

Calix[4]arene, Transition Metal and Crown Ether Based Anion and Ion-Pair Receptors

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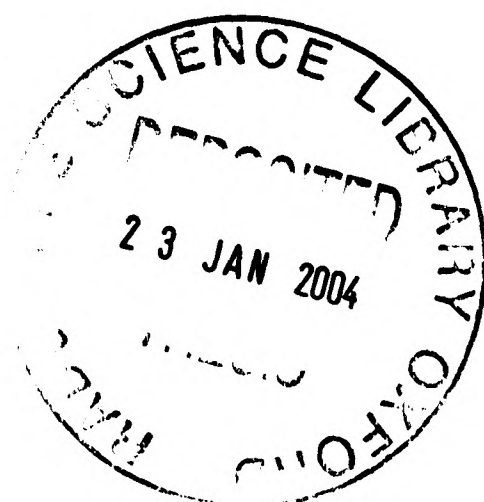
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The aim of this thesis is to develop novel receptors for the recognition of anions and ion-pairs. The guest binding and sensing properties of the receptors are studied by spectroscopic and electrochemical techniques. The ion-pair receptors described herein incorporate amide or urea functionalities for anion binding and crown ether moieties for alkali metal cation complexation. In addition, many receptors contain redox- and/or photo-active groups capable of sensing guest binding events.

Chapter One introduces the field of supramolecular chemistry. A review of synthetic cation, anion and ion-pair receptors reported in the literature is undertaken, and the formation of self-assembled architectures is discussed.

Chapter Two details the synthesis and study of a range of new upper-rim functionalised calix[4]arene anion and ion-pair receptors. The anion and ion-pair binding and sensing properties of the receptors are investigated by ^1H NMR spectroscopy, electrochemistry and luminescence spectroscopy. Two ion-pair receptors display a positive cooperative ion-pair effect, whereby the presence of potassium cations causes an enhancement in the strength of anion binding *via* electrostatic interactions and conformational effects.

Chapter Three centres on ion-pair receptors incorporating an azacrown group for alkali metal cation complexation together with amide functionalities for anion binding. Receptors containing either ferrocene or transition metal dithiocarbamate groups are capable of electrochemically and/or optically sensing the binding of anionic guests.

Chapter Four describes disulphide-appended receptors designed for self-assembly onto gold surfaces. A ferrocene- and disulphide-appended calix[4]arene receptor incorporating hydrogen bonding moieties forms self-assembled monolayers on gold electrodes which exhibit a surface sensing amplification in the electrochemical recognition of anions. In addition, the assembly of receptors onto gold nanoparticles is explored with the aim of producing UV-VIS spectroscopic sensors for guest binding.

Chapter Five reports the experimental procedures and characterisation for all products. The Appendices provide information on experimental techniques, list the crystallographic data and summarise all the receptors studied.

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Chapter One

Introduction

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Chapter One: Introduction

1.1 Supramolecular Chemistry

Supramolecular chemistry has been defined as ‘chemistry beyond the molecule’¹ and involves the study of systems in which the individual components are held together reversibly by non-covalent intermolecular forces. This is in contrast to traditional synthesis in which new molecules are formed by the making and breaking of covalent bonds.

Supramolecular chemistry is a truly interdisciplinary study drawing in particular on classical organic synthesis and coordination chemistry, gaining inspiration from biological systems and finding application in materials science, medicine and industry. The importance of this developing area was recognised in 1987 with the award of the Nobel Prize for chemistry to three of its pioneers: Lehn,¹ Pedersen² and Cram.³

Conceptually, the field may be divided into two areas, namely host-guest chemistry and self-assembly. In host-guest systems, the host (or receptor) is considered to spatially accommodate the guest (cationic, anionic or neutral) within a binding domain, the nature of which determines the strength and selectivity of guest complexation. An important concept here is complementarity, an idea introduced by Fischer in 1894 when he described enzymatic function according to a ‘lock and key’ principle.⁴ In general terms, successful molecular recognition requires that the binding sites on the host (lock) be sterically and electronically complementary for the guest (key).⁵ In self-assembly, many components spontaneously arrange themselves to form a molecular assembly (or supramolecular architecture). Both host-guest interactions and self-assembly rely on reversible intermolecular forces (such as hydrogen bonding and hydrophobic interactions) to form the resultant supermolecules.

The process of molecular recognition through complementarity is essential for the functioning of enzymes, which are designed to selectively bind the desired substrate before catalysing a specific chemical reaction. A demonstrative example is provided by carboxypeptidase-A, an enzyme that catalyses the hydrolysis of the C-terminal amino acid residues of proteins.⁶ Figure 1.1 shows the active site of the enzyme with a bound polypeptide chain, the anionic carboxylate terminus of which is hydrogen bonded to the positively charged guanidinium group of an arginine residue. The active site also contains a hydrophobic pocket which is ideally suited to accommodating the aromatic side chain of phenylalanine residues. This hydrophobic pocket provides the enzyme with a mechanism by which it can specifically select peptides with hydrophobic residues for hydrolysis, which is accomplished by the Lewis acidic zinc centre.

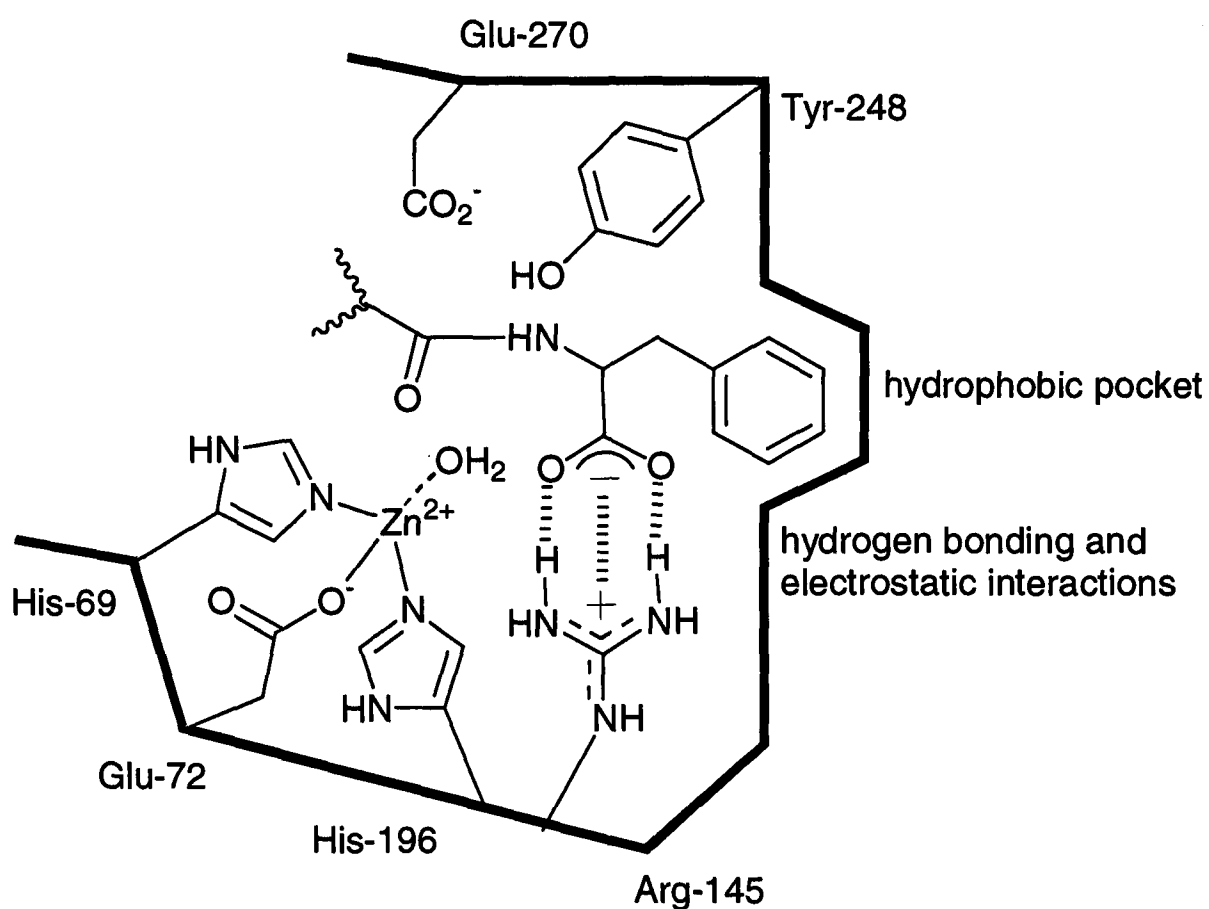


Figure 1.1: The active site of carboxypeptidase-A with a bound peptide chain.

This thesis is concerned with the synthesis and study of new receptors for binding charged guest species. The design of artificial receptors must address the nature of the guest, the

solvent environment and the function of the complex. A whole variety of hosts of different sizes, shapes, dimensionality, connectivity and flexibility have been reported in the literature, employing a diverse selection of non-covalent interactions to complex guest species. Some interesting examples of synthetic receptors which demonstrate strong and selective binding of cationic and anionic guests are given in the following sections. Solvent interactions affect both the entropy and enthalpy of guest complexation and can be manipulated in order to improve binding selectivity.⁷ Strong and specific recognition of a particular guest is often achieved by rigid receptors with a preorganised array of complementary binding sites. However, more adaptable and flexible hosts are often employed in catalysis and transport, where appreciable rates of guest complexation / decomplexation are required. In addition, hosts for use as molecular sensors may be designed with electrochemically- or optically-active reporter groups incorporated into their structures.

The above discussion has presented a brief introduction to supramolecular host-guest chemistry. In the following sections, the nature of the intermolecular forces used for binding guest species (Section 1.1.1) and some general design principles for such receptors (Section 1.1.2) will be addressed.

1.1.1 Non-covalent forces

Inspired by examples from nature, the supramolecular chemist uses various non-covalent forces to promote the association of molecules. These interactions include electrostatics (ion-ion, ion-dipole and dipole-dipole), hydrogen bonding, π - π stacking, dispersion and induction forces (van der Waals forces), and hydrophobic or solvatophobic effects. These non-covalent forces are weaker than covalent bonds, ranging in strength from 2 kJ.mol⁻¹ for dispersion forces to 20 kJ.mol⁻¹ for a hydrogen bond to 250 kJ.mol⁻¹ for an ion-ion interaction.⁸ The key

to supramolecular chemistry lies in the manipulation of multiple weak interactions to achieve strong and selective recognition of specific guests.

Electrostatic interactions are based on the Coloumbic attraction between opposite charges and have been used extensively in receptors for cations (such as crown ethers, cryptands and spherands) and anions (such as protonated polyammonium macrocycles) to achieve strong binding. Ion-ion interactions are non-directional whereas for ion-dipole interactions the dipole must be suitably aligned for optimal binding.⁹

Hydrogen bonds are ubiquitous in biological systems where their directional nature is responsible for the specificity of binding exhibited by many receptor-substrate complexes. Hydrogen bonding interactions have been employed in many synthetic receptors designed to coordinate to neutral species (such as barbiturates¹⁰ and ureas¹¹) and anionic guests.

π - π stacking forces occur between systems containing aromatic rings, with attractive interactions occurring for face-to-face and edge-to-face arrangements.¹² These forces have been used to enhance selectivity for guests with appropriately aligned aromatic groups, a feature which is elegantly demonstrated in a receptor for benzoquinone.¹³

Dispersion forces are attractive forces that occur between molecules due to the favourable interaction of their instantaneous dipoles.¹⁴ These forces are believed to provide additional enthalpic stabilisation to the inclusion of a hydrophobic guest into a hydrophobic cavity.¹⁵

The **hydrophobic effect** is the specific driving force for the association of apolar binding partners in aqueous solution. This has been utilised in receptors with hydrophobic interior cavities (such as cyclophanes¹⁶ and cyclodextrins¹⁷) for the encapsulation of organic guest molecules in water. The effect is due to both entropic and enthalpic contributions. Water molecules around the apolar surface of the host form an incomplete hydrogen bonded network

and are more ordered than free water molecules. Binding of the hydrophobic guest results in the release of these water molecules into the bulk solution which has a complete hydrogen bonded network (enthalpy gain) and is less organised (entropy gain).

Although not strictly a non-covalent bond, classical **coordination chemistry** is widely used in supramolecular chemistry, especially in the field of self-assembly. The geometric requirements of transition metal ions have been combined with rational ligand design to produce some remarkable supramolecular architectures.

1.1.2 Macrocyclic effect

Receptors for the binding of guest species usually employ chelating or macrocyclic ligands to increase the thermodynamic stability of their complexes.

The chelate effect refers to the enhanced stability of complexes containing multidentate chelating ligands compared to those derived from monodentate ones.¹⁸ For example, the copper(II) complex with ethylenediamine (en) is over eight orders of magnitude more stable than the analogous complex with ammonia (Figure 1.2).¹⁹ This is partly due to an entropic effect whereby the coordination of multidentate ligands results in an increase in the number of independent species in solution. Enthalpic factors also contribute to the chelate effect. Covalently linking the polar amino groups in ethylenediamine helps overcome part of their mutual repulsion, thereby making the binding more energetically favourable. In addition, the greater basicity of the amino groups of ethylenediamine results in their stronger coordination.

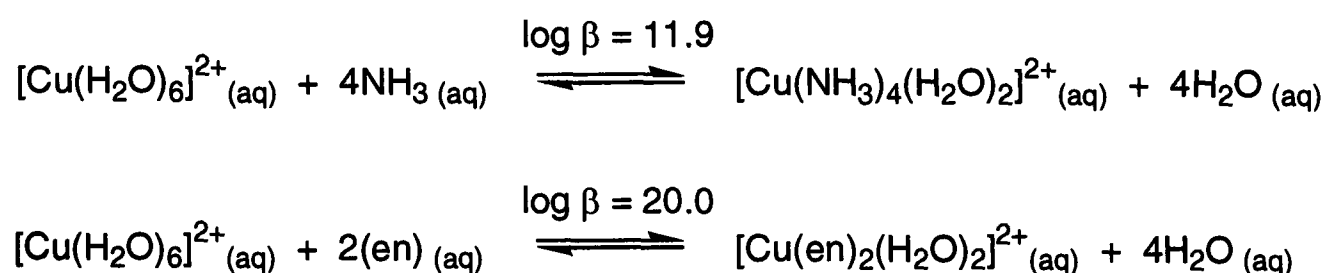


Figure 1.2: Chelating ligands bind metal ions more strongly.

The macrocyclic effect is a related phenomenon and concerns the increased thermodynamic stability of macrocyclic ligands compared to their acyclic counterparts.²⁰ For example, the zinc(II) complex of ligand **1.1** is over four orders of magnitude more stable than the complex with ligand **1.2** (Figure 1.3). This increased stability is caused by a combination of enthalpic and entropic factors. Macrocyclic hosts are less solvated than their acyclic counterparts and therefore less energy is required for desolvation. Furthermore, macrocyclic ligands are less flexible and consequently have less disorder to lose on complexation than their acyclic analogues.

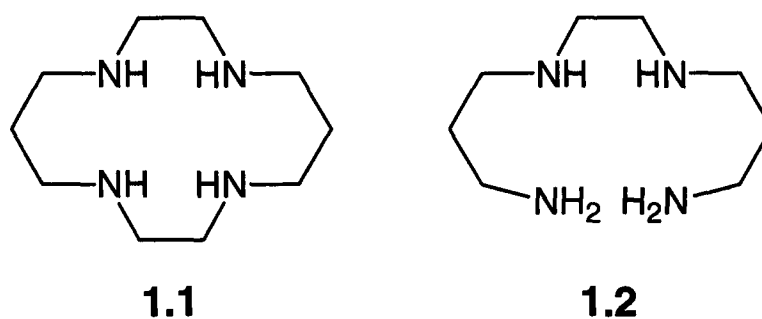


Figure 1.3: Macrocyclic **1.1** and acyclic **1.2** ligands.

The main objective of this thesis is the synthesis and characterisation of new receptors for anions and alkali metal cation-anion ion-pairs and the study of their guest binding and sensing properties. With this in mind, the following sections provide some illustrative examples of receptors for cations (Section 1.2), anions (Section 1.3) and ion-pairs (Section 1.4). This chapter is not intended to be a comprehensive review of supramolecular chemistry,²¹ but rather serves to highlight interesting and relevant examples from the literature.

1.2 Cation Receptors

Cations play a number of important roles in biological systems. For example, concentration differences of cations across cell membranes create potentials that are used to transport organic substrates in and out of cells. Metal cations are present in the active sites of many enzymes acting as catalysts for *in vivo* chemical reactions.²² Medically important metal

complexes include those of paramagnetic lanthanide cations that are used as contrast agents in magnetic resonance imaging.²³ Furthermore, the selective extraction of metal salts from aqueous systems is important for both industrial and environmental reasons. In response to these diverse applications, the study of synthetic receptors for cationic guest species is well established.

1.2.1 Crown ethers

One of the key moments in the development of supramolecular chemistry was the chance discovery of a polyether macrocycle by Pedersen in the late 1960s.²⁴ This crown ether, dibenzo[18]crown-6 **1.3** (Figure 1.4), was the first synthetically produced receptor for alkali metal cations. A sodium or potassium cation is bound in the cavity of the crown ether by the formation of six attractive electrostatic ion-dipole interactions with the oxygen donor atoms of the polyether ring.²⁵ This pioneering work opened up a whole new field of coordination chemistry involving the alkali and alkaline earth metal cations.²⁶

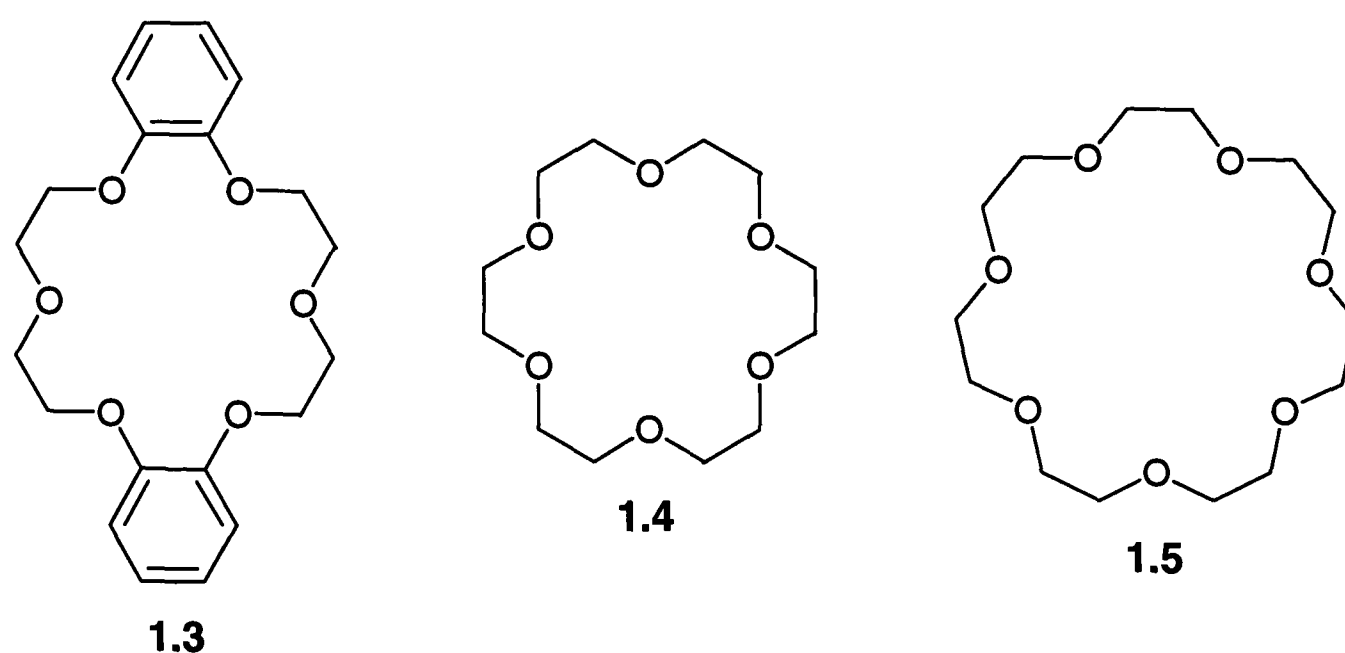


Figure 1.4: Crown ether macrocycles dibenzo[18]crown-6 **1.3**, [18]crown-6 **1.4** and [21]crown-7 **1.5**.

Following this initial discovery, a whole range of crown ethers were synthesised. Frensdorff and Pedersen measured the stability constants of these crown ethers with various cations in

methanol by potentiometry with ion-selective electrodes.²⁷ They discovered a simple relationship between the cavity size, cationic radius and the stability of the resulting complex now referred to as ‘optimal spatial fit’. Table 1.1 shows the size complementarity between the alkali metal cations and the crown ethers with which they form the most stable complexes. For example, [18]crown-6 **1.4** (Figure 1.4) forms the most stable complex with the potassium cation ($\log K = 6.10$ in methanol and 2.06 in water) whereas the larger [21]crown-7 **1.5** (Figure 1.4) is selective for caesium.

Cation	Diameter (Å)	Crown ether	Cavity diameter (Å)
Li ⁺	1.36	[12]crown-4	1.2 – 1.5
Na ⁺	1.94	[15]crown-5	1.7 – 2.2
K ⁺	2.66	[18]crown-6	2.6 – 3.2
Cs ⁺	3.34	[21]crown-7	3.4 – 4.3

Table 1.1: Alkali metal cation diameters and complementary crown ether cavity sizes.

The crystal structure of the potassium complex of [18]crown-6 shows the potassium cation lying in the centre of the macrocyclic ring where the electron density is highest, thereby maximising the electrostatic interactions and the binding strength.²⁸ For the smaller sodium cation however, the ring distorts around the cation and the resulting ring strain decreases the binding constant.²⁹ The larger caesium cation sits above the plane of the macrocycle, again decreasing the binding interactions.²⁸

Complexes of different stoichiometries are known to form between crown ethers and alkali metal cations of mis-matching sizes. For example, the crystal structure of $K^+ \cdot (\text{benzo}[15]\text{crown-5})_2$ (Figure 1.5) reveals the potassium cation sandwiched between two

crown ether molecules as it is too large to form a simple 1:1 complex.²⁵ Conversely, dibenzo[24]crown-8 encapsulates two potassium cations simultaneously.³⁰

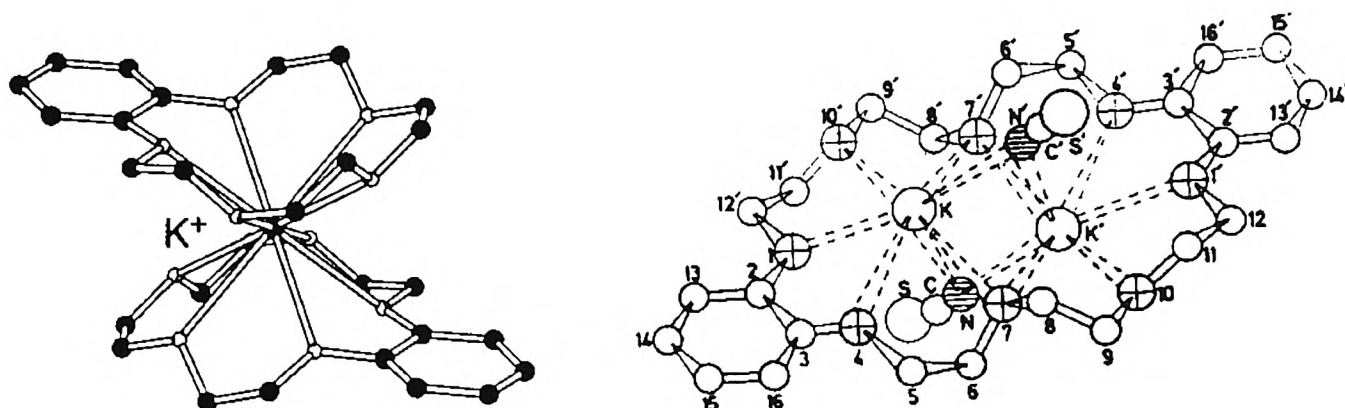


Figure 1.5: Crystal structures of benzo[15]crown-5 potassium sandwich complex and bis(potassium thiocyanate)dibenzo[24]crown-8.

In addition to alkali metal cations, transition metal and lanthanide cations may be bound by crown ethers.³¹ The selectivity characteristics of a crown ether can be manipulated by replacing the hard-donor oxygen atoms with soft-donor sulphur or nitrogen atoms. For example, replacing two diametrically opposed oxygen atoms in [18]crown-6 with nitrogen atoms gives a bis(aza)crown ether which exhibits a stability constant with silver over five orders of magnitude greater than with potassium.³²

Crown ethers can also form complexes with primary ammonium cations. For example, [18]crown-6 (unlike [15]crown-5) possesses C_3 symmetry which is ideal for the formation of three hydrogen bonds to an alkylammonium cation.³³

1.2.2 Lariat crown ethers

Crown ethers can be functionalised with pendant arms containing additional coordinating groups, thereby adding a three-dimensional character to cation complexation. These lariat crown ethers were designed as carrier species for cations across lipophilic membranes, because they possess higher binding constants than regular crown ethers but remain

kinetically labile due to the inherent flexibility of the sidearm.³⁴ For example, lariat ether **1.6** (Figure 1.6) binds sodium cation an order of magnitude more strongly than aza[15]crown-5.³⁵

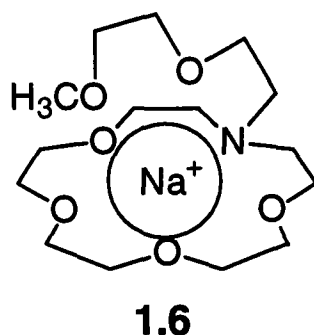


Figure 1.6: Lariat ether **1.6** complexing a sodium cation.

1.2.3 Cryptands

Lehn and co-workers first reported the synthesis of cryptands in 1969.³⁶ These three-dimensional cage-like molecules bind alkali and alkaline earth cations with stability constants much greater than those of analogous crown ethers.³⁷ For example, [2.2.2]cryptand (Figure 1.7) binds potassium in methanol four orders of magnitude more strongly than 18[crown]-6.³⁸ These higher stability constants may be attributed to a combination of factors, namely a positive entropic effect due to the desolvation of the cation upon complexation and a favourable enthalpic contribution due to the limited structural reorganisation of the rigid cavity required upon cation binding.³⁹

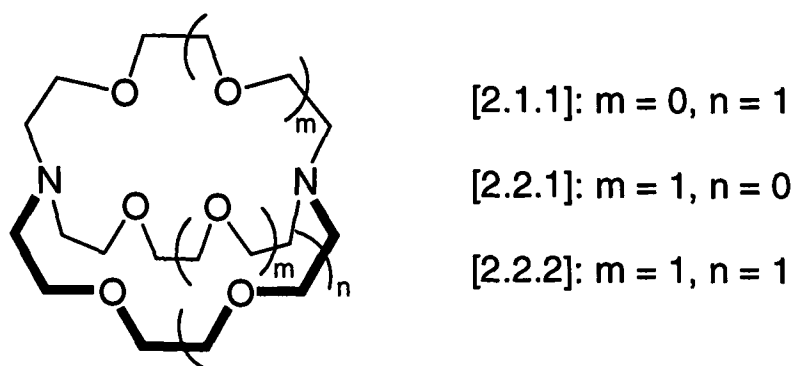


Figure 1.7: Three cryptands.

Cryptand cavities are quite rigid and hence they exhibit good cation selectivity. In a series of simple cryptands (Figure 1.7), the highest stability constants were observed for $\text{Li}^+ \cdot [2.1.1]$,

$\text{Na}^+ \cdot [2.2.1]$ and $\text{K}^+ \cdot [2.2.2]$, corresponding to a complementarity of cavity and alkali metal cation size.⁴⁰

1.2.4 Spherands

Cram designed a series of rigid ligands in which the donor atoms form an enforced spherical cavity.⁴¹ These spherands are highly selective for the appropriately sized alkali metal cation and form complexes of very high stability.⁴² For example, spherand **1.7** (Figure 1.8) binds sodium more than two orders of magnitude more strongly than [2.2.1]cryptand, and is completely unable to complex larger cations such as potassium.

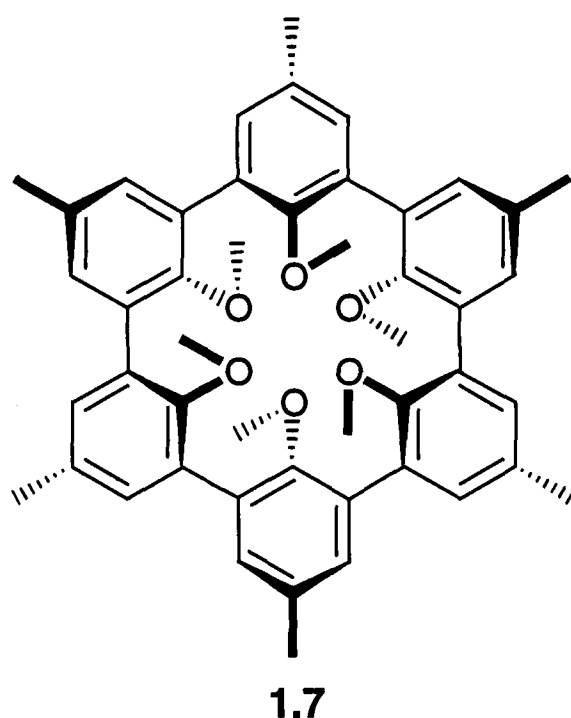


Figure 1.8: Highly preorganised spherand **1.7**.

From these studies Cram formalised the principle of preorganisation: “The more highly hosts and guests are organised for binding and low solvation prior to their complexation, the more stable will be their complexes”.³ As might be expected, these receptors show slow complexation / decomplexation kinetics.

1.2.5 Calixarene-based cation receptors

Calixarenes have been functionalised for use as cation receptors by appending appropriate donor groups to the three-dimensional framework. For example, the lower-rim tetra-ester appended calix[4]arene receptor **1.8** (Figure 1.9) is selective for sodium cations over other putative alkali metal guest species. The calix[4]tube **1.9** (Figure 1.9) is selective for potassium cations which are bound initially in the aromatic cavity of the calixarene *via* favourable π -cation interactions before passing through to the centre of the tube where they are bound by strong electrostatics with the eight ether oxygen donor atoms.⁴³

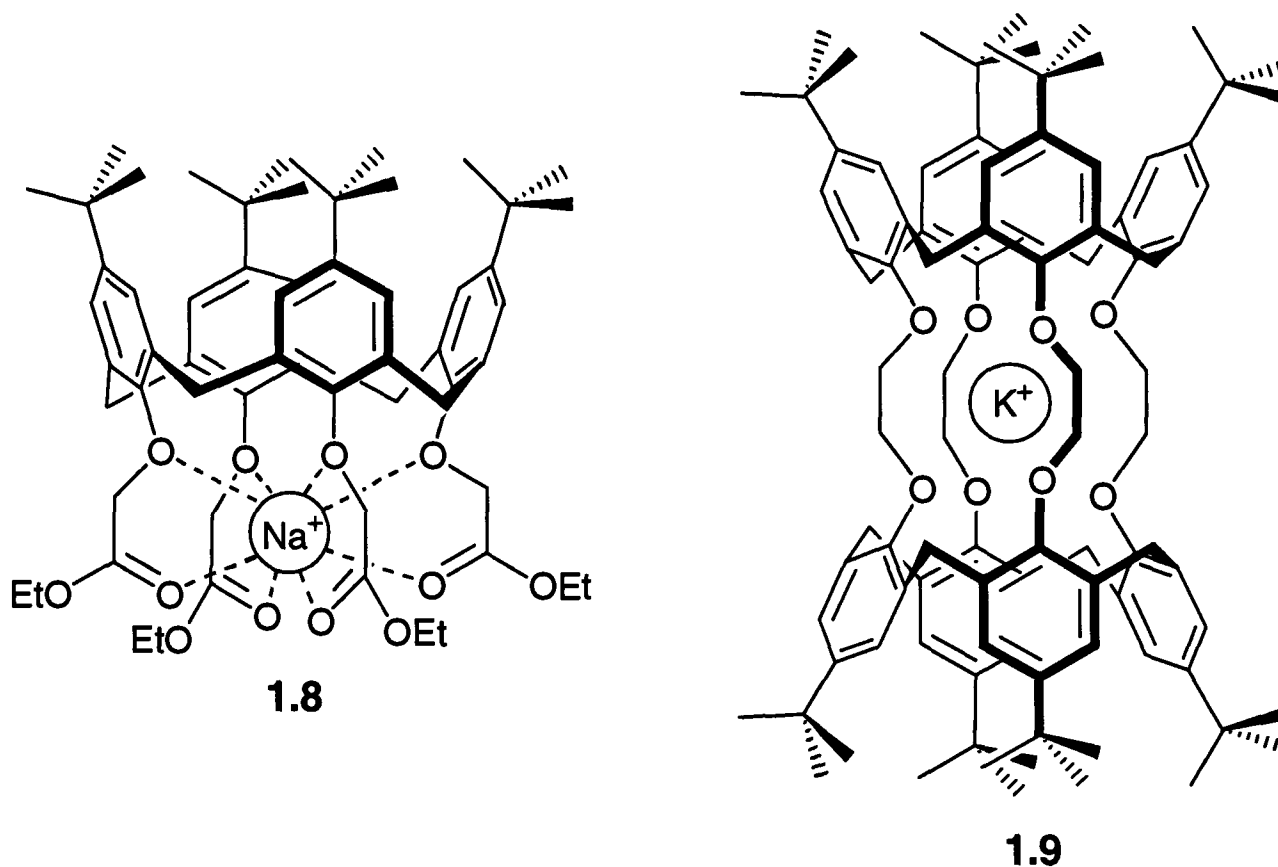


Figure 1.9: Calix[4]arene receptor **1.8** complexing a sodium cation and calix[4]tube **1.9** binding a potassium cation.

The calixarene scaffold has also been adapted for the complexation of lanthanide and actinide metal cations.⁴⁴ For example, Ungaro and co-workers have reported the synthesis of calix[4]arene derivative **1.10** (Figure 1.10) which forms very stable complexes with gadolinium(III) cations in water ($K = 1 \times 10^{13} \text{ M}^{-1}$ at pH 6.8).⁴⁵ The gadolinium cations are bound by the two acetamide and two ethyleneaminodicarboxy groups at the lower-rim of the

macrocycle. Such complexes show potential as new luminescent probes and as contrast agents for magnetic resonance imaging. In addition, these compounds have shown promise in the extraction of lanthanide metal cations from aqueous systems.⁴⁶

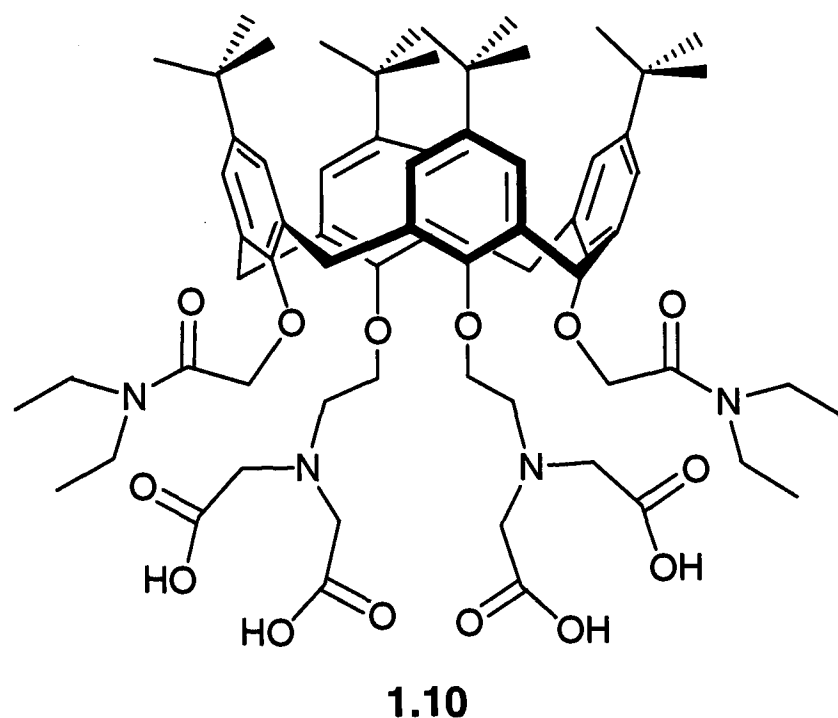


Figure 1.10: Calix[4]arene derivative **1.10** binds gadolinium cations at the lower-rim.

This section has served to highlight the factors which must be considered when designing hosts for cationic species. The focus of attention is now turned towards the related but more challenging field of anion recognition.

1.3 Anion Receptors

Synthetic hosts for anionic guest species have been known for over thirty years but only relatively recently has the interest in such anion receptors intensified.⁴⁷ The rapid emergence of this area of coordination chemistry has been encouraged by the realisation of the important roles played by anions. Many biologically important species are anionic, including nucleic acids and the majority of enzyme substrates,⁴⁸ and anion recognition *in vivo* is remarkably subtle. A large body of research has been devoted to biomimicry, in order to develop artificial catalysts and carrier systems.⁷ Anions play a role in diseases such as cystic fibrosis, which is

caused by the misregulation of chloride ion channels,⁴⁹ and the need for selective sensing of this anion has been emphasised in several reports.⁵⁰ In the environment, anions such as nitrate and phosphate can cause the eutrophication of waterways,⁵¹ and pertechnetate anions are a radioactive byproduct of nuclear power stations.⁵² Clearly, the design of receptors which can selectively bind, extract and/or sense anions is an important goal.

For the effective design of selective receptors for anionic guests, it is important to consider the following properties of anions.⁵³ Anions are negatively charged, requiring positive or electron deficient binding sites to be incorporated into the host framework. Anions are larger than their isoelectronic cations⁵⁴ and so recognition cavities must also be larger to enable guest encapsulation. In addition, the relatively larger size of many anions results in lower charge densities which may reduce the effectiveness of electrostatic binding interactions. Anions exhibit a range of geometries including spherical (chloride), linear (cyanate), trigonal (nitrate), tetrahedral (phosphate) and octahedral ($\text{Fe}(\text{CN})_6^{4-}$) which challenges the designer to create complementary binding sites. Anions display larger solvation energies than cations of a comparative size and hence competition effects between host and solvent for the guest species will be more pronounced. Many anions exist only over a limited pH range and so receptors must be designed to function within the pH window of their target anion. The following sections discuss the application of these design principles to synthetic anion receptors.⁵⁵

1.3.1 Positively charged receptors

Anionic guest species can be bound *via* strong electrostatic interactions by the incorporation of positive charges into a macrocyclic host. In addition, these receptors often utilise more subtle hydrogen bonding interactions to achieve selectivity of anion binding, an approach inspired by nature. For example, the first crystal structure of a chloride channel revealed that its outer portion was lined with positive charges to attract chloride anions, however the

chloride selectivity filter relied upon multiple hydrogen bonding interactions to achieve specificity.⁵⁶

1.3.1.1 Polyaza macrocycles

Park and Simmons were the first to demonstrate the use of electrostatics and hydrogen bonds to complex anionic guests with the report in 1968 of macrotricyclic anion receptor **1.11** (Figure 1.11).⁵⁷ NMR and crystallographic studies revealed that halide anions were encapsulated inside the host cavity, forming hydrogen bonds with the NH protons which complemented the attractive electrostatic forces.⁵⁸ The strength and selectivity of halide binding was found to be dependent on the size of the cage.

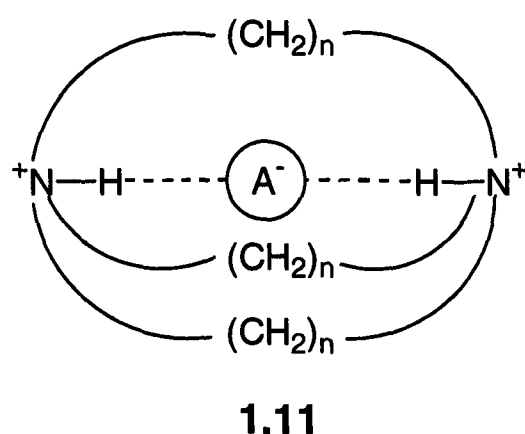


Figure 1.11: The halide anion complex of macrotricyclic receptor **1.11** ($n = 9$ or 10).

Lehn and co-workers realised the importance of this pioneering work and developed a range of polyaza macrocyclic anion receptors,⁵⁹ two examples of which are shown in Figure 1.12.

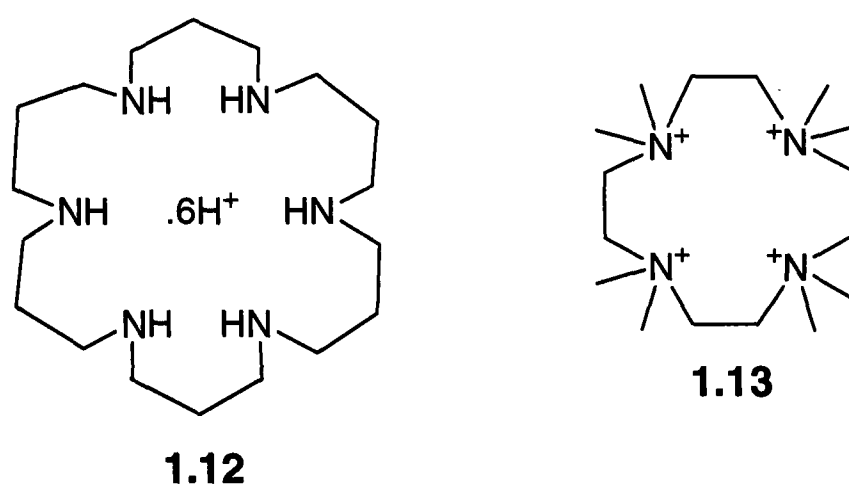


Figure 1.12: Polyaza macrocyclic receptors **1.12** and **1.13**.

In its fully protonated form, receptor **1.12** binds biologically relevant anions such as ATP^{4-} ($\log K = 8.9$) and AMP^{2-} ($\log K = 3.4$) in water. The higher the negative charge on the guest the stronger the binding by the positively charged host, demonstrating the importance of electrostatic interactions in the binding process. However, receptor **1.13** does not bind ATP^{4-} despite its high positive charge as it cannot form hydrogen bonds with the anionic guest.

The binding sites of such macrocycles can be sterically tuned. For example, ditopic receptor **1.14** (Figure 1.13) consists of two anion binding sites separated by alkyl chain spacers, and forms the strongest complexes with dicarboxylate anions of a complementary length to the internal cavity.⁶⁰

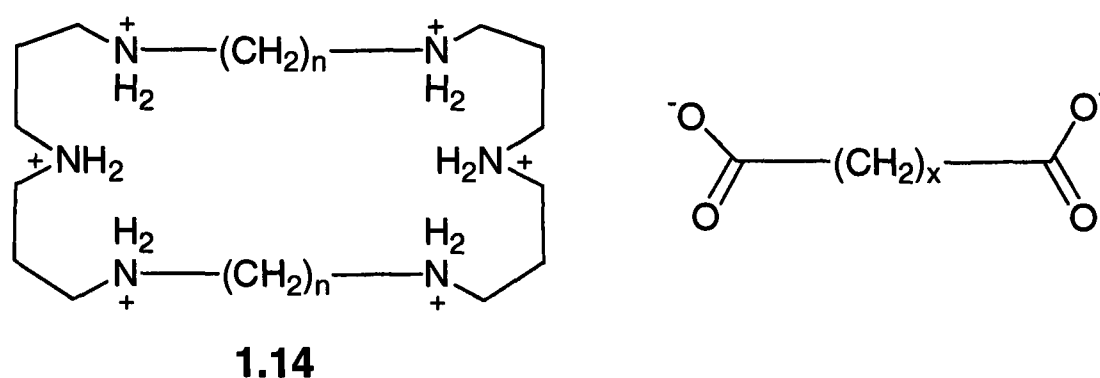


Figure 1.13: Ditopic receptor **1.14** ($n = 7$) binds complementary dicarboxylate anions ($x = 3$).

Lehn and co-workers synthesised macrotricyclic host **1.15** (Figure 1.14) which exhibits a fascinating chameleon-like response to guest recognition depending on the pH of the medium.⁶¹ The neutral host is similar to the cryptands described earlier (in Section 1.2.3) and is capable of recognising tetrahedral ammonium and spherical metal cations. The di-protonated host accommodates a water molecule in the cavity, whereas the tetra-protonated species binds halide anions. Anion binding studies reveal that macrotricyclic receptor **1.15** displays enhanced stability and selectivity compared to bicyclic analogues, showing good discrimination for chloride ($\log K > 4.0$) over bromide ($\log K < 1.0$) in water. This effect arises because the highly preorganised receptor possesses a well defined, rigid cavity which

directs strong, cooperative hydrogen bonds towards the anion and prevents the host from adjusting to changes in the size of the guest.

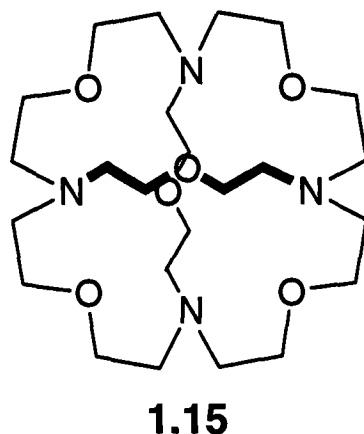


Figure 1.14: Macrotricyclic receptor **1.15**.

Recently, Nelson and McKee have developed a series of polyaza cryptands such as receptor **1.16** (Figure 1.15) capable of encapsulating and extracting oxoanions such as pertechnetate and perrhenate from aqueous to organic solution.⁶² The extraction efficiency was shown to depend importantly on the degree of protonation of the ligands. Although the highest anion stability constants in aqueous solution were obtained for the hexa-protonated species, the best extraction percentages were achieved for less highly charged (and hence less hydrophilic) ligands. The challenging task of designing functional ligands for the sequestration of oxoanions is of considerable interest for both environmental and medical reasons.

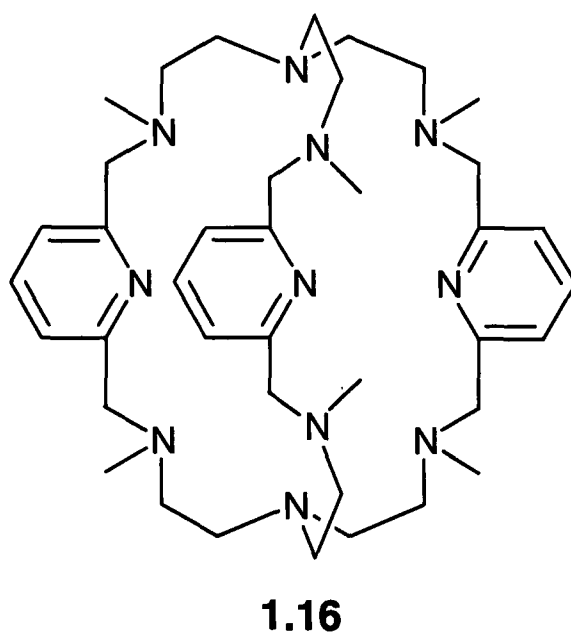


Figure 1.15: Polyaza cryptand receptor **1.16**.

These protonated ammonium hosts generally have the disadvantage of operating only at low to medium pH, conditions under which many anions also become protonated, leading to a narrow pH range over which the recognition of pH sensitive anions is possible.

1.3.1.2 Expanded porphyrins

Sessler and co-workers developed a receptor with an electron poor cavity based on an expanded protonated porphyrin structure.⁶³ This receptor bound fluoride anions over three orders of magnitude more strongly than chloride or bromide. The functionalisation of this sapphyrin produced the more complex receptor **1.17** for biologically important anions such as anti-viral nucleic acid phosphates. Selectivity was observed for guanine monophosphate, attributed to the complementary hydrogen bonding triad (Figure 1.16).⁶⁴

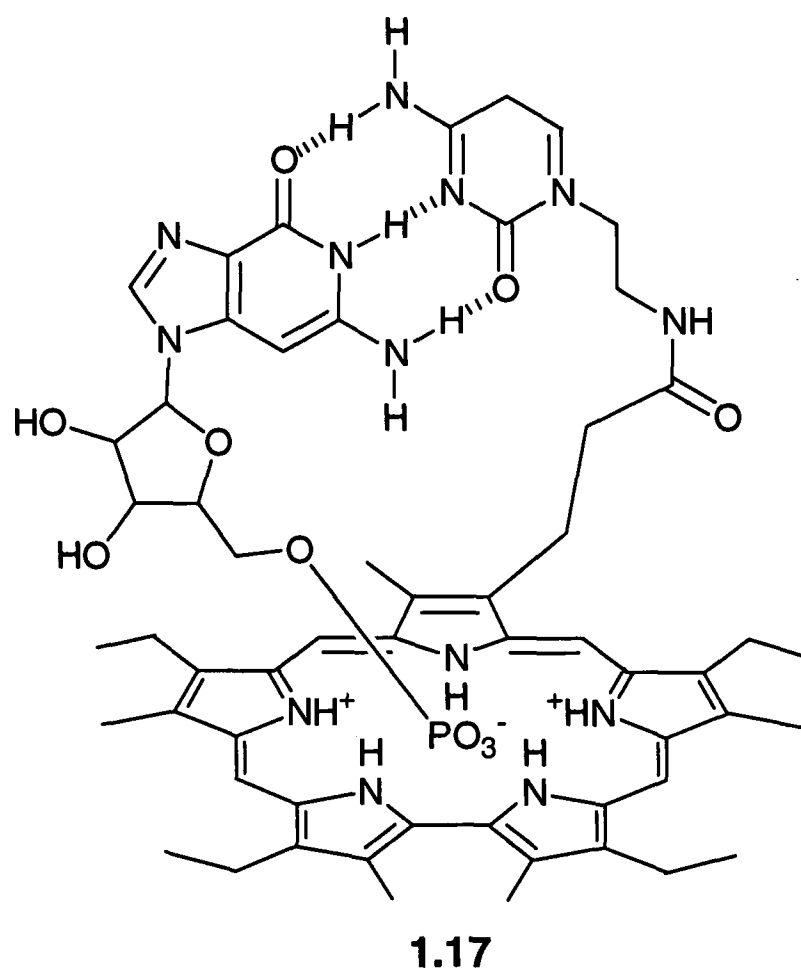


Figure 1.16: Functionalised di-protonated sapphyrin receptor **1.17** complexing guanine monophosphate.

1.3.1.3 Guanidinium receptors

One solution to the problem of the limited operational pH range of polyaza macrocycles is the use of guanidinium units in the receptor.⁶⁵ Charge delocalisation stabilises the guanidinium group such that it remains protonated even at relatively high pH.⁶⁶ Interestingly, the arginine amino acid side chain has a terminal guanidinium group which is used extensively for anion binding in biological systems.^{7, 67}

Schmidtchen and co-workers incorporated the guanidinium fragment into a bicyclic ring thereby rigidifying the receptor and ideally aligning the hydrogen bond donors for the recognition of bidentate anions.⁶⁸ Lehn, de Mendoza and co-workers synthesised receptor **1.18** (Figure 1.17) which extracted a complementary guest (*p*-nitrobenzoate) from water into chloroform through a combination of electrostatics, hydrogen bonding interactions and π - π stacking effects ($K = 1600 \text{ M}^{-1}$ in chloroform).⁶⁹

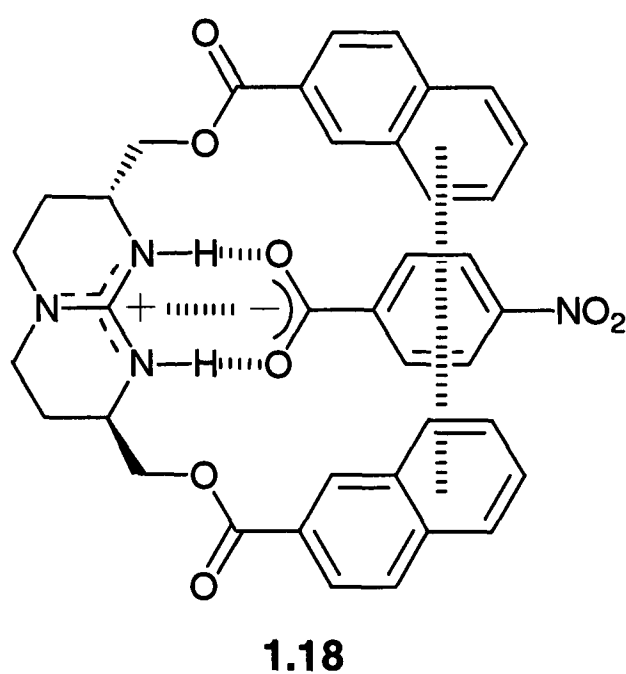
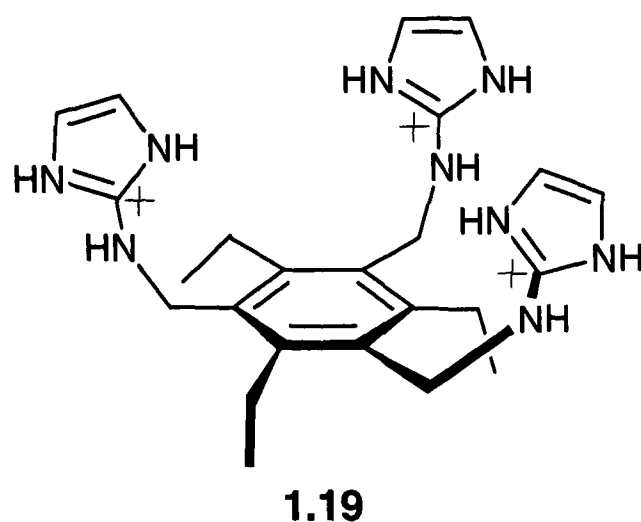


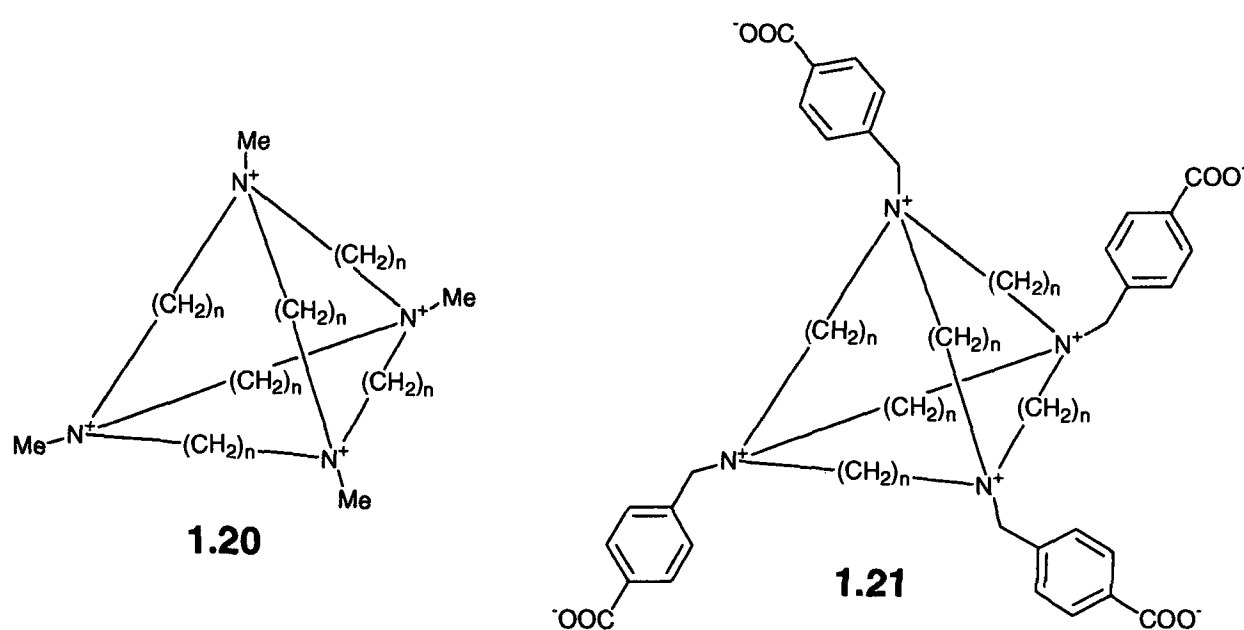
Figure 1.17: Guanidinium-based receptor **1.18** complexing *p*-nitrobenzoate.

Another example is host **1.19** (Figure 1.18) which contains three guanidinium moieties and is selective for trianions such as citrate.⁷⁰ This receptor has been used to produce a displacement-assay-type chemosensor for citrate in beverages.

Figure 1.18: Citrate selective receptor **1.19**.

1.3.1.4 Quaternary ammonium receptors

Schmidtchen and co-workers produced a number of receptors incorporating pH independent, positively charged quaternary nitrogen atoms for the electrostatic binding of anions. Macrotricyclic quaternary ammonium receptor **1.20** (Figure 1.19) forms 1:1 complexes with halide anions in water and demonstrates good size selectivity, forming the strongest complexes with anions having the best steric fit.⁷¹ However, the absence of hydrogen bonding groups resulted in lower stability constants than those observed for analogous protonated polyammonium receptors.

Figure 1.19: Quaternary ammonium receptors **1.20** and **1.21** ($n = 6$).

The problem with quaternary ammonium receptors is that they possess counter anions which may compete for the binding site. This was addressed by the synthesis of zwitterionic hosts such as **1.21** (Figure 1.19).⁷² NMR titrations showed that this net-neutral receptor binds halide anions more strongly than **1.20**.

Schneider and co-workers reported the synthesis of receptor **1.22** (Figure 1.20) containing a large hydrophobic cavity together with positively charged quaternary nitrogen atoms, which is selective for hydrophobic anions such as nucleic acid base anions.⁷³ This mirrors many biological anion binding sites which are often located in a hydrophobic pocket within the peptide structure.

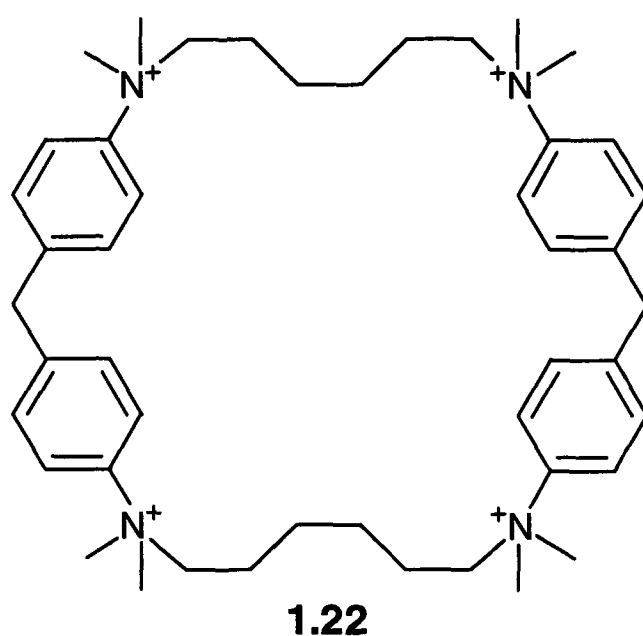
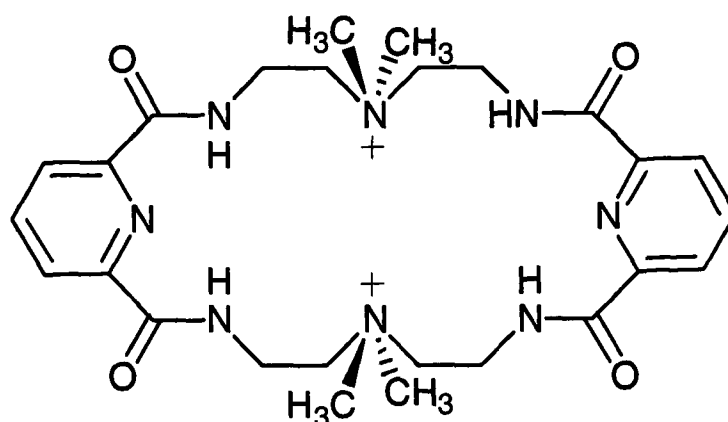


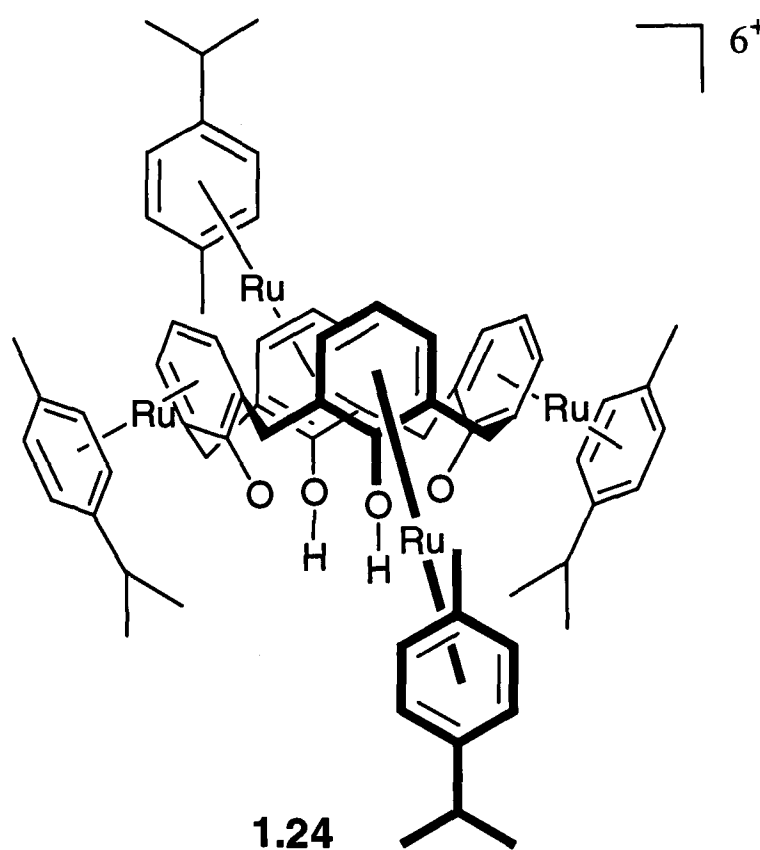
Figure 1.20: Positively charged cyclophane receptor **1.22**.

More recently, Bowman-James and co-workers synthesised anion receptor **1.23** (Figure 1.21) which incorporates two quaternary amines and four amide groups in a macrocyclic structure.⁷⁴ This host binds anions in a 1:1 stoichiometry *via* a combination of electrostatics and hydrogen bonding interactions, and exhibits higher affinities for anions ($\log K$ (chloride) = 4.75 in DMSO) compared to the corresponding neutral tetra-amide receptor ($\log K$ (chloride) = 2.69 in DMSO). Strong anion binding is observed in competitive solvents, with a marked selectivity for dihydrogen phosphate ($\log K$ = 5.32 in DMSO).

**1.23**Figure 1.21: Amide / quaternarised amine macrocyclic anion receptor **1.23**.

1.3.1.5 Metallated cavities

Another example of employing a positively charged hydrophobic cavity for anion binding comes from Atwood and Steed who have functionalised the aromatic framework of calix[4]arenes with positively charged organometallic groups.⁷⁵ This has produced electron deficient receptors such as **1.24** (Figure 1.22) which crystallographic studies show can encapsulate anions such as tetrafluoroborate inside the hydrophobic cavity.⁷⁶ Anion binding studies with an analogous iridium receptor revealed binding constants as high as 550 M^{-1} for chloride complexation in aqueous solution.⁷⁷

**1.24**Figure 1.22: Metallated calix[4]arene receptor **1.24**.

1.3.1.6 Transition metal containing receptors

Beer and co-workers have taken a different approach to combining electrostatics and hydrogen bonding interactions,⁷⁸ producing anion receptors containing positively charged ligated metal centres such as cobaltocenium (1.25) or ruthenium(II) tris(bipyridyl) (1.26) in conjunction with hydrogen bonding secondary amide groups (Figure 1.23).⁷⁹ As a consequence of anion binding being proximate to the transition metal centre, these receptors can sense the presence of a bound guest *via* changes in the electrochemical and/or optical properties of the metallocene or bipyridyl-coordinated transition metal ion (see Section 1.3.4).

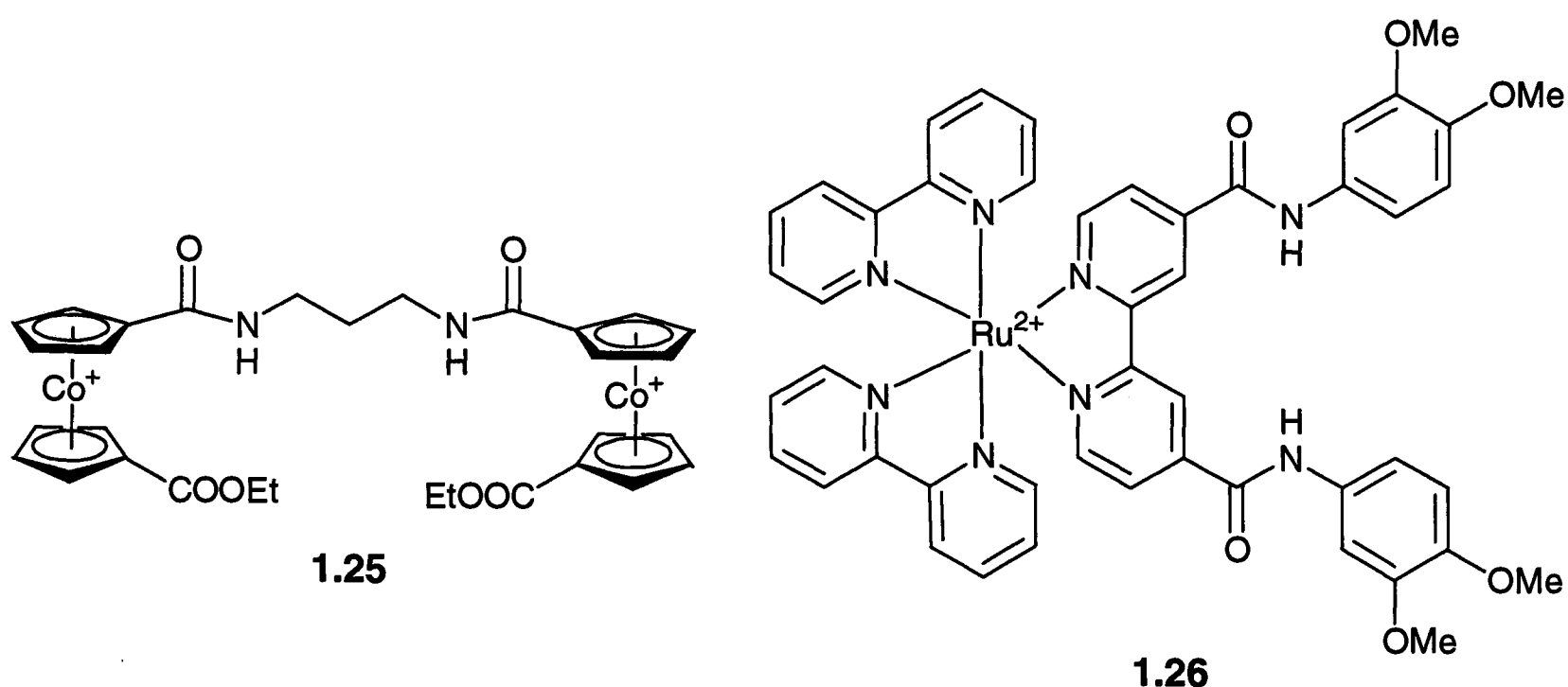


Figure 1.23: Cobaltocenium (1.25) and ruthenium(II) tris(bipyridyl) (1.26) containing receptors (the hexafluorophosphate counter anions are not shown).

1.3.2 Neutral hydrogen bonding hosts

Receptors containing electropositive hydrogen atoms (such as those present in amides, ureas, thioureas and pyrroles) are capable of complexing anions solely through hydrogen bonding interactions. Remarkable selectivity in the binding of anions is achieved in biological systems through subtle hydrogen bonding arrays. A particularly appropriate and striking example is provided by the *Salmonella typhimurium* sulphate binding protein, which displays an association constant for sulphate of 10^6 M^{-1} in water and discrimination over phosphate by a

factor of 10^5 .⁸⁰ The crystal structure of the protein-sulphate complex reveals the sulphate anion buried deep below the surface with the only stabilisation for the dinegative charge being provided by neutral hydrogen bond donors.

Compound **1.27** (Figure 1.24) was the first synthetic anion receptor to use only hydrogen bonding interactions for the complexation of anions. The three convergent amide protons pointing into the cavity were shown to bind fluoride anions in DMSO solution.⁸¹

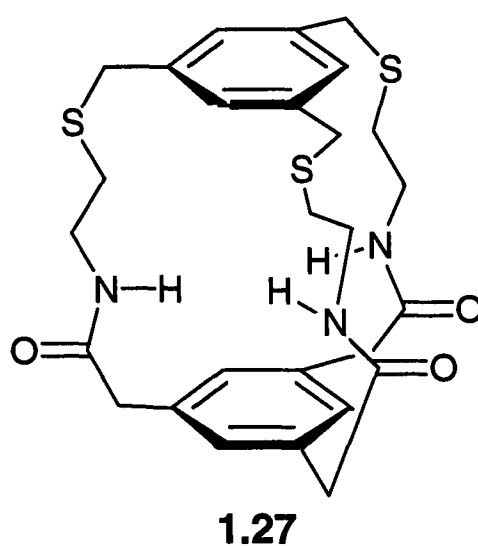
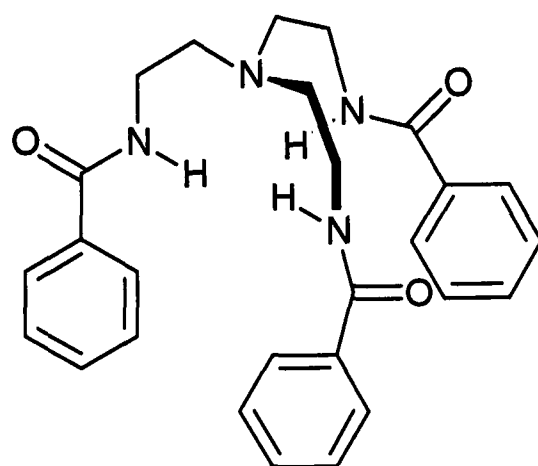
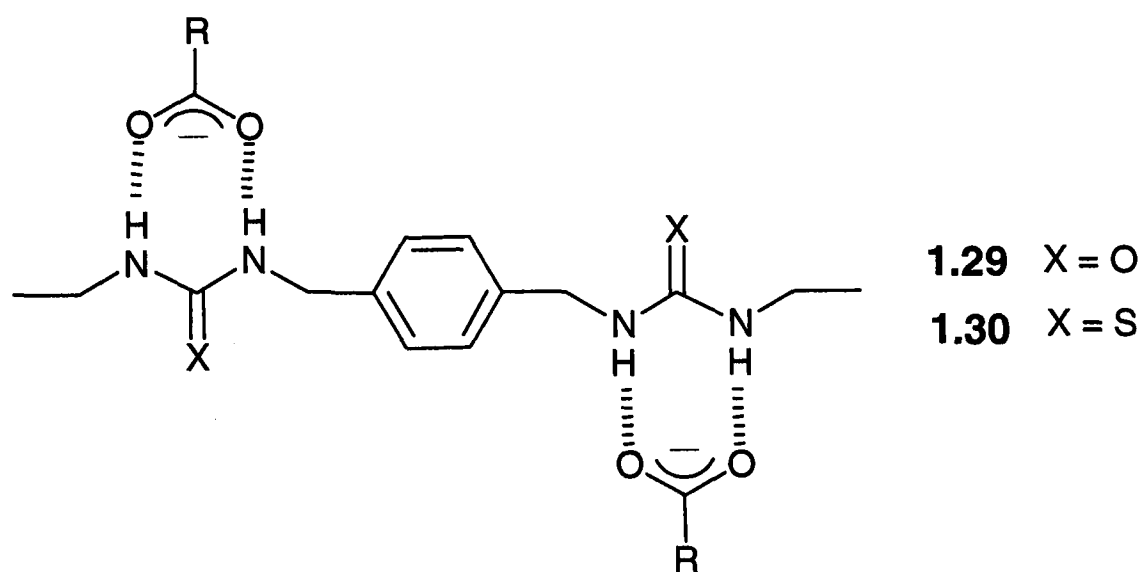


Figure 1.24: Hydrogen bonding receptor **1.27** for fluoride anions.

The directional nature of hydrogen bonds enables the design of receptors with specific orientations of binding sites capable of differentiating between anionic guests with different geometries or hydrogen bonding requirements.⁸² For example, hosts with a trigonal arrangement of hydrogen bond donor groups are complementary for biologically relevant tetrahedral organophosphate anions. Reinhoudt and co-workers have synthesised simple acyclic hosts such as receptor **1.28** based on triethylenediamine (tren, Figure 1.25).⁸³ These tripodal receptors have C_3 symmetry and display preferential binding of dihydrogen phosphate in polar organic solvents ($K = 870 \text{ M}^{-1}$ in acetonitrile).

**1.28**Figure 1.25: Tren-based receptor **1.28** is selective for dihydrogen phosphate.

Urea and thiourea groups are particularly good hydrogen bond donors, ideally constructed for the complexation of bidentate anions such as carboxylates. Urea-containing receptor **1.29** (Figure 1.26) binds bidentate anions in DMSO solution with the strength of the complex depending on the basicity of the guest.⁸⁴ Studies of urea (**1.29**), thiourea (**1.30**) and analogous amide receptors reveal that the strength of anion binding follows the order amide < urea < thiourea,⁸⁵ attributable to the increasing acidity of the respective hydrogen bond donor.

Figure 1.26: Urea (**1.29**) and thiourea (**1.30**) receptors binding complementary bidentate carboxylate anions.

Umezawa and co-workers produced a series of acyclic thiourea cleft molecules such as receptor **1.31** (Figure 1.27).⁸⁶ This highly preorganised system presents a hydrogen bonding

array which is complementary for dihydrogen phosphate anions which are bound strongly and selectively in DMSO solution ($K = 195000 \text{ M}^{-1}$).

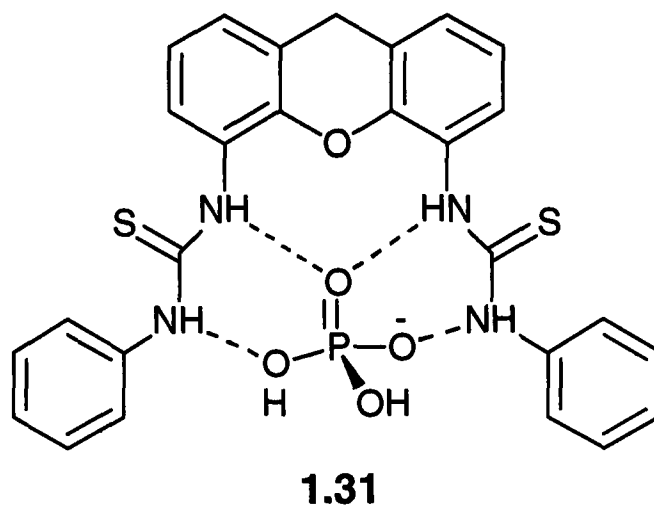


Figure 1.27: Preorganised bis(thiourea) cleft molecule **1.31** binding dihydrogen phosphate.

Another approach to anion binding *via* hydrogen bonding interactions is taken by Sessler and Gale who have studied calix[4]pyrrole-based receptors⁸⁷ such as **1.32** (Figure 1.28).⁸⁸ The free macrocycle is in a 1,3-alternate conformation, however upon halide anion binding the pyrrole rings align forming four convergent hydrogen bonds with the bound guest. Receptor **1.32** forms the strongest complexes with fluoride anions, with a stability constant of 17200 M^{-1} in CD_2Cl_2 . Such receptors have found application in calixpyrrole-modified solid supports for the separation of oligonucleotides by HPLC.⁸⁹

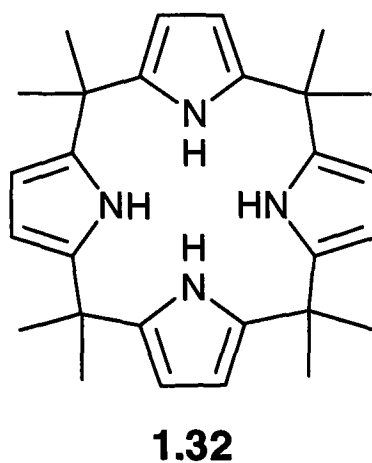


Figure 1.28: Calix[4]pyrrole-based receptor **1.32**.

Kubik and co-workers have recently synthesised the neutral cyclic hexa-peptide receptor **1.33** (Figure 1.29) which binds anions such as halides and sulphate in highly competitive aqueous solvent mixtures.⁹⁰ Structural investigations revealed that sandwich-type 2:1 complexes are formed, in which the anions are bound by six hydrogen bonds between two interdigitating cyclopeptide rings. Subsequent work has shown that these aggregates may be stabilised by covalently linking the two peptide units with an appropriate spacer.⁹¹ Furthermore, dynamic combinatorial chemistry has been exploited to optimise this linking unit, resulting in receptors which bind iodide ($K = 5.6 \times 10^4 \text{ M}^{-1}$) and sulphate ($K = 6.7 \times 10^6 \text{ M}^{-1}$) with unprecedented affinities for neutral hydrogen bonding hosts in 2:1 acetonitrile / water solution.⁹²

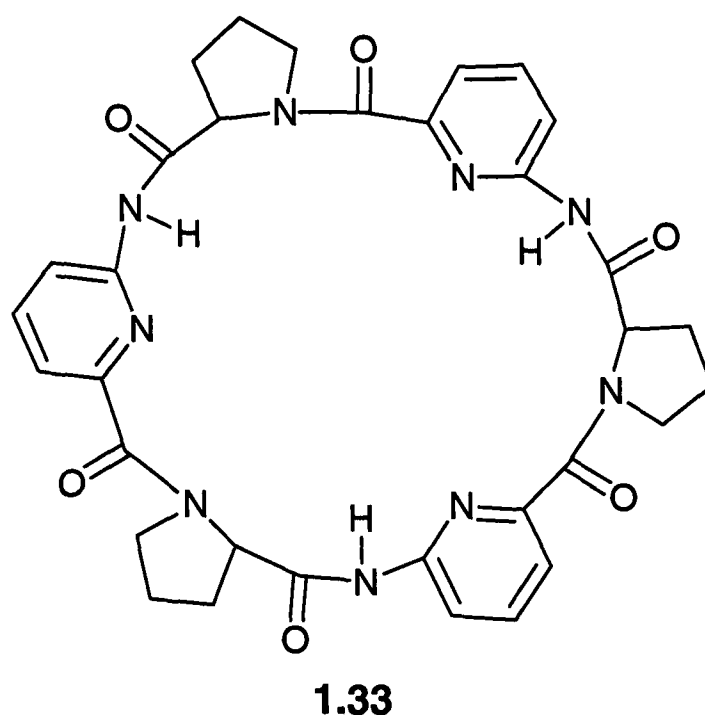


Figure 1.29: Cyclic peptide receptor **1.33**.

1.3.3 Neutral Lewis acidic hosts

Lewis acids, as electron pair acceptors, may be used in the complexation of anions. The first ligand to make use of Lewis acid-base interactions was organoboron compound **1.34** (Figure 1.30), reported by Shriver and Biallas in 1967, for which a chelate effect was observed in the binding of methoxide anions.⁹³ Subsequently Katz synthesised the more preorganised receptor

1.35 (Figure 1.30) which formed strong complexes with hard, electron rich anions such as hydride and fluoride.⁹⁴

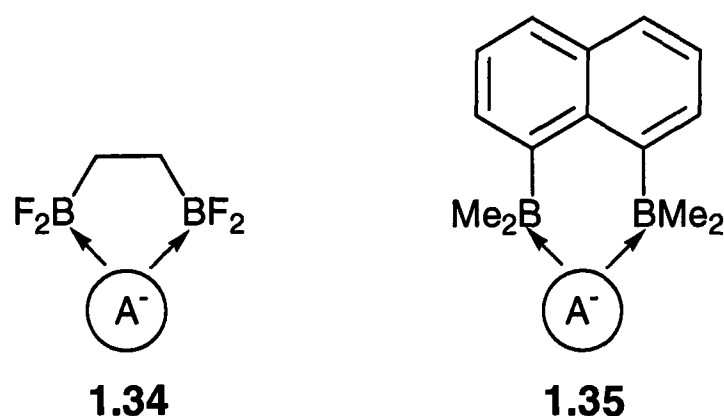


Figure 1.30: Organoboron anion receptors **1.34** and **1.35**.

Newcomb and co-workers have made extensive use of organotin macrocycles and cryptands for anion recognition.⁹⁵ Receptor **1.36** (Figure 1.31) encapsulates halide anions in a 1:1 stoichiometry and binds fluoride five times more strongly than chloride in chloroform solution.⁹⁶

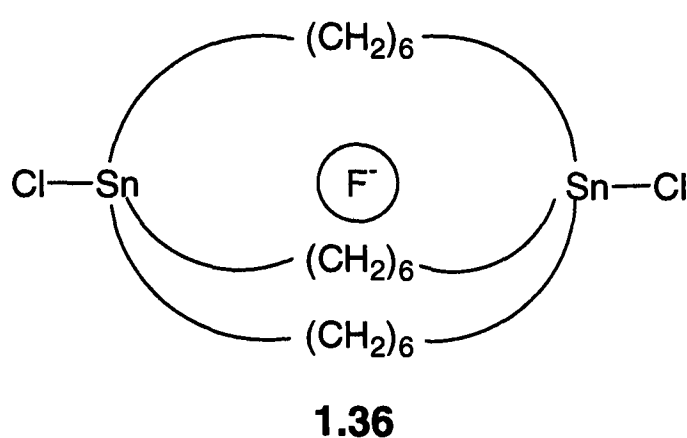


Figure 1.31: Organotin cryptand **1.36** encapsulating a fluoride anion.

Hawthorne and his research group have assembled organomercury anion receptors such as **1.37** (Figure 1.32).⁹⁷ The macrocyclic receptor comprises four carborane clusters linked by linear mercury-carbon bonds, and its formation is templated by the presence of chloride anions. Crystallography reveals that chloride binds in the plane of the macrocycle equidistant from all four mercury atoms, whereas the larger iodide anion binds in a 2:1 stoichiometry

above and below the plane. The electron-withdrawing nature of the carboranes enhances the Lewis acidity of the mercury centres, making such compounds good receptors for electron-rich guests. Substitution of the carborane cages allows these mercurocarborands to be tailored for a variety of applications including catalysis and ion-sensing.⁹⁸

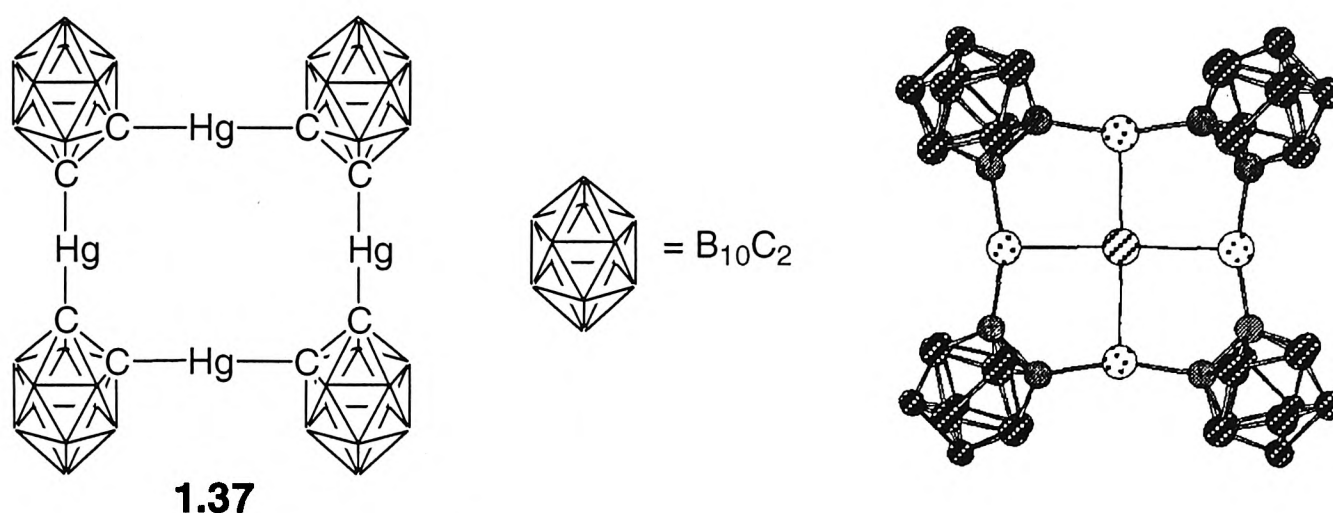


Figure 1.32: Organomercury macrocycle **1.37** and the crystal structure of the chloride complex.

Lewis acid centres have also been used in conjunction with secondary amides to create anion receptors. Reinhoudt and co-workers developed receptors such as **1.38** (Figure 1.33) containing a uranyl salene group which binds dihydrogen phosphate in DMSO solution with a relatively high stability constant ($K = 1500 \text{ M}^{-1}$).⁹⁹

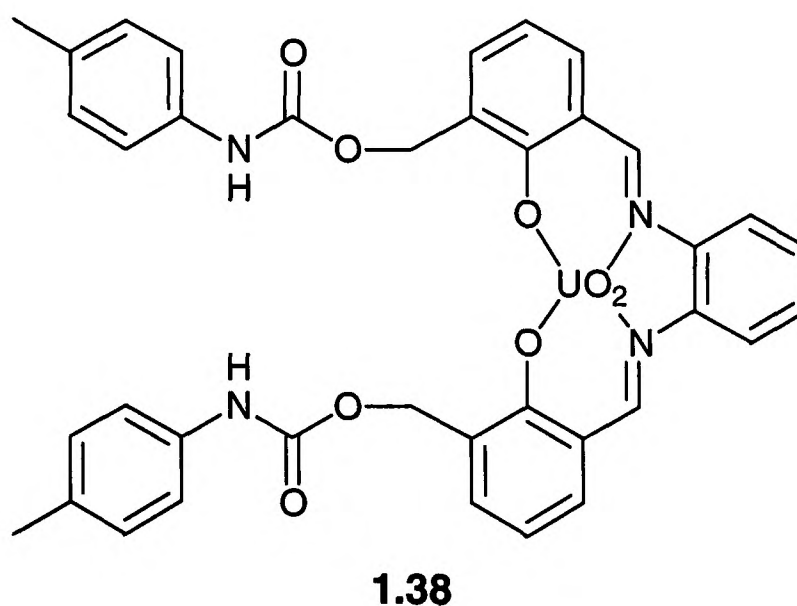


Figure 1.33: Uranyl salene receptor **1.38**.

1.3.4 Anion Sensors

Chemical sensors are molecules that undergo a measurable change in some physical property upon binding a guest species. The current interest in sensor technology has been driven by their potential medical and environmental applications. The incorporation of electrochemically or optically active groups into the structure of receptors has produced a variety of sensors which can report the binding of both charged and neutral species. Some examples of electrochemical, UV-VIS spectroscopic and luminescent sensors for anionic guests are given in the following sections.

1.3.4.1 Electrochemical anion sensors

Electrochemical anion recognition is an expanding research area at the interface of electrochemistry and supramolecular chemistry.¹⁰⁰ Receptors based on a bis(thiourea) cleft molecule have been incorporated into ion-selective electrodes to produce chloride-selective sensors¹⁰¹ and lipophilic uranylsalophane derivatives have been used in chemically modified field-effect transistor membranes.¹⁰² This section, however, focuses on voltammetric electrochemical sensors consisting of a redox-active group coupled to a guest binding site, in which anion complexation-induced changes in the redox properties of the host can be detected by electrochemical techniques such as cyclic or square wave voltammetry.

The first anion sensor based on the redox-active cobaltocenium group was reported by Beer and Keefe in 1989¹⁰³ and since then a plethora of acyclic, macrocyclic and calixarene-based receptors containing amide-linked cobaltocenium moieties have been prepared.¹⁰⁴ Receptors incorporating ferrocene units appended with secondary amides have also proved popular for reporting anion recognition events.¹⁰⁵ For example, receptors **1.39** and **1.40** (Figure 1.34) electrochemically sense anions *via* cathodic perturbations in the redox couple of the respective metallocene groups.

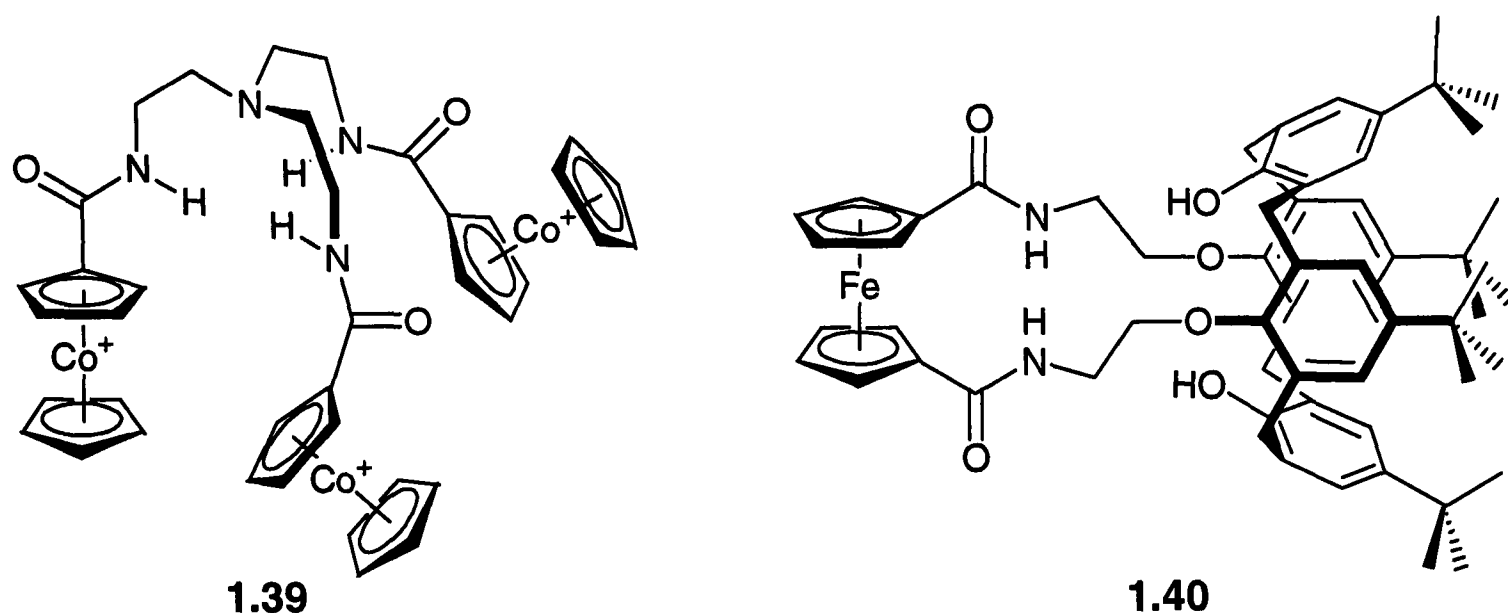
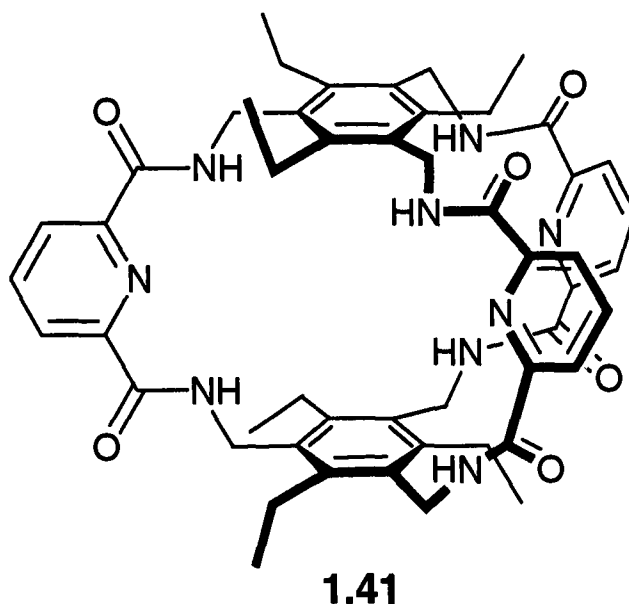


Figure 1.34: Cobaltocenium **1.39** and ferrocene **1.40** amide-containing anion sensors.

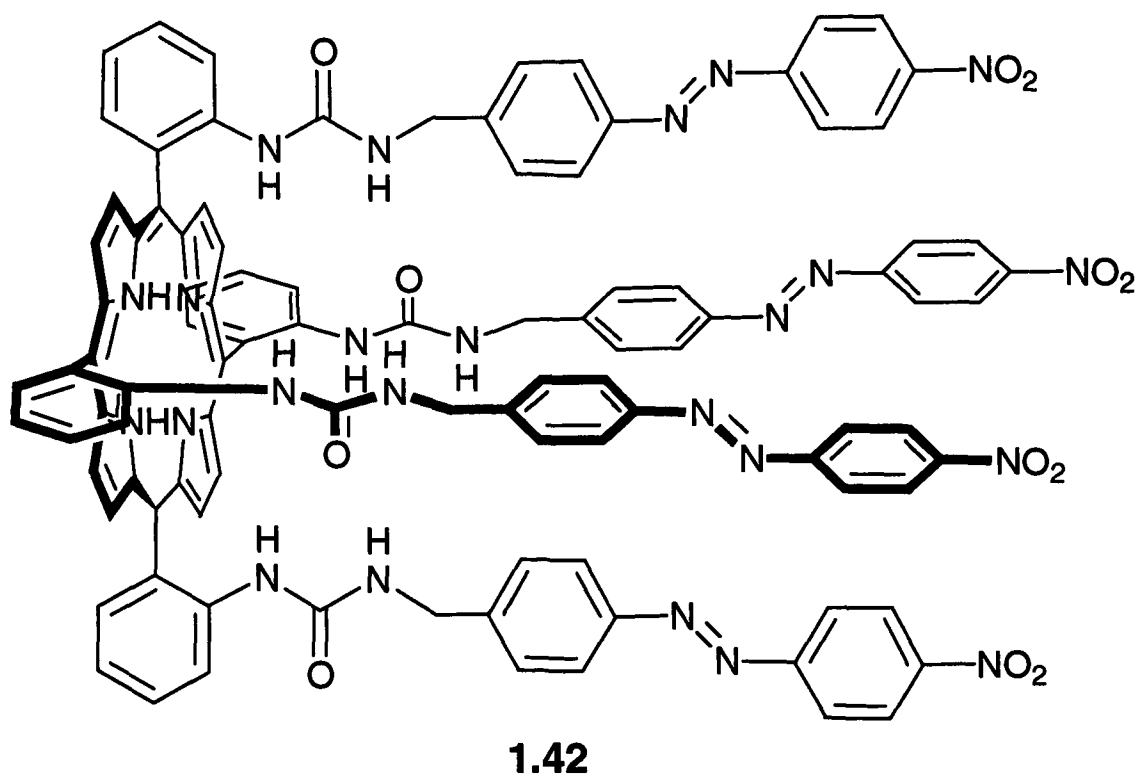
1.3.4.2 UV-VIS spectroscopic and colorimetric anion sensors

Chromogenic anion sensors function in one of two general ways.¹⁰⁶ The binding of an anion may induce changes in the electronic properties of a chromophoric moiety coupled to the binding site, or may cause the displacement of a chromophore from the binding site, thereby altering the UV-VIS spectroscopic properties of the system.

Anslyn and co-workers¹⁰⁷ developed a method of sensing anions using the C₃ symmetric receptor **1.41**, based on a 1,3,5-trisubstituted triethylbenzene scaffold (Figure 1.35).¹⁰⁸ The receptor binds anionic dyes such as methyl red, and upon addition of anions the equilibrium between the receptor and the dye is perturbed resulting in large changes in absorbance as measured by UV-VIS spectroscopy. Receptor **1.41** forms strong complexes with the C₃ symmetrical nitrate anion, typically a weakly coordinating species.

Figure 1.35: UV-VIS spectroscopic anion sensor **1.41**.

Hong and co-workers have recently reported receptor **1.42**, a porphyrin derivative with urea hydrogen bond donors and chromophoric units (Figure 1.36).¹⁰⁹ Solutions of the receptor undergo dramatic colour changes upon addition of fluoride, acetate and dihydrogen phosphate anions in acetonitrile solutions, while addition of other halide anions produces negligible colour change.

Figure 1.36: Colorimetric anion sensor **1.42**.

1.3.4.3 Luminescent anion sensors

Sensitive and selective sensors can be developed by coupling a guest binding site to a fluorescent unit.¹¹⁰ Beer has developed a number of fluorescent anion sensors based on acyclic, macrocyclic and calix[4]arene functionalised ruthenium(II) tris(bipyridyl) compounds¹¹¹ such as **1.43** (Figure 1.37).¹¹² Luminescence studies in DMSO solution revealed a blue shift in the MLCT emission band with significant intensity enhancement upon addition of chloride anions, but no response to dihydrogen phosphate. Analysis of the titration data indicated that receptor **1.43** formed extremely stable 1:1 complexes with chloride anions while dihydrogen phosphate anions were not bound at all.¹¹³ This remarkable selectivity may be attributed to the preorganisation of the macrocycle. Interestingly, increasing the size of the macrocyclic cavity by two or more methylene units dramatically reverses the trend in anion selectivity.

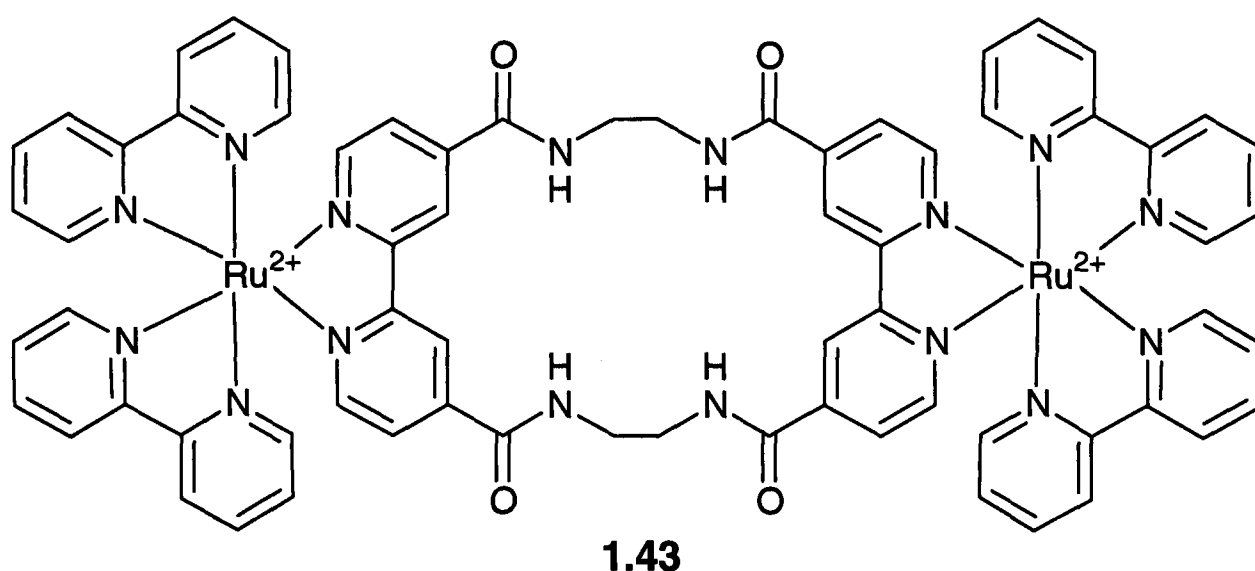


Figure 1.37: Chloride-selective ruthenium(II) tris(bipyridyl) based anion sensor **1.43**.

Parker and co-workers have studied a range of lanthanide complexes of ligands such as **1.44** (Figure 1.38), designed to sense various bioactive oxyanions in aqueous solution.¹¹⁴ The luminescent excited states of lanthanide complexes are highly sensitive to changes in the coordination environment of the lanthanide(III) ion. For example, the ytterbium complex of heptadentate ligand **1.44** can sense the binding of carboxylate anions in aqueous solution *via*

the enhancement of luminescence intensity caused by the displacement of two coordinated water molecules by the carboxylate anion.

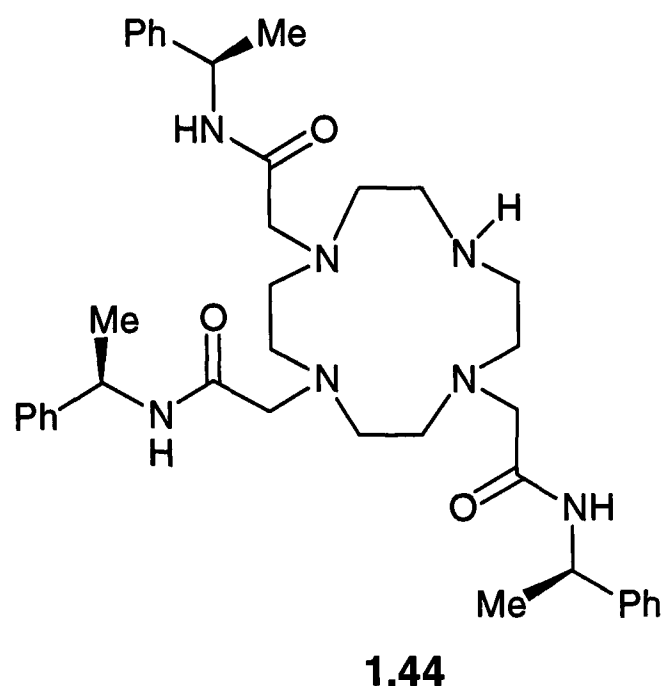


Figure 1.38: Lanthanide complexes of ligand **1.44** are luminescent anion sensors.

1.4 Ion-Pair Receptors

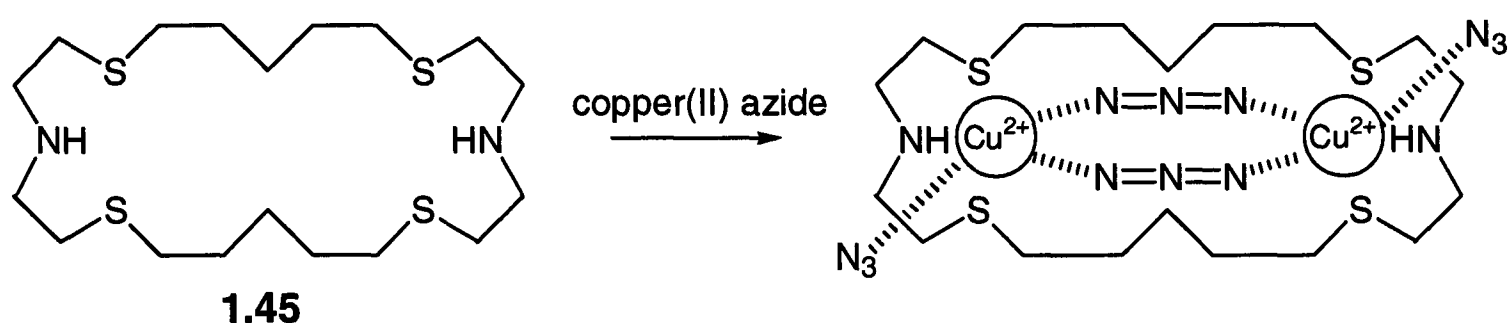
The previous two sections outlined the approaches taken towards binding cations and anions in separate receptor molecules. This section describes the development of heteroditopic receptors for the simultaneous complexation of both anionic and cationic guests.

1.4.1 Cascade complexes

These receptors are designed to bind two or more metal cations which are then able to bind anions between themselves and within the recognition cavity. The overall species is known as a cascade complex.

Lehn and his research group synthesised a range of receptors suitable for cascade complex formation. For example, macrocyclic host **1.45** can bind two copper(II) cations, thereby creating a positively charged ellipsoidal cavity ideally suited to binding two linear azide anions (Scheme 1.1).¹¹⁵ Azide guests bridge between the copper(II) centres, whereas smaller

spherical chloride anions coordinate separately to each metal cation. This cascade complex illustrates how a host molecule can control the relative positions of metal ions and hence manipulate the selectivity of subsequent anion binding. Interestingly, this cascade binding motif is analogous to the way in which some copper-based enzymes bind azide substrates.



Scheme 1.1: Receptor **1.45** and the cascade complex with copper(II) azide.

More recently, Fabbrizzi and co-workers developed a fluorescent chemosensor for amino acids which is selective for histidine.¹¹⁶ The coordination of two copper(II) ions by macrocycle **1.46** (Figure 1.39) enables the resulting complex to bind anions in a cooperative manner between the transition metal centres. Binding of the fluorescent indicator eosine-Y by the complex causes a complete quenching of emission. Subsequent addition of amino acids leads to the displacement of the indicator and an increase in emission intensity. The chemosensing ensemble is selective for histidine over other natural amino acids due to the preferential binding of the imidazole residue by the two copper(II) centres.

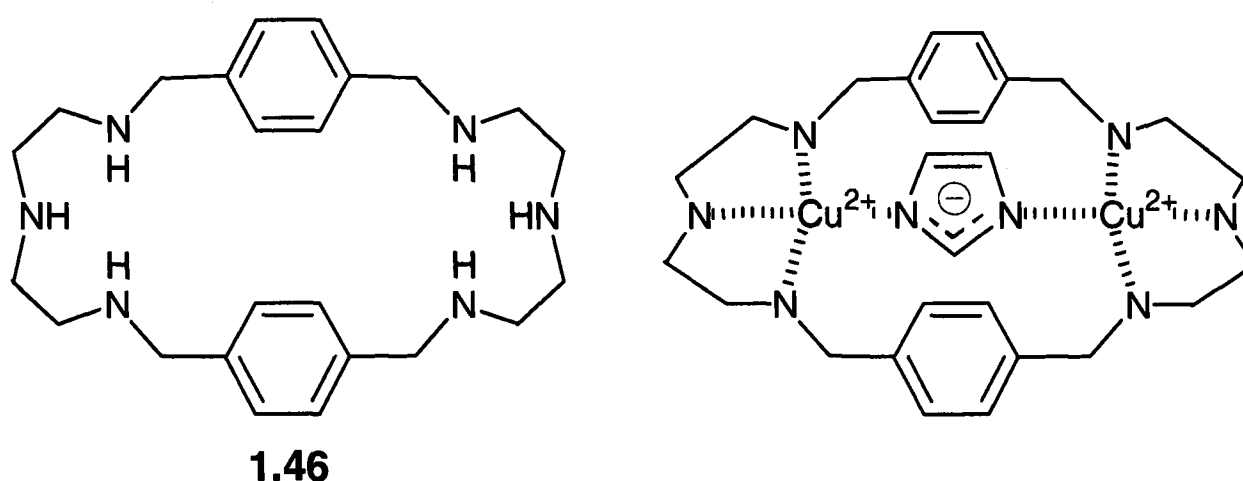


Figure 1.39: Macrocycle **1.46** and the copper(II) complex binding a bridging imidazolate anion.

Receptor **1.47** binds phosphate anions and catalyses the intramolecular hydrolysis of phosphodiester (Figure 1.40).¹¹⁷ This indicates the ability of cascade complexes to model not only the recognition properties of enzymes such as phosphatases but also their catalytic action.

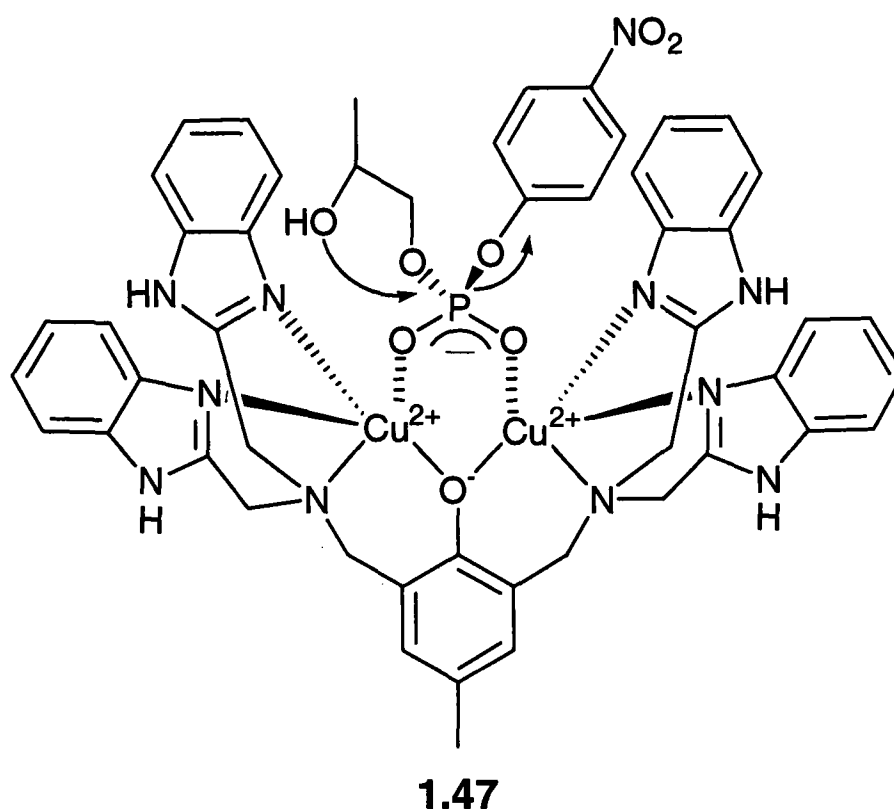
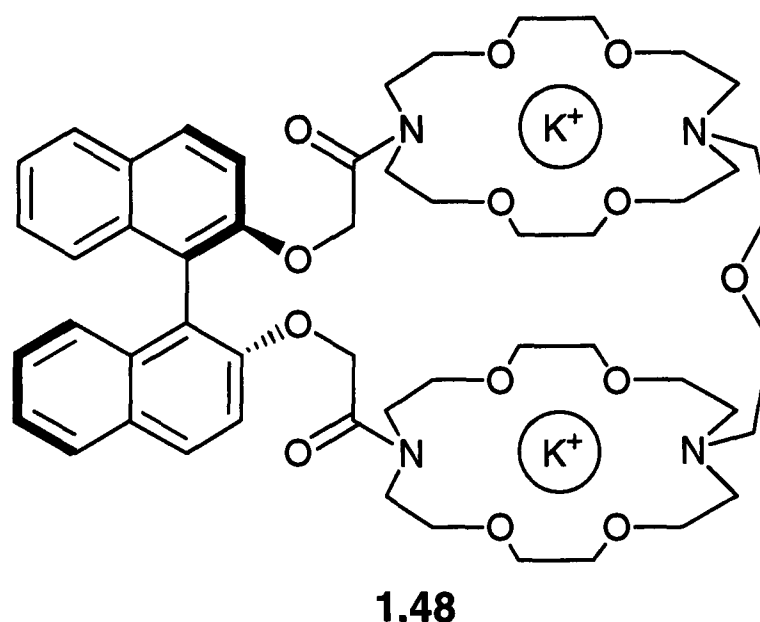


Figure 1.40: Cascade complex **1.47** catalysing the hydrolysis of a phosphodiester.

A cascade complex using non-coordinate interactions has also been reported.¹¹⁸ Receptor **1.48** binds two alkali metal cations (Figure 1.41) and is subsequently capable of co-binding an anionic substrate through electrostatic interactions. In addition, the presence of the chiral binaphthyl unit was shown to enhance the binding of one optical isomer of mandelate over the other.

Figure 1.41: Chiral receptor **1.48**.

1.4.2 Ion-pair receptors

The design and synthesis of new heteroditopic ligands for the simultaneous complexation of anionic and cationic guest species (ion-pair recognition) is a new, emerging and topical field of coordination chemistry.¹¹⁹ These multisite receptors are of significant interest for the selective extraction and transport of toxic, non-toxic and radioactive metal salt pollutants across lipophilic membranes, and their study is relevant to understanding biological membrane transport systems.¹²⁰ In addition, ion-pair receptors are capable of coordinating important biological molecules such as zwitterionic amino acids and peptides.¹²¹

Ion-pair receptors to date have been based on hydrogen bonding, positively charged or Lewis acidic groups to coordinate the anion, covalently linked to crown ethers or modified calixarenes to complex the cation. These ditopic host molecules often exhibit cooperative and allosteric effects whereby the association of one ion influences the binding affinity of the counter ion. The cooperativity can be positive or negative depending upon whether the binding affinity is respectively enhanced or reduced.¹²² Cooperative behaviour can result from several factors, such as through-space or through-bond electrostatic interactions between bound ion-pairs or conformational changes induced by binding.

The study of ion-pair receptors was established by Reetz who synthesised receptors such as **1.49** (Figure 1.42), containing both a crown ether group for cation binding and a Lewis acidic boron for anion binding.¹²³ This receptor is capable of dissolving solid potassium fluoride in dichloromethane solution, and both heteronuclear NMR and crystallography confirmed the ditopic mode of binding. Importantly, receptor **1.49** displays cooperative ion-pair binding, as it proved a more efficient receptor molecule than a simple 1:1 mixture of crown ether and boronic acid.

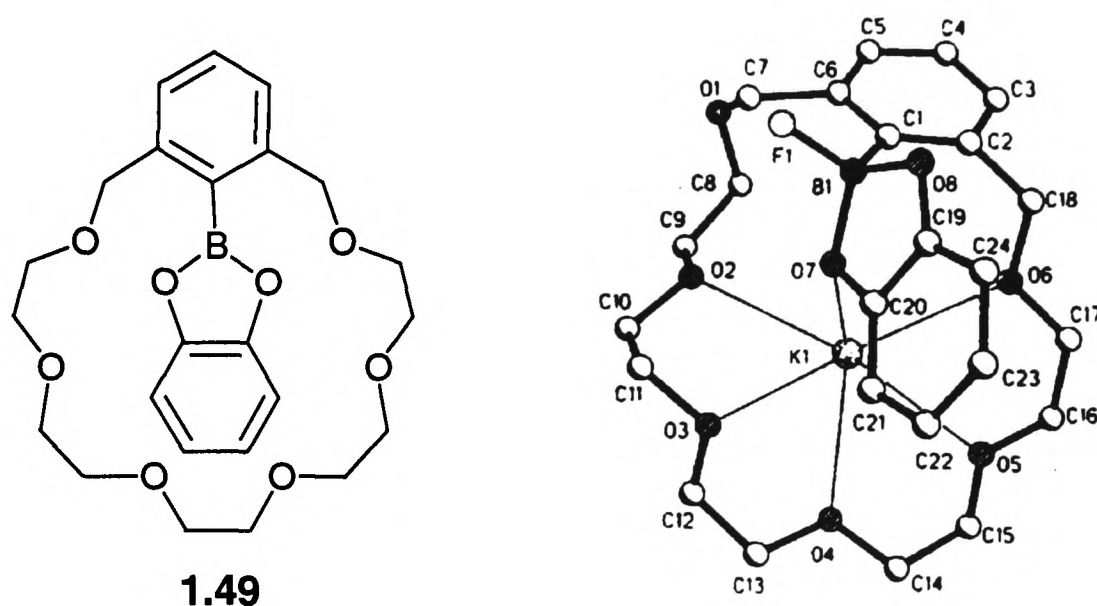


Figure 1.42: Ion-pair receptor **1.49** and the crystal structure of the potassium fluoride complex.

Reinhoudt and co-workers adapted their uranyl salene system for ion-pair recognition, synthesising receptors **1.50** and **1.51** (Figure 1.43).^{124, 125} These hosts employ the Lewis acidic uranyl group and hydrogen bonding amide functionalities to complex the anion in combination with crown ether or modified calixarene sites to bind the cation. The bis(benzo[15]crown-5) unit of receptor **1.50** is designed to form a sandwich complex in the presence of a potassium cation, thereby preorganising the two amide groups for cooperative anion binding. Solid / liquid extraction experiments and FAB mass spectrometry demonstrated the ion-pair binding of KH_2PO_4 by receptor **1.50**. The related receptor **1.51**

employs a sodium-selective calix[4]arene tetra-ester and is therefore a ditopic receptor for NaH_2PO_4 .

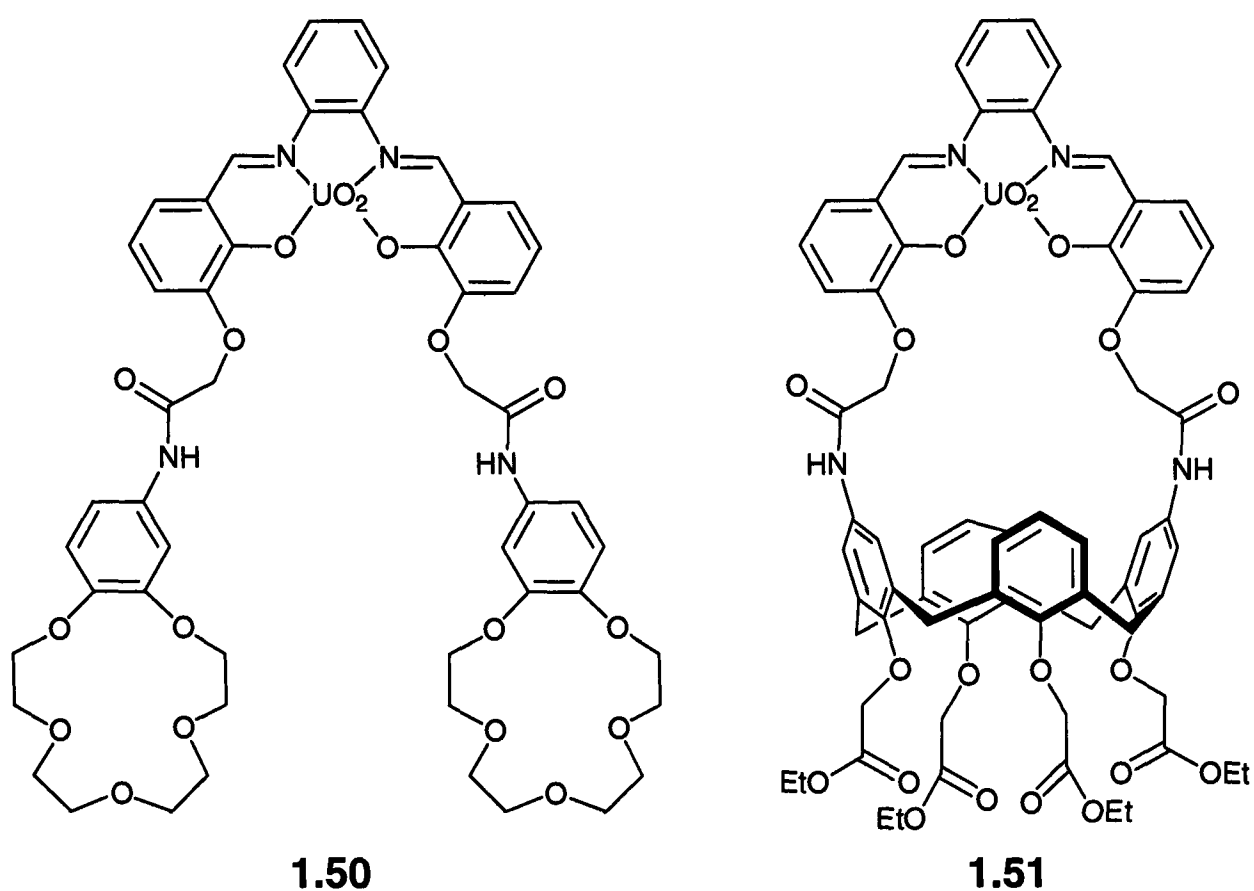
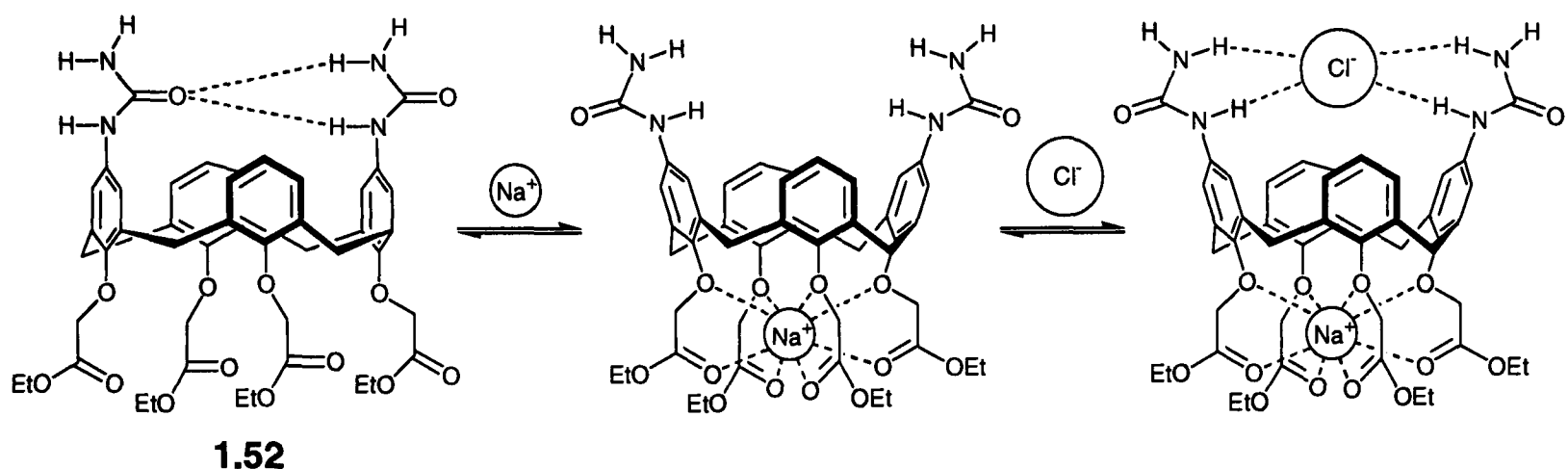


Figure 1.43: Uranyl salene based ion-pair receptors **1.50** and **1.51**.

Another example of a ditopic receptor based on a calixarene framework is receptor **1.52** which displays elegant cation-anion cooperativity (Scheme 1.2).¹²⁶ The receptor consists of a calix[4]arene with the sodium-selective tetra-ester group at the lower-rim and anion binding urea groups at the upper rim. In chloroform solution, intramolecular hydrogen bonding of the urea groups means that anion binding is disfavoured ($K < 10 \text{ M}^{-1}$). However sodium cation complexation causes a contraction of the lower-rim which forces the upper rim urea moieties apart making them available for binding anionic species such as chloride ($K = 10000 \text{ M}^{-1}$ in chloroform). This receptor exhibits a heterotopic allosteric effect, whereby cation coordination induces a structural change essential for anion binding.



Scheme 1.2: Ion-pair receptor **1.52** exhibits positive cooperative binding of sodium chloride.

A simple illustration of the combination of hydrogen bonding and crown ether sites in ion-pair recognition has been reported by Teramae and co-workers who synthesised the thiourea crown ether **1.53** (Figure 1.44).¹²⁷ ^1H NMR studies showed an enhancement in anion binding when sodium was located in the crown ether. The cooperative effect of sodium binding on anion coordination may be ascribed to two factors. Firstly, the hydrogen bond donor ability of the thiourea group is increased in $\text{Na}^+\cdot\mathbf{1.53}$ relative to **1.53**, due to the electron withdrawing nature of the sodium ion. Secondly, the bound ions experience mutual electrostatic attraction due to their proximity in the complex.

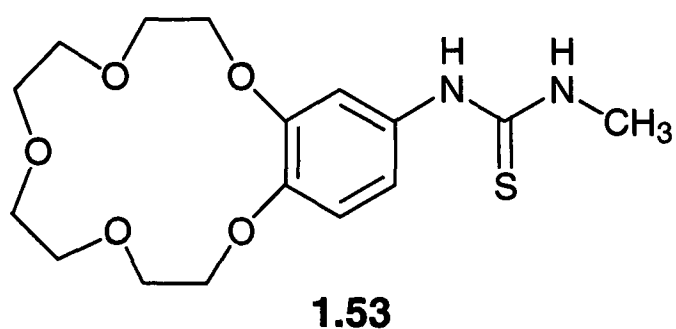


Figure 1.44: A simple thiourea crown ether ion-pair receptor **1.53**.

Beer and Dent have synthesised a heteroditopic rhenium(I) bipyridyl bis(benzo[15]crown-5) receptor **1.54** (Figure 1.45) which complexes potassium chloride ion-pairs in a cooperative manner.¹²⁸ In the absence of potassium cations, the receptor is selective for dihydrogen phosphate ($K = 205 \text{ M}^{-1}$) over chloride ($K = 55 \text{ M}^{-1}$), whereas following the formation of the intramolecular sandwich complex the reverse selectivity of chloride ($K = 300 \text{ M}^{-1}$) over

dihydrogen phosphate ($K = 35 \text{ M}^{-1}$) is exhibited in acetonitrile solution. The potassium-induced cooperativity of chloride binding may be a consequence of favourable electrostatic attraction and conformational effects, wherein the sandwich complex results in a pseudo-macrocyclic preorganised structure suitable for chloride binding.

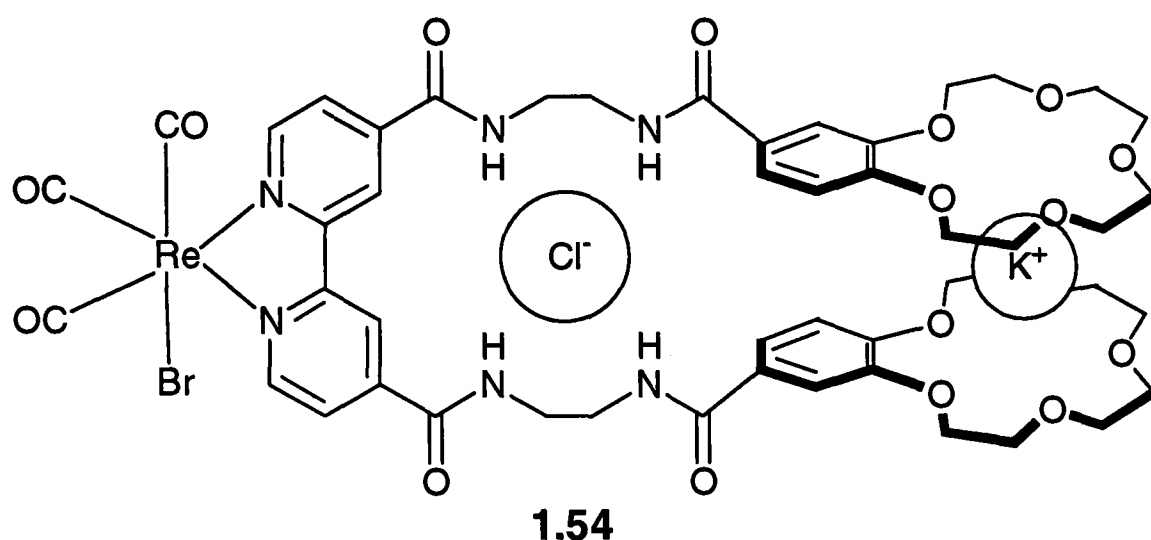


Figure 1.45: Ion-pair receptor **1.54** cooperatively binding potassium chloride.

Recently, Smith and co-workers combined an azacrown ether and an isophthalic acid based amide cleft receptor to produce a host capable of recognising potassium chloride contact ion-pairs.¹²⁹ ^1H NMR titrations revealed that the association constant of receptor **1.55** (Figure 1.46) with chloride in d_6 -DMSO is enhanced from 35 M^{-1} to 460 M^{-1} in the presence of one equivalent of potassium tetraphenylborate.

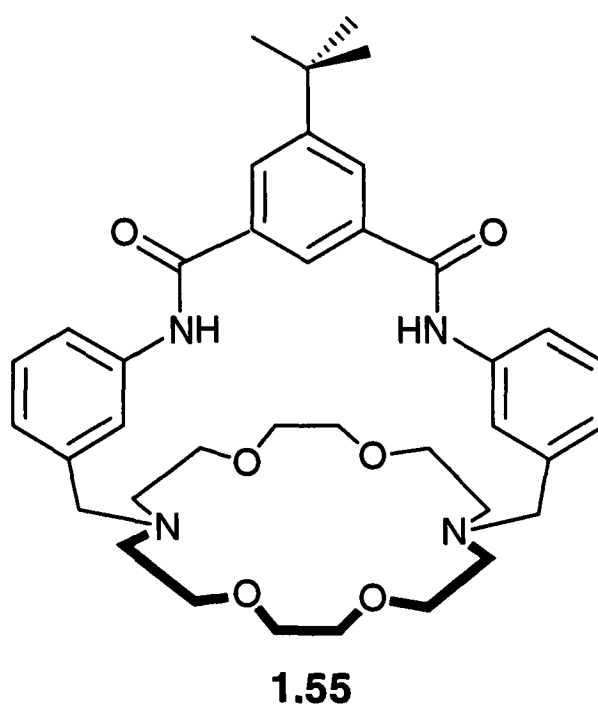
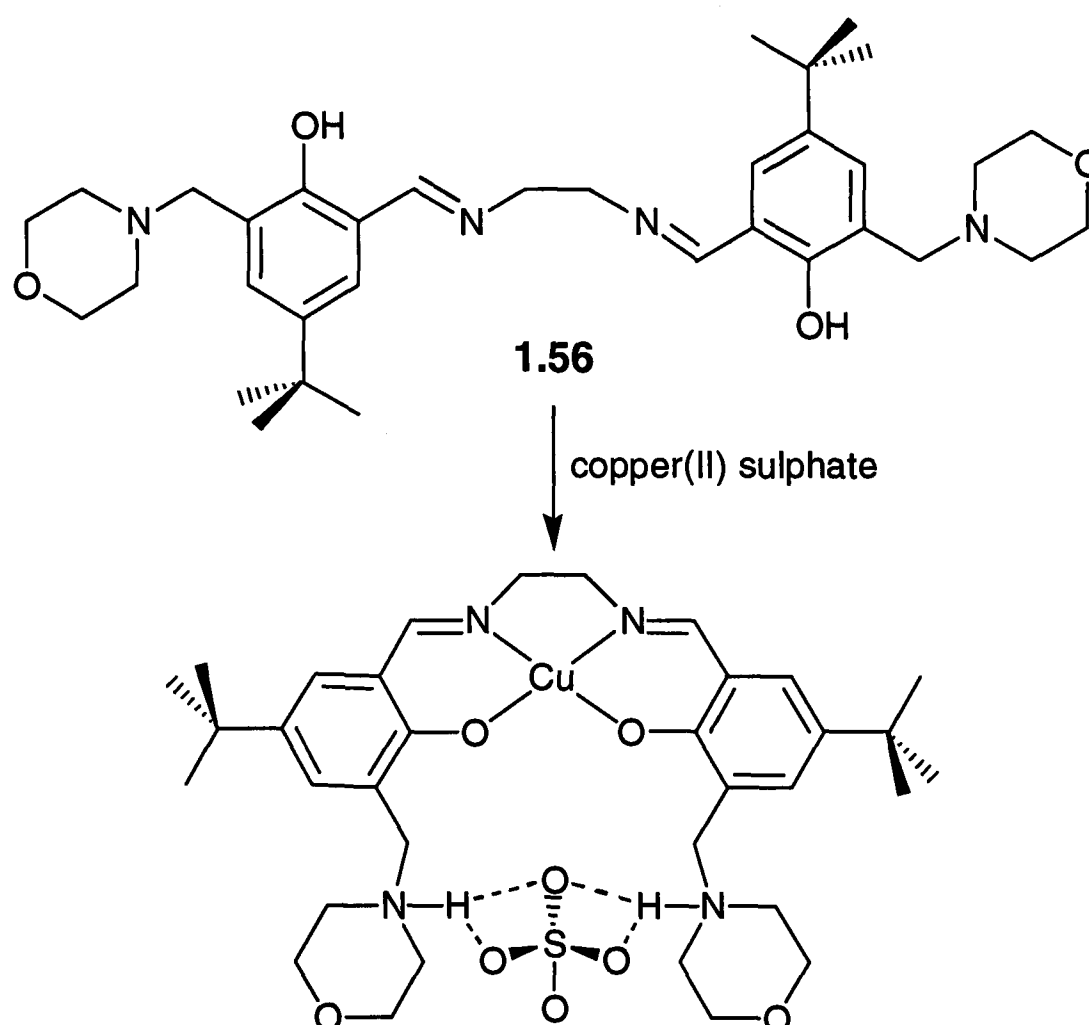


Figure 1.46: Receptor **1.55** recognises potassium chloride ion-pairs.

As mentioned previously, the study of ion-pair receptors is of particular relevance to the selective extraction and transport of metal salts. Tasker and co-workers have synthesised ditopic receptors for the extraction of transition metal salts (such as copper¹³⁰ and nickel¹³¹ sulphates) from aqueous to organic solvents for application in industrial metal separation and purification processes. A range of tetradentate H₂salen-type molecules bearing tertiary amine groups *ortho* to the phenolic OH-groups such as ligand **1.56** were synthesised. Incorporation of a metal ion such as copper(II) into the salen binding site preorganises the morpholinium groups for complexation of sulphate anions (Scheme 1.3). The key to the performance of these ditopic receptors is that the metal salt is bound to the zwitterionic form of the ligand generated by the transfer of the phenolic protons from the metal binding site to the pendant amine groups, thus creating a dipositive cavity wherein the anion is bound by a combination of electrostatic interactions and favourable hydrogen bonding effects.



Scheme 1.3: Copper(II) sulphate binding by ligand **1.56**.

1.4.3 Ion-pair receptors for zwitterions

Zwitterion recognition is of significant biological importance. Receptor **1.57** (Figure 1.47), synthesised by de Mendoza and co-workers, demonstrates a sophisticated spatial arrangement of various subunits for the selective extraction of amino acids with aromatic side chains from aqueous solution into dichloromethane.¹³² The carboxylate anion is bound by the guanidinium unit, the protonated amine by the azacrown ether group, and π - π interactions between the phenyl side chain of the amino acid and the naphthalene unit of the receptor further enhances the strength and selectivity of complex formation. Although a range of similar receptors have been studied,¹³³ optically-active host **1.57** demonstrates the best chiral selectivity, achieving an enantiomeric excess of *L*-amino acids over *D*-amino acids of 80 % in extraction studies and transport across model membranes.

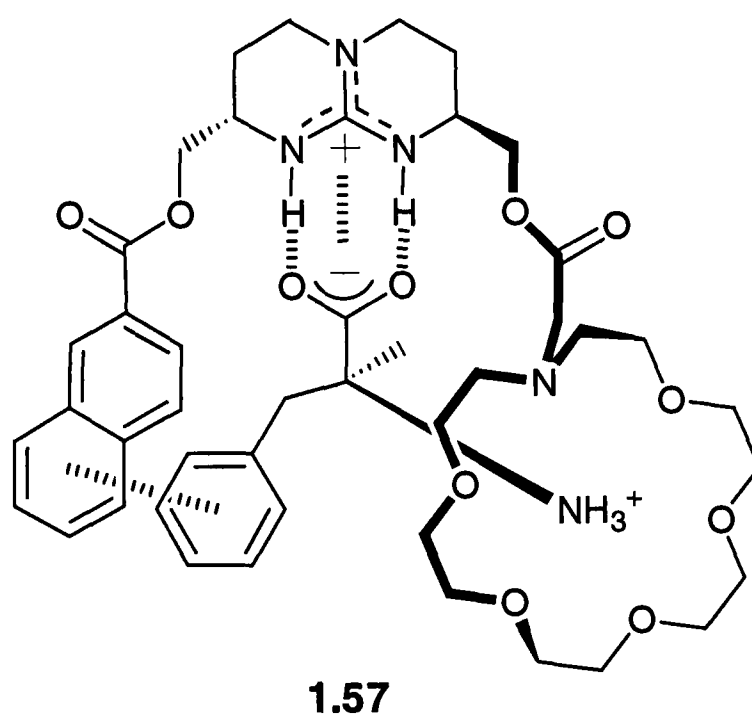


Figure 1.47: Zwitterionic receptor **1.57** complexing a complementary amino acid.

1.5 Self-Assembly

In order to complete this introduction to supramolecular chemistry, the area of self-assembly should be briefly mentioned. Self-assembly involves utilising intermolecular forces to reversibly assemble molecular building blocks into novel supramolecular architectures.

Nature provides many examples of the formation of complex structures through the self-assembly of simple molecules. For example, the tobacco mosaic virus consists of an RNA strand and 2130 protein subunits.¹³⁴ The proteins spontaneously assemble themselves around the RNA strand *via* non-covalent forces to form the virus superstructure.

Various non-covalent forces have been exploited in the formation of self-assembled products. For example, hydrogen bonding interactions¹³⁵ have been used to create assemblies such as the hexameric superstructure shown in Figure 1.48,¹³⁶ the formation of which was confirmed by NMR and crystallographic studies. It is held together by pairs of complementary acceptor-acceptor-donor and donor-donor-acceptor hydrogen bonding arrays at an angle of 120° to each other.

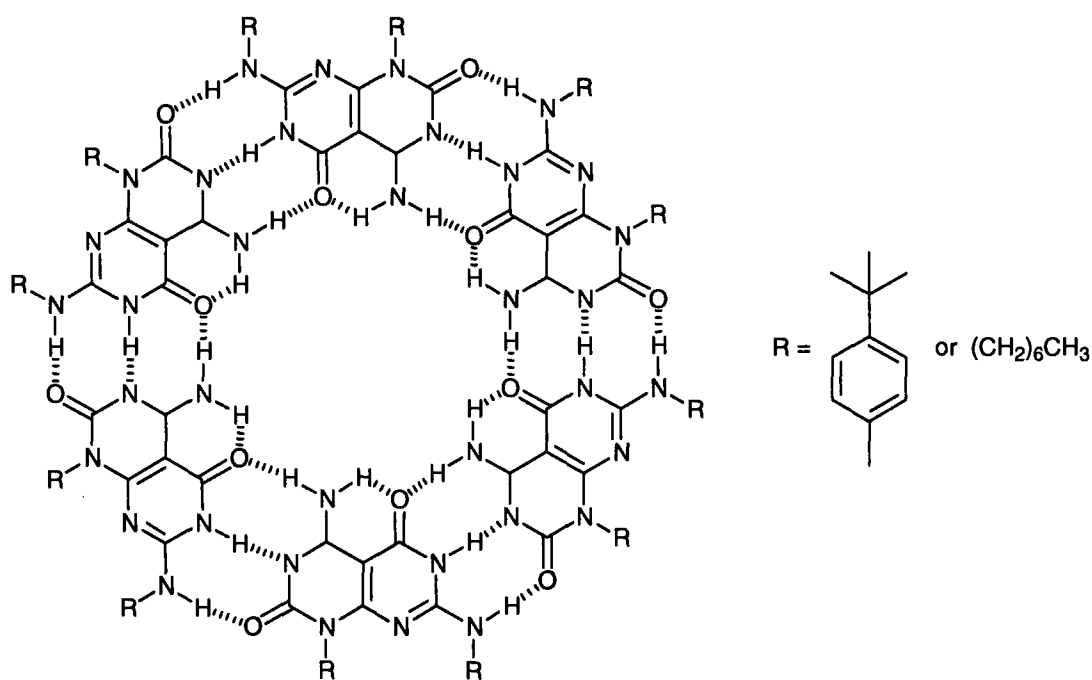
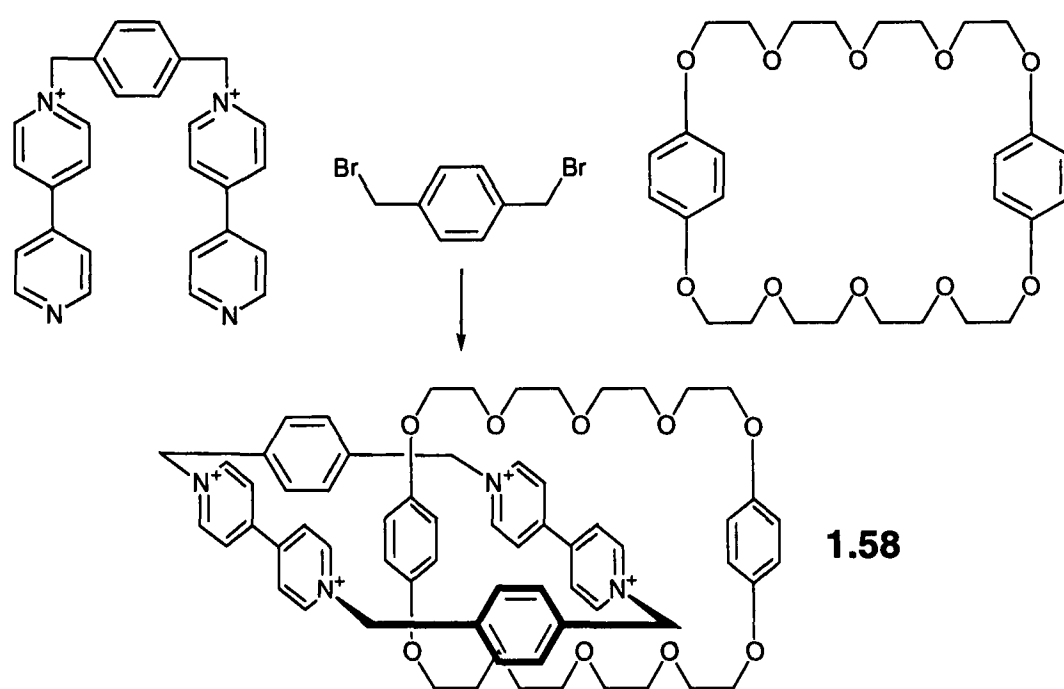


Figure 1.48: A hexameric hydrogen bonded assembly.

Combinations of hydrogen bonding, electrostatic and π - π stacking interactions have been used to associate molecular components for the formation of rotaxanes¹³⁷ and catenanes.¹³⁸ For example, Stoddart and co-workers synthesised the [2]catenane **1.58** from bis(paraphenylene)-[34]crown-10, a pyridine compound and 1,4-bis(bromomethyl)benzene as shown in Scheme 1.4.¹³⁹ The pyridine nitrogen acts as a nucleophile to create a tri-cationic

strand which threads through the macrocycle. The complex is stabilised by π - π stacking interactions between the electron rich crown ether macrocycle and the electron poor paraquat cation, together with hydrogen bonding interactions between the aromatic hydrogens of the paraquat and the oxygens of the crown ether ring. The [2]catenane is formed by a ring closing intramolecular nucleophilic reaction.



Scheme 1.4: Formation of [2]catenane **1.58**.

Of particular relevance to the work presented in Chapter Three of this thesis is metal-directed self-assembly,^{140, 141, 143} which will be discussed in the remainder of this section. Transition metals have been extensively used to direct the self-assembly of many interesting supramolecular architectures such as double and triple helices,¹⁴¹ knots,¹⁴² boxes¹⁴³ and grids.¹⁴⁴ The specific geometric requirements of coordination to transition metals have been employed to control the arrangements of ligands in these systems.

For example, Lehn has produced a series of polymetallic double helices based on poly-bipyridine ligand strands with ether linkages between each bipyridine subunit. In the presence of copper(I) ions, these ligands spontaneously assemble around the metal centres, producing helicates containing up to five copper(I) ions (Figure 1.49).¹⁴⁵ The copper(I) ions enforce a

tetrahedral coordination geometry resulting in the formation of the helical structure. Interestingly, if poly-bipyridine strands of different lengths are mixed together with copper(I) ions, only helices containing two strands of the same length are formed (self-recognition).¹⁴⁶

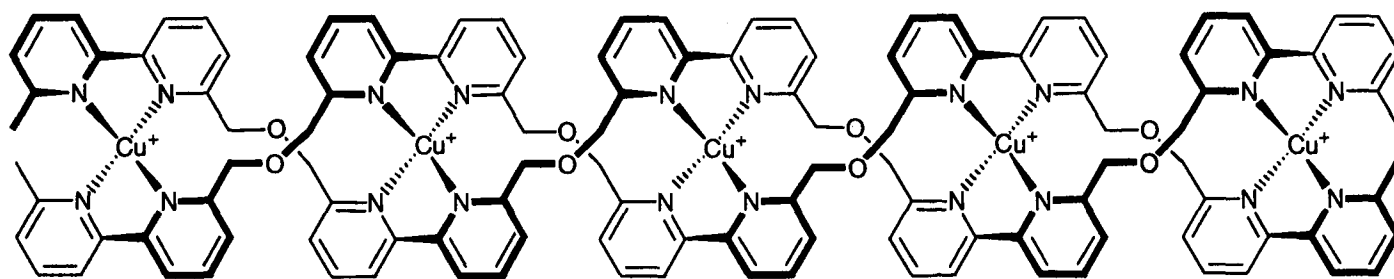
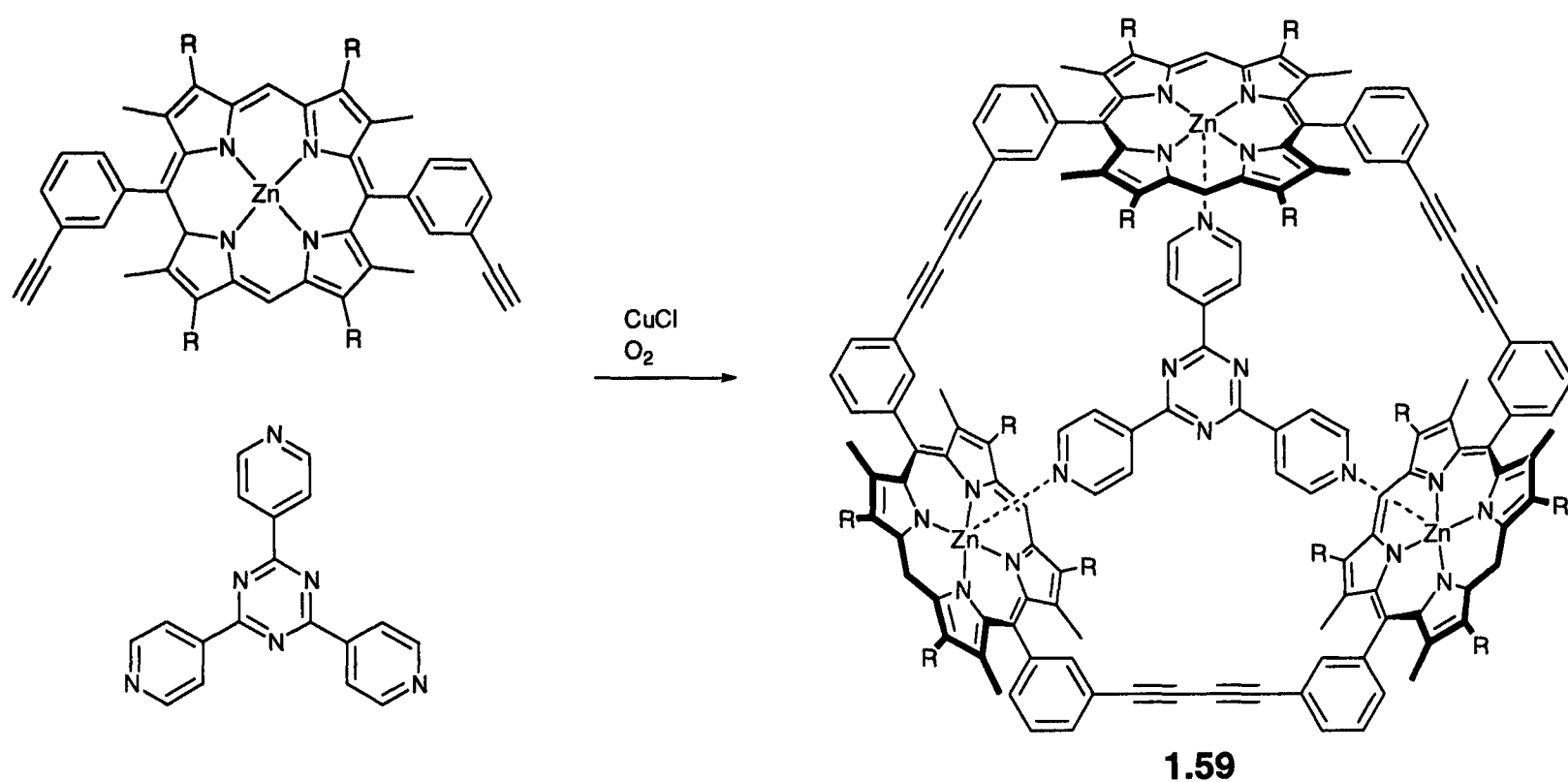
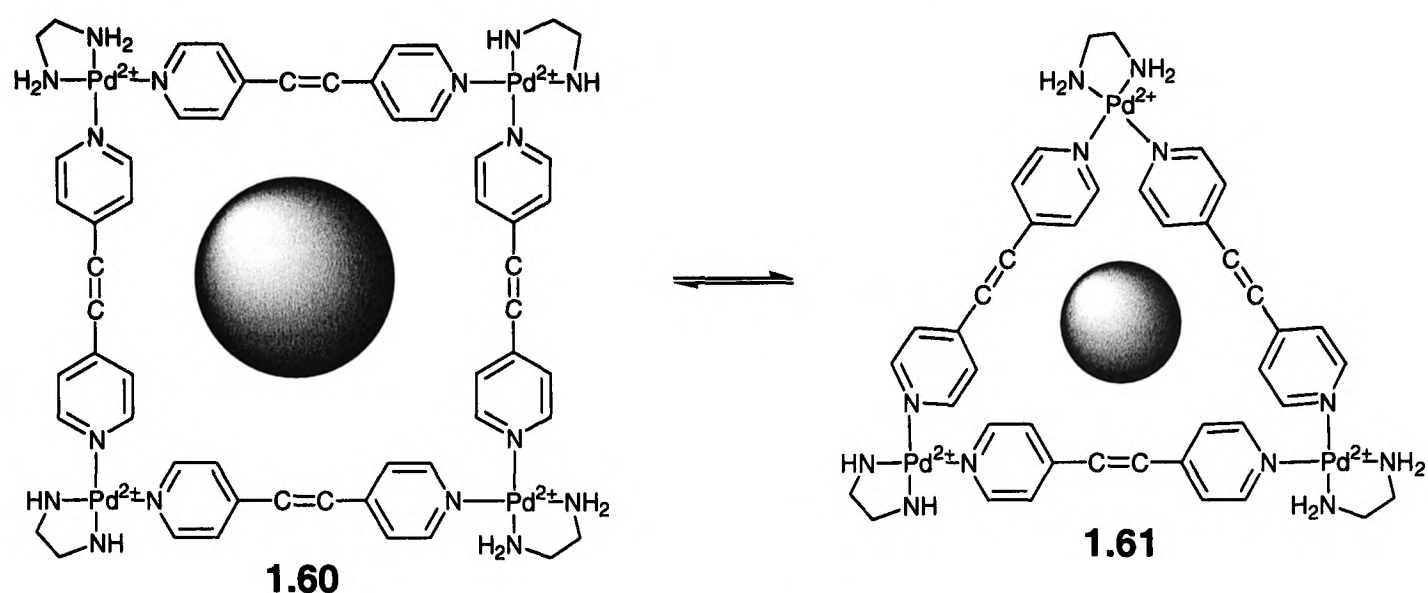


Figure 1.49: A pentametallic double helicate.

Sanders and co-workers have used self-assembly to create porphyrin-containing macrocycles. Addition of 1,3,5-tris(4-pyridyl)triazene to the dialkyne metalloporphyrin and subsequent copper catalysed coupling of the alkyne groups formed trimeric macrocycle **1.59** (Scheme 1.5).¹⁴⁷ Replacement of the triazene compound with bis-coordinating 4,4'-bipyridine led to the formation of the dimeric capsule, indicating that coordination of pyridine to the metal centres templates the formation of the macrocycle. The trimeric molecule **1.59** has been used as a molecular reaction vessel with Diels-Alder reactions being catalysed within the central cavity.¹⁴⁸

Scheme 1.5: Self-assembly of trimeric macrocycle **1.59**.

The combination of pyridine-based ligands and palladium(II) or platinum(II) salts has resulted in the self-assembly of a whole range of structures such as octahedrons, cones, tetrahedrons and hexahedrons.¹⁴⁹ For example, Fujita and co-workers reported the self-assembly of macrocyclic squares and triangles such as **1.60** and **1.61** (Scheme 1.6).¹⁵⁰ Reaction of $\text{Pd}(\text{en})(\text{NO}_3)_2$ with *trans*-1,2-bis(4-pyridyl)ethylene in water resulted in an equilibrium between the two macrocyclic species. Hong and co-workers showed that this equilibrium could be controlled by the addition of a guest *via* ‘induced-fit’ molecular recognition.¹⁵¹ Addition of a small guest (such as *p*-dimethoxybenzene) led to increased formation of triangle **1.61**, whereas addition of a large guest (such as 1,3-adamantanedicarboxylic acid disodium salt) caused the equilibrium to shift entirely in favour of square **1.60**.



Scheme 1.6: The equilibrium between square **1.60** and triangle **1.61** is influenced by the size of the guest species ('induced-fit' molecular recognition).

Hupp synthesised tetranuclear metallomacrocyclic **1.62** (Figure 1.50) which contains both rhenium(I) and palladium(II) metal centres.¹⁵² Addition of perchlorate anions to acetonitrile solutions of **1.62** caused an increase in the luminescence intensity, presumably by inclusion of the anion in the molecular cavity. This demonstrates the possible exploitation of metallocyclophanes in the development of molecular sensing devices.

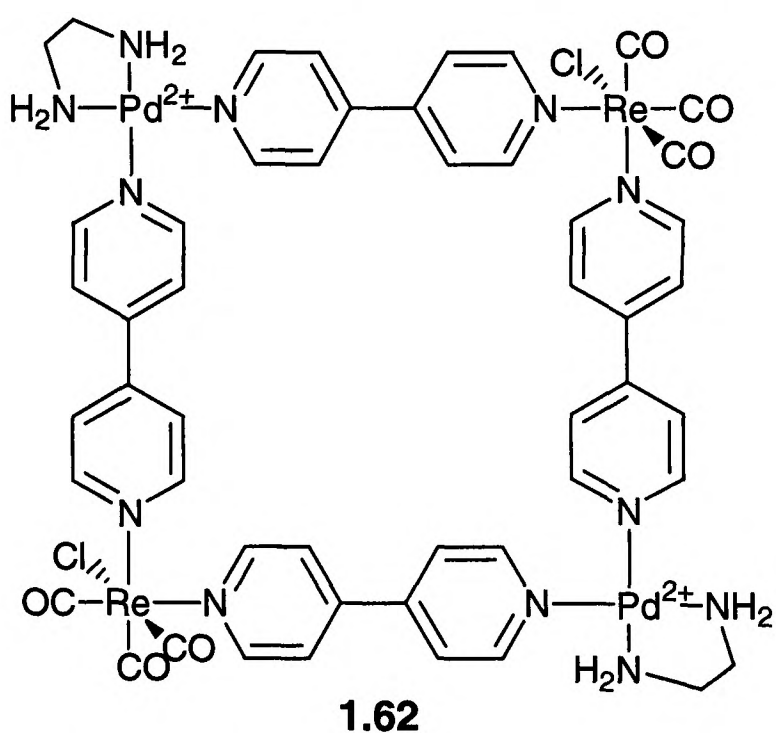
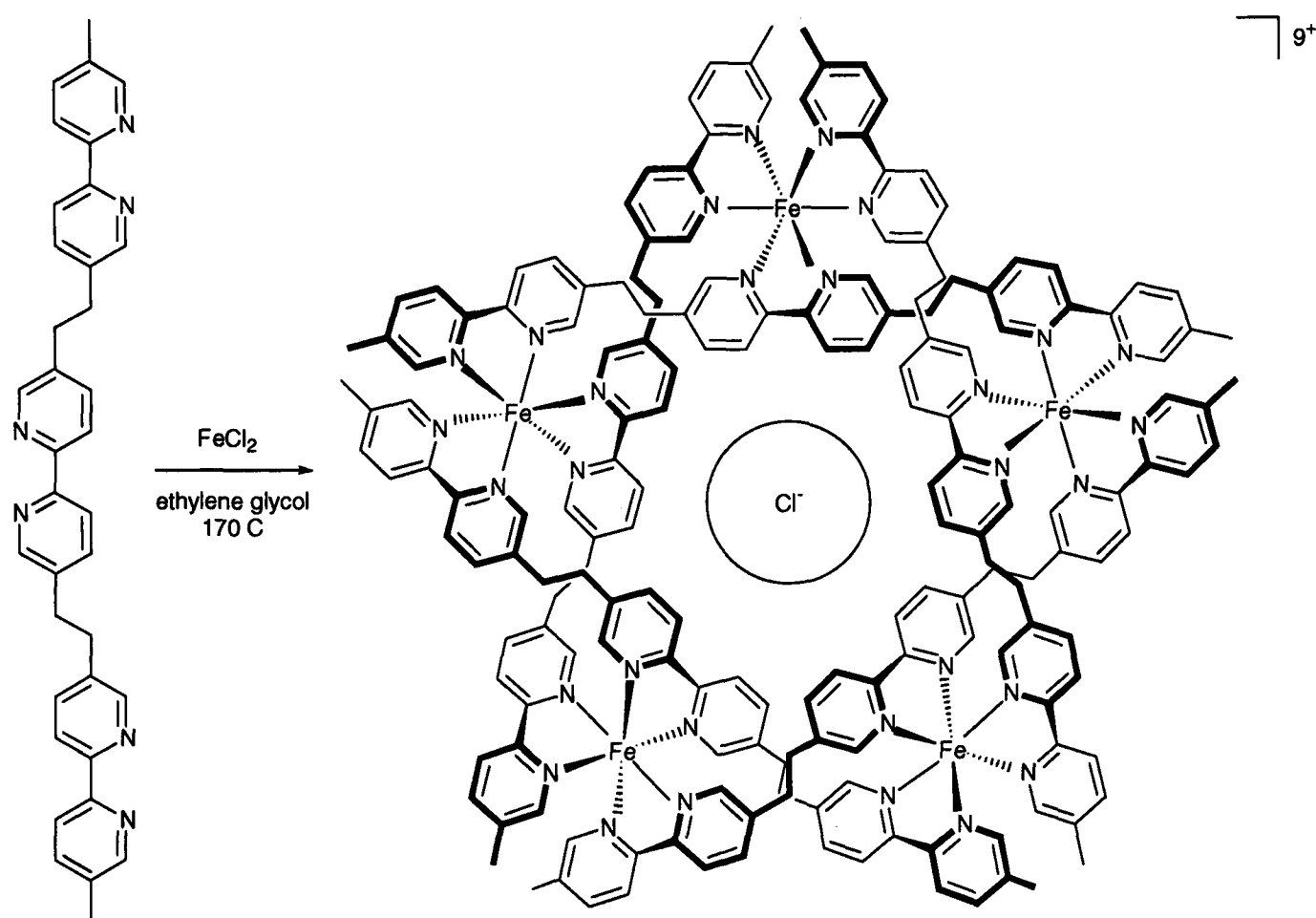


Figure 1.50: Metallomacrocyclic **1.62**.

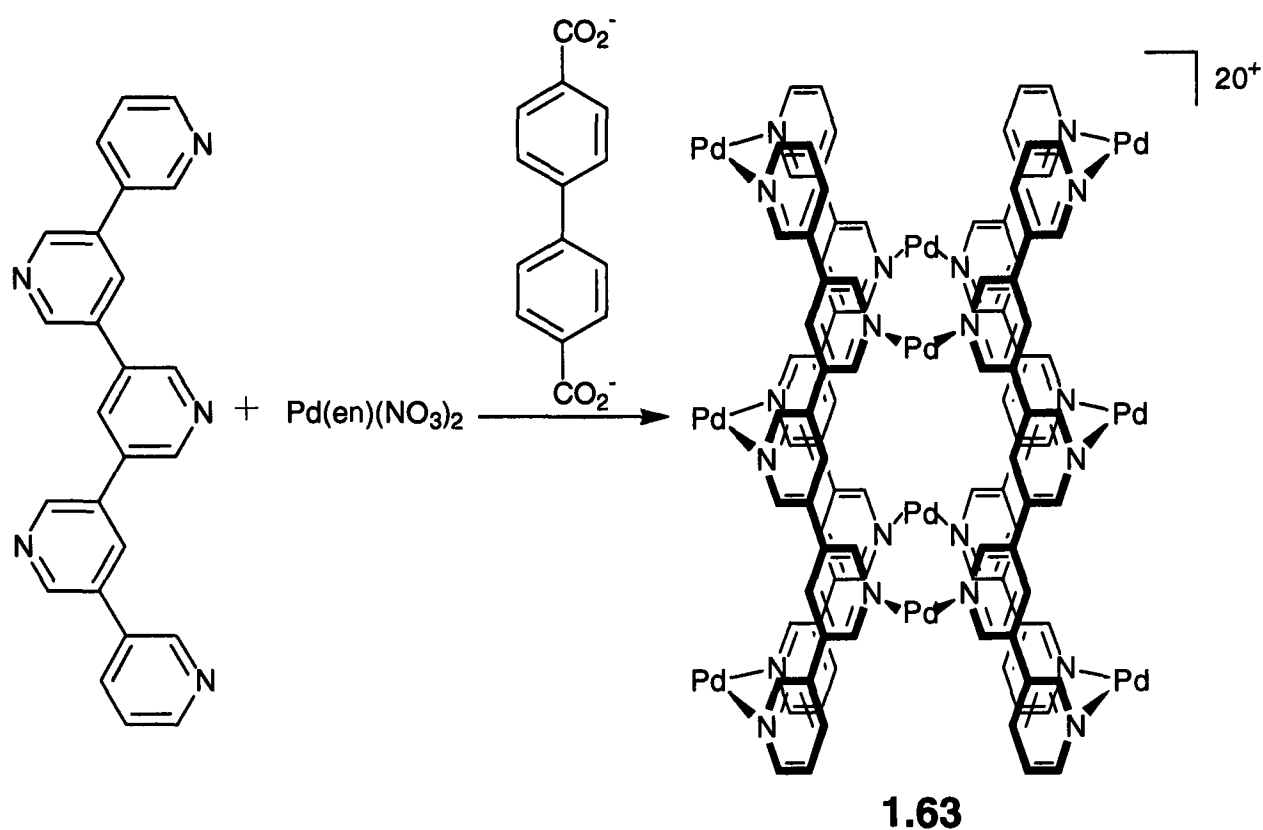
The role of anions in templating self-assembly processes has only recently been recognised.¹⁵³ Lehn demonstrated that the pentametallic circular helicate shown in Scheme 1.7 forms when

the tris-bipyridine ligand is mixed with an equimolar amount of iron(II) chloride.¹⁵⁴ Crystallography confirmed the presence of a chloride anion located in the centre of the structure. If an alternative iron(II) salt is used in the reaction, the pentametallic structure does not form, clearly demonstrating the templating role of the chloride anion.



Scheme 1.7: The formation of a circular double helicate templated around a chloride anion.

Fujita and co-workers have used carboxylate guest ions to template the formation of metal complexes, and have recently succeeded in constructing coordination nanotubes. For example, reaction of pentakis(3,5-pyridine) with $\text{Pd}(\text{en})(\text{NO}_3)_2$ in the presence of a linear template such as 4,4'-biphenylenedicarboxylate results in the formation of coordination nanotube **1.63** (Scheme 1.8).¹⁵⁵ Crystallography reveals that the anionic template is bound within the tube by π - π and CH - π interactions. Importantly, the tubular structure did not assemble in the absence of a suitable guest species.



Scheme 1.8: Coordination nanotube **1.63** templated by 4,4'-biphenylenedicarboxylate.

1.6 Thesis Objectives

The main objective of this thesis is the synthesis and characterisation of new receptors for anions and ion-pairs and the study of their guest binding and sensing properties by spectroscopic and electrochemical techniques. The ion-pair receptors described in this thesis incorporate amide or urea functionalities capable of hydrogen bonding to anionic guests and crown ether groups suitable for complexing sodium and potassium cations. Typically these receptors have a macrocyclic structure and contain redox- and/or photo-active reporter groups capable of sensing the guest binding events.

Chapter Two is concerned with the synthesis and study of a range of new upper-rim functionalised calix[4]arene receptors designed to bind anions and ion-pairs in organic solvents. The calix[4]arene-based receptors are synthesised *via* the condensation of upper-rim amino-derivatised calix[4]arene compounds with various acid chloride or protected isocyanate synthons. The anion and ion-pair binding and sensing properties of the receptors are investigated by ^1H NMR spectroscopy, electrochemistry and luminescence spectroscopy.

Chapter Three centres on ion-pair receptors incorporating an azacrown group for alkali metal cation complexation together with amide functionalities for anion binding. In addition, these receptors incorporate either ferrocene or transition metal dithiocarbamate groups for the electrochemical and/or optical sensing of guest binding. The dithiocarbamate-containing receptors are synthesised *via* metal-directed self-assembly to form macrocyclic hosts. Anion and ion-pair recognition is monitored by electrochemistry and UV-VIS spectroscopy.

Chapter Four focuses on disulphide-appended receptors designed for self-assembly onto gold surfaces. Upper-rim functionalised calix[4]arene receptors incorporating ferrocene and disulphide groups together with hydrogen bonding moieties are synthesised and their anion binding and sensing properties investigated by ^1H NMR spectroscopy and voltammetry. The formation and anion sensing ability of self-assembled monolayers of the receptors on gold electrodes is investigated by electrochemical techniques. In addition, the assembly of receptors onto gold nanoparticles is explored with the aim of producing optical sensors for guest binding.

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Chapter Two

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Chapter Two: Calix[4]arene-Based Anion and Ion-Pair Receptors

2.1 Introduction

Calix[n]arenes are a family of synthetic macrocyclic receptors consisting of cyclic arrays of n phenol moieties linked by methylene groups, and are formed *via* the base-catalysed condensation of *p-t*-butylphenol and formaldehyde.¹ Calix[4]arenes may adopt one of four conformations, namely cone, partial cone, 1,2-alternate or 1,3-alternate.¹ The functionalisation of calix[4]arenes has been studied in detail, and they have been shown to undergo a wide variety of reactions at their upper- and lower-rims.² The work described in this thesis is concerned solely with the upper-rim functionalisation of calix[4]arenes in the cone conformation.

Modified calixarenes have been extensively employed in the field of host-guest chemistry, and the literature contains numerous examples of synthetic receptors designed around a calix[4]arene framework.² The widespread development of calix[4]arene-based receptors has been encouraged by their versatile chemistry, enabling the attachment and modification of various functional groups on the calixarene scaffold. In addition, the bowl-shaped macrocyclic structure of calix[4]arenes provides an attractive three-dimensional building motif from which to append ligating groups. Importantly, the upper-rim functionalisation of calix[4]arenes allows the spatial preorganisation of an array of binding sites around the hydrophobic cavity.

This chapter reports the synthesis, characterisation and binding properties of a range of new upper-rim functionalised calix[4]arene anion and ion-pair receptors. A general discussion of anion and ion-pair receptors has been undertaken previously (in Sections 1.3 and 1.4 of the

Introduction), however the following section presents a few relevant and recent examples of calix[4]arene-based receptors.

Calix[4]arene-based receptors that contain positively charged groups (such as ammonium³ or guanidinium⁴) or Lewis acidic groups⁵ to bind anions have been reported. Of particular relevance to this thesis are receptors containing amide or urea functionalities for hydrogen bonding to anionic guests. For example, Stibor and co-workers have recently reported the upper-rim urea-functionalised anion receptor **2.1** (Figure 2.1) which additionally incorporates porphyrin moieties to enable detection of chloride and bromide anions in dichloromethane *via* UV-VIS spectroscopy.⁶

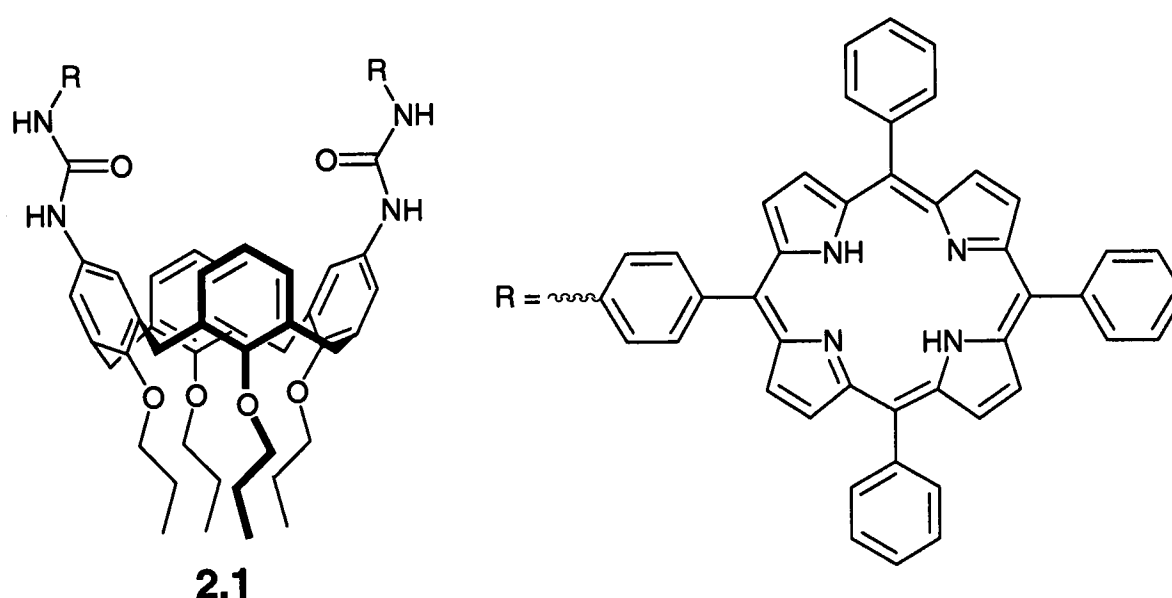


Figure 2.1: Urea-porphyrin-functionalised calix[4]arene anion receptor **2.1**.

Calix[4]arene-based ion-pair receptors reported to date have typically employed either crown ether or lower-rim tetra-ester groups for alkali metal cation complexation in addition to anion binding sites. Compound **2.2** is an early example of a lower-rim substituted calix[4]arene-based ditopic receptor employing amide groups for anion recognition and benzo[15]crown-5 ether moieties for alkali metal cation complexation (Figure 2.2).⁷ The free receptor is unable to bind anions ($K < 10 \text{ M}^{-1}$), however in the presence of potassium cations the formation of an intramolecular sandwich complex organises the amide units into a suitable geometry for the

cooperative binding of anions. Complexes with a 1:1:1 host / cation / anion stoichiometry are formed in acetonitrile solution with a selectivity for dihydrogen phosphate ($K > 10000 \text{ M}^{-1}$) over hydrogen sulphate, chloride ($K = 3500 \text{ M}^{-1}$) and nitrate.

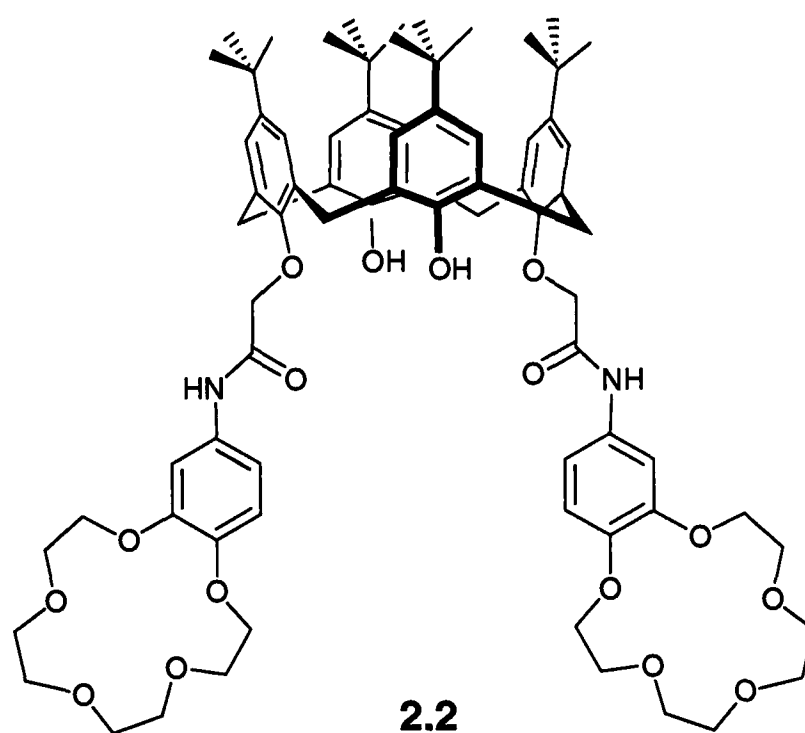


Figure 2.2: Bis(benzo[15]crown-5) calix[4]arene-based ion-pair receptor **2.2**.

Stibor and colleagues have investigated a number of amide-containing calix[4]arene receptors featuring the sodium-selective tetra-ester ligand arrangement at the lower-rim. For example, receptor **2.3** displays a marked allosteric response to binding in acetonitrile solution (Figure 2.3).⁸ In the absence of a complexing cation, halide anions are bound in a 1:2 host / guest stoichiometry, whereas the dicarboxylate anions adipate and terephthalate are bound in a 1:1 manner between the two amide units. Sodium complexation causes a rearrangement of the receptor which enables cooperative 1:1 binding of halide anions by the two amide units and prevents the binding of dicarboxylates.

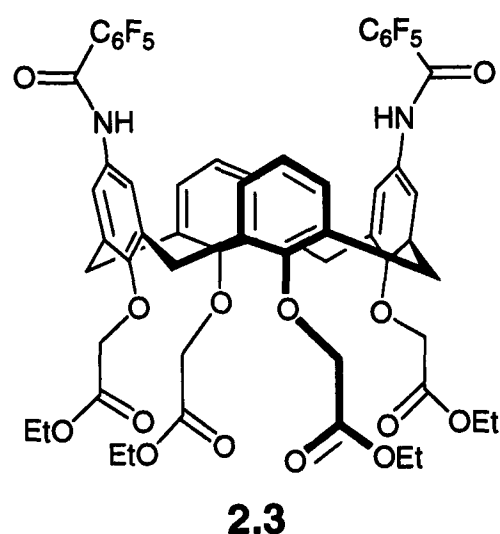


Figure 2.3: Lower-rim tetra-ester calix[4]arene-based ditopic receptor **2.3**.

The previous two examples demonstrate the importance of alkali metal cation complexation-induced conformational change on both the stoichiometry and strength of anion binding. However, electrostatic interactions are equally important for cooperative ion-pair recognition. For example, the upper-rim 1,3-bis(urea) functionalised receptor **2.4** exhibits selectivity for dihydrogen phosphate over halide anions with non-complexing cations (Figure 2.4).⁹ Sodium complexation at the lower-rim appended crown ether moiety results in substantial anion binding enhancements, for example a five-fold increase in dihydrogen phosphate binding in d_6 -DMSO. This binding enhancement is mainly attributable to electrostatic interactions rather than allosteric effects, as evidenced by the absence of changes in the ^1H NMR signals of the calixarene core upon cation binding.

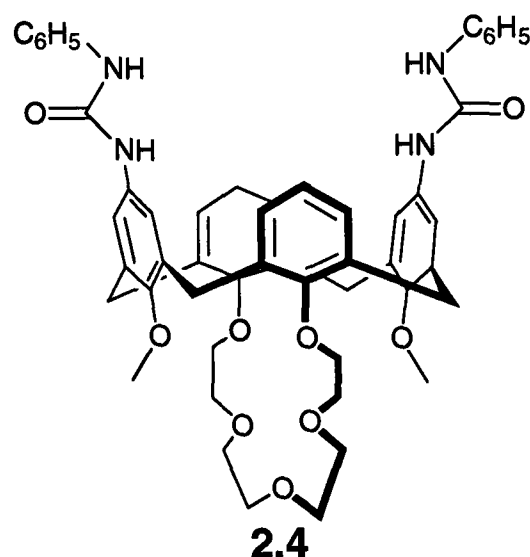


Figure 2.4: Crown ether appended calix[4]arene ion-pair receptor **2.4**.

Metallocene¹⁰ and ruthenium(II) / rhenium(I) bipyridyl¹¹ groups have also been incorporated into calix[4]arene-based ion-pair receptors in order to enable the sensing of guest binding by electrochemical or optical methods. One such example is the clam receptor **2.5** which links two calix[4]arenes containing lower-rim alkali metal binding regions with a ferrocene amide anion binding site (Figure 2.5). The receptor is selective for carboxylates, with acetate producing a cathodic shift of 155 mV in the ferrocene / ferrocenium redox couple. Although weak halide binding is exhibited by the receptor alone, lithium complexation ‘switches on’ halide binding due to both rigidification of the calixarene and electrostatic effects. The addition of lithium cations caused a more than ten-fold enhancement in bromide binding in acetonitrile solution.

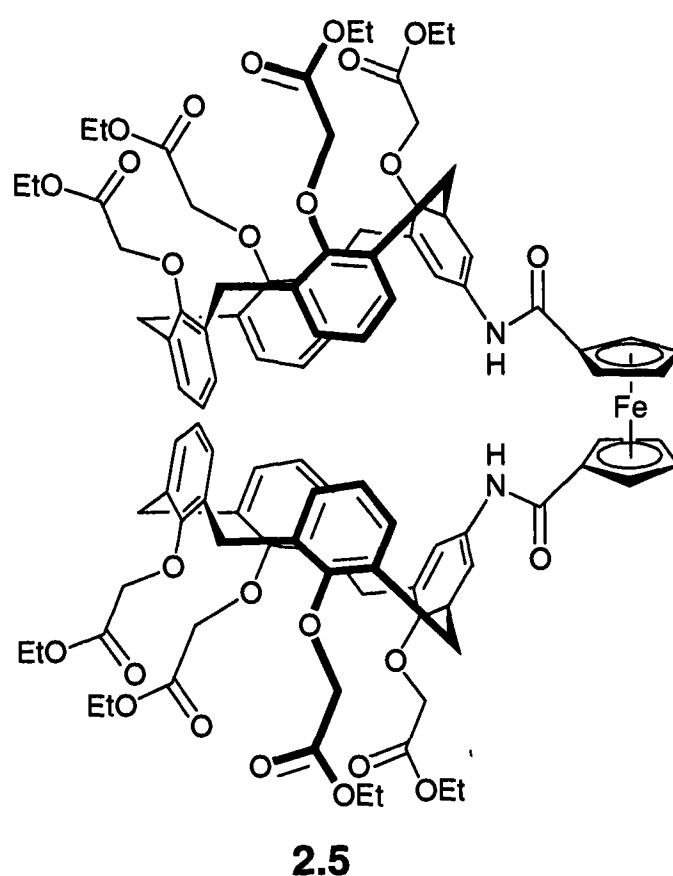


Figure 2.5: Bis(calix[4]arene) ditopic receptor **2.5**.

The objective of the research presented in this chapter was the synthesis and investigation of a range of new regioselective upper-rim functionalised calix[4]arene compounds for the complexation of anions and ion-pairs in organic solvents. These receptors were designed to incorporate amide or urea functionalities capable of binding anions through hydrogen bonding

interactions, and benzo[15]crown-5 moieties for binding alkali metal cations. In addition, photo- and/or redox-active groups (such as ferrocene or ruthenium(II) / rhenium(I) bipyridyl groups) were integrated into the host design in order to create receptors with the potential to sense anion and ion-pair binding events *via* electrochemical and/or spectroscopic techniques.

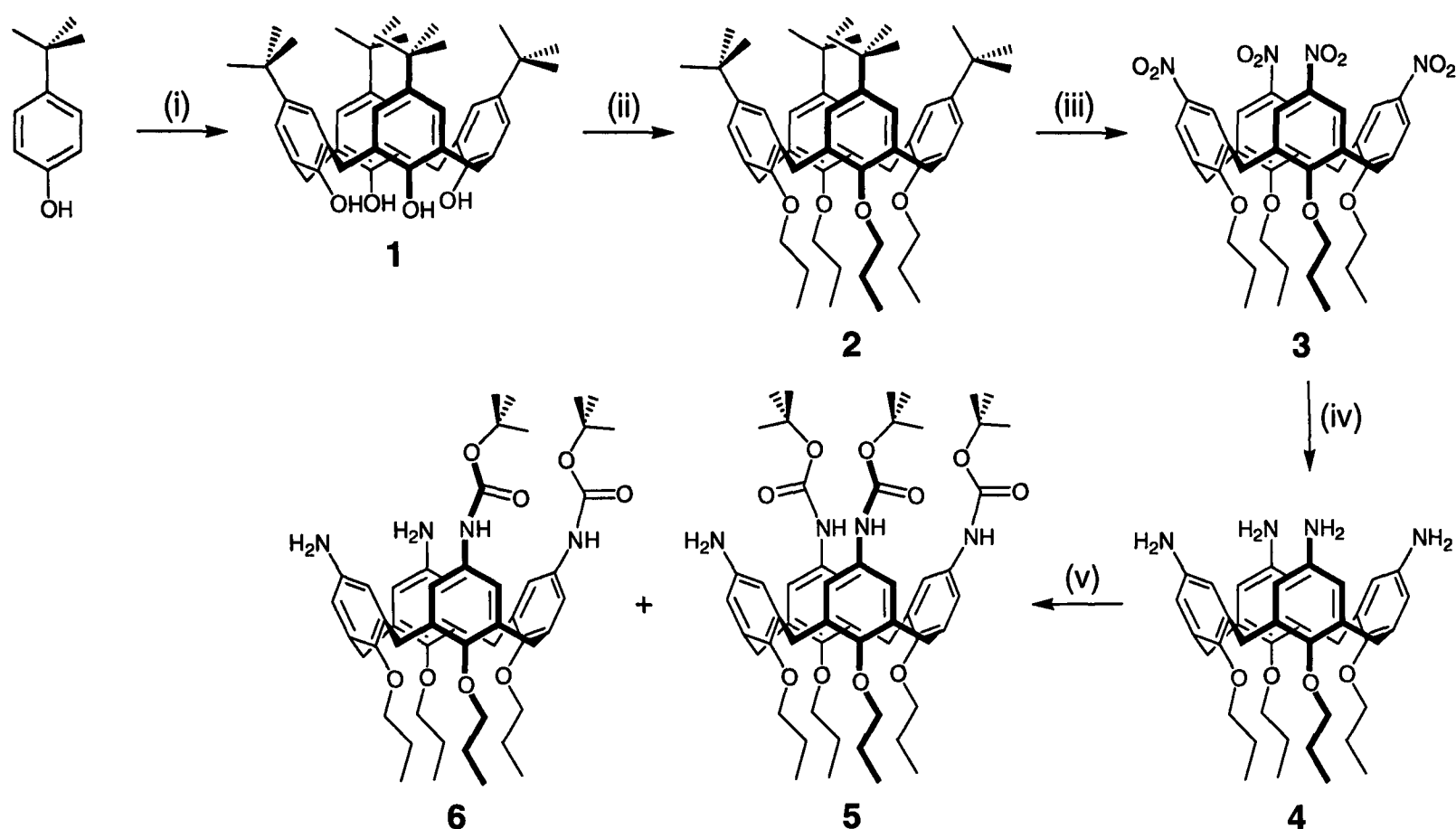
The following section describes the synthesis of these calixarene-based receptors by the condensation of various regioselective-protected upper-rim amino-derivatised calix[4]arene compounds with acid chloride or protected isocyanate synthons. Subsequent sections detail the investigation of receptor binding properties by ^1H NMR spectroscopy (Section 2.3), electrochemistry (Section 2.4) and luminescence spectroscopy (Section 2.5).

2.2 Synthesis and Characterisation

The preparation of a range of new calix[4]arene-based anion and ion-pair receptors was achieved in the following way. Condensation of tetra-amino upper-rim functionalised calix[4]arene compound **4** (Section 2.2.1) with various acid chloride or protected isocyanate synthons (chlorocarbonyl ferrocene **9**, 4-chlorocarbonyl-4'-methyl-2,2'-bipyridine **11**, 4-(chlorocarboxy)benzo[15]crown-5 **15** or ferrocene mononitrophenolate **18**, Section 2.2.2) produced four tetra-substituted calix[4]arene receptors (Section 2.2.3). Analogous coupling reactions between 1,3-bis(amino) upper-rim calix[4]arene derivative **24** and chlorocarbonyl ferrocene **9** or 4-(chlorocarboxy)benzo[15]crown-5 **15** afforded two 1,3-bis-substituted calix[4]arene receptors (Section 2.2.5). Selective BOC-protection of the amine groups of **4** gave tri- and di-BOC-protected calix[4]arene compounds **5** and **6** (Section 2.2.1). Condensation of these calixarene derivatives with one acid chloride synthon followed by deprotection and coupling with a different acid chloride synthon gave two 'mixed' calix[4]arene receptors (Sections 2.2.6 and 2.2.7).

2.2.1 Synthesis of the calix[4]arene framework

The synthesis of the upper-rim amine-functionalised calix[4]arene precursor compounds **4**, **5** and **6** was achieved by following established literature methods,¹³⁻¹⁶ Scheme 2.1.



Scheme 2.1: (i) CH_2O , NaOH , Ph_2O , reflux, 54 %; (ii) NaH , ${}^n\text{PrI}$, dmf , 68 %; (iii) 1:1 glacial AcOH / fuming HNO_3 , CH_2Cl_2 , 80 %; (iv) hydrazine hydrate, Raney Ni , CH_3OH , reflux, 89 %; (v) BOC-anhydride, CH_2Cl_2 , 47 % **5** and 23 % **6**.

Tetra-*t*-butylcalix[4]arene **1** was synthesised in 54 % yield by the base-catalysed condensation reaction of *p*-*t*-butylphenol and formaldehyde.¹² Tetra-*O*-alkylation of **1** with *n*-propyl iodide in the presence of sodium hydride gave **2** in 68 % yield.¹³ The attachment of four propyl groups to the lower-rim prevents conformational exchange in solution, as the propyl groups are too large to pass through the annulus of the calixarene. The ${}^1\text{H}$ NMR spectrum of **2** reveals that it exists exclusively in the cone conformation. Ipsom-nitration of **2** using a 1:1 mixture of glacial acetic acid and fuming nitric acid gave **3** in 80 % yield, in which the tertiary butyl groups were replaced by nitro groups.¹⁴ Reduction with hydrazine hydrate and Raney nickel gave tetra-amino upper-rim functionalised calix[4]arene **4** in 89 % yield.¹⁵

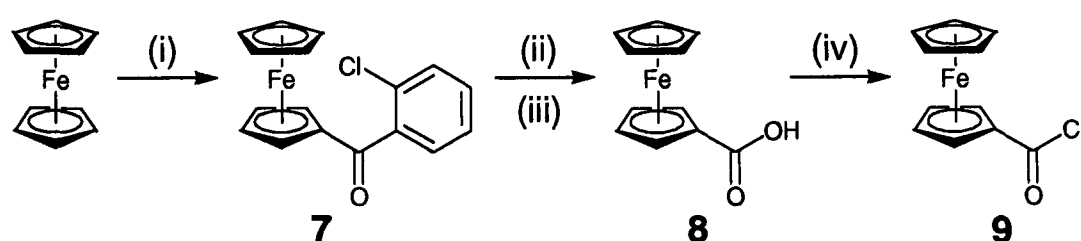
Selective protection of the upper-rim amino groups of **4** was achieved by reaction with di-*t*-butyl-dicarbonate (BOC-anhydride) followed by purification of the resulting mixture by column chromatography (silica, hexane / ethylacetate).¹⁶ The tri- and di-BOC-protected calix[4]arenes **5** and **6** were obtained in 47 % and 23 % yields (respectively) upon reaction of **4** with 2.7 equivalents of BOC-anhydride. A small amount of tetra-BOC-protected calix[4]arene **38** was also isolated. It should be noted that in the selective BOC-protection of tetra-amino calix[4]arene **4**, of the two possible bis-substituted products, only the 1,2-substituted compound is produced; no 1,3-di-BOC-protected product is obtained.¹⁶

2.2.2 Synthesis of acid chloride and protected isocyanate synthons

The synthesis of acid chloride and protected isocyanate synthons (chlorocarbonyl ferrocene **9**, 4-chlorocarbonyl-4'-methyl-2,2'-bipyridine **11**, 4-(chlorocarboxy)benzo[15]crown-5 **15** and ferrocene mononitrophenolate **18**) for reaction at the upper-rim of the amine-functionalised calix[4]arene precursor compounds (**4**, **5** and **6**) is described below.

2.2.2.1 Chlorocarbonyl ferrocene **9**

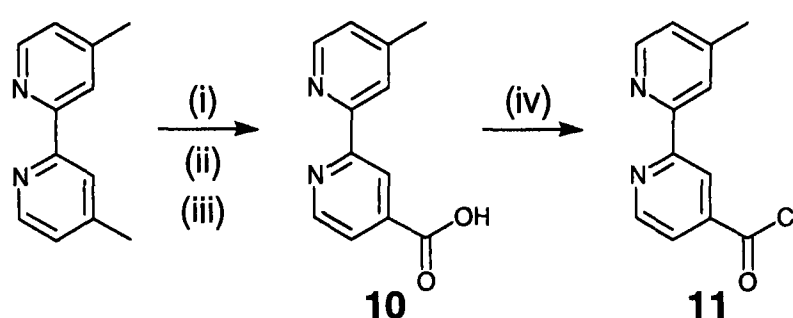
The acylation (Friedel-Crafts) of ferrocene with 2-chlorobenzoyl chloride and aluminium(III) chloride gave compound **7** (Scheme 2.2).¹⁷ Reaction with water under strongly basic conditions followed by acidification gave ferrocene carboxylic acid **8** in 40 % yield, which on reaction with oxalyl chloride gave chlorocarbonyl ferrocene **9** in 66 % yield. The acid chloride synthon **9** was used immediately in subsequent reactions.



Scheme 2.2: (i) 2-chlorobenzoyl chloride, AlCl₃, CH₂Cl₂, 5 °C; (ii) KO^tBu, H₂O, 1,2-dimethoxyethane, reflux; (iii) HCl_(aq), 40 %; (iv) oxalyl chloride, CH₂Cl₂, reflux, 66 %.

2.2.2.2 4-Chlorocarbonyl-4'-methyl-2,2'-bipyridine 11

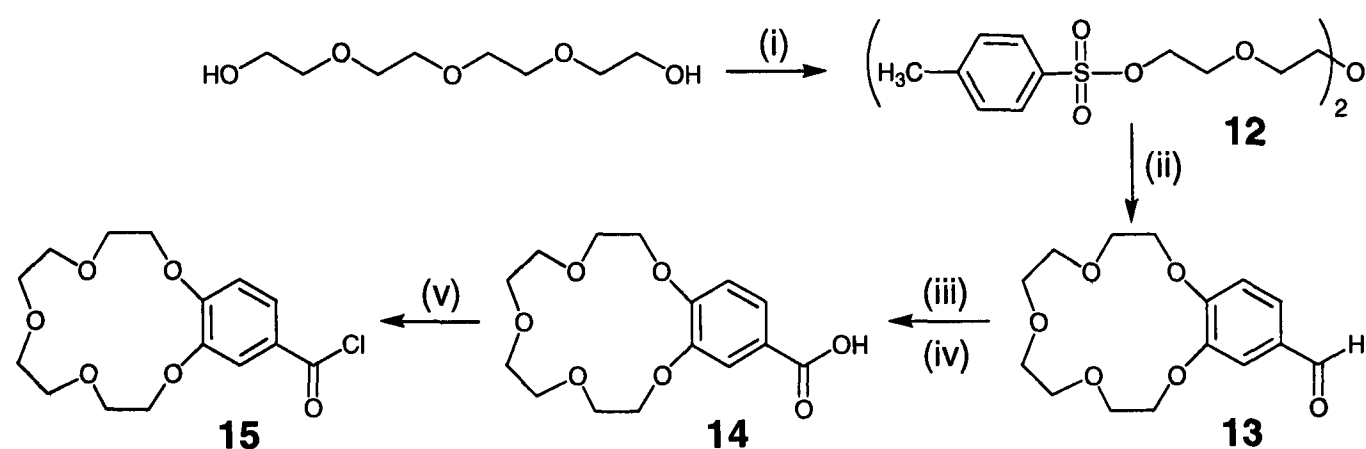
Bipyridine monoacid **10** was synthesised in 30 % yield by the selective oxidation of 4,4'-dimethyl-2,2'-bipyridine with selenium dioxide (Scheme 2.3).¹⁸ Reaction with thionyl chloride gave 4-chlorocarbonyl-4'-methyl-2,2'-bipyridine **11**.



Scheme 2.3: (i) SeO_2 , 1,4-dioxane, reflux; (ii) $\text{AgNO}_{3(\text{aq})}$, $\text{NaOH}_{(\text{aq})}$, EtOH; (iii) $\text{HCl}_{(\text{aq})}$, 30 %; (iv) SOCl_2 , reflux.

2.2.2.3 4-(Chlorocarboxy)benzo[15]crown-5 15

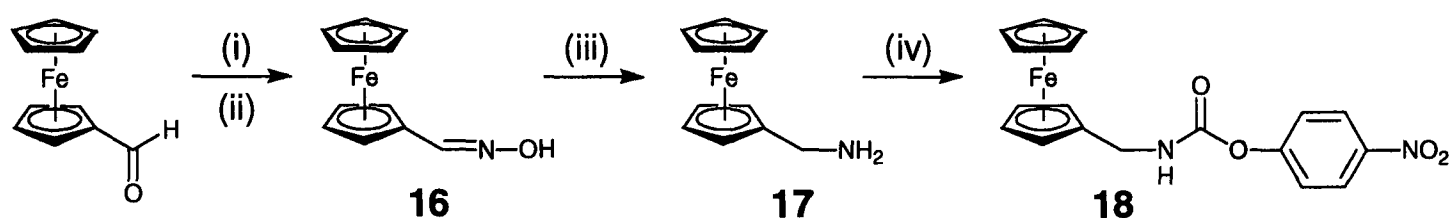
Tosylation of tetraethyleneglycol by reaction with *p*-toluenesulfonyl chloride under basic conditions gave tetraethyleneglycol ditosylate **12** in 91 % yield (Scheme 2.4).¹⁹ This was reacted with 3,4-dihydroxybenzaldehyde in a metal-templated cyclisation reaction to form crown ether **13** in 71 % yield.²⁰ Oxidation with potassium permanganate followed by acidification gave **14** in 72 % yield,²¹ which was reacted with oxalyl chloride to give 4-(chlorocarboxy)benzo[15]crown-5 **15**.



Scheme 2.4: (i) *p*-toluenesulfonyl chloride, NaOH, 2:1 thf / H_2O , 5 °C, 91 %; (ii) 3,4-dihydroxybenzaldehyde, CsF, CH_3CN , reflux, 71 %; (iii) KMnO_4 , Na_2CO_3 , H_2O ; (iv) $\text{HCl}_{(\text{aq})}$, 72 %; (v) oxalyl chloride, pyridine, CH_2Cl_2 .

2.2.2.4 Ferrocene mononitrophenolate 18

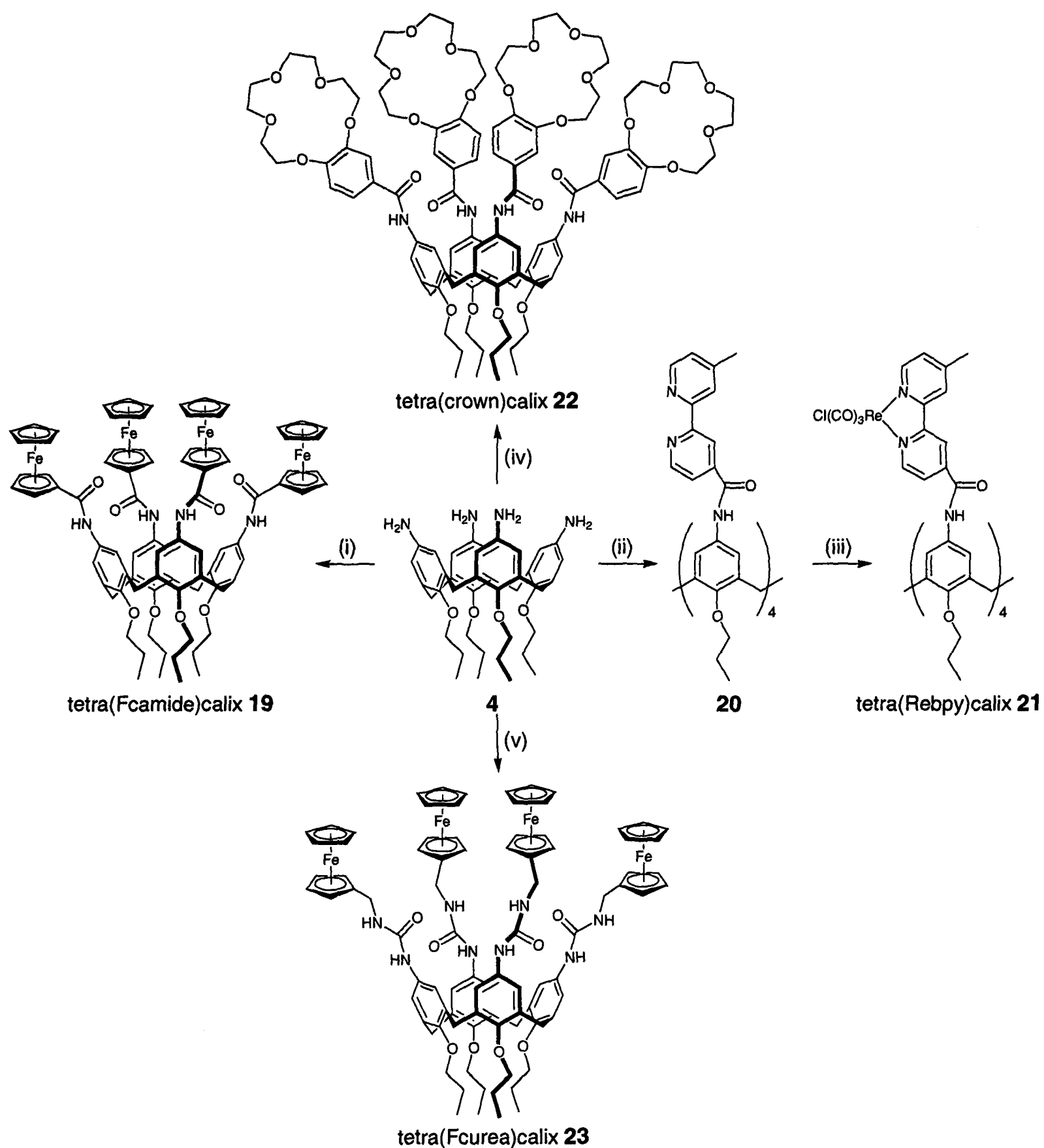
Ferrocene carboxaldehyde was reacted with hydroxylamine hydrochloride under basic conditions (Scheme 2.5).²² The solution was neutralised by bubbling with carbon dioxide resulting in the precipitation of the oxime **16** in 72 % yield, which was reduced with lithium aluminium hydride to give ferrocene methylamine **17** in 81 % yield. Reaction with *p*-nitrophenol chloroformate in the presence of ethyldiisopropylamine followed by purification by column chromatography (silica, 4:1 ethylacetate / hexane) gave the protected isocyanate synthon **18** as an orange solid in 87 % yield.



Scheme 2.5: (i) $\text{NH}_2\text{OH}\cdot\text{HCl}_{(\text{aq})}$, NaOH, EtOH, reflux; (ii) $\text{CO}_{2(\text{g})}$, 72 %; (iii) LiAlH_4 , thf, 81 %; (iv) *p*-nitrophenol chloroformate, $\text{Et}^i\text{Pr}_2\text{N}$, CH_2Cl_2 , 87 %.

2.2.3 Synthesis of tetra-substituted upper-rim calix[4]arene receptors

Condensation reactions of tetra-amino upper-rim functionalised calix[4]arene **4** with the acid chloride or protected isocyanate synthons gave four new tetra-amide or tetra-urea substituted receptors, Scheme 2.6. In order to prevent the formation of a mixture of di-, tri- and tetra-substituted products, in all cases **4** was reacted with six equivalents of the various synthons, thereby ensuring complete reaction of the amine functional groups.



Scheme 2.6: (i) chlorocarbonyl ferrocene **9**, Et₃N, CH₂Cl₂, 90 %; (ii) 4-chlorocarbonyl-4'-methyl-2,2'-bipyridine **11**, Et₃N, CH₂Cl₂, 73 %; (iii) Re(CO)₅Cl, thf, reflux, 44 %; (iv) 4-(chlorocarboxy)benzo[15]crown-5 **15**, Et₃N, CHCl₃, reflux, 57 %; (v) ferrocene mononitrophenolate **18**, Et(ⁱPr)₂N, DMAP, CH₂Cl₂, 48 %.

2.2.3.1 Tetra(Fcamide)calix 19

Tetra-amino calix[4]arene **4** was reacted with an excess (six equivalents) of chlorocarbonyl ferrocene **9** in the presence of triethylamine base in dichloromethane to form the tetra-ferrocene-amide upper-rim functionalised calix[4]arene receptor tetra(Fcamide)calix **19**

(Scheme 2.6). Precipitation from chloroform / hexane gave the desired product as a pale orange powder in 90 % yield. Excess reagent **9** was removed in the workup by washing the product thoroughly with hexane. An assigned ^1H NMR spectrum of **19** in d_6 -DMSO is shown in Figure 2.6.

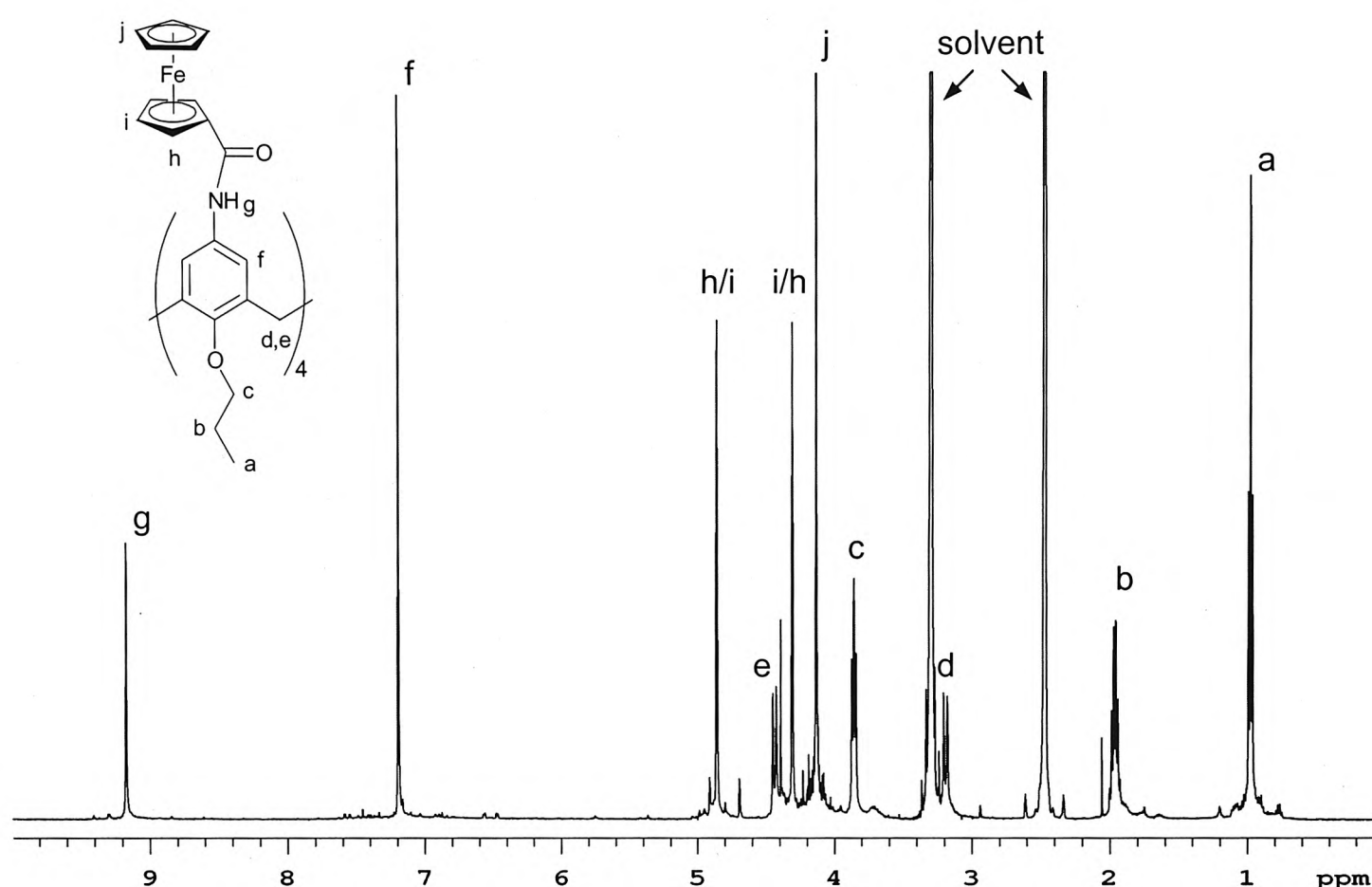


Figure 2.6: ^1H NMR spectrum (500 MHz) of tetra(Fcamide)calix **19** in d_6 -DMSO.

2.2.3.2 Tetra(Rebpy)calix **21**

Tetra-amino calixarene **4** was condensed with excess 4-chlorocarbonyl-4'-methyl-2,2'-bipyridine **11** in the presence of triethylamine base in dichloromethane (Scheme 2.6). Precipitation from chloroform / hexane gave **20** as a light brown solid in 73 % yield. The coordination of rhenium(I) to each of the four bipyridine groups was achieved by reacting **20** with six equivalents of rhenium(I) pentacarbonyl chloride in tetrahydrofuran. Column chromatography (silica, 30:1 dichloromethane / methanol) followed by precipitation from dichloromethane / hexane afforded tetra(Rebpy)calix **21** as a yellow-brown solid in 44 % yield.

Synthesis of the analogous tetra-(ruthenium(II) tris(bipyridyl)) complex was attempted by reacting **20** with cis-bis(2,2'-bipyridyl)dichlororuthenium(II) **39**.²³ The mass spectrum of the resulting material showed no evidence for the formation of the desired tetra-substituted product, and the ¹H NMR spectrum revealed a forest of peaks. This may indicate that the complete reaction of **20** and **39** is opposed by the resulting steric crowding at the calixarene upper-rim. Unfortunately, repeated efforts to purify this reaction mixture were unsuccessful.

2.2.3.3 Tetra(crown)calix **22**

Tetra-amino calixarene **4** was reacted with excess 4-(chlorocarboxy)benzo[15]crown-5 **15** in the presence of triethylamine base by heating to reflux in chloroform (Scheme 2.6). The organic solution was stirred overnight with aqueous lithium hydroxide to remove excess starting material **15**. Precipitation from chloroform / hexane gave tetra(crown)calix **22** as a white solid in 57 % yield.

The synthesis and purification of tetra-(benzo[15]crown-5)-amide calix[4]arene receptor **22** proved challenging. Firstly, whereas the analogous condensation reactions (shown in Scheme 2.6) readily occurred in dichloromethane at room temperature, the reaction of **4** and **15** under these conditions resulted in a mixture of di-, tri- and tetra-substituted products. Complete reaction of **4** and **15** required heating to reflux in chloroform. The need for more vigorous reaction conditions in this case may indicate some steric difficulty in appending four bulky benzo[15]crown-5 groups to the calix[4]arene upper-rim.

Secondly, it proved difficult to remove excess benzo[15]crown-5 starting material in the workup. Unfortunately, column chromatography was of no help in the purification of the receptor, and even repeated washing of a chloroform solution of the receptor with aqueous lithium hydroxide failed to remove all the excess starting material. However, it was finally

established that stirring a chloroform solution of the receptor with aqueous lithium hydroxide overnight enabled pure tetra(crown)calix **22** to be obtained.

Elemental analysis of purified receptor **22** revealed the complete absence of sodium or potassium. However, the mass spectrum of tetra(crown)calix **22** showed peaks corresponding to MNa_3^{3+} , $\text{MNa}_2\text{K}^{3+}$, MNa_2^{2+} , MNaK^{2+} , MNa^+ and MK^+ , highlighting the ease with which the benzo[15]crown-5 groups pick up sodium or potassium cations. These cations originate from alkali metal salts which are used to calibrate the spectrometer.²⁴

2.2.3.4 Tetra(Fcurea)calix **23**

A variety of approaches to the preparation of calixarene ureas have been reported, the majority based on the use of commercially available isocyanates²⁵ or isocyanate derivatives of calixarenes.²⁶ In the synthesis of tetra(Fcurea)calix **23**, the protected isocyanate synthon **18** was used to introduce ferrocene-urea groups onto the upper-rim calix[4]arene skeleton.²⁷ This method has the advantages of allowing the isolation of a less toxic reagent and enabling a convergent approach whereby both amide- and urea-derivatised products can be synthesised from the same amino-functionalised calixarene. In addition, this method is readily adaptable to the introduction of other more complex urea substituents.

Tetra-amino calixarene **4** was reacted with ferrocene mononitrophenolate **18** in the presence of ethyldiisopropylamine base and a catalytic amount of DMAP in dichloromethane to form the tetra-ferrocene-urea upper-rim functionalised calix[4]arene receptor tetra(Fcurea)calix **23** (Scheme 2.6). Column chromatography (silica, 10 % methanol in chloroform) followed by precipitation from chloroform / hexane gave the desired product as a pale yellow powder in 48 % yield.

Tetra(Fcurea)calix **23** exists as the monomer in competitive solvents such as DMSO, however it forms dimeric capsules in non-competitive solvents such as benzene. The investigation of this interesting behaviour is discussed in detail in Section 2.2.8.

2.2.4 X-ray structural investigations of tetra(Fcamide)calix **19** and tetra(Fcurea)calix **23**

The slow diffusion of methanol into a chloroform solution of tetra(Fcamide)calix **19** yielded X-ray quality orange crystals of $19 \cdot 3\text{CH}_3\text{OH} \cdot 3\text{CHCl}_3$. The structure was solved by Dr. A. R. Cowley (Chemical Crystallography Laboratory, University of Oxford) and is shown in Figure 2.7; full data are given in Appendix F.2.

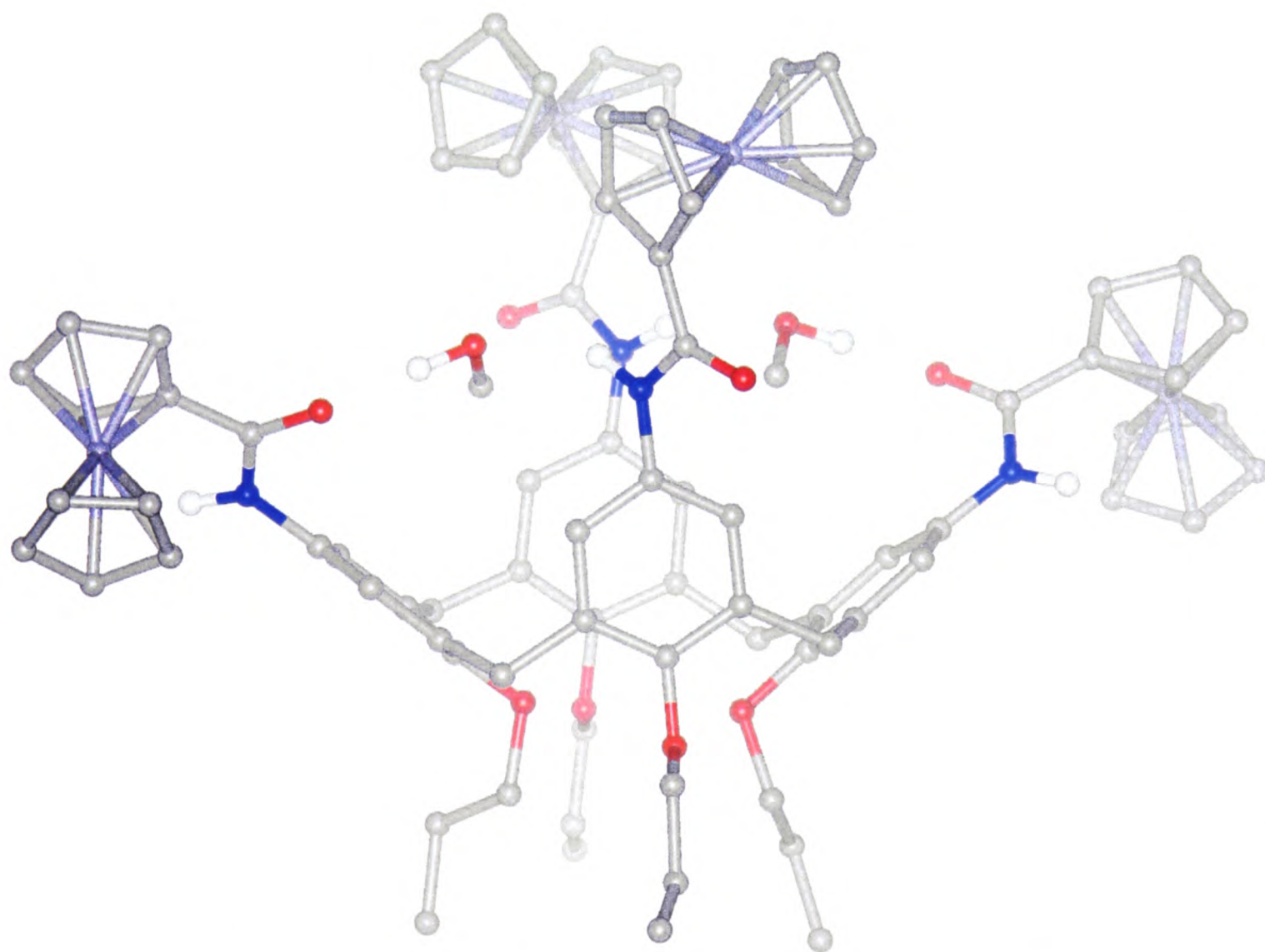


Figure 2.7: General view of tetra(Fcamide)calix **19**, showing two methanol molecules hydrogen bonded within the calix[4]arene cavity (most of the hydrogen atoms have been omitted for clarity).

Although it has no crystallographic symmetry (triclinic system, $P\bar{1}$ space group), the calixarene core of the receptor closely approximates to two-fold symmetry. The calix[4]arene adopts a flattened cone conformation in which opposed phenyl rings have parallel (interplanar angle 0.6°) or sharply inclined (interplanar angle 100.7°) positions. Associated with each receptor are three methanol molecules, the hydroxyl groups of which are hydrogen bonded to the carbonyl oxygen atoms of the inclined fragments of the tetramer. As shown in Figure 2.7, two of these occupy sites within the ‘cusps’ between the inclined and parallel fragments ($\text{O}(9)\text{--O}(1) = 2.781(3) \text{ \AA}$, $\text{O}(10)\text{--O}(3) = 2.764(3) \text{ \AA}$). These hydrogen bonds are well positioned, having $\text{O}\cdots\text{H}\text{--O}$ distances of $\sim 1.77 \text{ \AA}$ and $\text{O}\cdots\text{H}\text{--O}$ angles of 180° . A further hydrogen bond is formed by the interaction of the NH group of one of the adjacent parallel fragments with the oxygen atom of each ($\text{N}(4)\text{--O}(9) = 2.912(4) \text{ \AA}$, $\text{N}(2)\text{--O}(10) = 2.888(4) \text{ \AA}$). These hydrogen bonds are longer ($\text{N}\text{--H}\cdots\text{O} \sim 2.00 \text{ \AA}$) and less well aligned ($\text{N}\text{--H}\cdots\text{O}$ angle $\sim 21^\circ$). The remaining methanol molecule (not shown in Figure 2.7) lies alongside the receptor, to which it is linked by a single hydrogen bond ($\text{O}(11)\text{--O}(1) = 2.833(6) \text{ \AA}$). In addition, the NH groups of the inclined fragments form intermolecular hydrogen bonds to carbonyl oxygen atoms of parallel fragments of adjacent tetramers ($\text{N}(1)\text{--O}(3') = 2.779(4) \text{ \AA}$, $\text{N}(3)\text{--O}(7'') = 2.775(4) \text{ \AA}$).

The slow diffusion of methanol into a chloroform solution of tetra(Fcurea)calix **23** yielded X-ray quality crystals (orange-yellow blocks) of **23**·3CH₃OH·3CHCl₃. The structure was solved by Dr. A. R. Cowley (Chemical Crystallography Laboratory, University of Oxford) and is shown in Figure 2.8; full data are given in Appendix F.3.

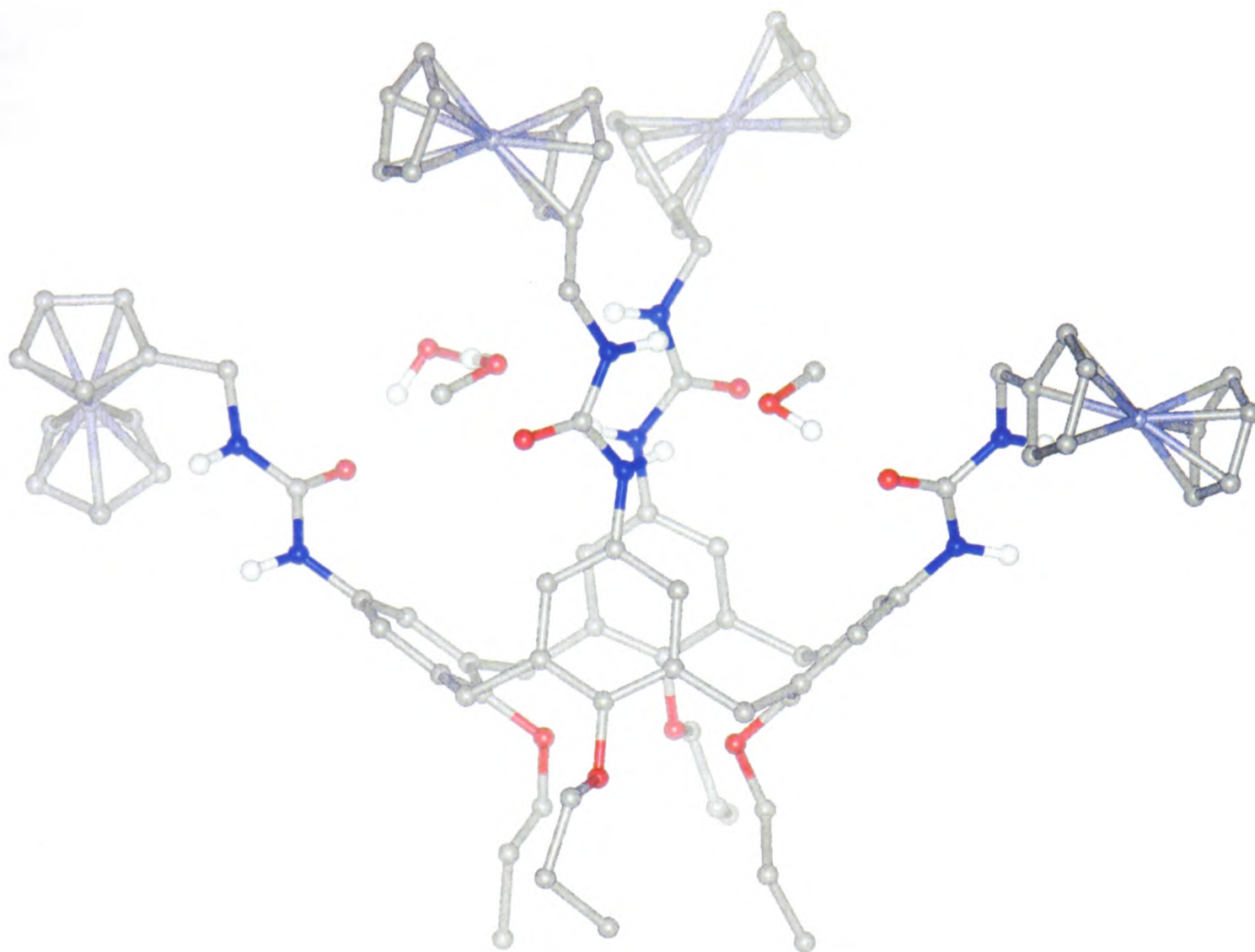
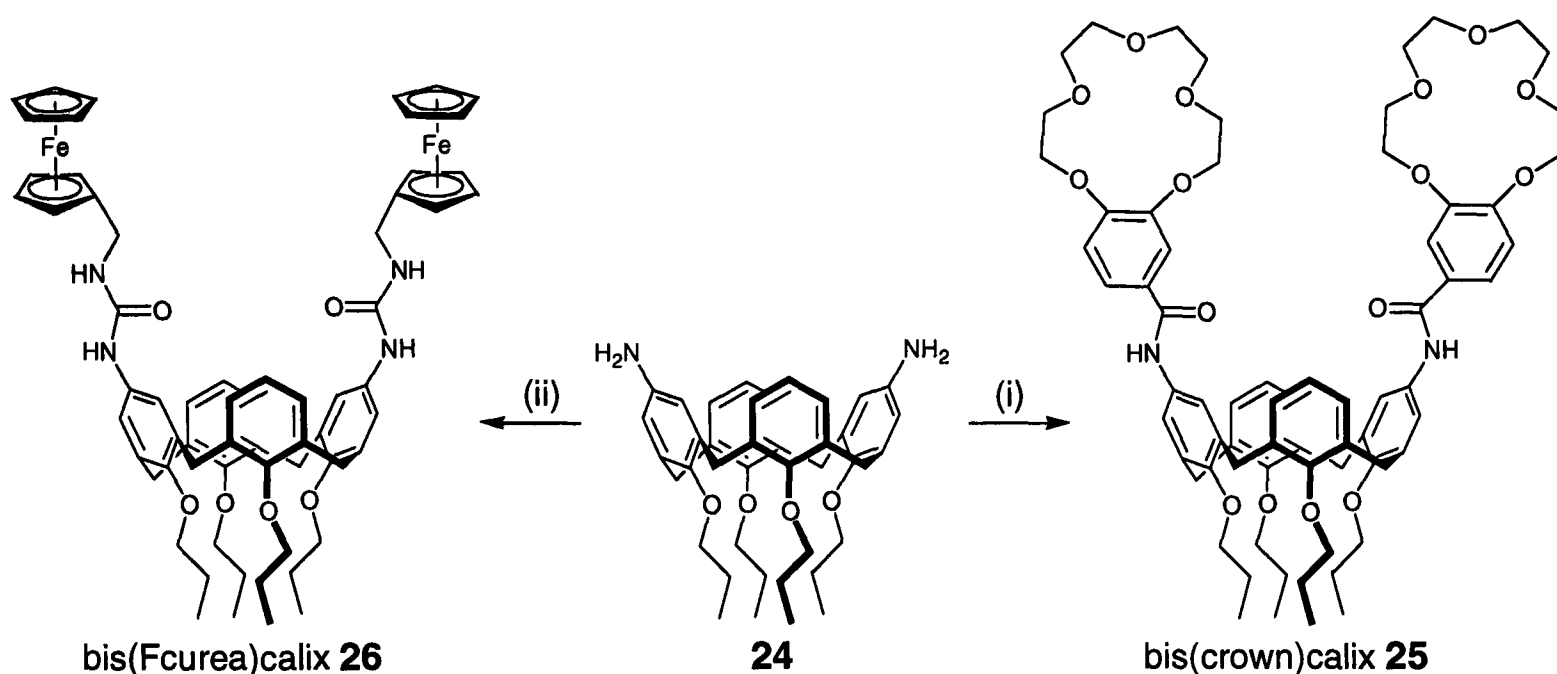


Figure 2.8: General view of tetra(Fcurea)calix **23**, showing three included methanol molecules (most of the hydrogen atoms have been omitted for clarity).

The structure is similar to that of the tetra-ferrocene-amide analogue. The calix[4]arene adopts a flattened cone conformation, and three methanol molecules are hydrogen bonded to the urea groups of the receptor. Unfortunately, the crystals were not of sufficient quality to enable good refinement of the data, and consequently a detailed discussion of bond lengths and angles is not appropriate.

2.2.5 Synthesis of 1,3-bis-substituted upper-rim calix[4]arene receptors

The synthesis of two 1,3-bis-substituted upper-rim calix[4]arene receptors (bis(Fcurea)calix **26** and bis(crown)calix **25**) is outlined in Scheme 2.7. The 1,3-bis(amino) calix[4]arene derivative **24** was synthesised by Dr. S. E. Matthews according to a literature method.²⁸



Scheme 2.7: (i) 4-(chlorocarboxy)benzo[15]crown-5 **15**, Et_3N , CHCl_3 , reflux, 63 %; (ii) ferrocene mononitrophenolate **18**, $\text{Et}(\text{iPr})_2\text{N}$, DMAP, CH_2Cl_2 , 68 %.

The calix[4]arene precursor **24** was reacted with three equivalents of either 4-(chlorocarboxy)benzo[15]crown-5 **15** or ferrocene mononitrophenolate **18**, as described previously for the tetra-substituted analogues in Section 2.2.3. After purification and precipitation from chloroform / hexane, bis(crown)calix **25** was obtained as a white solid in 63 % yield. After column chromatography, bis(Fcurea)calix **26** was obtained as an orange solid in 68 % yield. An assigned ^1H NMR spectrum of **25** in d_6 -DMSO is shown in Figure 2.9.

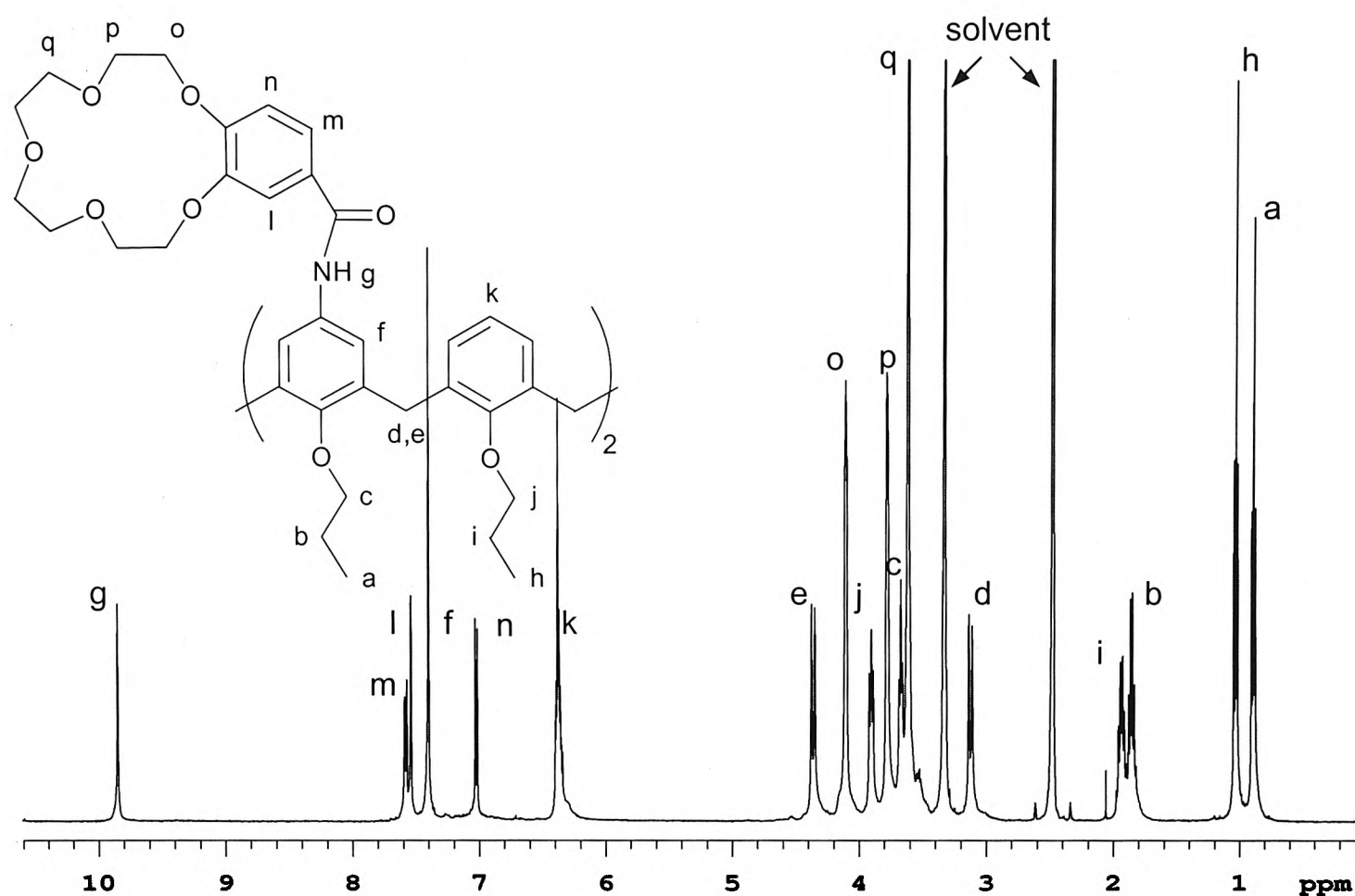
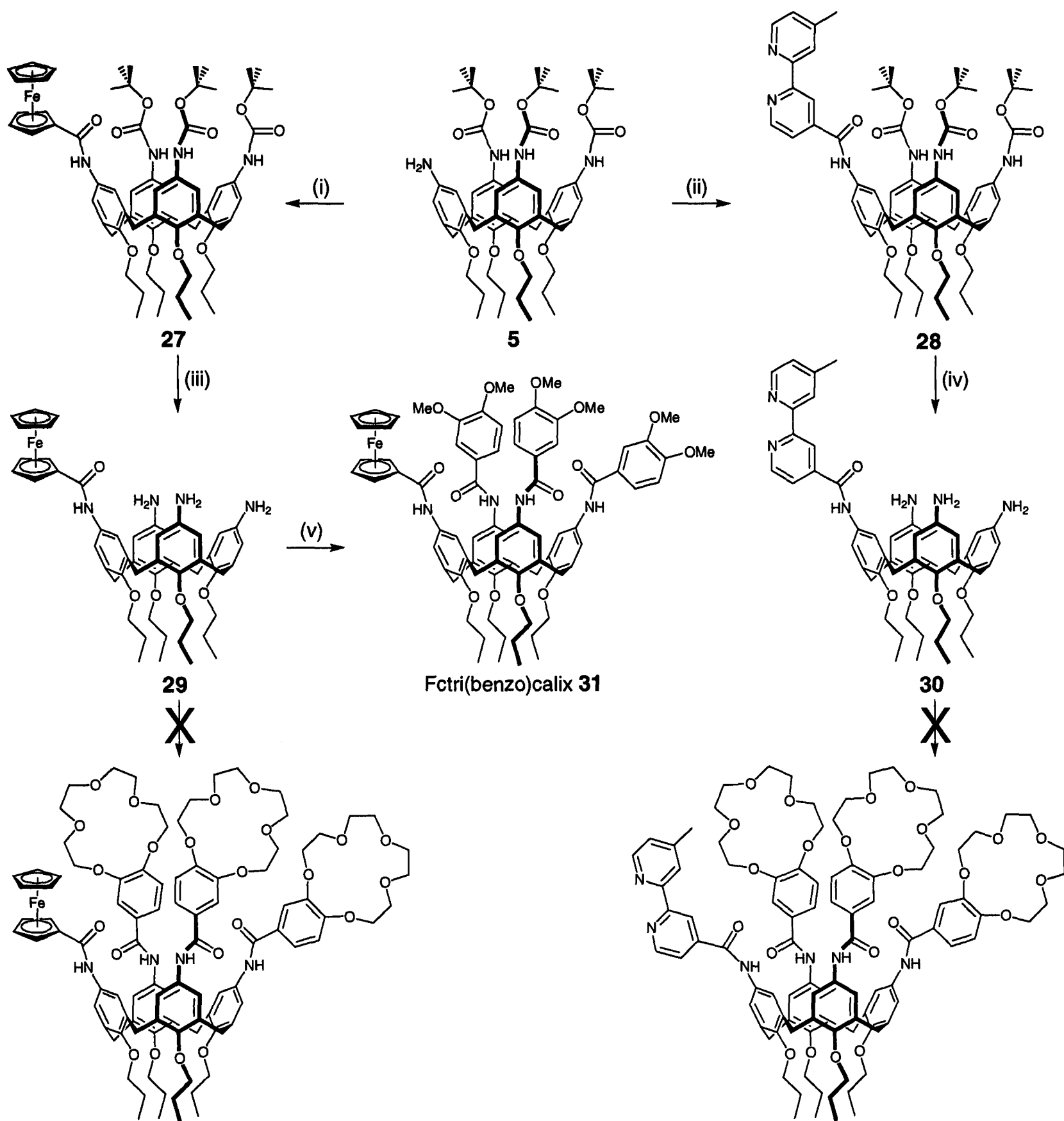


Figure 2.9: ^1H NMR spectrum (500 MHz) of bis(crown)calix **25** in d_6 -DMSO.

2.2.6 Synthesis of mixed receptors from tri-BOC-protected calix[4]arene **5**

The tri-BOC-protected calix[4]arene precursor **5** was prepared in order to facilitate the synthesis of mixed receptor systems in which two different groups are appended to the calixarene upper-rim. The general synthetic strategy was to (i) couple **5** with a redox- and/or photo-active group by reaction with the ferrocene or bipyridine acid chloride synthons **9** or **11**; (ii) remove the BOC protecting groups; and (iii) condense the resulting mono-functionalised tri-amino calixarene with the alkali metal cation-binding benzo[15]crown-5 acid chloride synthon **15** (Scheme 2.8).



Scheme 2.8: (i) chlorocarbonyl ferrocene **9**, Et₃N, CH₂Cl₂, 68 %; (ii) 4-chlorocarbonyl-4'-methyl-2,2'-bipyridine **11**, Et₃N, CH₂Cl₂, 55 %; (iii) TFA, CH₂Cl₂, 99 %; (iv) TFA, CH₂Cl₂, 78 %; (v) 3,4-dimethoxybenzoyl chloride, Et₃N, CHCl₃, reflux, 48 %.

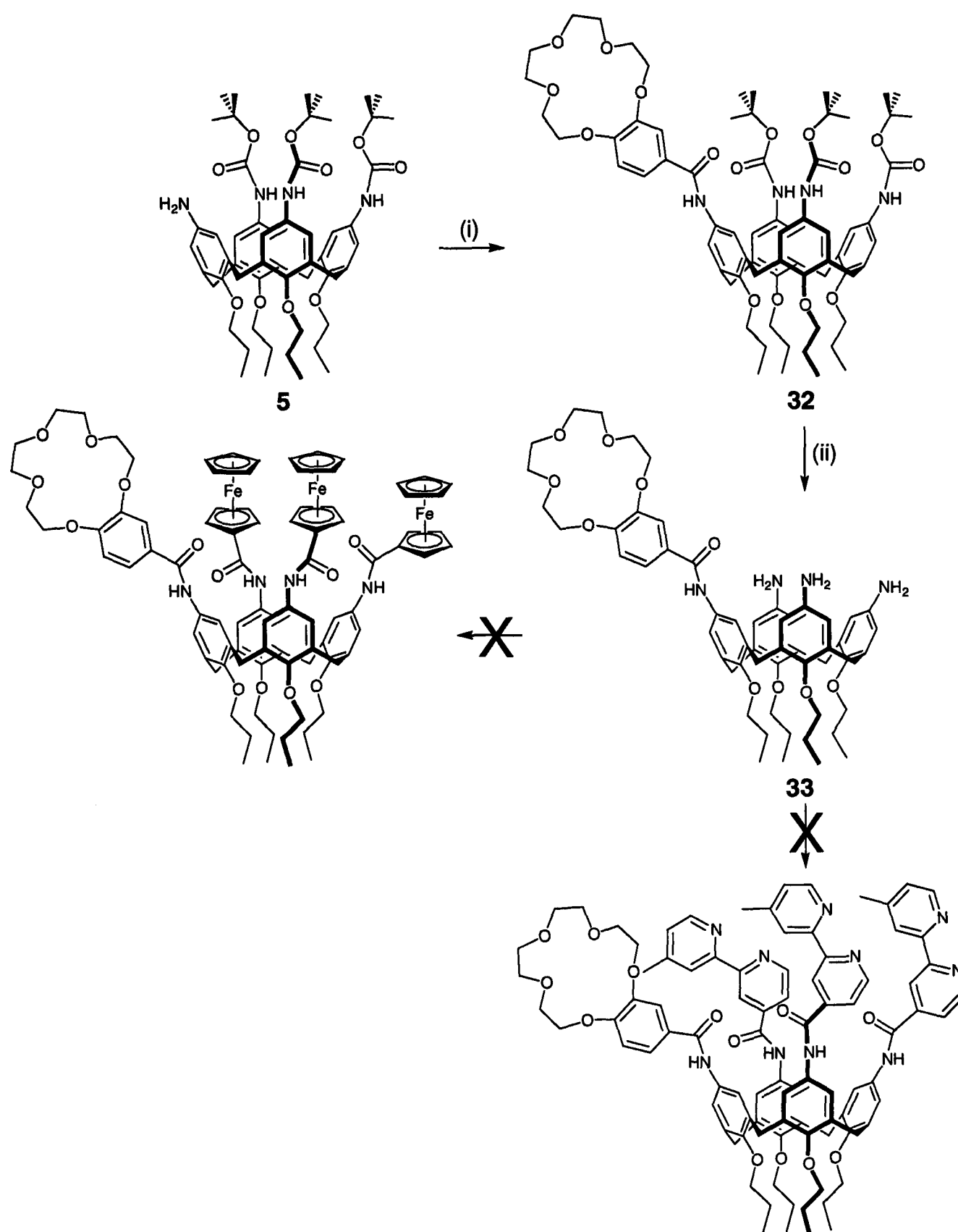
Calix[4]arene precursor **5** was reacted with one and a half equivalents of chlorocarbonyl ferrocene **9** in the presence of triethylamine base in dichloromethane. Precipitation from chloroform / hexane gave **27** as a pale orange powder in 68 % yield. Similarly, reaction of **5** with 4-chlorocarbonyl-4'-methyl-2,2'-bipyridine **11** followed by precipitation from

chloroform / hexane gave **28** as a cream solid in 55 % yield. Deprotection of **27** and **28** using trifluoroacetic acid (TFA) in dichloromethane gave **29** and **30** as their TFA salts in 99 % and 78 % yields, respectively.

Unfortunately, the attempted condensation reactions of **29** and **30** with excess 4-(chlorocarboxy)benzo[15]crown-5 **15** were unsuccessful. ¹H NMR spectroscopic and mass spectrometric analyses of the reaction mixtures indicated that the major products were indeed the desired ones. However, these reaction mixtures could not be purified as the benzo[15]crown-5-derivatised calix[4]arenes were not amenable to column chromatography. Despite repeated attempts, the desired receptors could not be isolated in sufficient purity for further study.

Mono-ferrocene tri-amino calix[4]arene **29** was reacted with 3,4-dimethoxybenzoyl chloride in the presence of triethylamine by heating to reflux in chloroform. Purification by column chromatography (silica, 30:1 chloroform / methanol) followed by precipitation from chloroform / hexane gave Ftri(benzo)calix **31** as pale yellow solid in 48 % yield.

In addition, attempts were made to synthesise mixed receptor systems by firstly coupling tri-BOC-protected calix[4]arene precursor **5** with the benzo[15]crown-5 acid chloride synthon **15** then deprotecting and condensing with ferrocene or bipyridine acid chloride synthons **9** or **11** (Scheme 2.9).



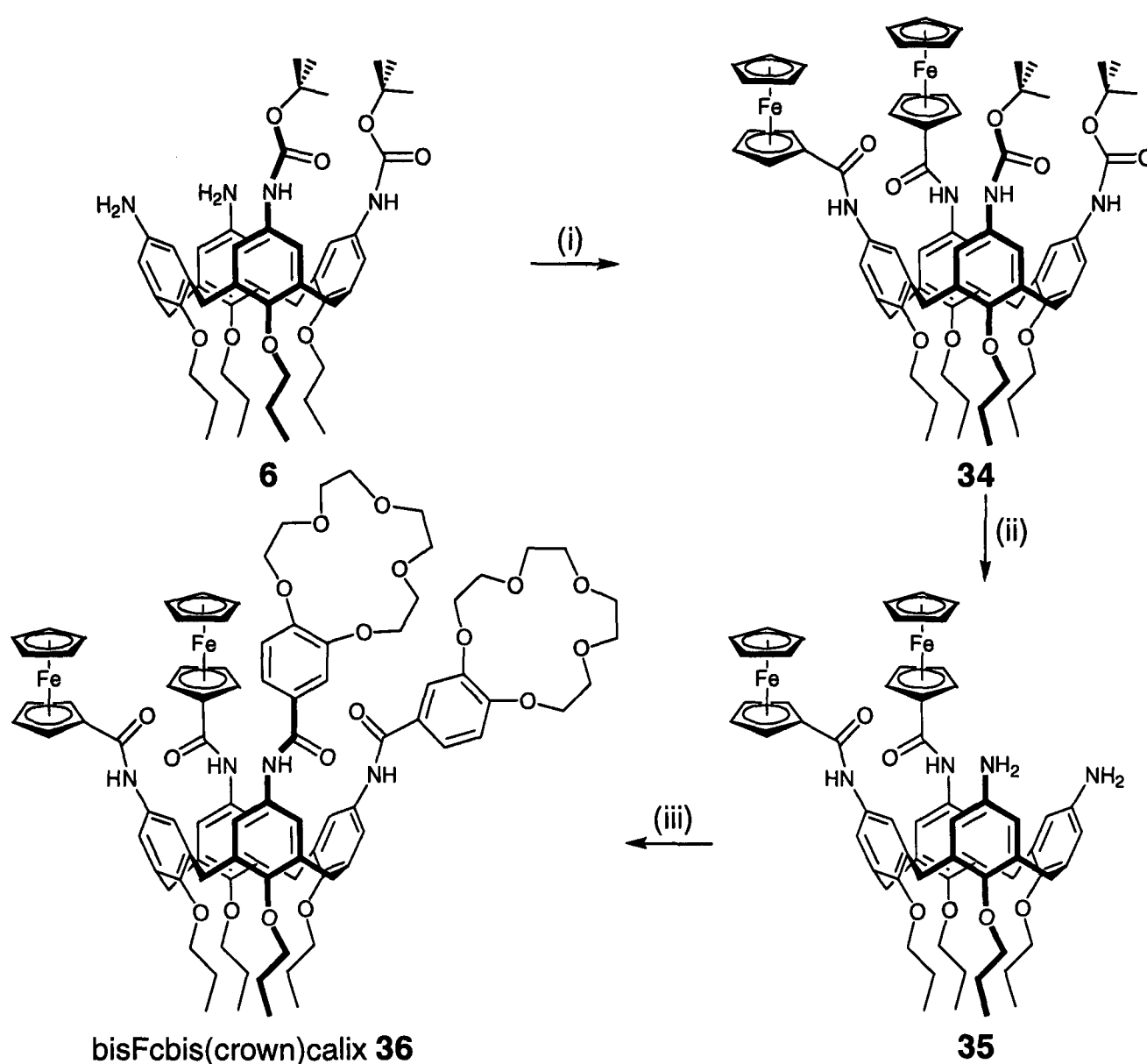
Scheme 2.9: (i) 4-(chlorocarboxy)benzo[15]crown-5 **15**, Et₃N, CHCl₃, reflux, 66 %; (ii) TFA, CH₂Cl₂, 73 %.

Calix[4]arene precursor **5** was reacted with one and a half equivalents of 4-(chlorocarboxy)benzo[15]crown-5 **15** in the presence of triethylamine base by heating to reflux in chloroform. The organic solution was stirred overnight with aqueous lithium hydroxide to remove excess starting material **15**. Precipitation from chloroform / hexane gave **32** as a white solid in 66 % yield. Deprotection of **32** using trifluoroacetic acid (TFA) in

dichloromethane followed by precipitation from chloroform / hexane gave **33** in 66 % yield. However, the coupling of **33** with **9** or **11** was surprisingly unsuccessful. As noted above, the reaction mixtures could not be purified sufficiently for further studies.

2.2.7 Synthesis of mixed receptors from di-BOC-protected calix[4]arene **6**

Following a similar synthetic methodology to that outlined above in Section 2.2.6, 1,2-di-BOC-protected calix[4]arene precursor **6** was reacted with three equivalents of chlorocarbonyl ferrocene **9** in the presence of triethylamine base in dichloromethane (Scheme 2.10). Precipitation from chloroform / hexane gave **34** as a pale orange powder in 81 % yield. Deprotection of **34** using trifluoroacetic acid in dichloromethane afforded the TFA salt of **35** in quantitative yield. Bis-ferrocene bis-amino calix[4]arene **35** was reacted with three equivalents of 4-(chlorocarboxy)benzo[15]crown-5 **15** in the presence of triethylamine base by heating to reflux in chloroform. The organic solution was stirred overnight with aqueous lithium hydroxide to remove excess starting material **15**. Precipitation from chloroform / hexane gave bisFc₂bis(crown)calix **36** as a pale orange solid in 49 % yield.



Scheme 2.10: (i) chlorocarbonyl ferrocene **9**, Et₃N, CH₂Cl₂, 81 %; (ii) TFA, CH₂Cl₂, 99 %; (iii) 4-(chlorocarboxy)benzo[15]crown-5 **15**, Et₃N, CHCl₃, reflux, 49 %.

2.2.8 Further investigation of tetra(Fcurea)calix **23**

As has been previously observed for other tetra-urea functionalised calixarenes,²⁹ tetra(Fcurea)calix **23** forms dimeric capsules in non-competitive organic solvents such as benzene or chloroform. Clearly, an understanding of such behaviour is important when considering possible anion binding interactions (see Section 2.3), and so the solution-phase association of receptor **23** in non-polar solvents was investigated in further detail.

In non-competitive solvents such as benzene or chloroform, tetra(Fcurea)calix **23** forms dimeric capsules in which the eight urea functions align themselves in a head-to-tail fashion (Figure 2.10). Sixteen hydrogen bonds effectively zipper the dimer together, restricting rotation around the phenyl-nitrogen bonds, resulting in a loss of equivalency for the aromatic

protons on the calixarene phenyl rings. Consequently, the ^1H NMR spectrum of **23** in C_6D_6 (Figure 2.10 (a)) shows two peaks for these aromatic protons at 6.69 ppm (H_C) and 8.18 ppm (H_D), both doublets with a typical meta-coupling of 2.5 Hz. In addition, the strong hydrogen bonds in the dimer cause deshielding of the urea protons. This results in the peaks for H_A and H_B appearing well downfield in the ^1H NMR spectrum, at 7.46 ppm and 8.04 ppm respectively.

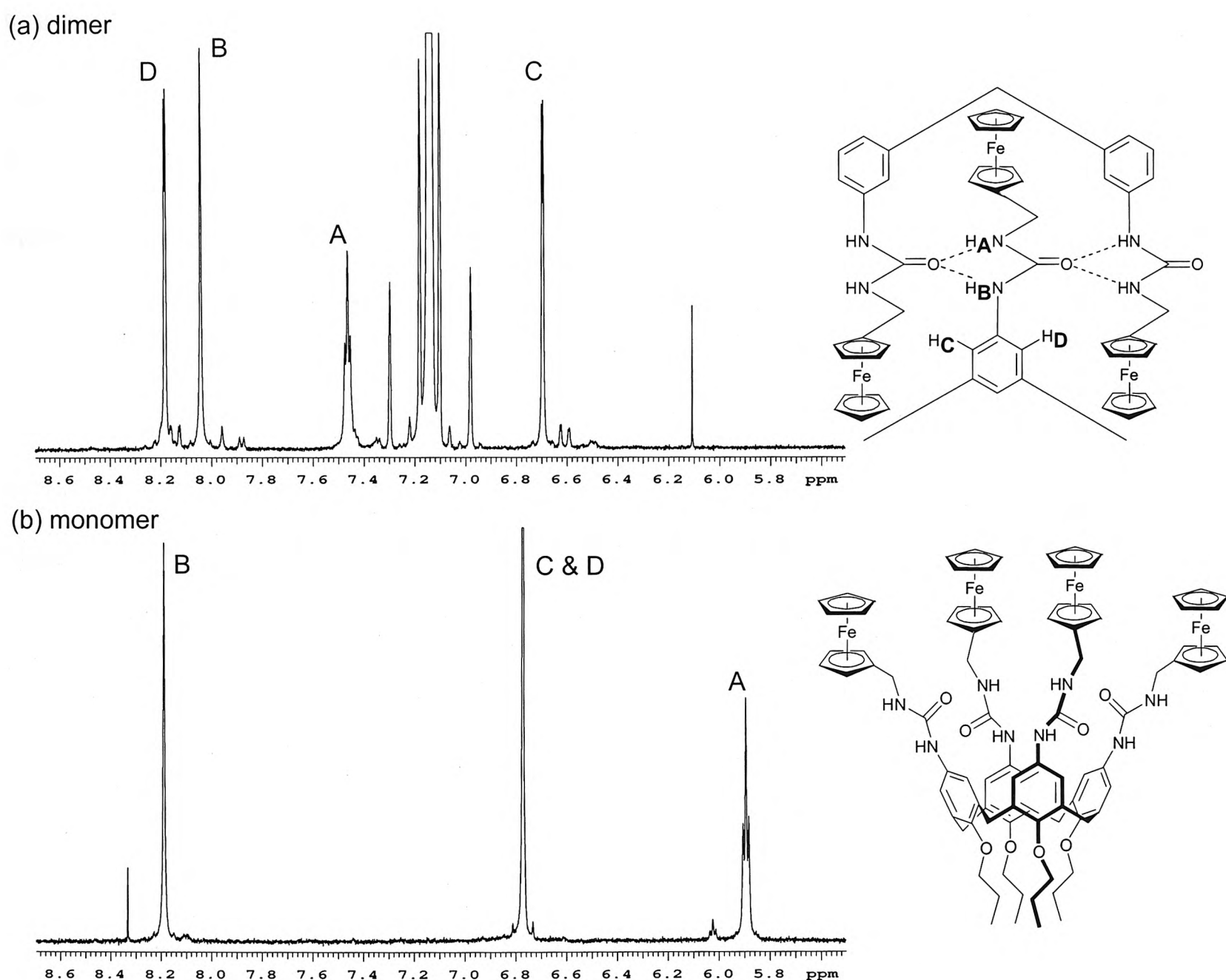


Figure 2.10: Partial ^1H NMR spectra of tetra(Fcurea)calix **23** in (a) C_6D_6 and (b) d_6 -DMSO (500 MHz, 5 - 9 ppm).

Solvents such as DMSO effectively compete for the urea hydrogen bonds thereby disrupting the dimeric structure. The ^1H NMR spectrum of **23** in d_6 -DMSO (Figure 2.10 (b)) is typical of

a monomeric species, showing peaks for the two urea protons at 5.90 ppm (H_A) and 8.19 ppm (H_B) and a single peak for the aromatic protons at 6.77 ppm (H_C and H_D).

Interestingly, the internal cavities of these tetra-urea calix[4]arene dimers are not empty but rather contain a single guest molecule of solvent. In fact, these species have been shown to encapsulate various aromatic, aliphatic and cationic guests.²⁹ The 1H NMR spectrum of tetra(Fcurea)calix **23** in 1:1 C_6D_6 / C_6H_6 shows a new peak at 3.99 ppm corresponding to the encapsulation of benzene. As has been observed in other studies,³⁰ the peak for the encapsulated solvent is shifted well upfield compared to that for the free solvent. Integration of the relevant peaks confirms the stoichiometry of one benzene molecule per dimeric capsule.

Further evidence for the encapsulation of solvent comes from the 1H NMR spectrum of **23** in 1:1 C_6D_6 / $CDCl_3$ (Figure 2.11). This shows two sets of signals (as confirmed by 1H - 1H correlation spectroscopy (COSY)) corresponding to the two different dimers present in solution, one encapsulating a molecule of benzene (H_D , H_B and H_C) and one encapsulating a molecule of chloroform (H_D^* , H_B^* and H_C^*).

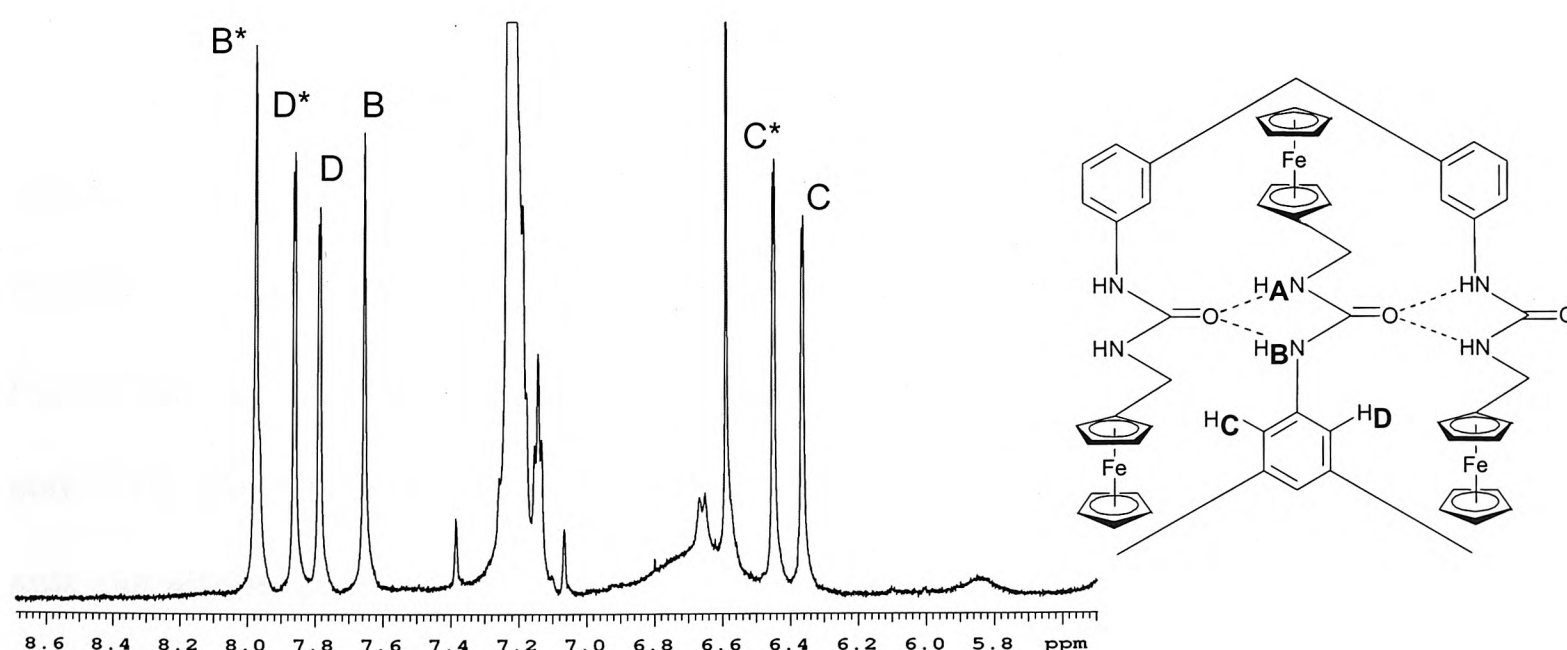


Figure 2.11: Partial 1H NMR spectrum of tetra(Fcurea)calix **23** in 1:1 C_6D_6 / $CDCl_3$ (500 MHz, 5 - 9 ppm).

The kinetic lability of these dimeric capsules may be demonstrated in the following way. The tetra-phenyl-urea calix[4]arene analogue **37** was synthesised by reacting tetra-amino calix[4]arene **4** with phenylisocyanate in dichloromethane to give the product as a cream coloured solid in 58 % yield.³¹ The ^1H NMR spectrum of a mixture of tetra(Fcurea)calix **23** and **37** in C_6D_6 (Figure 2.12) shows peaks corresponding to both homodimers and the heterodimer. In Figure 2.12, the peaks marked (+) are assigned to the **23**·**23** homodimer, those marked (*) are due to the **37**·**37** homodimer, and the rest are from the **23**·**37** heterodimer.

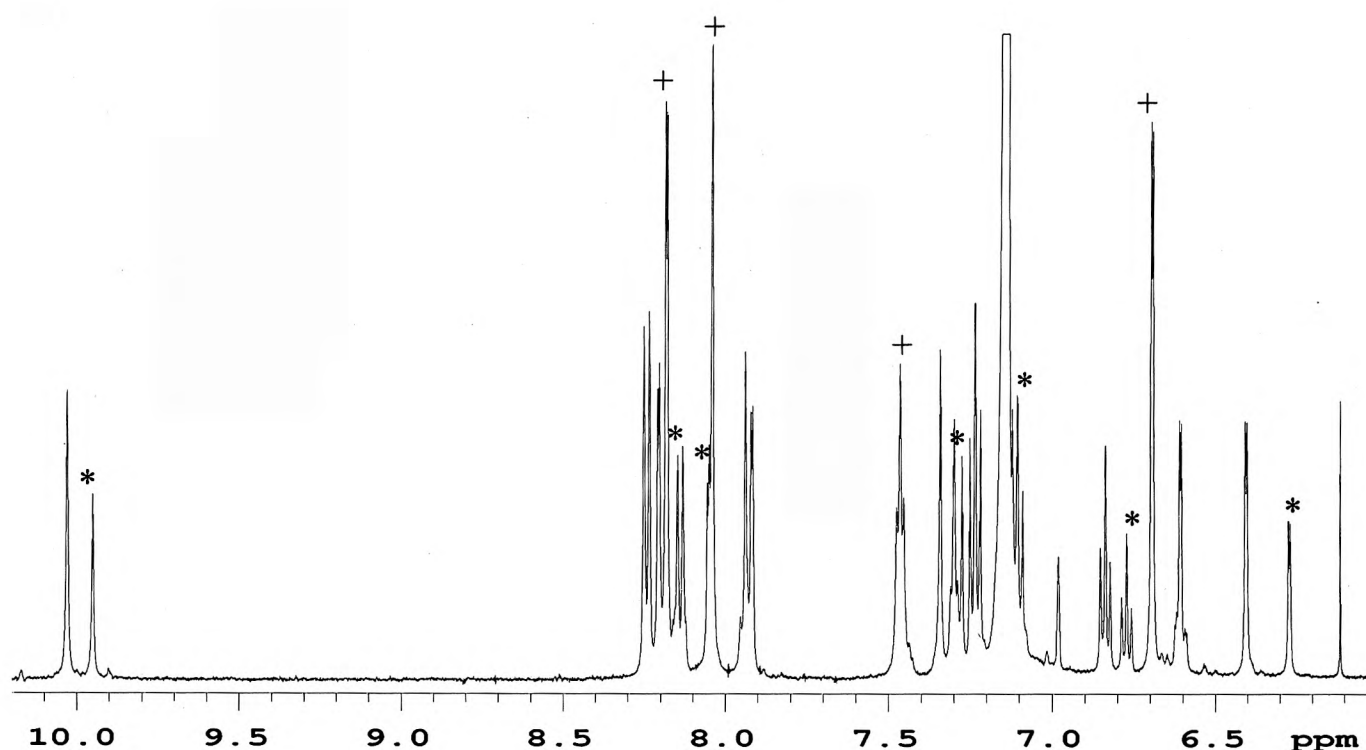


Figure 2.12: Partial ^1H NMR spectrum of a mixture of tetra(Fcurea)calix **23** and **37** in C_6D_6 (500 MHz, 5 - 9 ppm). + = **23**·**23** homodimer, * = **37**·**37** homodimer.

In order to quantify this behaviour, the rate of capsule association / dissociation was determined with the help of Dr. N. Rees (Inorganic Chemistry Laboratory, University of Oxford). The experiment involved measuring the rate of exchange between H_C and H_D (Figure 2.13) for a solution of tetra(Fcurea)calix **23** in C_6D_6 . After dissociation, a dimeric capsule can reform in one of two ways, either with the hydrogen bonds in the same direction as before (in which case there is no exchange) or with the hydrogen bonds in the opposite

direction (in which case H_C 'becomes' H_D and visa versa). The rate of this proton exchange was measured at 60 °C as the exchange was too slow to be determined at room temperature.

Slow exchange rates were determined from 1D-EXSY ($\pi/2 - t_1 - \pi/2 - t_m - \pi/2 - \text{obs}$) experiments. This involved varying the delay time t_m between the selective excitation of one proton (H_C) and the recording of the ^1H NMR spectrum. Figure 2.13 shows the change in the observed peak intensity of H_D as the delay time t_m is increased. As t_m is increased, the signal intensity decreases at first as more time is allowed for proton exchange (that is, for the excited H_C to exchange with H_D). However as the delay becomes longer, more time is allowed for the excited H_C to relax resulting in the signal intensity increasing back to its original value.

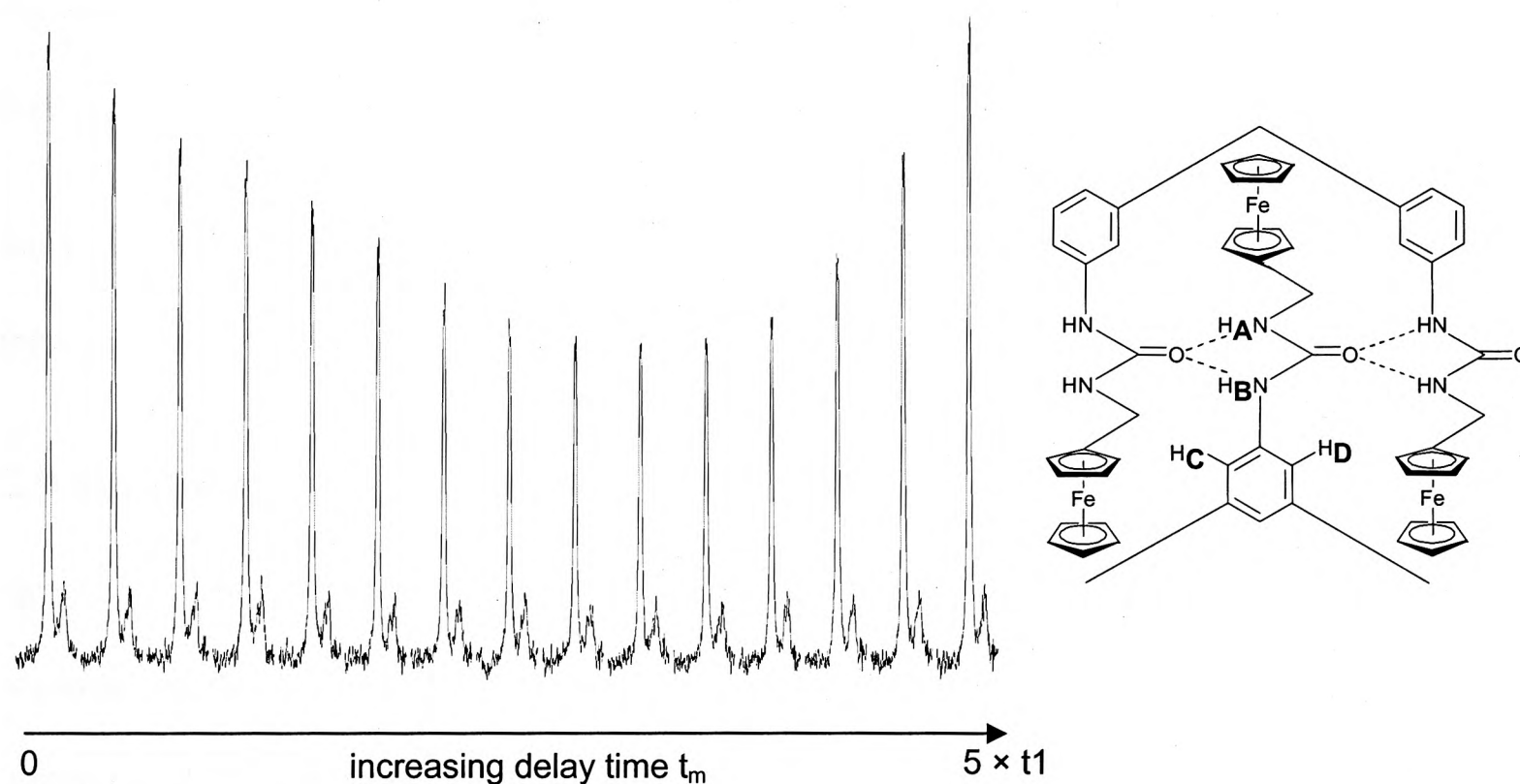


Figure 2.13: Results of a 1D-EXSY experiment with tetra(Fcurea)calix **23** in C_6D_6 , showing the change in peak intensity of H_D with increasing delay time t_m .

Rate constants were calculated using the program CIFIT³² with t_1 relaxation rates estimated from inversion recovery experiments. The rate of exchange between H_C and H_D for tetra(Fcurea)calix **23** in C_6D_6 at 60 °C was determined to be $3.0 \pm 0.1 \text{ s}^{-1}$. As noted above,

there are two pathways *via* which the dimeric capsule can dissociate and reform again, only one of which results in proton exchange. Therefore, the measured exchange rate corresponds to a rate of capsule association / dissociation of 6 s^{-1} .

Similar rate constants have been reported for the association kinetics of other tetra-urea calixarene compounds.³³ Interestingly, the *N*-functionalisation of tetra-urea-functionalised calix[4]arenes with bulky trityl and *p*-tritylphenyl groups has recently led to the formation of kinetically stable dimers with half lives of up to four days in DMSO solution.³⁴

The incorporation of ferrocene groups into the dimeric structure suggests the intriguing possibility of redox control of guest encapsulation. Although this was not investigated further, it is conceivable that a guest species held within the neutral dimeric capsule would be released upon oxidation of the ferrocene groups, as the oxidised receptors would not be expected to dimerise because of mutual repulsive charge effects.

Finally, it should be noted that neither tetra(Fcamide)calix **19** nor bis(Fcurea)calix **26** form dimers in benzene solution.

2.2.9 Summary

Reactions of the calixarene precursors **4**, **5** and **6** with the acid chloride or protected isocyanate synthons **9**, **11**, **15** and **18** resulted in the synthesis of a range of new upper-rim functionalised calix[4]arene anion and ion-pair receptors (see Appendix G). Five new anion receptors (tetra(Fcamide)calix **19**, tetra(Rebpy)calix **21**, tetra(Fcurea)calix **23**, bis(Fcurea)calix **26** and Fctri(benzo)calix **31**) and three new ion-pair receptors (tetra(crown)calix **22**, bis(crown)calix **25** and bisFc(bis(crown)calix **36**) were synthesised and characterised by ^1H NMR spectroscopy, mass spectrometry and elemental analysis.³⁵ Crystal

structures of tetra(Fcamide)calix **19** and tetra(Fcurea)calix **23** were obtained and the dimerisation of tetra(Fcurea)calix **23** in benzene solution was investigated.

2.3 ^1H NMR Anion and Ion-Pair Binding Studies

2.3.1 Introduction

The anion and ion-pair binding properties of the calix[4]arene-based receptors were studied initially by ^1H NMR spectroscopy. The anions chosen for these investigations were chloride, benzoate, acetate and dihydrogen phosphate as they possess contrasting shapes, sizes and basicities. Tetrabutylammonium was used as the counter cation as it is large and non-coordinating. Binding studies were carried out in several different solvent systems namely CDCl_3 , 1:1 CD_3CN / d_6 -DMSO and d_6 -DMSO.

^1H NMR spectroscopy has often been used to provide information about the structure of receptor-guest complexes in solution and to calculate receptor-guest stability constants.³⁶ Formation of a receptor-guest complex can alter the magnetic environments of the protons which are in close proximity to the binding site, leading to a change in the observed chemical shift in the spectrum. In all cases in this thesis, the receptor and receptor-guest complexes interconvert rapidly on the NMR timescale and a weighted mean of their chemical shifts is observed.³⁷

Typically, anion titration experiments involved the addition of aliquots of an anion solution (0.5 M), corresponding to between 0 and 10 equivalents of anion, to a solution of the receptor (0.01 M) and recording the ^1H NMR spectra (see Appendix A for details). The chemical shift of a specific proton (usually an amide or urea proton) on the receptor was monitored as it moved downfield upon addition of anions. The resulting titration data was analysed by the

computer program EQNMR³⁸ to yield stability constants for the anion-receptor binding processes.

In addition, Job plot analyses were often carried out in order to confirm the receptor-anion binding stoichiometry (see Appendix A). In cases where there was insufficient compound available for such studies, the binding stoichiometry was determined from the best fit of data in EQNMR.

2.3.2 Anion binding studies in CDCl₃

Initially, anion binding studies were undertaken in the non-competitive solvent CDCl₃. ¹H NMR titrations were carried out with tetra(Fcamide)calix **19** with chloride, benzoate, acetate and dihydrogen phosphate anions, added as their tetrabutylammonium salts. In all cases, addition of anions resulted in significant downfield perturbations of the receptor amide signal, indicating that the anions are bound by the hydrogen bonding moieties. Additional evidence for the binding of anions in the vicinity of the upper-rim was provided by the downfield shifts of the signal for the calix[4]arene aromatic protons *ortho* to the point of substitution. EQNMR analysis of the titration data (with chloride, benzoate and acetate) obtained from monitoring the receptor amide signal, indicated 1:1 anion / receptor binding stoichiometries and gave stability constant values shown in Table 2.1. EQNMR was unable to fit the data with dihydrogen phosphate. Job plot analyses were undertaken and confirmed the 1:1 binding stoichiometry between tetra(Fcamide)calix **19** and chloride, benzoate and acetate, and indicated a mixture of complex equilibria between receptor **19** and dihydrogen phosphate.

	tetra(Fcamide)calix 19
chloride	45
benzoate	160
acetate	160
dihydrogen phosphate	– ^a

Table 2.1: Anion stability constants (K / M^{-1}) determined in $CDCl_3$ (errors $\leq 10\%$). ^a EQNMR was unable to fit the data.

The stability constant values displayed in Table 2.1 show tetra(Fcamide)calix **19** binds carboxylate anions more strongly than chloride anions, following the trend in anion basicities.³⁹ Importantly, Job plot analyses revealed 1:1 anion / receptor binding stoichiometries, indicating that the four amide groups arranged around the calix[4]arene upper-rim bind a single anion in a concerted manner.

Analogous 1H NMR titrations were undertaken with the other anion receptors (tetra(Fcurea)calix **23**, bis(Fcurea)calix **26**, tetra(Rebpy)calix **21** and Fctri(benzo)calix **31**) in $CDCl_3$, however stability constant data could not be obtained for the reasons outlined below.

As discussed previously (in Section 2.2.8), tetra(Fcurea)calix **23** forms dimeric capsules in non-competitive solvents such as chloroform. Interestingly, addition of anions to chloroform solutions of **23** caused the disruption of the hydrogen bonding array and resulted in the dissociation of the dimer. In the 1H NMR spectrum of **23** in $CDCl_3$, the signals corresponding to the dimer gradually disappeared upon addition of anions, while those of the monomer gradually appeared and shifted downfield. Although indicative of anion binding by the urea groups of the receptor, the complexity of this process prevented accurate titration data from being obtained.

Job plot analyses with bis(Fcurea)calix **26** and various anions in CDCl₃ revealed an equilibrium between both 1:1 and 2:1 anion / receptor complexes. Anion titrations with receptor **26** resulted in significant downfield shifts of the urea protons of the receptor, however the complex nature of the binding processes prevented accurate determination of stability constants. Anion titrations could not be performed with tetra(Rebpy)calix **21** in CDCl₃ due to the poor solubility of the receptor. ¹H NMR titrations with Fctri(benzo)calix **31** and various anions in CDCl₃ resulted in a broadening of the amide signals of the receptor to such an extent that the chemical shift of the peaks could not be followed throughout the course of the titration.

Consequently, the anion binding properties of these receptors were investigated in other solvent systems. As most of the receptors showed poor solubility in acetonitrile, further ¹H NMR anion titrations were performed in either 1:1 CD₃CN / *d*₆-DMSO or 100 % *d*₆-DMSO.

2.3.3 Anion binding studies in 1:1 CD₃CN / *d*₆-DMSO

¹H NMR titrations were carried out with tetra(Fcamide)calix **19**, tetra(Fcurea)calix **23** and bis(Fcurea)calix **26** with chloride, benzoate and dihydrogen phosphate anions in 1:1 CD₃CN / *d*₆-DMSO. In all cases, addition of anions resulted in significant downfield perturbations of the amide or urea signals of the receptors. Downfield shifts of up to Δδ = 2.32 ppm were observed (in the case of **26** and benzoate), indicating a favourable interaction between the anion and the receptor hydrogen bonding moieties. For example, Figure 2.14 shows the ¹H NMR spectra of receptor **19** upon titration with dihydrogen phosphate. As observed previously for the titrations in CDCl₃, in addition to the amide protons, the aromatic protons *ortho* to the point of upper-rim substitution also shift downfield.

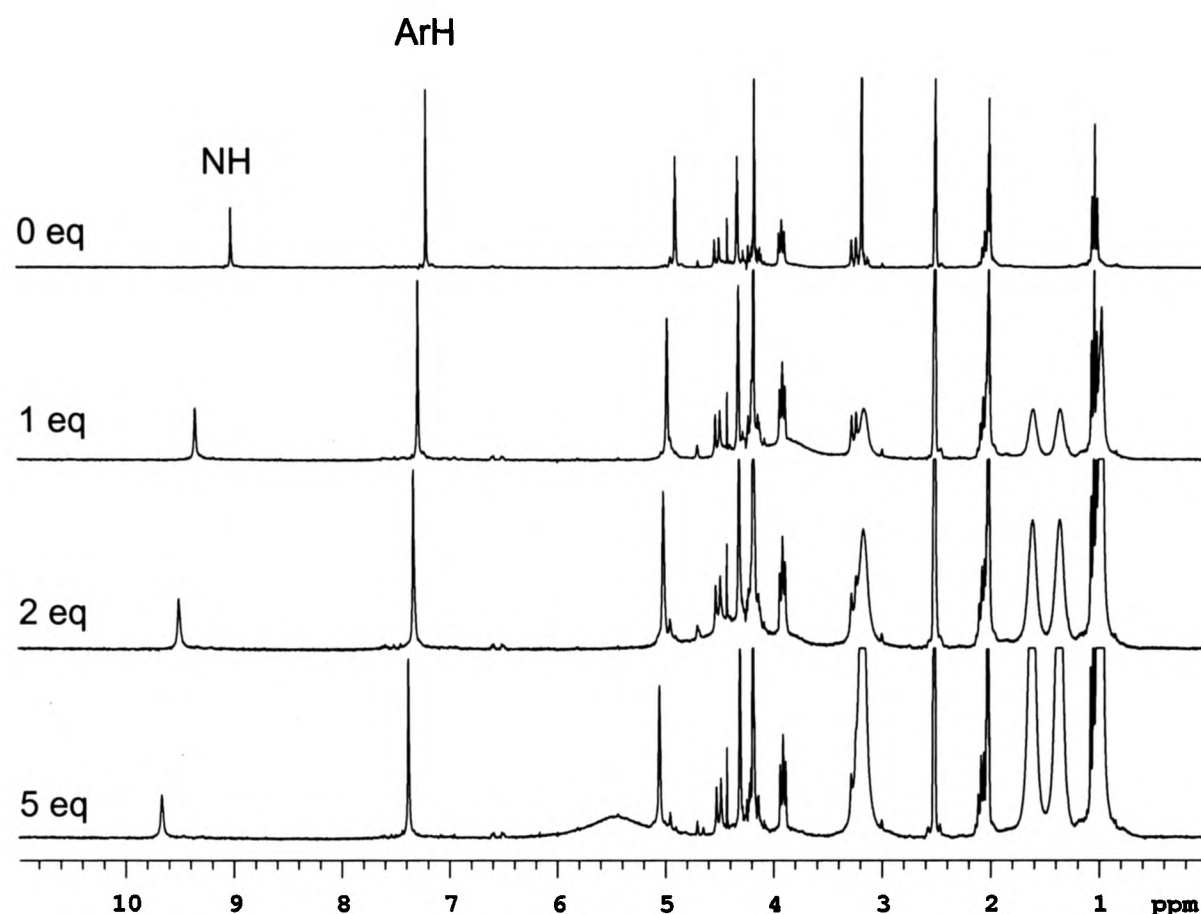


Figure 2.14: ^1H NMR spectra of tetra(Fcamide)calix **19** in 1:1 CD_3CN / d_6 -DMSO upon addition of 0, 1, 2 and 5 equivalents of dihydrogen phosphate.

The anion binding-induced downfield shifts of the amide or urea signals of the receptors were monitored and the resulting titration data analysed by EQNMR. For example, Figure 2.15 shows the titration curves obtained for receptor **19** upon addition of chloride, benzoate and dihydrogen phosphate anions.

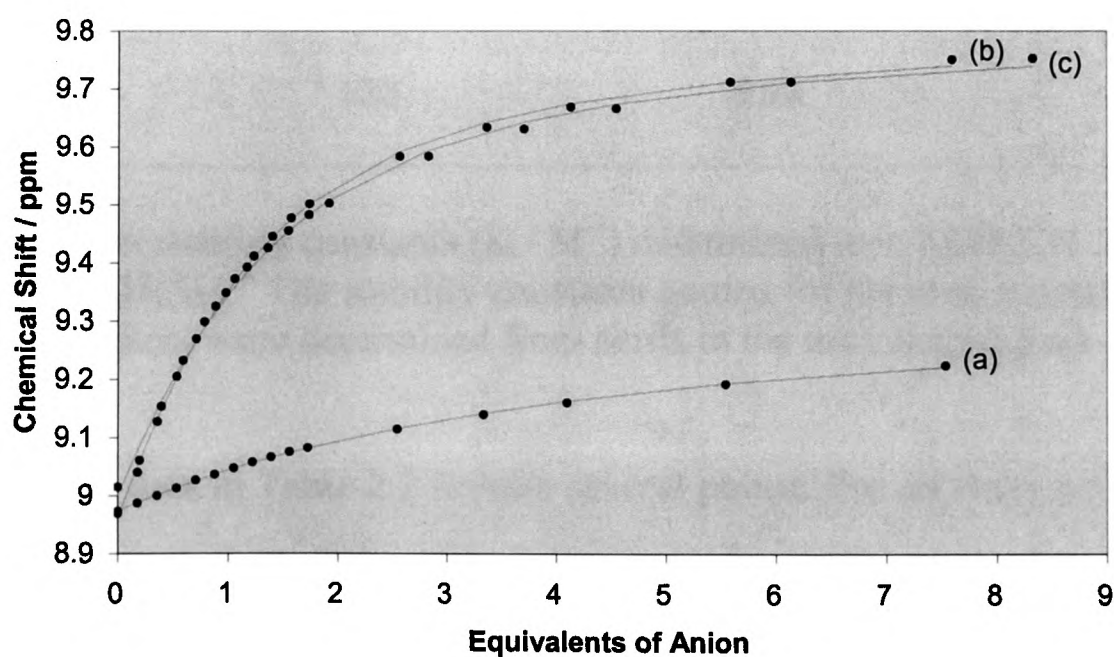


Figure 2.15: ^1H NMR titration curves for tetra(Fcamide)calix **19** upon addition of (a) chloride, (b) benzoate and (c) dihydrogen phosphate.

In all cases, the titration data fitted a 1:1 anion / receptor binding model to give the stability constant values shown in Table 2.2. Job plot analyses were undertaken for both tetra(Fcurea)calix **23** and bis(Fcurea)calix **26** with chloride, benzoate and dihydrogen phosphate, and in all cases the results confirmed a 1:1 binding stoichiometry. For example, Figure 2.16 shows the Job plot for receptor **26** with benzoate.

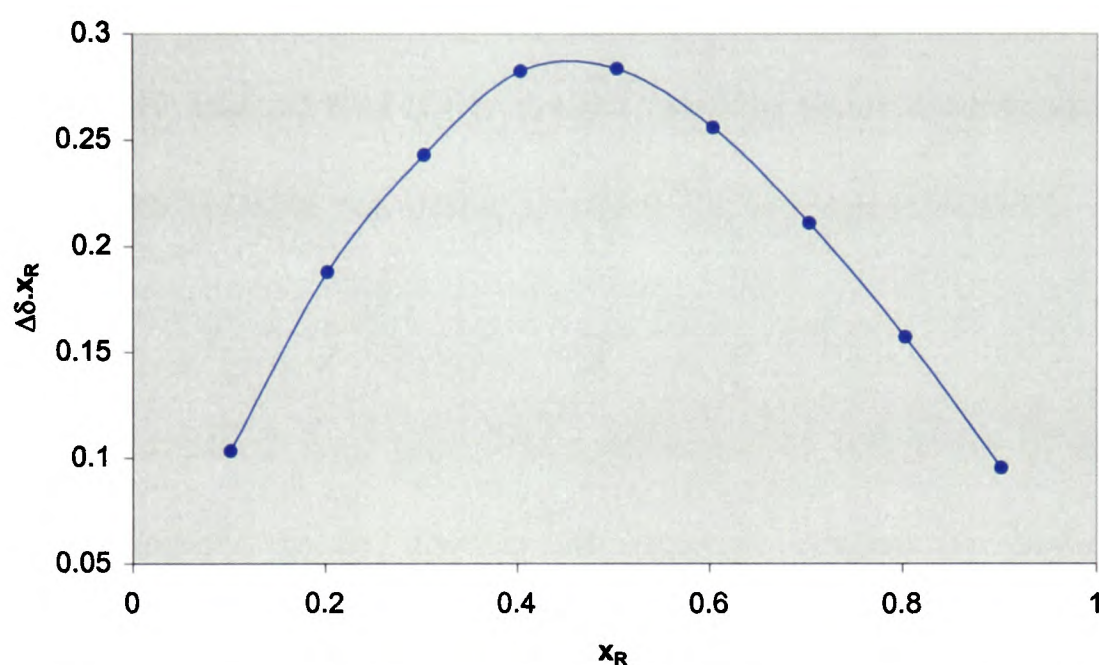


Figure 2.16: Job plot for bis(Fcurea)calix **26** with benzoate in 1:1 CD₃CN / *d*₆-DMSO revealing a 1:1 anion / receptor binding stoichiometry.

	tetra(Fcamide)calix 19	tetra(Fcurea)calix 23 ^a	bis(Fcurea)calix 26 ^a
chloride	30	15	15
benzoate	150	30	40
dihydrogen phosphate	120	150	25

Table 2.2: Anion stability constants (K / M⁻¹) determined in 1:1 CD₃CN / *d*₆-DMSO (errors ≤10 %). ^a The stability constants quoted for the urea-containing receptors were determined from shifts in the urea singlet peak.

Consideration of the data in Table 2.2 reveals several points. For all three receptors, chloride is bound most weakly, as expected for the least basic anion. It is evident that the degree of upper-rim substitution has a marked effect on the binding properties of the receptors. The bis-substituted receptor **26** exhibits modest association constants for all three anions and shows

limited topological discrimination. In contrast, the tetra-substituted receptors **19** and **23**, in which additional hydrogen bond donor sites are available, generally show larger association constants, in particular for the dihydrogen phosphate anion.

It is interesting to note that whereas tetra(Fcamide)calix **19** binds benzoate more strongly than dihydrogen phosphate (in line with anion basicities), the opposite selectivity preference is shown by tetra(Fcurea)calix **23** which binds dihydrogen phosphate five times more strongly than benzoate. This may indicate that the hydrogen bonding functionalities of the tetra-urea-substituted calix[4]arene receptor are better arranged for binding tetrahedral anions such as dihydrogen phosphate.

Disappointingly, the introduction of urea functionalities does not result in markedly larger stability constants compared to the tetra-amide receptor despite the higher acidity and increased anion binding ability of the urea NH protons.

2.3.4 X-ray structural investigation of the bis(benzoate) complex of bis(Fcurea)calix **26**

X-ray quality crystals (pale orange blocks) of $26 \cdot 2[\text{N}(\text{C}_4\text{H}_9)_4][\text{C}_6\text{H}_5\text{CO}_2]$ were obtained from a 1:1 CD_3CN / d_6 -DMSO solution of bis(Fcurea)calix **26** containing a ten-fold excess of tetrabutylammonium benzoate. The crystals formed in the NMR tube after the ^1H NMR titration of **26** with benzoate anions. The structure was solved by Dr. A. R. Cowley (Chemical Crystallography Laboratory, University of Oxford) and is shown in Figure 2.17; full data are given in Appendix F.4.

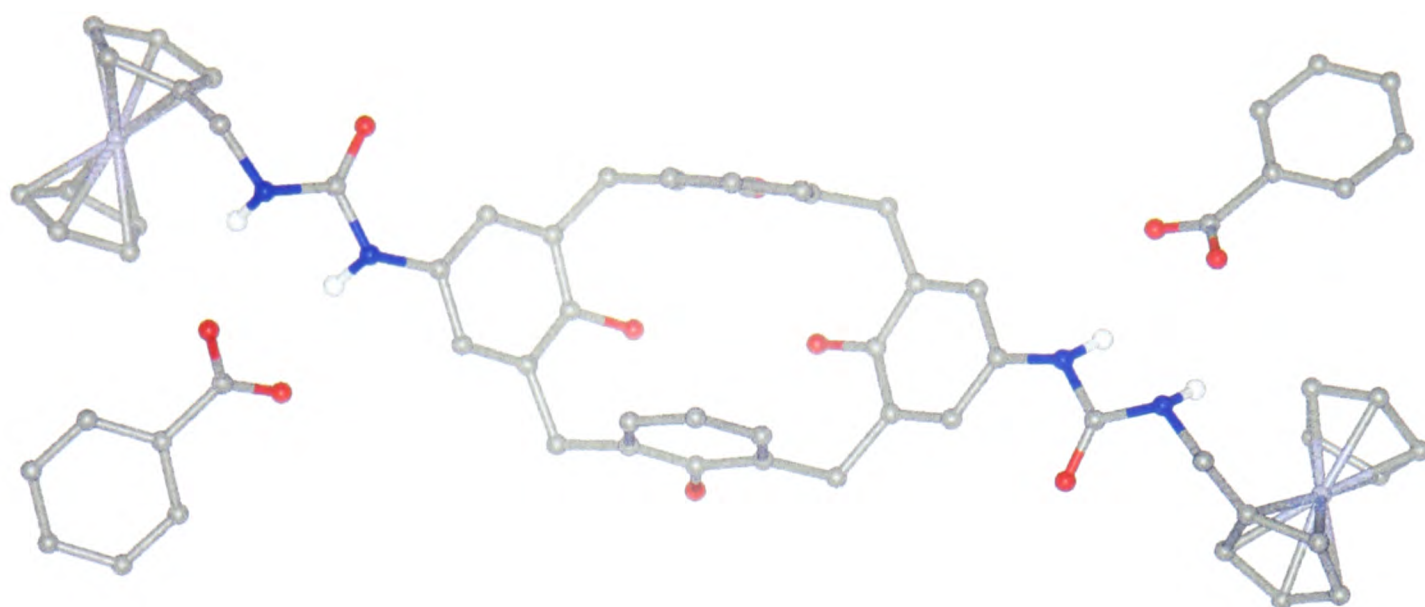


Figure 2.17: General view of the bis(benzoate) complex of bis(Fcurea)calix **26** (the lower-rim propyl groups and most of the hydrogen atoms have been omitted for clarity).

The calix[4]arene molecule is situated on a crystallographic two-fold axis of rotation (monoclinic system, $C 2/c$ space group). It adopts a flattened cone conformation in which the two urea-substituted aromatic rings are angled away from each other (the interplanar angle between the best planes of the attached phenyl groups is 113.2°) and the other two aromatic rings taper inward slightly (interplanar angle 17.1°). Each urea functionality is hydrogen bonded through both NH groups to a benzoate anion ($N(1)-O(4) = 2.949(2) \text{ \AA}$, $N(2)-O(5) = 2.813(2) \text{ \AA}$), the urea and carboxylate groups not being coplanar (the interplanar angle between the NCN and OCO planes is 36.3°).

It is interesting to compare the anion binding properties of bis(Fcurea)calix **26** in solution and solid state. Job plot analyses (Figure 2.16) reveal that receptor **26** binds anions in a 1:1 stoichiometry in solution, with the two urea groups acting cooperatively in the complexation of anions. In contrast, the crystal structure of the bis(benzoate) complex of **26** (Figure 2.17) reveals that in the solid state the two urea groups act independently, binding benzoate in a 2:1 anion / receptor stoichiometry. The presence of a ten-fold excess of benzoate anions in solution could have encouraged the crystallisation of the bis(benzoate) complex by favouring

the formation of the 2:1 species in solution. In addition, the doubly-charged 2:1 complex would be expected to be less soluble in organic solution than the singly-charged 1:1 species, and hence solubility factors could have caused the preferential crystallisation of the bis(benzoate) complex of **26**.

2.3.5 Anion binding studies in d_6 -DMSO

^1H NMR titrations were carried out with tetra(Fcamide)calix **19**, tetra(Rebpy)calix **21** and Fctri(benzo)calix **31** with chloride, benzoate, acetate and dihydrogen phosphate anions in d_6 -DMSO. The binding of an anion by the amide groups at the upper-rim of a receptor was indicated by the observation of significant downfield shifts of the receptor amide signals upon addition of anions. EQNMR analysis of the titration data indicated 1:1 anion / receptor binding stoichiometries in all cases and gave the stability constant values shown in Table 2.3.

^1H NMR titrations with receptor **21** and dihydrogen phosphate resulted in a broadening of the amide signals of the receptor to such an extent that the chemical shift of the peak could not be followed throughout the course of the titration. Job plot analyses were undertaken for receptor **19** with chloride, benzoate, acetate and dihydrogen phosphate and confirmed the 1:1 binding stoichiometry.

	tetra(Fcamide)calix 19	tetra(Rebpy)calix 21	Fctri(benzo)calix 31 ^b
chloride	5	35	15
benzoate	40	75	55
acetate	90	70	190
dihydrogen phosphate	95	– ^a	210

Table 2.3: Anion stability constants (K / M^{-1}) determined in d_6 -DMSO (errors $\leq 10\%$). ^a The amide peak became too broad to monitor. ^b The three different amide peaks of the receptor gave the same stability constants.

Table 2.3 reveals that all three receptors exhibit a similar trend in anion binding affinity. Interestingly, receptor **31** displays significantly larger stability constants with acetate and dihydrogen phosphate than observed for the other receptors. For **19** and **31**, the anion preference order is dihydrogen phosphate $\approx$ acetate $>$ benzoate $>$ chloride; for **21**, the order is acetate $\approx$ benzoate $>$ chloride.

A comparison of the anion stability constants for tetra(Fcamide)calix **19** in different solvents (Tables 2.1 – 2.3) reveals that, as expected, the binding of anions is stronger in non-competitive solvents (such as CDCl₃) than in competitive solvents (such as *d*₆-DMSO).

2.3.6 Ion-pair binding studies

Bis(crown)calix **25**, bisFc(bis(crown)calix **36** and tetra(crown)calix **22** were designed to simultaneously bind cations and anions such that the presence of co-bound alkali metal cations would enhance the strength of anion binding *via* favourable electrostatic interactions and preorganisation / conformational effects. ¹H NMR titration experiments (see Appendix A) were conducted with all three heteroditopic receptors with chloride, benzoate and dihydrogen phosphate anions (added as their tetrabutylammonium salts), both in the absence and presence of equivalents of sodium and potassium cations (added as their perchlorate salts). The tetrabutylammonium and perchlorate counter-ions chosen for these studies are non-coordinating, and were shown to have no influence on the binding of the cations and anions of interest.

The choice of solvent for these experiments was limited because all possible species that might exist in the titration experiment (most importantly the ion-pair salt being studied, the receptor and the receptor ion-pair complex) need to be soluble in the selected solvent. Also, ideally the metal cation must be bound strongly so as to minimise ion-pairing outside of the receptor. Taking this into account, the cation and anion coordination properties of

bis(crown)calix **25**, bisFc(bis(crown)calix **36** and tetra(crown)calix **22** were investigated by ^1H NMR titration experiments in 1:1 CD_3CN / d_6 -DMSO (in the majority of cases).

The addition of sodium perchlorate and potassium perchlorate salts to solutions of the receptors in 1:1 CD_3CN / d_6 -DMSO caused small but significant upfield perturbations of the crown ether OCH_2 signals in the respective ^1H NMR spectra. This is indicative of alkali metal cation binding by the benzo[15]crown-5 ether moieties of the receptors. However, cation stability constant values could not be determined, as it proved impossible to continually monitor a specific signal throughout the titration experiment.

Interestingly, the addition of potassium cations to solutions of these receptors also resulted in upfield shifts of the amide resonances in the respective ^1H NMR spectra. In particular, the amide proton signal for bis(crown)calix **25** shifted from 9.58 ppm to 8.80 ppm upon addition of one equivalent of potassium perchlorate, however no perturbation was observed upon addition of sodium perchlorate. These results may be explained by potassium complexation-induced conformational effects (which are discussed in detail below).

Electrospray mass spectrometry (ESMS) has been used to assess alkali metal cation binding with crown ether complexes.⁴⁰ ESMS results with excess sodium cations gave predominant receptor-alkali metal complex species where the sodium cation was bound in each of the benzo[15]crown-5 moieties of the respective receptor. That is, when solutions of the receptors were co-injected into the mass spectrometer with excess sodium perchlorate, the major peaks in the corresponding mass spectra were $[\mathbf{25} + 2\text{Na}]^{2+}$, $[\mathbf{36} + 2\text{Na}]^{2+}$ and $[\mathbf{22} + 4\text{Na}]^{4+}$. Analogous ESMS experiments with potassium cations revealed 1:1 intramolecular sandwich complex species as the major molecular ions with bis(crown)calix **25** and bisFc(bis(crown)calix **36**. Bis(benzo[15]crown-5) ether ligands are well known to form sandwich complexes with potassium cations.⁴¹

Interestingly, ESMS competition experiments with bis(crown)calix **25** with five equivalents each of lithium, sodium, potassium, rubidium and cesium cations in acetonitrile solutions revealed $[25 + K]^+$ as the most intense singularly charged molecular species (Figure 2.18) and $[25 + 2Na]^{2+}$ as the most prominent doubly charged species. The peaks corresponding to the complexation of other alkali metal cations were much less intense.

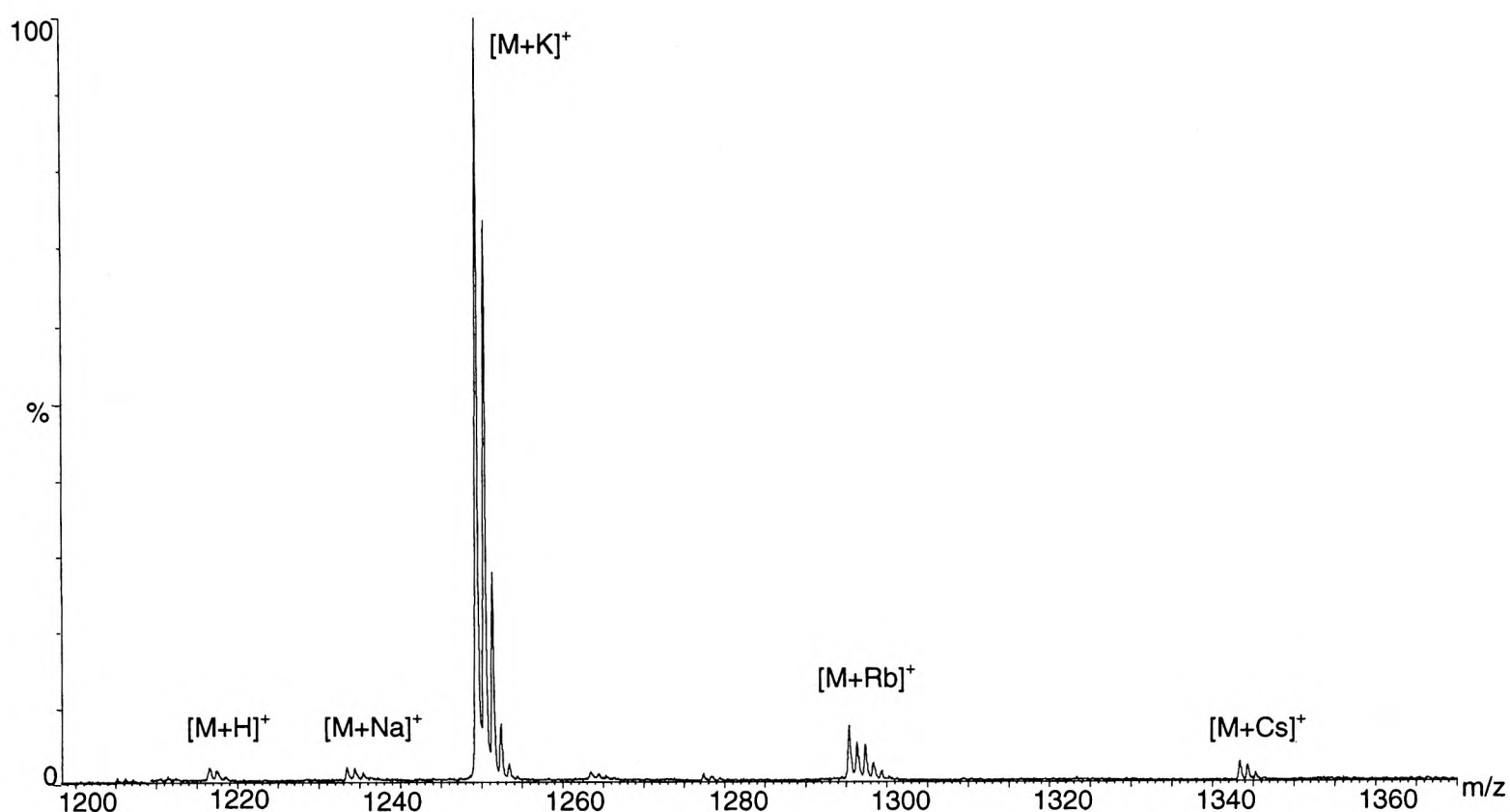


Figure 2.18: ESMS competition experiment with bis(crown)calix **25** and alkali metal perchlorate salts.

The ^1H NMR and ESMS studies described above established the ability of the receptors to strongly bind sodium and potassium cations and indicated the preferred binding stoichiometries for these cations with the benzo[15]crown-5 ether moieties. ^1H NMR titration experiments were performed with bis(crown)calix **25**, bisFcbis(crown)calix **36** and tetra(crown)calix **22** with chloride, benzoate and dihydrogen phosphate anions in 1:1 CD_3CN / d_6 -DMSO in the absence / presence of sodium (one equivalent of sodium perchlorate per benzo[15]crown-5 group in the respective receptor) and potassium (0.5 equivalents of potassium perchlorate per crown ether) cations. EQNMR analysis of the titration curves (Figure 2.19), monitoring the amide protons of the respective receptor, indicated 1:1 anion /

receptor binding stoichiometries and gave the stability constant values for anion binding shown in Table 2.4. In the case of dihydrogen phosphate, precipitation problems necessitated titration experiments being undertaken in 100 % d_6 -DMSO. The previously determined anion stability constants for tetra(Fcamide)calix **19** (which does not contain a crown ether cation binding site) are also given in Table 2.4 for comparison purposes.

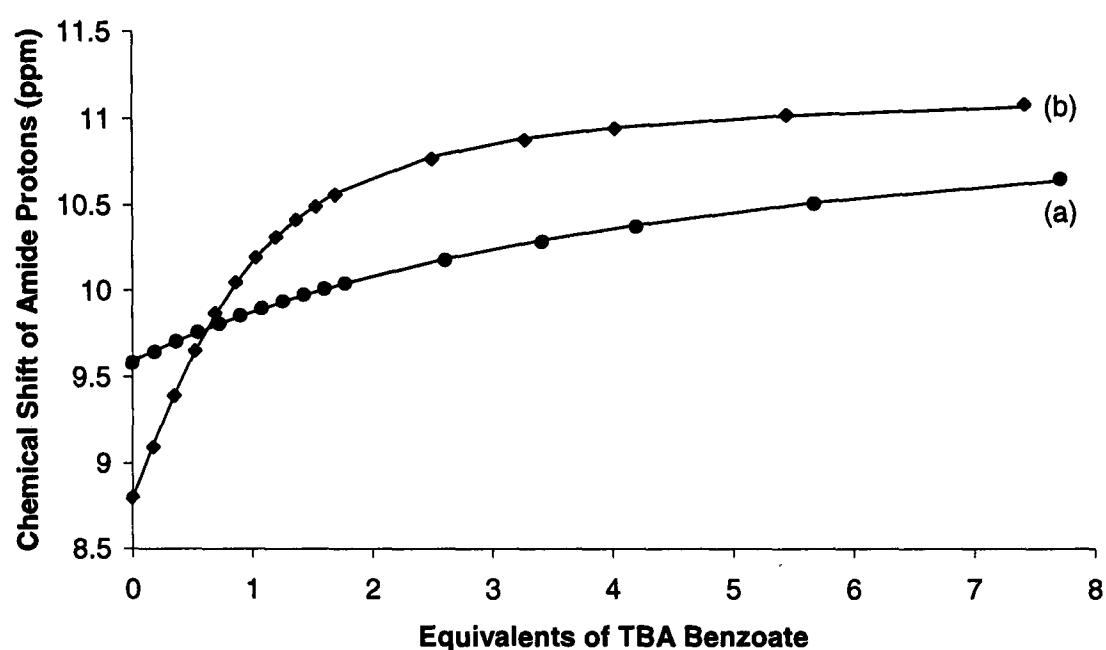


Figure 2.19: ^1H NMR titration curves for (a) bis(crown)calix **25** and (b) **25**· K^+ upon addition of benzoate anions in 1:1 CD_3CN / d_6 -DMSO.

	bis(crown)calix 25	bisFc 36 ^f bis(crown)calix	tetra(crown)calix 22	tetra(Fcamide)calix 19
chloride ^a	5	25	10	30
+ 2 Na ⁺	< 5	< 5	< 5 ^d	— ^g
+ K ⁺	15	150	15 ^e	— ^g
benzoate ^a	25	105	30	150
+ 2 Na ⁺	< 5	20	< 5 ^d	— ^g
+ K ⁺	270	205	30 ^e	— ^g
dihydrogen phosphate ^b	10	80	^c	95
+ 2 Na ⁺	< 5	< 5	< 5 ^d	— ^g
+ K ⁺	60	^c	^c	— ^g

Table 2.4: Anion stability constants (K / M^{-1}) (errors $\leq 10 \%$). ^a Titrations carried out in 1:1 CD₃CN / *d*₆-DMSO. ^b Titrations carried out in 100 % *d*₆-DMSO. ^c EQNMR was unable to fit the data. ^d 4 equivalents of Na⁺. ^e 2 equivalents of K⁺. ^f The two different amide peaks of the receptor gave the same stability constants. ^g Titrations were not performed.

Consideration of the data in Table 2.4 reveals a number of trends. All four receptors (**25**, **36**, **22** and **19**) bind anions with modest stability constant values and show the same order of anion selectivity. That is, all four receptors bind benzoate most strongly, followed by dihydrogen phosphate then chloride, a trend in line with anion basicities (the pK_a values of the respective acids of benzoate, dihydrogen phosphate and chloride in water are 4.2, 2.2 and -6.1 respectively).³⁹ All three anions are bound most strongly by tetra(Fcamide)calix **19**, followed by bisFc**36** then tetra(crown)calix **22** then bis(crown)calix **25**. This indicates that, broadly speaking, stronger anion complexes are formed by the tetra-substituted receptors compared to the bis-substituted one, as the tetra-substituted receptors contain additional amide functionalities capable of hydrogen bonding to the anions. In addition, the receptors containing the more acidic ferrocenoyl amide protons form stronger anion complexes than those without these groups.

It is important to note that with the bis(benzo[15]crown-5) containing calix[4]arene receptors bis(crown)calix **25** and bisFcabis(crown)calix **36**, the presence of one equivalent of potassium cations results in a significant increase in the strength of chloride, benzoate and dihydrogen phosphate binding by up to an order of magnitude in the case of **25** and benzoate. This anion binding enhancement in the presence of potassium cations is shown graphically in Figure 2.20. In contrast, with two equivalents of sodium cations a general decrease in the strength of anion binding is observed.

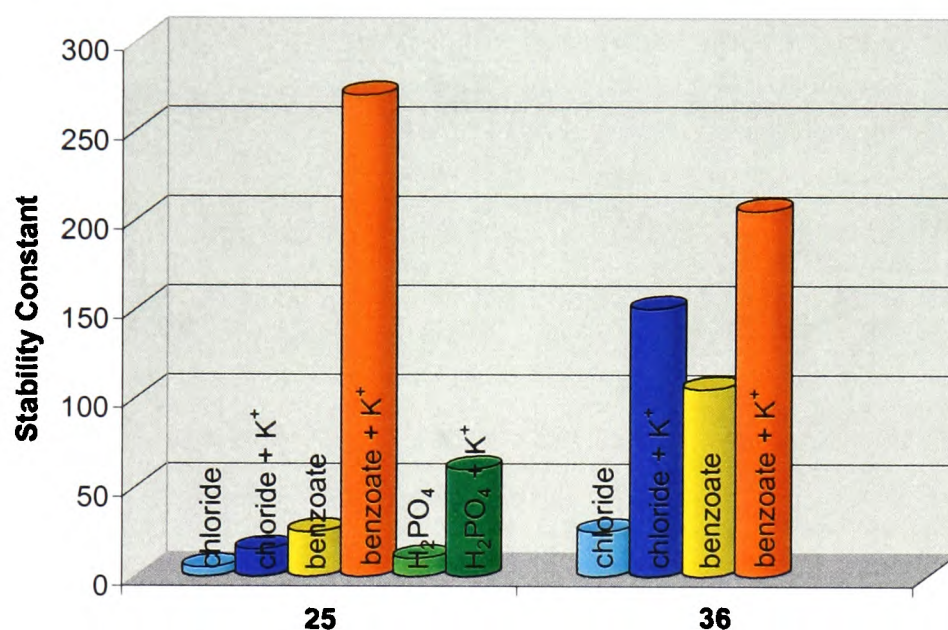


Figure 2.20: Anion stability constants (K / M^{-1}) for bis(crown)calix **25** and bisFcabis(crown)calix **36** in the absence / presence of potassium cations showing a positive cooperative ion-pair effect.

These observations may be rationalised by the fact that the potassium cation forms a 1:1 intramolecular sandwich complex with the benzo[15]crown-5 ether moieties of bis(crown)calix **25** and bisFcabis(crown)calix **36** which in effect preorganises the amide groups for anion binding (Figure 2.21 (a)). In addition to this positive allosteric effect, mutual electrostatic potassium cation-anion attraction and through bond inductive electrostatic effects of the complexed metal cation may enhance the relative acidity of the receptors' amide protons leading to stronger hydrogen bonding with the guest anion. In contrast, the 2:1 sodium cation / receptor stoichiometry, in which each crown ether complexes a sodium

cation, results in the amide groups being unable to cooperatively complex an anion due to mutual repulsive sodium cation crown ether electrostatic effects (Figure 2.21 (b)). This negative allosteric effect was also noted with the tetra(benzo[15]crown-5) derivative tetra(crown)calix **22** and four equivalents of sodium. Interestingly, receptor **22** exhibited little difference in binding strength of chloride or benzoate anions in the presence of one or two equivalents of potassium cations.

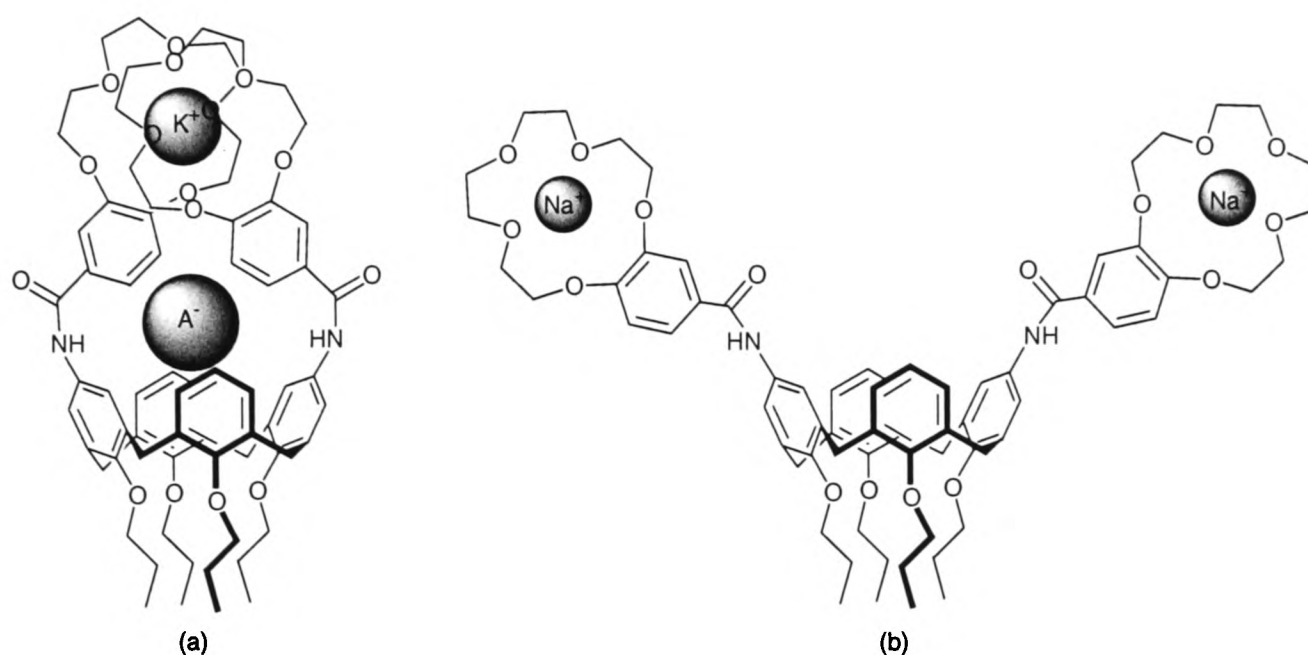


Figure 2.21: Schematic representation of (a) 1:1 potassium cation sandwich complex of bis(crown)calix **25** favouring anion complexation and (b) 2:1 sodium / receptor complex which is unable to cooperatively bind an anion.

Finally, 1H NMR titrations were carried out with tetra(Fcamide)calix **19** with chloride, benzoate and dihydrogen phosphate anions in 1:1 CD_3CN / d_6 -DMSO in the presence of a mixture of one equivalent of benzo[15]crown-5 and either one equivalent of sodium or 0.5 equivalents of potassium perchlorate. The stability constants determined were the same (within error) as those determined for tetra(Fcamide)calix **19** on its own. This demonstrates that, in this solvent mixture, the potassium and sodium cations are indeed bound strongly by the crown ether moieties and ion-pairing (between the alkali metal cation and titrated anion) outside the receptor is minimal. This provides further support for the above explanation of the observed binding enhancement in terms of conformational effects.

2.3.7 Solid / liquid extraction studies

One of the potential applications of neutral ion-pair receptors (as outlined in Section 1.4.2 of the Introduction) is the extraction and transport of metal salts. The ability of bis(crown)calix **25** to extract and solubilise various sodium and potassium salts into non-polar organic solvents was therefore investigated. In a typical experiment, the receptor was dissolved in CDCl_3 and stirred with an excess of solid KCl , KOAc , KH_2PO_4 , NaCl , NaOAc or NaH_2PO_4 for 24 hours. After filtration, ^1H NMR spectra were recorded and compared to that of the free receptor. No changes were observed in the ^1H NMR spectra except in the case of KOAc (Figure 2.22). After extraction, the spectrum revealed the amide proton of the receptor was shifted downfield by 2.8 ppm and a peak corresponding to the acetate anion had appeared at 1.99 ppm. Integration of this signal indicated that bis(crown)calix **25** extracts KOAc with 100 % efficiency. It should be noted that stirring KOAc in CDCl_3 in the absence of the ion-pair receptor results in no extraction, indicating that receptor **25** does indeed extract solid KOAc into organic solvents.

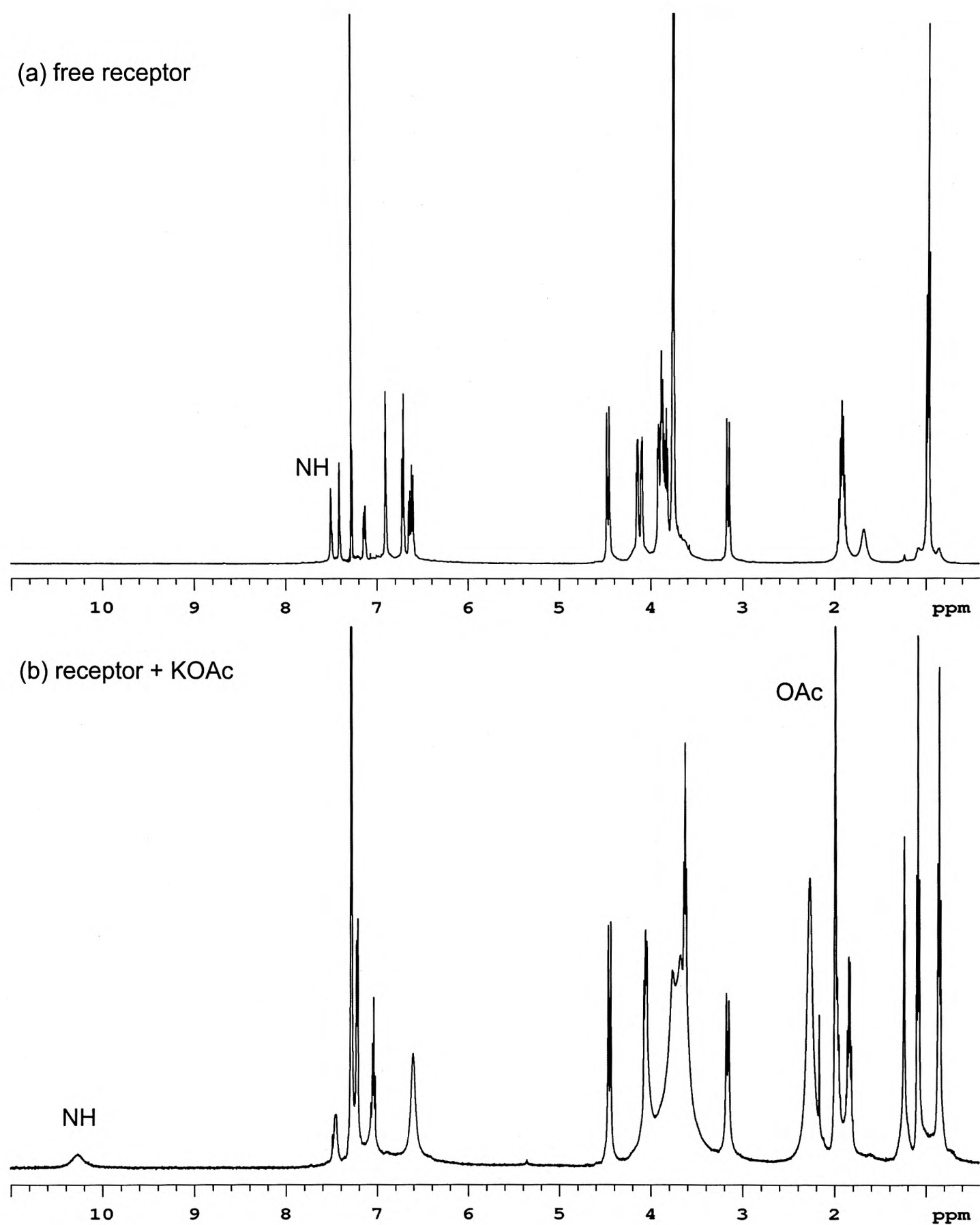


Figure 2.22: ^1H NMR spectra of bis(crown)calix **25** in CDCl_3
(a) before and (b) after addition of solid KOAc.

2.4 Electrochemical Anion and Ion-Pair Sensing

2.4.1 Electrochemical data

The electrochemical properties of the ferrocene-containing receptors (tetra(Fcamide)calix **19**, bisFcbis(crown)calix **36**, tetra(Fcurea)calix **23** and bis(Fcurea)calix **26**) were investigated using cyclic voltammetry (CV) and square wave voltammetry (SWV). The instrumentation and general procedure for these experiments is outlined in Appendix B.

Electrochemical studies of the receptors (5×10^{-4} M in electrolyte solution) were conducted in 0.1 M tetrabutylammonium tetrafluoroborate in 1:1 dichloromethane / acetonitrile. Electrochemical data for the receptors are given in Table 2.5. Cyclic voltammograms (CVs) were recorded at a scan rate of 100 mV.s^{-1} using a glassy carbon working electrode, a platinum wire auxiliary electrode and a silver / silver nitrate reference electrode which was calibrated against ferrocene before and after each set of measurements. The electrochemical potentials of the anodic (E_{pa}) and cathodic (E_{pc}) peaks and the calculated $E_{1/2}$ values are quoted relative to the internal standard ferrocene. CVs of the four receptors are shown in Figure 2.23. Square wave voltammograms (SWVs) were recorded at a frequency of 25 Hz and a scan increment of 2 mV. The $E_{1/2}$ values determined from SWV were the same as those calculated from CV.

	tetra(Fcamide)calix	bisFc 36 bis(crown)calix	tetra(Fcurea)calix	bis(Fcurea)calix
	19	36	23	26
E_{pa}	210	204	27	28
E_{pc}	110	111	-69	-57
ΔE^a	100	93	96	85
$E_{1/2}^b$	160	158	-21	-14
I_{pa} / I_{pc}	1.10	1.05	1.05	1.05

Table 2.5: Electrochemical data for the free receptors. CVs were recorded under the following conditions: 5×10^{-4} M solutions of receptor in 0.1 M Bu_4NBF_4 in 1:1 CH_2Cl_2 / CH_3CN , scan rate 100 mV.s^{-1} , glassy carbon working electrode, $Ag / AgNO_3$ reference electrode. Electrochemical potentials are $\pm 5\text{ mV}$ and are quoted relative to ferrocene. ^a $\Delta E = E_{pa} - E_{pc}$ ^b $E_{1/2} = (E_{pa} + E_{pc}) / 2$

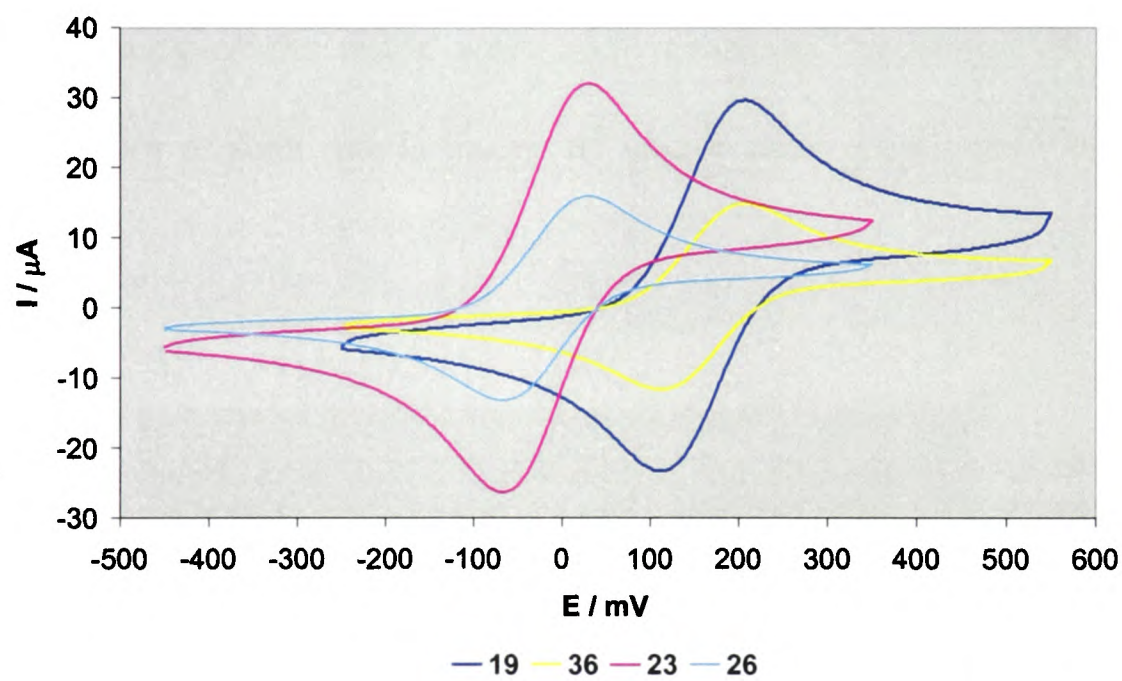


Figure 2.23: CVs of the free receptors.

The CVs of each receptor (Figure 2.23) show only one redox wave, indicating that all ferrocene centres in a receptor undergo oxidation and reduction at the same potential. That is, there is no communication between ferrocene redox centres. As expected, the peak heights are proportional to the number of ferrocene groups in the receptor, as current is a measure of the number of electrons transferred in the redox process.

The $E_{1/2}$ values of tetra(Fcamide)calix **19** and bisFc₂bis(crown)calix **36** both occur about 160 mV positive of ferrocene, due to the electron withdrawing nature of the carbonyl group attached directly to the cyclopentadienyl ring. The $E_{1/2}$ values of tetra(Fcurea)calix **23** and bis(Fcurea)calix **26** both occur about 20 mV negative of ferrocene, due to the slightly electron donating nature of the methylene group.

The electrochemical response of the receptors at different scan rates was investigated by recording CVs at scan rates of 20, 40, 60, 80, 100, 200, 400, 600, 800 and 1000 mV.s^{-1} and plotting current ($I_{\text{pa}} - I_{\text{pc}}$) against the square root of scan rate. For example, Figures 2.24 and 2.25 show the results for tetra(Fcurea)calix **23** and demonstrate two features typical of all four receptors. Firstly, as the scan rate is increased, E_{pa} shifts anodically and E_{pc} shifts cathodically leading to a broadening of the redox wave (ΔE increases). Secondly, the plot of current against the square root of scan rate is linear. R^2 values were greater than 0.996 for all four receptors.

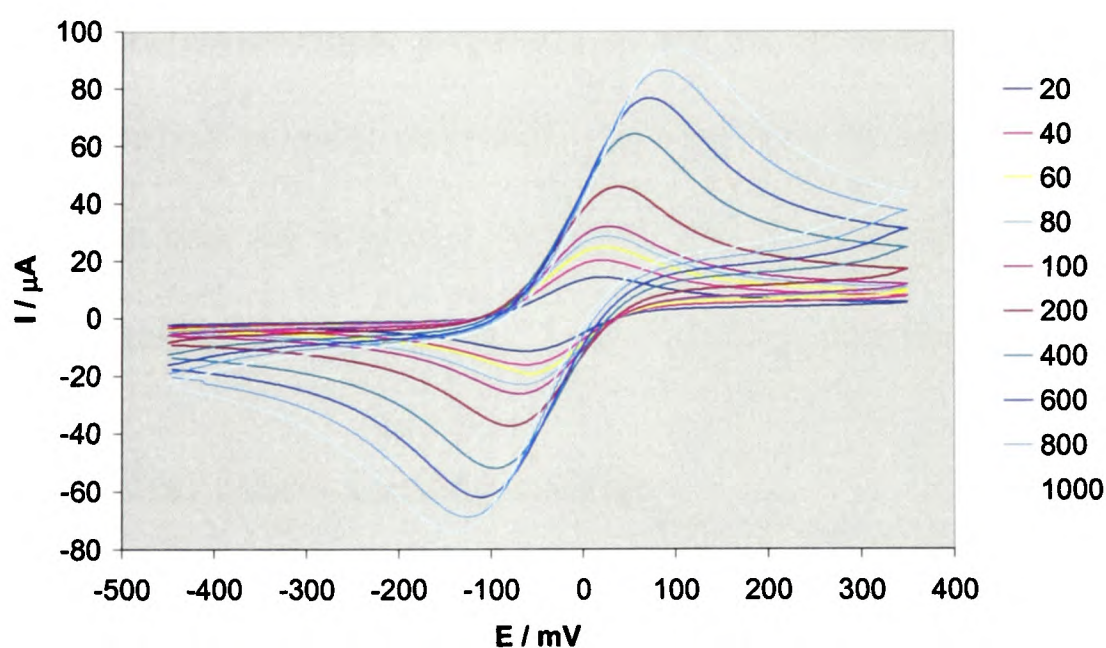


Figure 2.24: CVs of tetra(Fcurea)calix **23** recorded at various scan rates. CVs were recorded under the following conditions: 5×10^{-4} M solutions of receptor in 0.1 M Bu_4NBF_4 in 1:1 CH_2Cl_2 / CH_3CN , glassy carbon working electrode, Ag / AgNO_3 reference electrode.

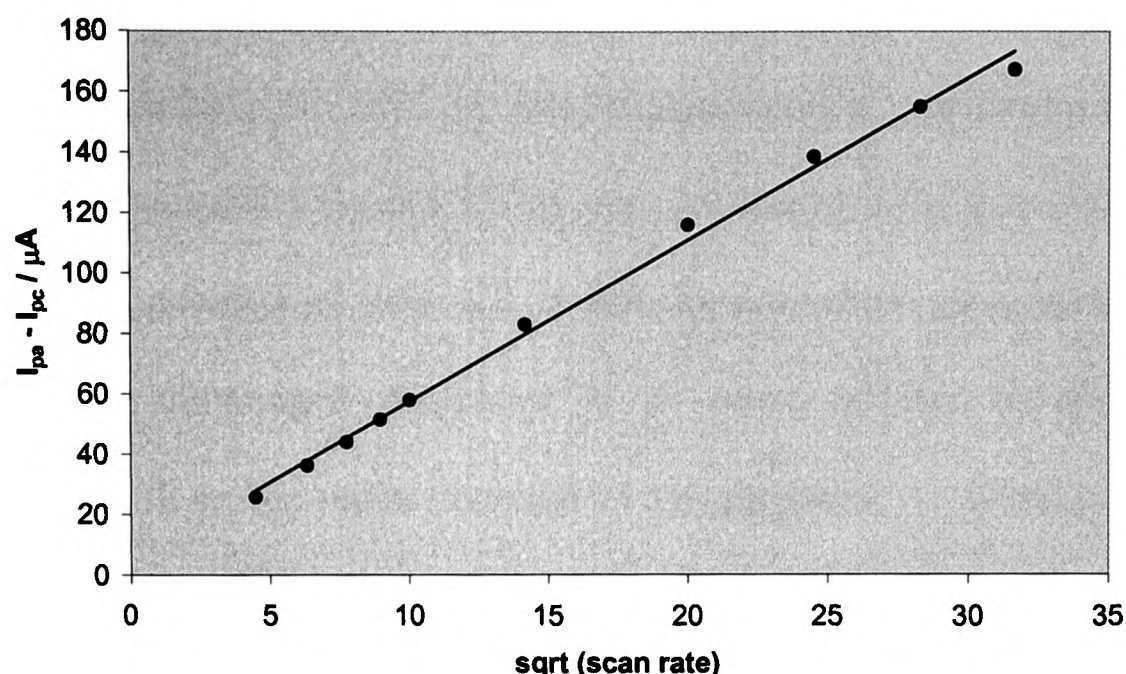


Figure 2.25: Plot of current against the square root of scan rate for tetra(Fcurea)calix **23**.

An electrochemically reversible system⁴² is characterised by a fast rate of electron transfer such that Nernstian conditions exist at the electrode surface at all times. In order to be described as reversible, the following criteria must be satisfied: $\Delta E = 59/n$ mV (where n = number of electrons transferred in the redox process), E_{pa} and E_{pc} are independent of the scan rate, $I_{pa} / I_{pc} = 1$, and I_{pa} and I_{pc} are proportional to the square root of the scan rate. Consideration of the electrochemical properties of **19**, **36**, **23** and **26** indicates that these systems are best described as quasi-reversible. Although the current is proportional to the square root of the scan rate, ΔE is greater than $59/n$ mV, E_{pa} shifts anodically and E_{pc} shifts cathodically with increasing scan rate and I_{pa} / I_{pc} is slightly greater than unity.

2.4.2 Electrochemical anion sensing studies

The ability of redox-active receptors to sense / report guest binding events is a well documented phenomenon. As discussed previously (in Section 1.3.4.1 of the Introduction), receptors incorporating ferrocene moieties have been widely employed for the sensing of anionic guests.

Electrochemical anion sensing studies were conducted on solutions of the receptors (5×10^{-4} M in electrolyte solution) in 0.1 M tetrabutylammonium tetrafluoroborate in 1:1 dichloromethane / acetonitrile. CVs and SWVs were recorded for the free receptors (**19**, **36**, **23** and **26**) and upon addition of 0.5, 1, 2, 5 and 10 equivalents of tetrabutylammonium chloride, benzoate or dihydrogen phosphate. In all cases, addition of anions caused a significant cathodic shift in the redox potential of the receptors. As noted previously with simple acyclic amide-substituted ferrocene derivatives,⁴³ this anion-induced cathodic perturbation can be attributed to the complexation of an anionic guest by the NH protons of the amide and urea groups in close proximity to the ferrocene redox centres, thereby facilitating their oxidation to ferrocenium.

Upon addition of anions the electrochemical response of the receptors becomes increasingly irreversible. CV reveals that in all cases the reduction peak becomes smaller (I_{pa} / I_{pc} increases) and the redox wave broadens (ΔE increases) in the presence of anions. For example, after the addition of 5 equivalents of chloride to bisFcbis(crown)calix **36**, I_{pa} / I_{pc} increases from 1.05 to 1.60 and ΔE increases from 93 to 132 mV; after the addition of 5 equivalents of benzoate or dihydrogen phosphate to receptor **36**, the reduction peak has disappeared entirely.

The disappearance of the reduction wave on anion addition indicates that a bound anion-ferrocenium cation ion-pair may be disfavoured reduction back to ferrocene or that an EC (electrochemical – chemical) mechanism is in operation, where after the electron transfer of the oxidation, a chemical reaction process occurs which prevents reduction from being observed. Similar electrochemical anion recognition behaviour has been observed with simple alkyl and aryl amide-substituted ferrocene receptors.⁴³

This tendency towards irreversibility (which is more pronounced for the ferrocene-amide receptors **19** and **36** than for the ferrocene-urea receptors **23** and **26**) often prevented the determination of cathodic shift magnitudes from CV data. Consequently, SWV was used to obtain quantitative shift data for the anion sensing studies. The advantage of SWV is that non-faradaic, capacitative currents (those which do not involve electron transfer) are largely eliminated due to the short pulse time. This leaves a well defined faradaic peak (that arising from electron transfer) making SWV a more sensitive technique than CV, especially for the study of irreversible systems.

The magnitudes of the cathodic shifts in the redox potentials of the receptors upon addition of five equivalents of anion (as determined from SWV) are given in Table 2.6. As an illustrative example, the SWVs recorded after the addition of 0, 2 and 5 equivalents of anions to tetra(Fcurea)calix **23** are shown in Figures 2.26 – 2.28. For all receptors, the redox waves shift gradually upon addition of chloride or benzoate, whereas addition of dihydrogen phosphate results in the evolution of a new cathodically shifted peak and the concurrent disappearance of the initial one. This behaviour suggests that the binding of dihydrogen phosphate is kinetically slow on the CV or SWV timescale. As well as shifting, the peaks decrease in intensity (especially for benzoate and dihydrogen phosphate), indicative of the increasing irreversibility discussed above.

	tetra(Fcamide)calix 19	tetra(Fcurea)calix 23	bis(Fcurea)calix 26	bisFcbis(crown)calix 36
chloride	50	40	40	50
benzoate	20	50	70	30
dihydrogen phosphate	200	220	180	170

Table 2.6: Cathodic shifts in the $E_{1/2}$ values of the receptors upon addition of 5 equivalents of anions (errors ± 10 mV). SWVs were recorded under the following conditions: 5×10^{-4} M solutions of receptor in 0.1 M Bu_4NBF_4 in 1:1 $\text{CH}_2\text{Cl}_2 / \text{CH}_3\text{CN}$, frequency 25 Hz, scan increment 2 mV, glassy carbon working electrode, Ag / AgNO_3 reference electrode.

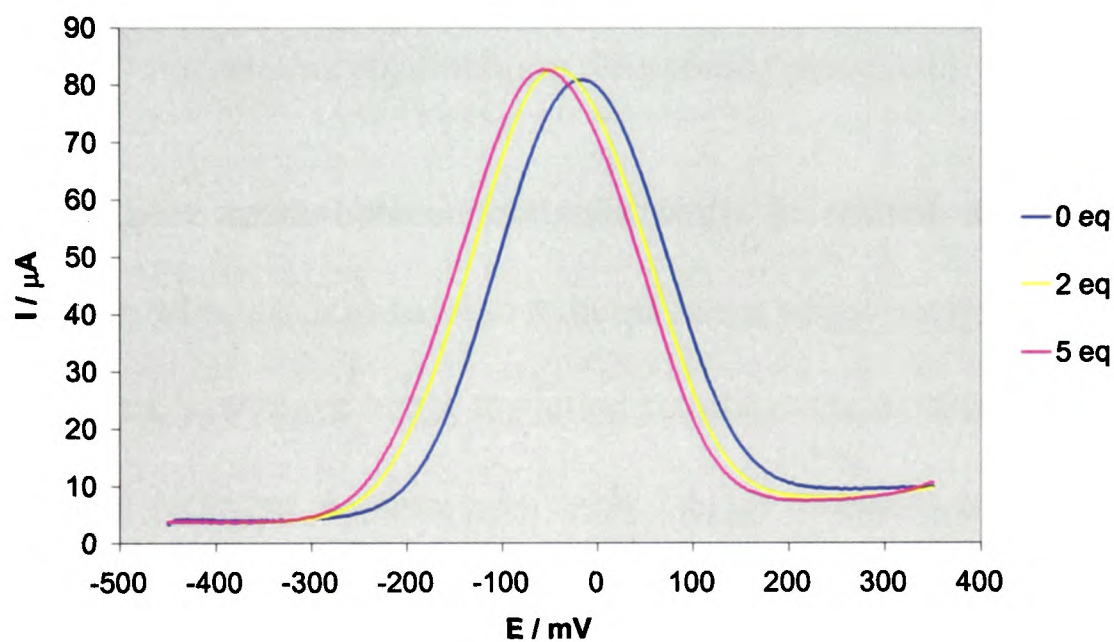


Figure 2.26: SWVs of tetra(Fcurea)calix **23** upon addition of tetrabutylammonium chloride.

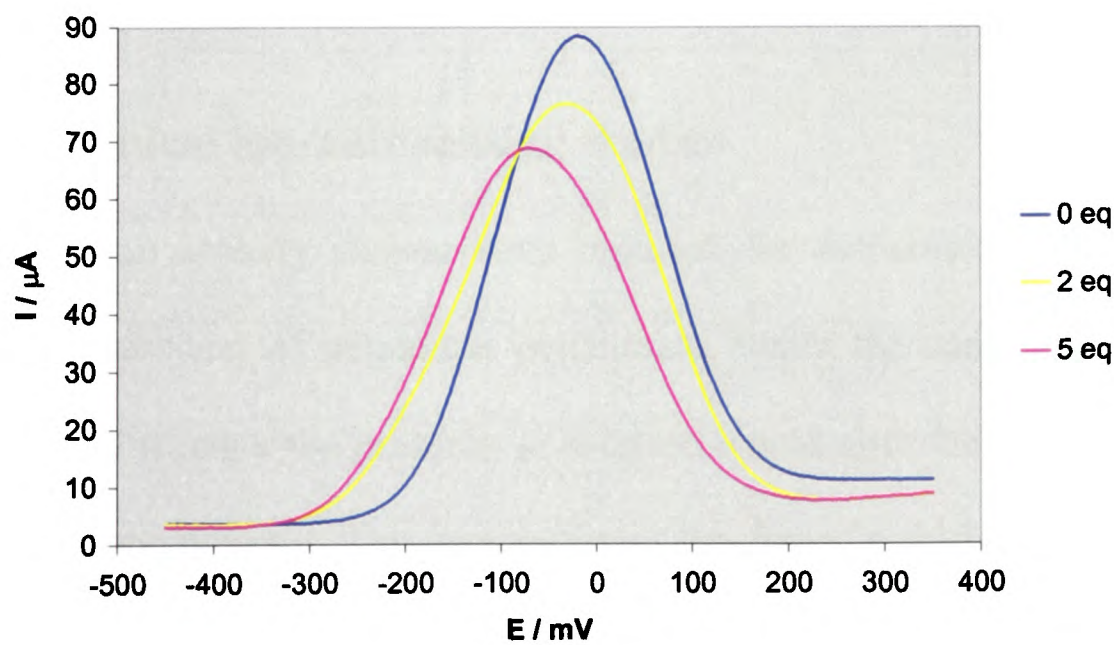


Figure 2.27: SWVs of tetra(Fcurea)calix **23** upon addition of tetrabutylammonium benzoate.

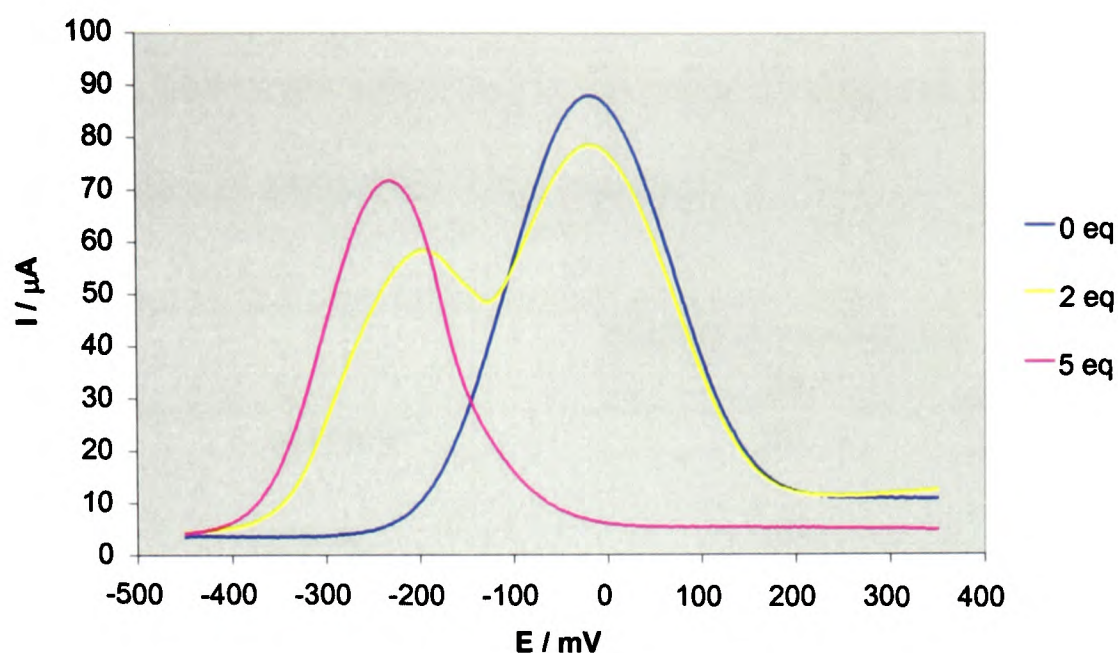


Figure 2.28: SWVs of tetra(Fcurea)calix **23** upon addition of tetrabutylammonium dihydrogen phosphate.

The magnitude of these anion-induced cathodic shifts is related to the relative binding constants of the anion with the oxidised and reduced forms of the receptor. In other words, the size of the shift reveals how much better the anion stabilises the oxidised form of the receptor relative to the neutral receptor. As shown in Table 2.6, all receptors exhibit similar shifts for chloride (40 – 50 mV). The shifts upon addition of benzoate are larger for the ferrocene-urea receptors (**23** and **26**) than for the ferrocene-amide receptors (**19** and **36**). The shift magnitudes upon addition of dihydrogen phosphate are much larger than those for chloride or benzoate, up to 220 mV in the case of tetra(Fcurea)calix **23**.

2.4.3 Electrochemical ion-pair sensing studies

Electrochemical anion sensing studies were repeated for bisFc₂bis(crown)calix **36** in the presence of one equivalent of potassium perchlorate, under the same conditions outlined above, to investigate whether the presence of a cation would alter the electrochemical anion sensing response of the receptor. The magnitudes of the cathodic shifts in the redox potential of receptor **36** upon addition of five equivalents of anion, for the free receptor and in the presence of one equivalent of potassium perchlorate, are given in Table 2.7. It should be noted

that no change occurred in the SWV of the receptor upon addition of one equivalent of potassium perchlorate. This is not surprising as the cation binding site is located too far away from the ferrocene centres to affect their redox potential.

	bisFcbis(crown)calix 36
chloride	50
+ K ⁺	60
benzoate	30
+ K ⁺	75
dihydrogen phosphate	170
+ K ⁺	165

Table 2.7: Cathodic shifts in the $E_{1/2}$ values of bisFcbis(crown)calix **36** upon addition of 5 equivalents of anions, for the free receptor and in the presence of one equivalent of potassium perchlorate (errors ± 10 mV). SWVs were recorded under the following conditions: 5×10^{-4} M solutions of receptor in 0.1 M Bu₄NBF₄ in 1:1 CH₂Cl₂ / CH₃CN, frequency 25 Hz, scan increment 2 mV, glassy carbon working electrode, Ag / AgNO₃ reference electrode.

The presence of potassium makes little difference to the electrochemical response of receptor **36** to chloride or dihydrogen phosphate anions. However, the redox response to benzoate anions is more cathodically shifted by 45 mV in the presence of potassium cations.

2.5 Luminescence Spectroscopic Anion Binding Studies

The luminescent properties of Re(CO)₃XL complexes (X = halide, L = polypyridyl) are well documented.⁴⁴ The design of receptor molecules with an anion binding site in close proximity to a luminescent group such as this enables the spectroscopic sensing of anion binding *via* changes in the emission spectrum.

The UV-VIS absorption spectrum of a solution of tetra(Rebpy)calix **21** (2×10^{-5} M) in acetonitrile was recorded (see Appendix C). Table 2.8 displays the wavelengths, molar extinction coefficients and assignments for the absorption maxima. In addition, absorption data for a simple complex, Re(bpy)(CO)₃Br, are given for comparison.

tetra(Rebpy)calix 21	Re(bpy)(CO) ₃ Br	assignment
297 (57.1)	291 (17.7)	LC
378 (25.4)	384 (3.2)	MLCT

Table 2.8: Wavelengths (λ / nm) and molar extinction coefficients (ϵ / $10^3 \text{ M}^{-1} \text{ cm}^{-1}$) of the absorption maxima of tetra(Rebpy)calix **21** in CH₃CN.

The absorption spectrum of receptor **21** is typical of a rhenium(I)-bipyridine complex, showing a ligand centred (LC) transition at 297 nm and a metal to ligand charge transfer (MLCT) transition at 378 nm. The metal centred (MC) transitions are thought to be hidden under the more intense LC and MLCT bands.⁴⁵ The extinction coefficients observed for **21** are considerably higher than those for Re(bpy)(CO)₃Br, as there are four rhenium(I)-bipyridine centres in the receptor compared to just one in the model complex.

The emission spectrum of a solution of tetra(Rebpy)calix **21** (2×10^{-5} M) in acetonitrile was recorded (see Appendix D). Excitation of the MLCT transition at 378 nm resulted in a broad emission at 598 nm.

The anion binding ability of receptor **21** was investigated by emission (luminescence) spectroscopy. Anion titrations were carried out with solutions of **21** (2×10^{-5} M) in acetonitrile by recording the emission spectra upon addition of tetrabutylammonium chloride, benzoate, acetate or dihydrogen phosphate. The addition of dihydrogen phosphate, acetate or benzoate caused a quenching of the luminescence, with the emission intensity decreasing by

55 – 70 % after the addition of ten equivalents of anion. This quenching of luminescence is surprising, as addition of anions to other rhenium(I)-bipyridine-amide receptors reported in the literature typically caused an enhancement of emission intensity, attributed to the bound anion rigidifying the receptor and thereby inhibiting collisional deactivation.⁴⁶ Such behaviour was observed upon addition of chloride, which resulted in a 33 % increase in the emission intensity.

Addition of anions also resulted in hypsochromic shifts (of up to 10 nm with acetate) in the emission maximum. Such shifts indicate that the MLCT state moves to higher energy in the presence of the anion. The MLCT $d\pi^*$ state has the electron formally residing on the bipyridine ligand, and this configuration is presumably less favourable when the negatively charged guest binds to the bipyridine-amide group.

The titration data was analysed by the computer program Specfit[™],⁴⁷ yielding the stability constants (log K values) given in Table 2.9. Good agreement between experimental and calculated intensities was obtained using a 1:1 anion / receptor binding model in all cases. As an example, Figure 2.29 shows the results of the titration of **21** with acetate.

	tetra(Rebpy)calix 21
chloride	4.71
benzoate	4.65
acetate	4.81
dihydrogen phosphate	4.60

Table 2.9: Stability constants (log K values) determined for titrations of tetra(Rebpy)calix **21** with anions in CH₃CN. Specfit[™] determined errors < 1 %.

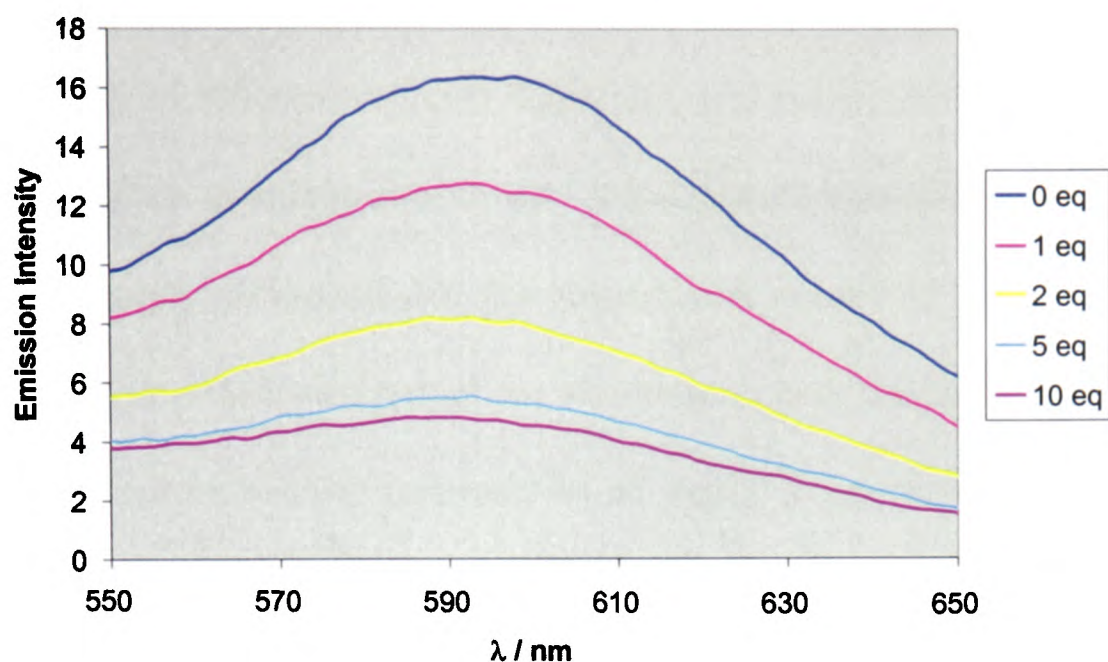


Figure 2.29: Emission spectra recorded upon addition of acetate to tetra(Rebpy)calix **21** in CH₃CN solution.

Surprisingly, the data in Table 2.9 reveal that tetra(Rebpy)calix **21** demonstrates no particular selectivity for the binding of one anion over another. The stability constants are much the same for all four anions.

2.6 Summary

A range of new upper-rim functionalised calix[4]arene anion and ion-pair receptors have been synthesised *via* the condensation of upper-rim amino-derivatised calix[4]arene compounds with various acid chloride or protected isocyanate synthons. All these new calix[4]arene-based receptors were characterised by ¹H NMR spectroscopy, mass spectrometry and elemental analysis, and by X-ray crystallography in the cases of tetra(Fcamide)calix **19** and tetra(Fcurea)calix **23**. Receptor **23** was observed to form hydrogen bonded solvent-containing dimeric capsules in non-competitive organic solvents such as benzene (as evidenced by ¹H NMR spectroscopy experiments), and the rate of capsule association / dissociation was determined to be 6 s⁻¹ in benzene solution at 60 °C.

The anion and ion-pair binding properties of the receptors were investigated by ^1H NMR spectroscopy in a range of different solvents. Typically, addition of chloride, benzoate, acetate and dihydrogen phosphate anions to solutions of the receptors caused downfield shifts in the amide or urea resonances, indicating that the anions were bound by the hydrogen bonding moieties. Job plot and EQNMR analyses of the resulting titration curves revealed 1:1 binding stoichiometries and modest stability constants in all cases. X-ray structural investigation of the bis(benzoate) complex of bis(Fcurea)calix **26** revealed a 2:1 anion / receptor stoichiometry, in contrast to the 1:1 stoichiometry observed in solution.

The (benzo[15]crown-5)-amide appended receptors were designed to simultaneously bind cations and anions such that the presence of co-bound alkali metal cation would enhance the strength of anion binding *via* favourable electrostatic interactions and preorganisation effects. ^1H NMR titration experiments were undertaken with the heteroditopic receptors with anions both in the presence and absence of equivalents of sodium and potassium cations. For the bis(benzo[15]crown-5) calix[4]arene receptors **25** and **36**, the presence of potassium cations resulted in significant increases in the strength of chloride, benzoate and dihydrogen phosphate binding, by up to an order of magnitude in the case of **25** and benzoate. In contrast, with sodium cations a general decrease in the strength of anion binding was observed. These observations may be rationalised by the fact that the potassium cation forms a 1:1 intramolecular sandwich complex with the benzo[15]crown-5 ether moieties of bis(crown)calix **25** and bisFc(bis(crown)calix **36**, which in effect preorganises the amide groups for anion binding. However, sodium cations are bound in a 2:1 cation / receptor stoichiometry whereby each benzo[15]crown-5 group complexes one sodium cation, resulting in the amide groups being unable to cooperatively complex an anion due to mutual repulsive sodium cation crown ether electrostatic effects. Solid / liquid extraction experiments revealed receptor **25** was capable of solubilising solid potassium acetate into chloroform solution.

The ability of the ferrocene-containing receptors to electrochemically sense the binding of anions was investigated by cyclic and square wave voltammetry. These receptors were shown to electrochemically recognise chloride, benzoate and dihydrogen phosphate anions by substantial cathodic perturbations of the metallocene redox couple of up to 220 mV in 1:1 dichloromethane / acetonitrile. In particular, in the presence of potassium cations, the electrochemical response of bisFc(bis(crown)calix **36** to benzoate was amplified significantly.

Tetra(Rebpy)calix **21** was shown to optically sense anions in acetonitrile solutions, generally *via* quenching of luminescence.

2.7 References

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Chapter Three

Azacrown and Transition Metal Dithiocarbamate Based Ion-Pair Receptors

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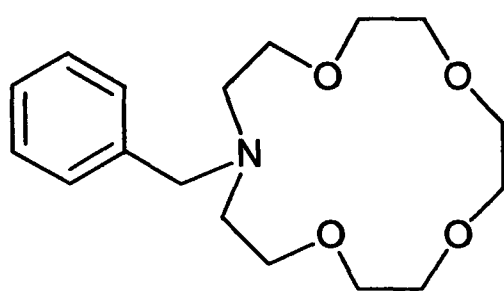
Chapter Three: Azacrown and Transition Metal Dithiocarbamate Based Ion-Pair Receptors

3.1 Introduction

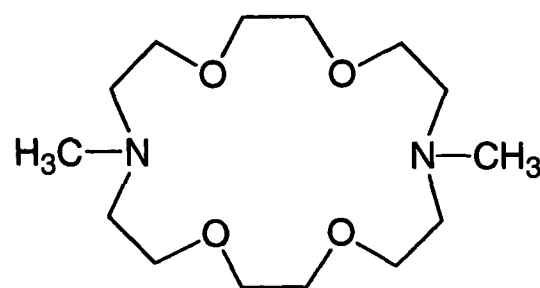
The objective of the work presented in this chapter was the synthesis and investigation of new ion-pair receptors incorporating an azacrown ether group for alkali metal cation complexation together with amide functionalities for anion binding. Furthermore, these receptors were designed to contain ferrocene or transition metal dithiocarbamate groups for the electrochemical and/or optical sensing of guest binding.

As discussed previously, the complexation of alkali metal cations by crown ethers is a well established phenomenon and a plethora of cation receptors exploiting this interaction have been described in the literature (see Section 1.2 of the Introduction). More recently, ion-pair receptors incorporating crown ether groups together with anion binding moieties have been reported (see Section 1.4 of the Introduction). These receptors often exhibit positive cooperativity whereby alkali metal cation complexation enhances the strength of anion binding *via* favourable electrostatic interactions and conformational effects.

The receptors described in this chapter contain either *N*-functionalised aza[15]crown-5 or *N,N'*-functionalised 1,10-bis-aza[18]crown-6 groups which are known to form strong complexes with alkali metal cations. For example, calorimetric titrations in methanol solution revealed the stability constants shown in Figure 3.1.^{1,2} Clearly, *N*-benzyl-aza[15]crown-5 **3.1** demonstrates a preference for sodium cations, whereas *N,N'*-dimethyl-1,10-bis-aza[18]crown-6 **3.2** is selective for potassium.



3.1 $\log K (\text{Na}^+) = 2.49$
 $\log K (\text{K}^+) = 1.83$



3.2 $\log K (\text{Na}^+) = 3.53$
 $\log K (\text{K}^+) = 5.18$

Figure 3.1: Stability constants for *N*-functionalised aza[15]crown-5 and *N,N'*-functionalised 1,10-bis-aza[18]crown-6 compounds **3.1** and **3.2** with sodium and potassium cations in methanol solution.

The synthesis of a number of receptors reported in this chapter was achieved by exploiting the metal-directed self-assembly properties of the dithiocarbamate group. Self-assembly is an attractive method for the formation of macrocyclic structures. In many cases, self-assembly enables the synthesis of complex architectures in fewer steps and in higher yields than could be achieved by covalent synthesis alone. There are many reports of the metal-directed self-assembly of structures which use either polypyridine-based ligands with transition metals such as palladium(II) or platinum(II),³ or catechol ligands with gallium(III) or iron(III),⁴ and several examples have already been discussed (in Section 1.5 of the Introduction). The use of other ligands, however, is less common.

The coordination chemistry of the dithiocarbamate ligand has been extensively investigated⁵ but only recently exploited in the field of self-assembly. *N*-substituted dithiocarbamates can be prepared readily *via* reaction of primary or secondary amines with carbon disulphide in the presence of a base. Addition of a transition metal salt results in the formation of the transition metal dithiocarbamate complex. The dithiocarbamate group is an attractive unit for self-assembly as it forms complexes with a range of metal ions and can stabilise metals in high oxidation states. Despite these appealing features, it is only recently that the dithiocarbamate ligand has been used in self-assembly.

Beer and co-workers reported the remarkable formation of a nano-dimensional molecular loop and tetrahedron by the reaction of a tetra-dithiocarbamate-functionalised resorcarene ligand with zinc(II)⁶ and copper(II)⁷ ions, respectively. UV-VIS spectroscopic studies revealed that molecular loop **3.3** (Figure 3.2) bound C₆₀ very strongly in benzene or toluene solution. Molecular modelling of C₆₀ inside the cavity revealed a possible mode of binding involving charge donation from the sulphur atoms of the dithiocarbamate linkages to the electron deficient C₆₀.

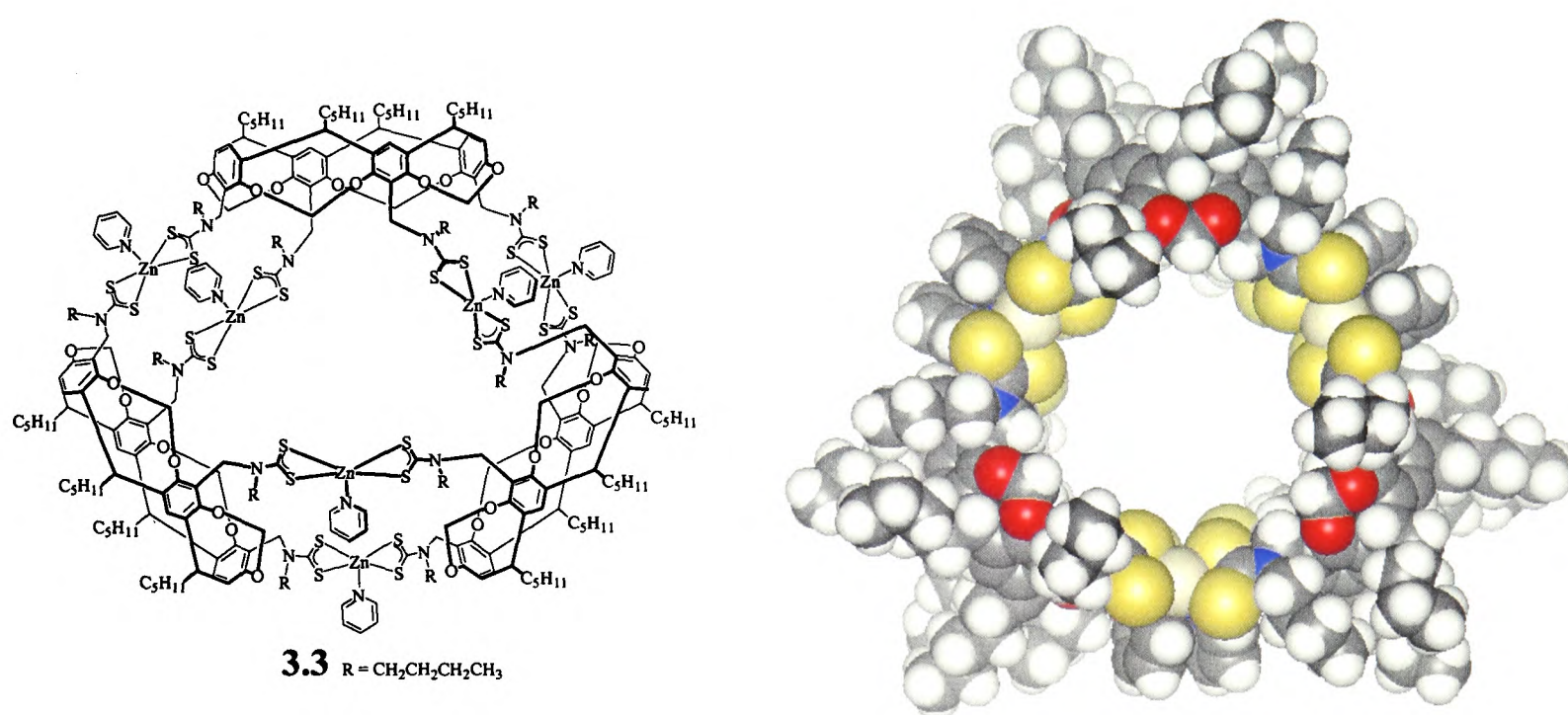


Figure 3.2: Zinc(II)-dithiocarbamate self-assembled molecular loop **3.3** and the crystal structure.

The dithiocarbamate ligand has also been exploited in the metal-directed self-assembly of heteroditopic nickel(II)- and copper(II)-dithiocarbamate receptors containing crown ether and amide recognition sites for the simultaneous complexation of cations and anions.⁸ ¹H NMR titrations in *d*₆-DMSO revealed that receptor **3.4** (Figure 3.3) exhibited a six-fold enhancement of acetate binding in the presence of one equivalent of potassium cations. In addition, receptor **3.5** (Figure 3.3) was capable of electrochemically sensing the presence of

anions in 4:1 chloroform / acetonitrile solutions *via* cathodic perturbations in the copper(II) / copper(III) dithiocarbamate redox wave.

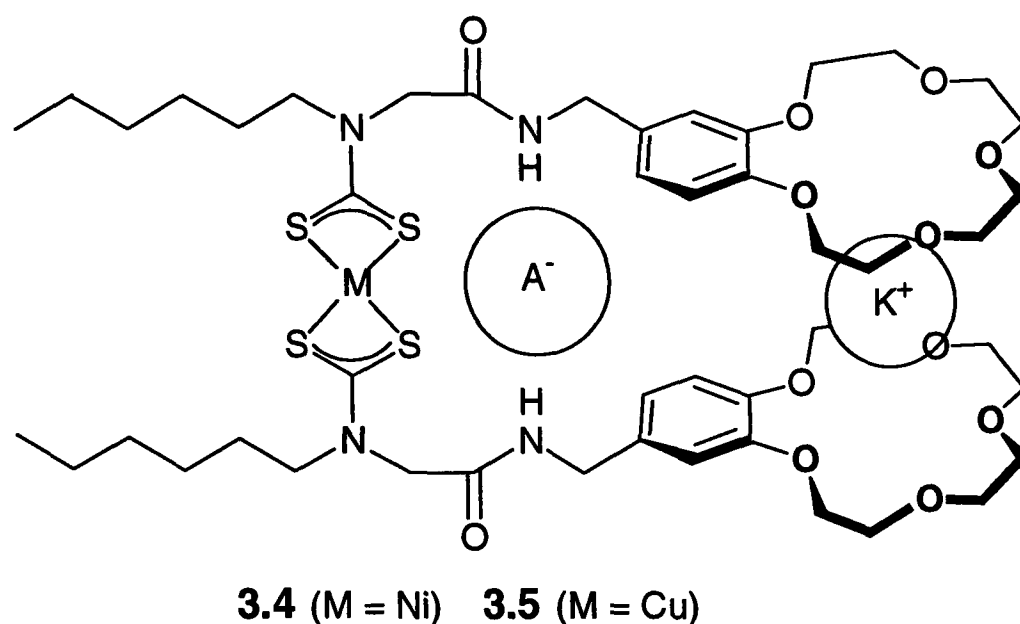


Figure 3.3: Self-assembled transition metal dithiocarbamate receptors **3.4** and **3.5** binding a potassium cation-anion ion-pair.

This chapter describes the synthesis and investigation of a range of new azacrown-containing ion-pair receptors, a number of which were prepared by exploiting the metal-directed self-assembly properties of the dithiocarbamate group. The following sections outline the synthesis and characterisation of the ion-pair receptors (Section 3.2) and detail the investigation of receptor binding properties by ^1H NMR spectroscopy (Section 3.3), electrochemistry (Section 3.4) and UV-VIS spectroscopy (Section 3.5).

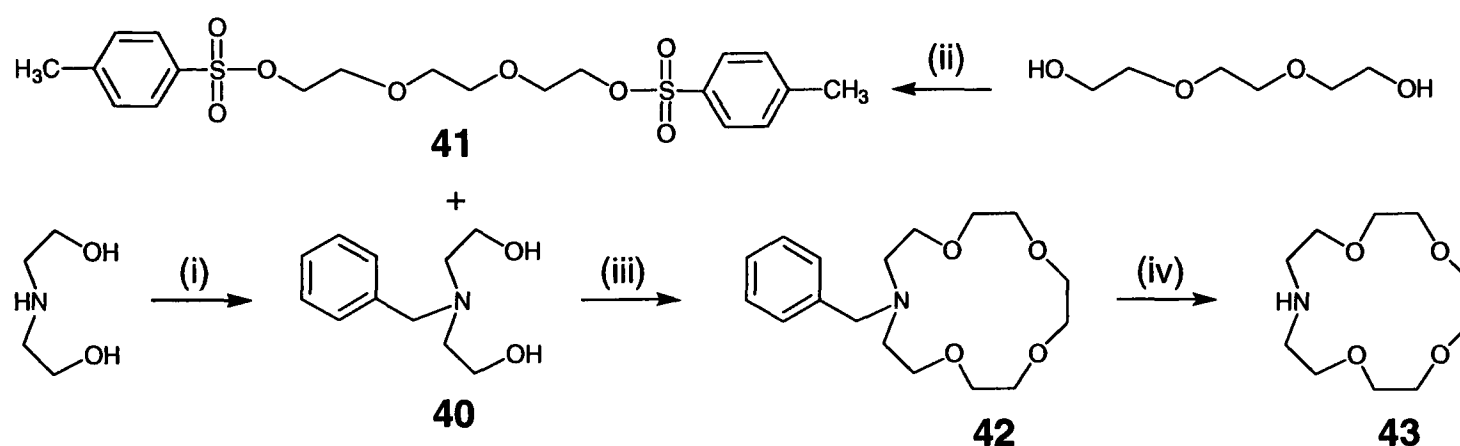
3.2 Synthesis and Characterisation

The *N*-functionalisation of aza[15]crown-5 and 1,10-bis-aza[18]crown-6 gave two primary amine-derivatised compounds which were condensed with acid chloride synthons (3,4-dimethoxybenzoyl chloride, chlorocarbonyl ferrocene or 1,1'-bis(chlorocarbonyl)ferrocene) to produce four new ion-pair receptors (Sections 3.2.2 and 3.2.4). The reaction of secondary amine-functionalised 1,10-bis-aza[18]crown-6 compounds with carbon disulphide and potassium hydroxide afforded dithiocarbamate-derivatised ligands, which upon addition of

nickel(II) or copper(II) salts self-assembled to form several new macrobicyclic receptors (Section 3.2.5).

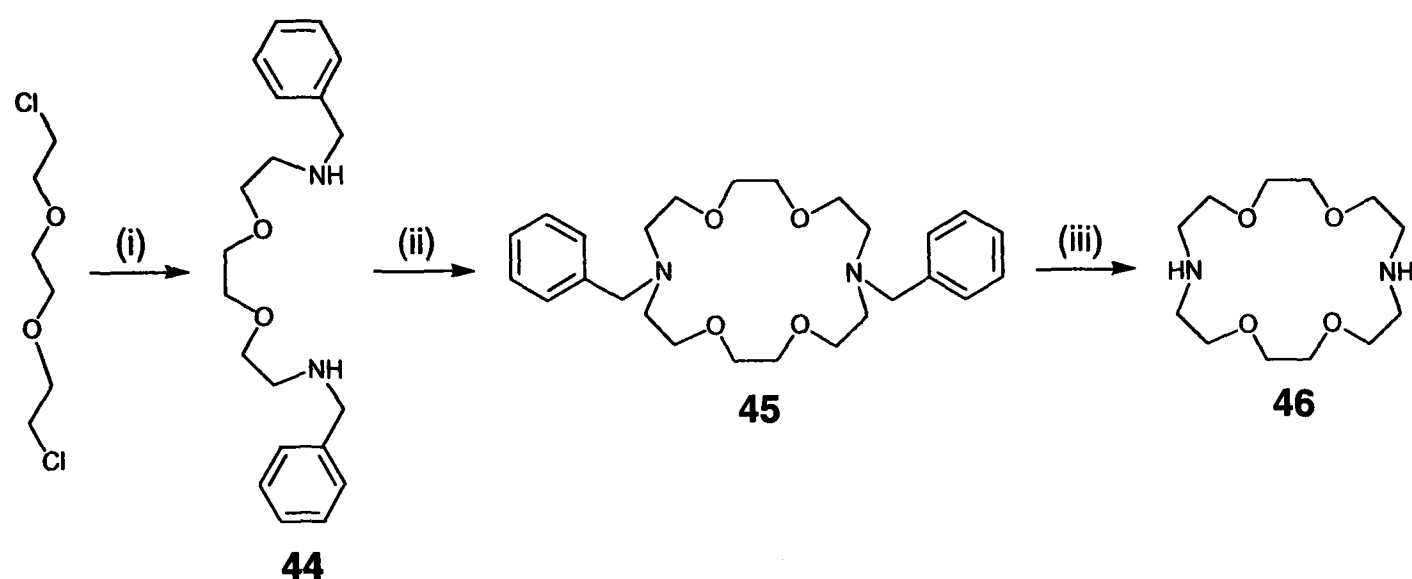
3.2.1 Synthesis of the azacrown precursors

Aza[15]crown-5 **43** was synthesised according to a literature method (Scheme 3.1).⁹⁻¹¹ Reaction of diethanolamine and benzyl chloride by heating under basic conditions gave the benzyl-protected product **40** in 77 % yield.⁹ Tosylation of triethyleneglycol by reaction with *p*-toluenesulfonyl chloride under basic conditions gave **41** in 96 % yield.¹⁰ Cyclisation was achieved by heating **40** and **41** to reflux in the presence of sodium hydride, producing the benzyl-protected azacrown product **42** in 42 % yield.⁹ Deprotection of **42** by Parr hydrogenation afforded aza[15]crown-5 **43**¹¹ as a soft, white, hygroscopic solid in 96 % yield.



Scheme 3.1: (i) benzyl chloride, Na_2CO_3 , 77 %; (ii) *p*-toluenesulfonyl chloride, NaOH, 2:1 thf / H_2O , 5 °C, 96 %; (iii) NaH, thf, reflux, 42 %; (iv) H_2 (4 atm), 10 % Pd-C, EtOH, 96 %.

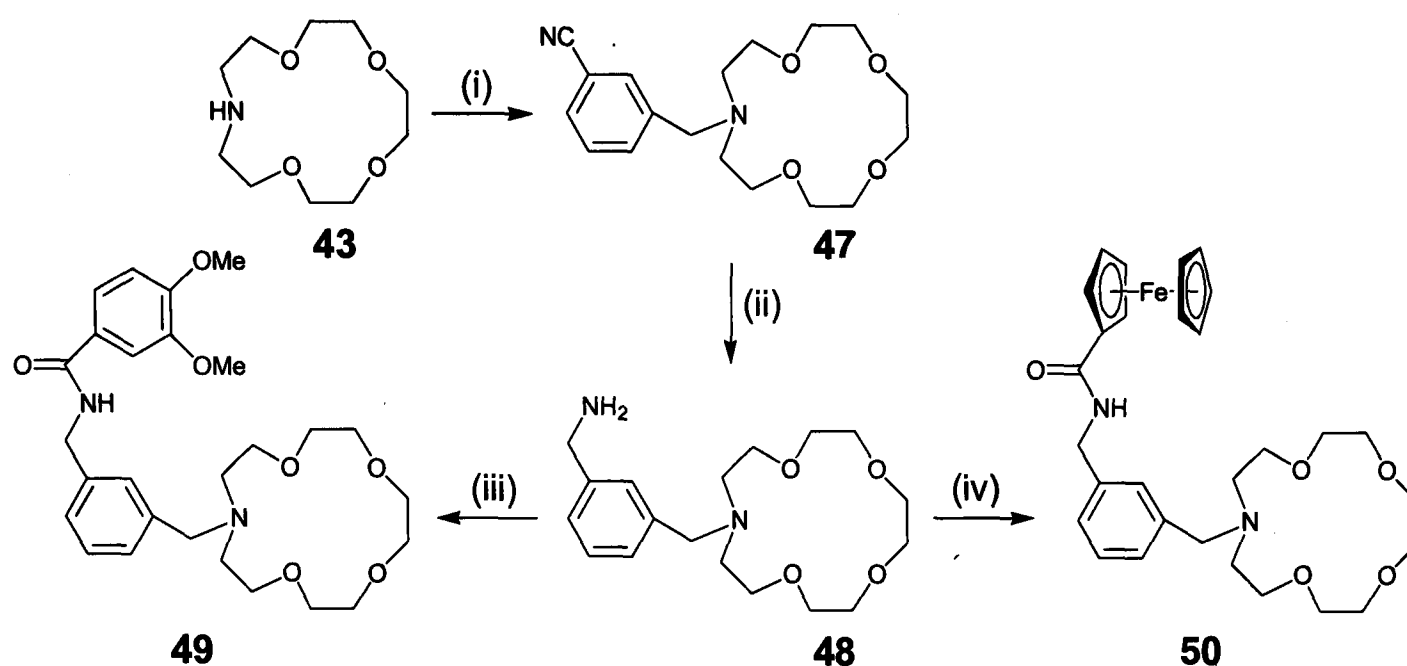
1,10-Bis-aza[18]crown-6 **46** was synthesised according to a literature method (Scheme 3.2).¹² Reaction of 1,2-bis(2-chloroethoxy)ethane with benzylamine under basic conditions gave **44** (in 93 % yield) which was cyclised by reaction with 1,2-bis(2-iodoethoxy)ethane under basic conditions to give the benzyl-protected bis-azacrown product **45** in 52 % yield. Deprotection by Parr hydrogenation afforded 1,10-bis-aza[18]crown-6 **46** as a cream, microcrystalline solid in 58 % yield after recrystallisation from hexane.



Scheme 3.2: (i) benzylamine, NaOH, 120 °C, 93 %; (ii) 1,2-bis(2-iodoethoxy)ethane, Na₂CO₃, NaI, CH₃CN, reflux, 52 %; (iii) H₂ (3 atm), Pd(OH)₂-C, EtOH, 58 %.

3.2.2 Synthesis of simple azacrown ion-pair receptors

Aza[15]crown-5 **43** was reacted with one equivalent of α -bromo-*m*-tolunitrile in the presence of potassium carbonate by heating to reflux in acetone (Scheme 3.3). Purification by column chromatography (silica, 3 % methanol in chloroform) gave **47**¹³ as a yellow oil in 89 % yield. Reduction of the nitrile groups of **47** was achieved using lithium aluminium hydride and heating to reflux in tetrahydrofuran. Solvent removal gave the oily product **48**¹³ in 79 % yield. Amine **48** was condensed with one equivalent of the commercially available 3,4-dimethoxybenzoyl chloride in the presence of triethylamine base by heating to reflux in chloroform. Purification by preparative thin layer chromatography (silica, 20 % methanol in chloroform) afforded receptor **49** as a pale yellow oil in 56 % yield. Amine **48** was also condensed with one equivalent of chlorocarbonyl ferrocene **9** (see Scheme 2.2, Chapter Two) under similar conditions. Purification by preparative thin layer chromatography (silica, 10 % methanol in chloroform) gave receptor **50** as a dark orange oil in 61 % yield. An assigned ¹H NMR spectrum of **50** in *d*₆-DMSO is shown in Figure 3.4.



Scheme 3.3: (i) α -bromo-*m*-tolunitrile, K_2CO_3 , acetone, reflux, 89 %; (ii) LiAlH_4 , thf, reflux, 79 %; (iii) 3,4-dimethoxybenzoyl chloride, Et_3N , CHCl_3 , reflux, 56 %; (iv) chlorocarbonyl ferrocene **9**, Et_3N , CHCl_3 , reflux, 61 %.

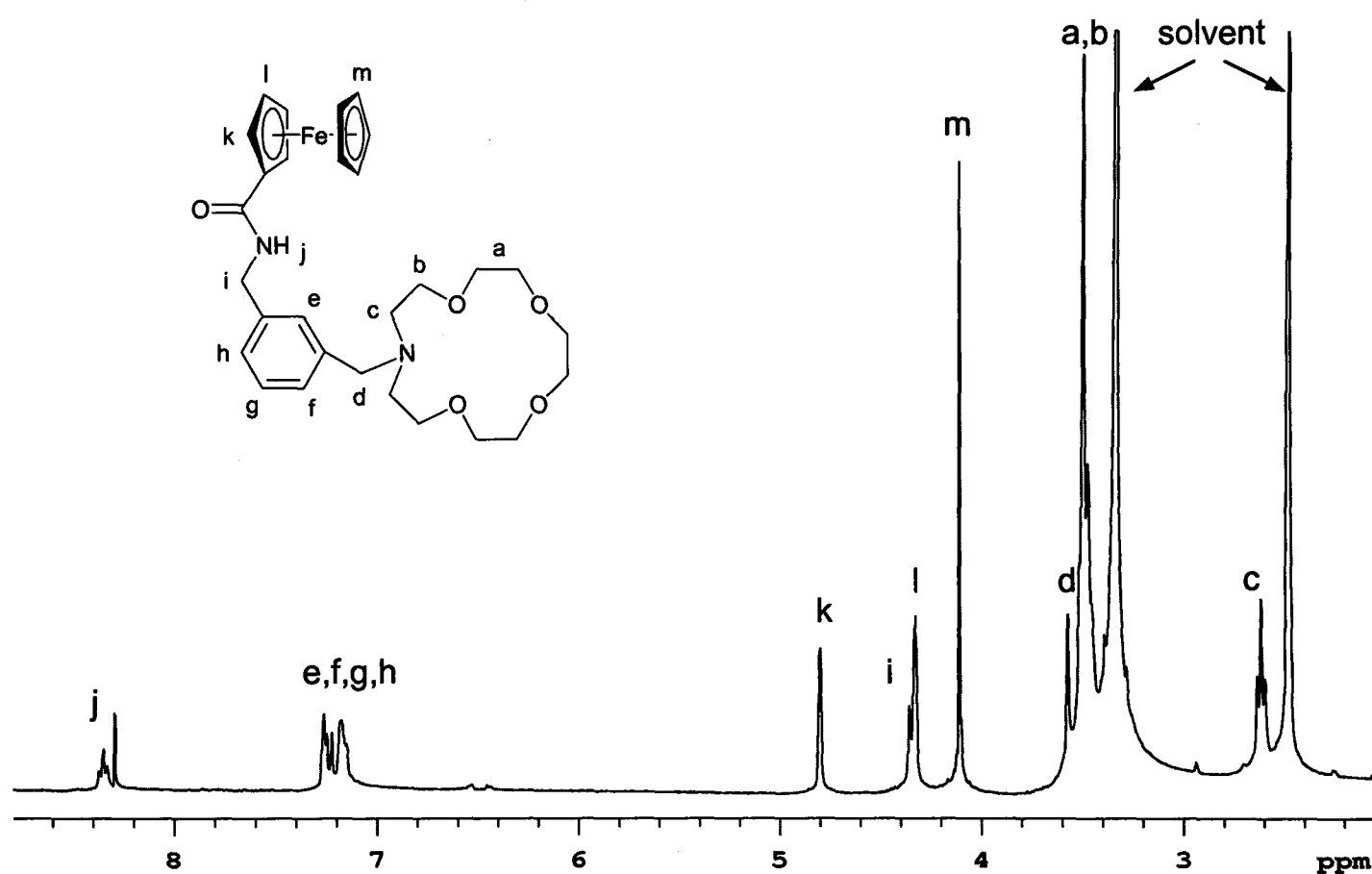
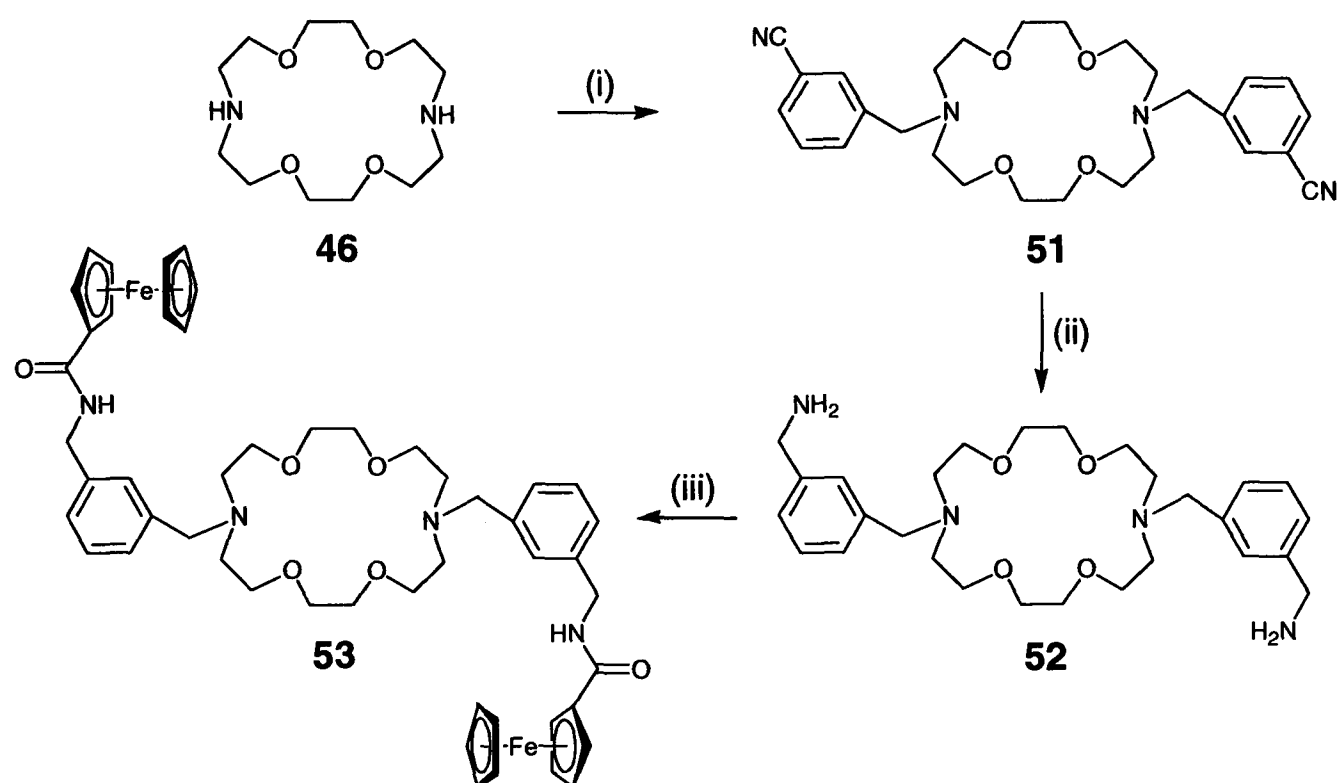


Figure 3.4: ^1H NMR spectrum (300 MHz) of receptor **50** in d_6 -DMSO.

The synthesis of receptor **53** from azacrown precursor **46** was achieved in an analogous manner to the synthesis of receptor **50** described above (Scheme 3.4). 1,10-Bis-aza[18]crown-6 **46** was reacted with two equivalents of α -bromo-*m*-tolunitrile to give **51**¹³ as a yellow powder in quantitative yield. Reduction with lithium aluminium hydride produced **52**¹³ as a

yellow oil in 85 % yield. Bis-amine-functionalised 1,10-bis-aza[18]crown-6 **52** was condensed with two equivalents of chlorocarbonyl ferrocene **9**, and purification by preparative thin layer chromatography (silica, 20 % methanol in chloroform) afforded receptor **53** as a red oil in 64 % yield.



Scheme 3.4: (i) α -bromo-*m*-tolunitrile, K_2CO_3 , acetone, reflux, 99 %; (ii) $LiAlH_4$, thf, reflux, 85 %; (iii) chlorocarbonyl ferrocene **9**, Et_3N , $CHCl_3$, reflux, 64 %.

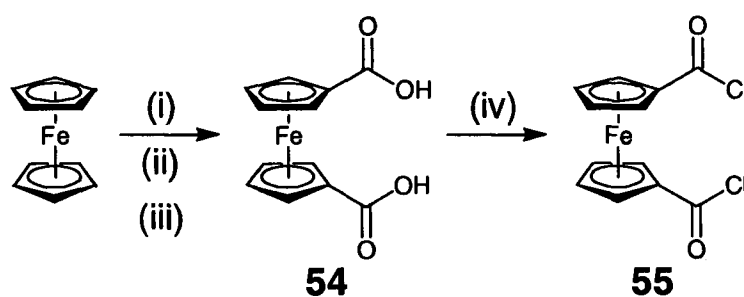
Attempts to make an analogous bipyridine-appended receptor by reacting compound **52** with two equivalents of 4-chlorocarbonyl-4'-methyl-2,2'-bipyridine **11** unfortunately failed. Despite repeated attempts, the desired compound could not be isolated in sufficient purity for further study.

Following the successful syntheses of these three simple azacrown ion-pair receptors (**49**, **50** and **53**), the preparation of several macrobicyclic receptors was undertaken. Cyclisation was achieved either by reacting bis-amine-functionalised 1,10-bis-aza[18]crown-6 **52** with a bis-acid chloride synthon (Section 3.2.4) or by exploiting the self-assembly properties of transition metal dithiocarbamate interactions (Section 3.2.5). The synthesis of two bis-acid chloride synthons is described below (Section 3.2.3).

3.2.3 Synthesis of bis-acid chloride synthons

3.2.3.1 1,1'-Bis(chlorocarbonyl)ferrocene **55**

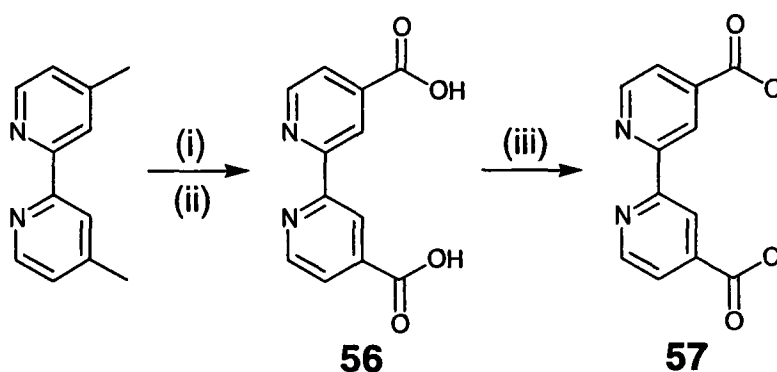
Ferrocene was reacted with *n*-butyl lithium and TMEDA in hexane (Scheme 3.5).¹⁴ Carbon dioxide was bubbled through the solution to precipitate the bis-lithiate which was acidified to give the bis-acid **54** as a tan solid in 68 % yield after recrystallisation from toluene. Reaction with oxalyl chloride gave 1,1'-bis(chlorocarbonyl)ferrocene **55**, which was used immediately in subsequent reactions.



Scheme 3.5: (i) ⁿBuLi, TMEDA, hexane; (ii) CO_{2(g)}, Et₂O; (iii) HCl_(aq), H₂O, 68 %; (iv) oxalyl chloride, reflux.

3.2.3.2 4,4'-Bis(chlorocarbonyl)-2,2'-bipyridine **57**

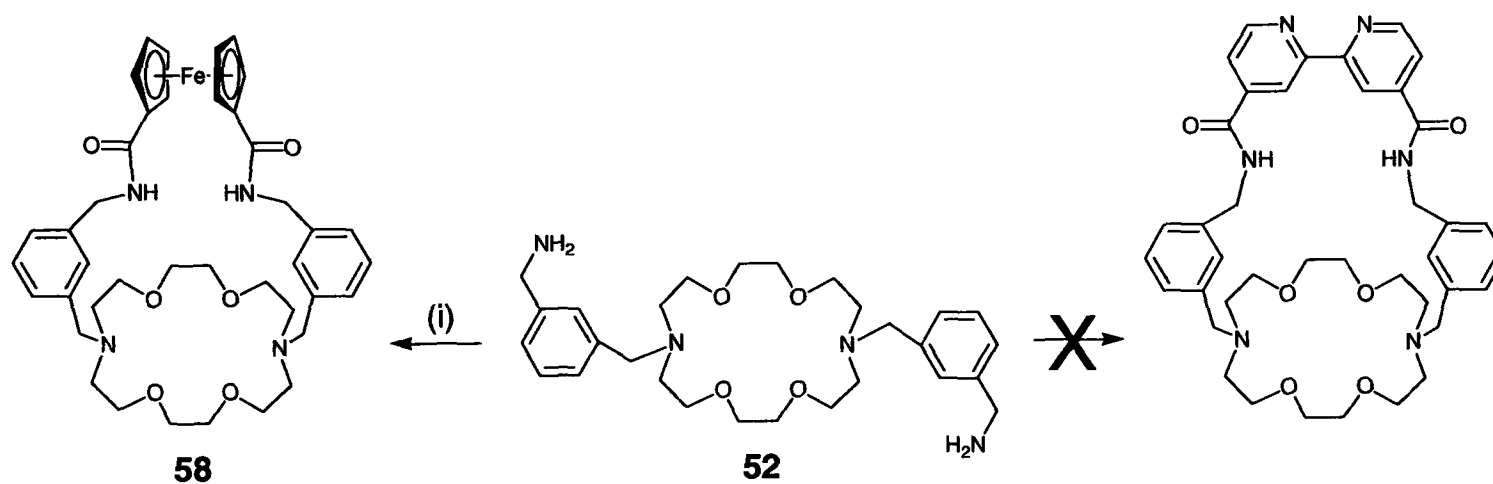
The oxidation of 4,4'-dimethyl-2,2'-bipyridine with chromium(VI) oxide and concentrated sulphuric acid gave the bipyridine bis-acid **56** as a white solid in 87 % yield (Scheme 3.6).¹⁵ Reaction with thionyl chloride gave 4,4'-bis(chlorocarbonyl)-2,2'-bipyridine **57**.



Scheme 3.6: (i) CrO₃, conc. H₂SO₄; (ii) HCl_(aq), 87 %; (iii) SOCl₂, reflux.

3.2.4 Synthesis of macrobicyclic ferrocene-bridged azacrown ion-pair receptor **58**

The condensation cyclisation reaction of bis-amine-functionalised 1,10-bis-aza[18]crown-6 **52** with the ferrocene bis-acid chloride synthon **55** (Scheme 3.7) was carried out in the presence of triethylamine base by heating to reflux in chloroform. To encourage the formation of the 1:1 cyclisation product, the reaction was performed under high dilution conditions. Purification by preparative thin layer chromatography (silica, 20 % methanol in chloroform) followed by precipitation from chloroform / diethylether gave receptor **58** as an orange solid in 12 % yield. The low yield of this product highlights the difficulties associated with [1+1] cyclisation reactions.



Scheme 3.7: (i) 1,1'-bis(chlorocarbonyl)ferrocene **55**, Et₃N, CHCl₃, reflux, 12 %.

Obviously, ¹H NMR spectroscopy and elemental analysis are unable to distinguish between the desired 1:1 product and other larger cyclisation products. Importantly, the electrospray mass spectrum of **58** (Figure 3.5) only revealed peaks for the 1:1 product – $m/z = 739.4$ (MH⁺), 761.3 (MNa⁺) and 777.3 (MK⁺). No peaks for other possible cyclisation products were observed.

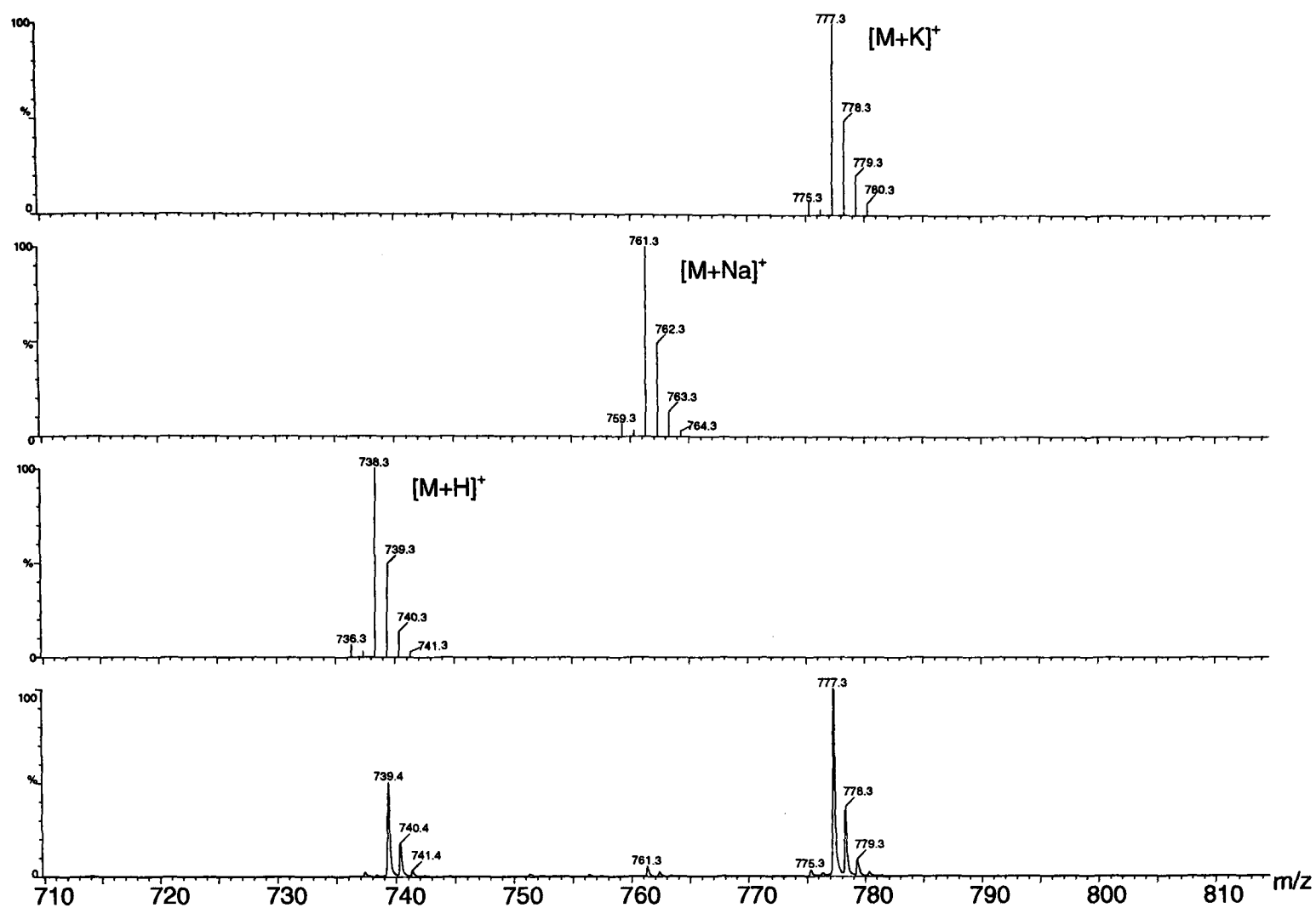


Figure 3.5: Electropray mass spectrum of receptor **58** (bottom) together with the calculated isotopic patterns (top).

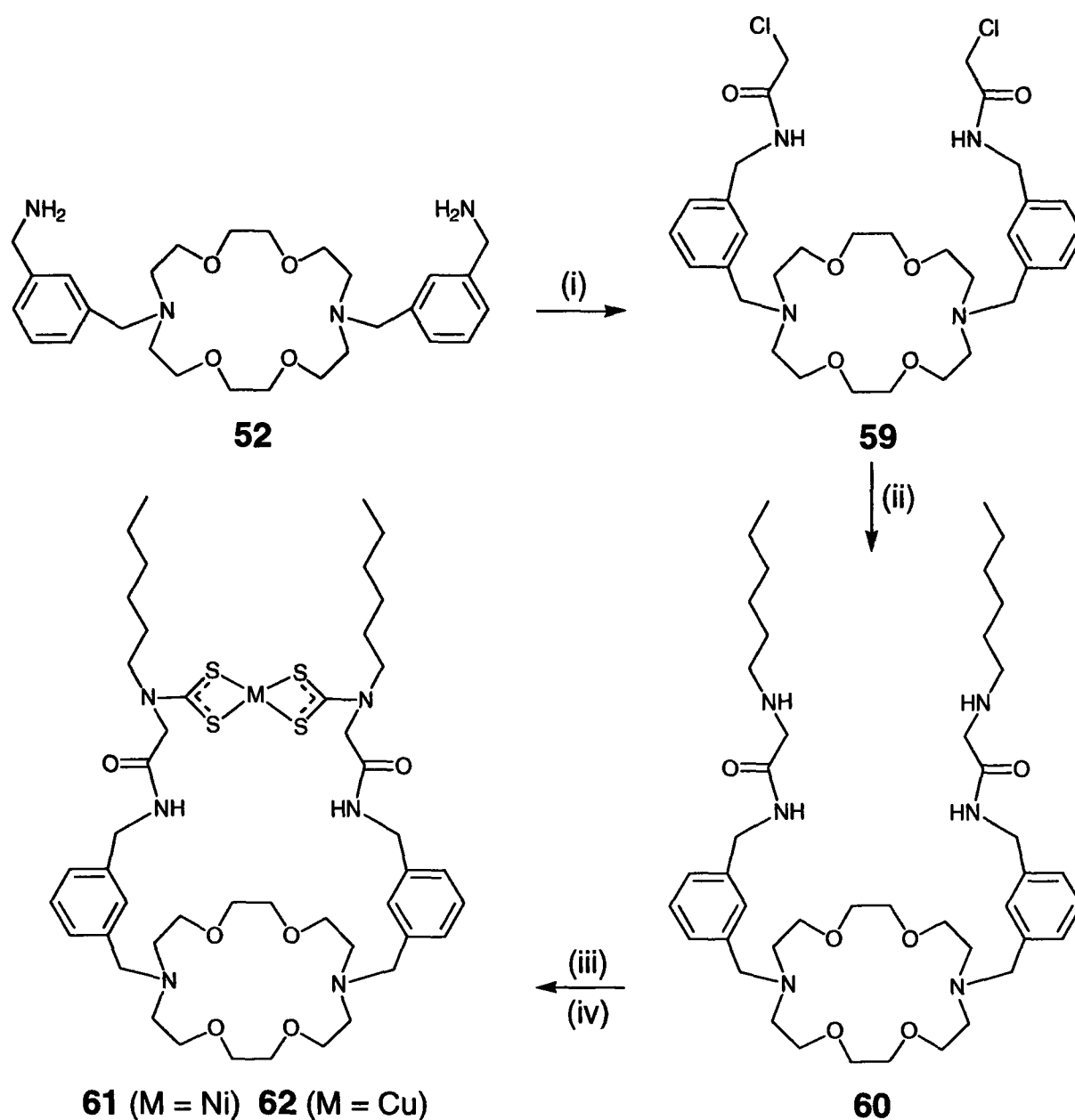
The attempted cyclisation of compound **52** with the bipyridine bis-acid chloride synthon **57** was unfortunately unsuccessful. ^1H NMR spectroscopic analysis of the reaction mixture indicated that the desired product had formed, however the receptor could not be isolated in sufficient purity or quantity for further study.

3.2.5 Synthesis of macrobicyclic transition metal dithiocarbamate-bridged azacrown ion-pair receptors

As discussed in Section 3.1, the reaction of secondary amines with carbon disulphide and potassium hydroxide to give dithiocarbamate ligands is well established, and the addition of transition metal salts to these polydentate dithiocarbamate ligands has resulted in the self-assembly of some interesting molecular architectures. In this section, the metal-directed self-assembly of dithiocarbamate groups was exploited in the synthesis of a number of new macrobicyclic transition metal dithiocarbamate-bridged azacrown ion-pair receptors. In

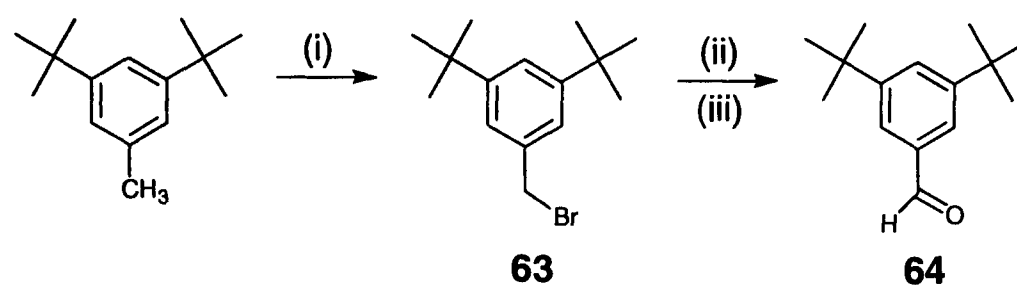
addition to the structural effects of rigidifying the receptors and creating preorganised binding sites, the redox-active transition metal dithiocarbamate groups are capable of electrochemically and spectroscopically sensing anion or ion-pair binding processes (see Sections 3.4 and 3.5).

The synthesis of potential heteroditopic receptors **61** and **62** is outlined in Scheme 3.8. A solution of chloroacetyl chloride in chloroform was added to a biphasic mixture of bis-amine-functionalised 1,10-bis-aza[18]crown-6 **52** in chloroform and sodium hydroxide in water to produce compound **59** as a dark orange oil in quantitative yield. This was heated with excess hexylamine to give the secondary amine **60** as an orange oil in 93 % yield. It was envisaged that the addition of two hexyl chains would enhance the solubility of the target receptors in organic solvents. The secondary amine **60** was reacted with carbon disulphide and potassium hydroxide in 9:1 tetrahydrofuran / water. The addition of nickel(II) acetate tetrahydrate resulted in the formation of the nickel(II)-dithiocarbamate complex. This was extracted into dichloromethane and washed with aqueous lithium hydroxide to ensure the complete removal of all inorganic salts. Precipitation from chloroform / methanol afforded receptor **61** as a tan solid in 48 % yield. In a similar fashion, addition of copper(II) acetate monohydrate followed by precipitation from chloroform / methanol gave receptor **62** as a dark brown solid in 43 % yield.



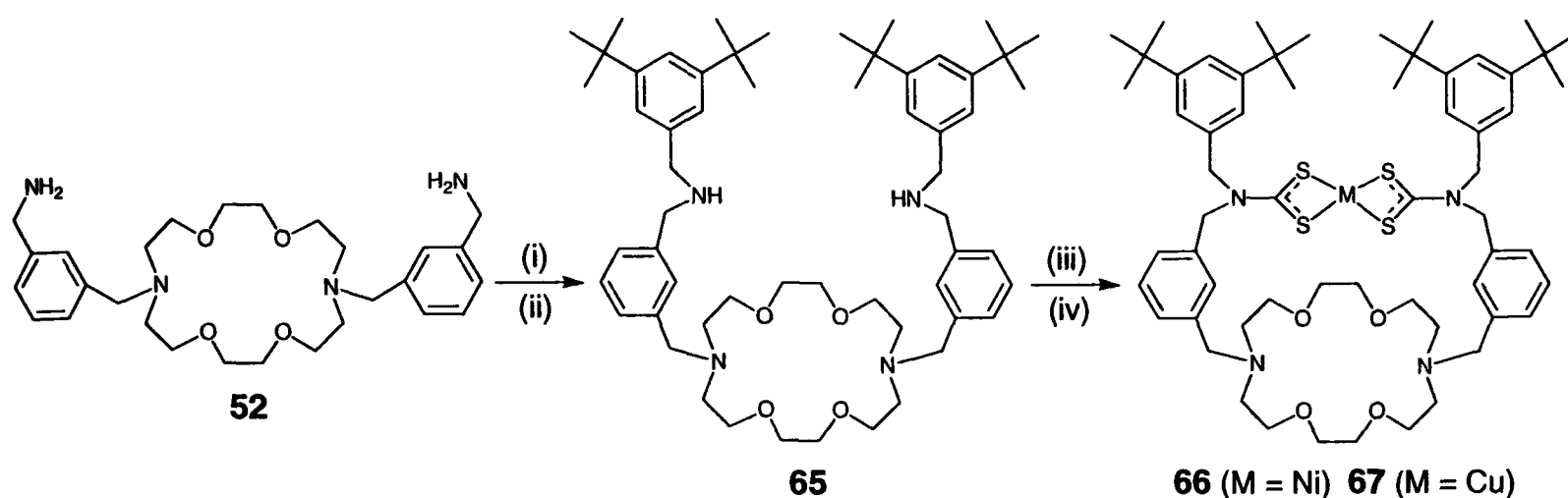
Scheme 3.8: (i) chloroacetyl chloride, NaOH, 5:1 CHCl₃ / H₂O, 98 %; (ii) hexylamine, CHCl₃, 50 °C, 93 %; (iii) CS₂, KOH, 9:1 thf / H₂O; (iv) Ni(OAc)₂·4H₂O, 48 % or Cu(OAc)₂·H₂O, 43 %.

The synthesis of receptors **66** and **67** is outlined in Scheme 3.10. In order to promote the solubility of these receptors in organic solvents, reductive amination was carried out with aldehyde synthon **64**, the synthesis of which is shown in Scheme 3.9.¹⁶ Radical bromination of 3,5-di-*t*-butyltoluene with *N*-bromosuccinimide in the presence of a catalytic amount of the radical initiator AIBN gave compound **63**. Reaction of **63** *in situ* with hexamethylenetetramine followed by acidification gave 3,5-di-*t*-butylbenzaldehyde **64** as a yellow crystalline solid in 91 % yield.



Scheme 3.9: (i) NBS, AIBN, 1,2-dichloroethane, reflux; (ii) hexamethylenetetramine, 1:1 EtOH / H₂O, reflux; (iii) HCl_(aq), 91 %.

Reductive amination of aldehyde **64** with bis-amine-functionalised 1,10-bis-aza[18]crown-6 **52** was achieved in two steps (Scheme 3.10). The reactants **52** and **64** were heated to reflux in toluene using a Dean-Stark apparatus whereby the condensation reaction was driven by the azeotropic removal of water. The resulting imine was reduced *in situ* with sodium borohydride in methanol to give the secondary amine **65** as a pale yellow oil in 95 % yield. Reaction with carbon disulphide and potassium hydroxide followed by addition of nickel(II) acetate tetrahydrate resulted in the formation of the nickel(II)-dithiocarbamate complex, which was extracted into dichloromethane and washed with aqueous lithium hydroxide. Precipitation from dichloromethane / methanol afforded receptor **66** as a green solid in 53 % yield. In a similar fashion, addition of copper(II) acetate monohydrate followed by precipitation from dichloromethane / methanol gave receptor **67** as a dark brown microcrystalline solid in 46 % yield. Although these new receptors do not contain amide groups for anion binding, they were prepared in order to provide a comparison to ion-pair receptors **61** and **62**.



Scheme 3.10: (i) 3,5-di-*t*-butylbenzaldehyde **64**, toluene, reflux, Dean-Stark;
(ii) NaBH₄, CH₃OH, 95 %; (iii) CS₂, KOH, 9:1 thf / H₂O;
(iv) Ni(OAc)₂·4H₂O, 53 % or Cu(OAc)₂·H₂O, 46 %.

All new receptors were characterised by ¹H NMR spectroscopy, mass spectrometry and elemental analysis. For example, the electrospray mass spectrum observed for **61** (Figure 3.6) is typical of these receptors. It reveals peaks at $m/z = 991.4$ (MH⁺), 1013.4 (MNa⁺) and 1029.3 (MK⁺) with good agreement between the theoretical and experimental isotopic patterns. Although elemental analysis confirmed that the ion-pair receptors were free from sodium and potassium, they readily picked up these cations in the mass spectrometer.

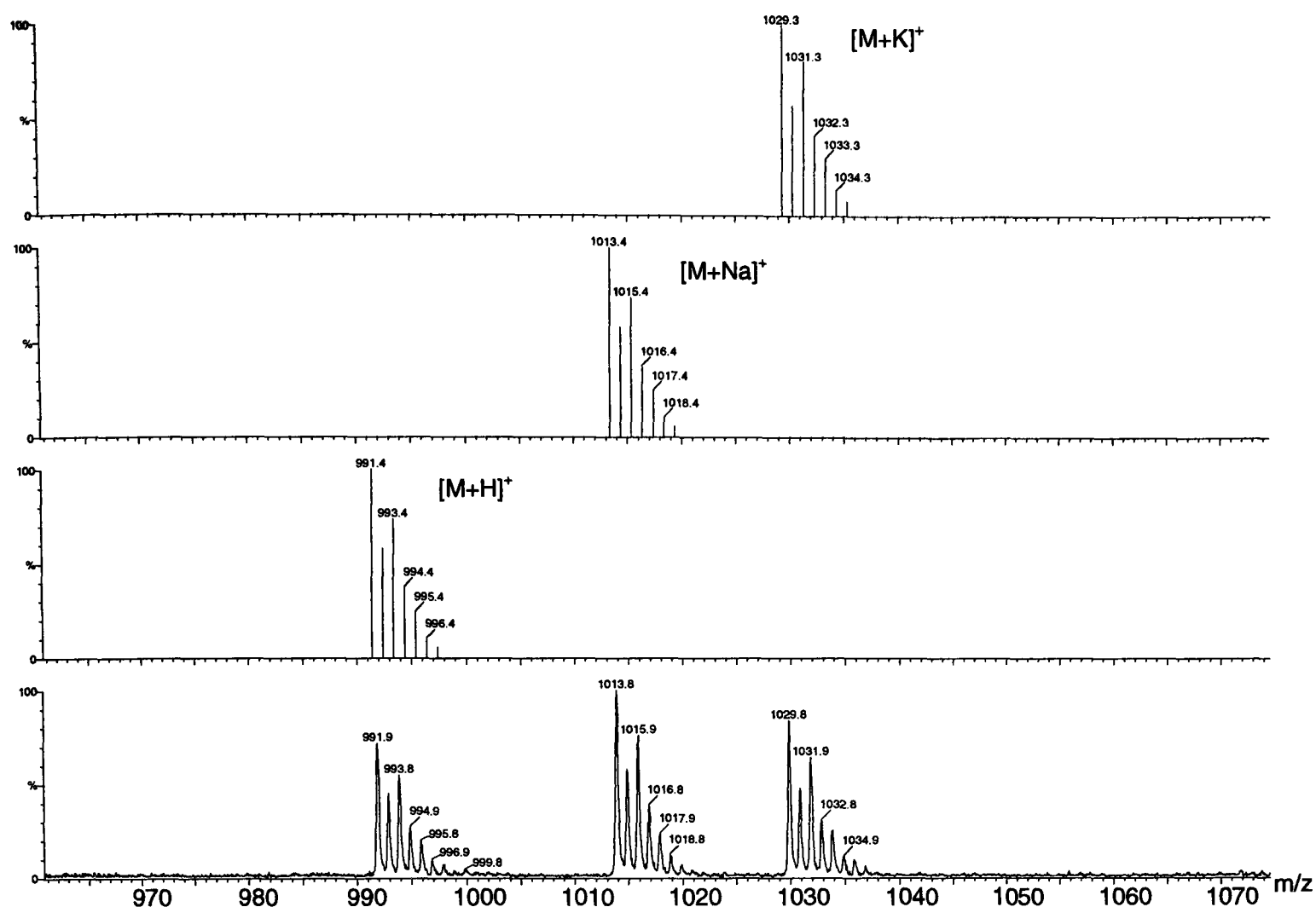


Figure 3.6: Electrospray mass spectrum of receptor **61** (bottom) together with the calculated isotopic patterns (top).

The assigned ^1H NMR spectrum of receptor **66** in CDCl_3 is shown in Figure 3.7. Interestingly, the two aromatic protons H_e are not equivalent (giving rise to two peaks at 7.81 and 7.83 ppm) and the peak for H_i is broad (perhaps due to two overlapping signals). This evidence indicates that the structure of **66** is not as symmetrical as expected. The ^1H NMR spectrum of the parent secondary amine **65** is characteristic of an entirely symmetrical molecule free to rotate in solution. However, the formation of the intramolecular nickel(II)-dithiocarbamate linkage leads to a rigidification of the receptor whereby it is locked into a less symmetrical structure. The N–C bonds of metal-dithiocarbamate complexes are known to have significant double bond character,⁵ and the resulting restricted rotation about this bond means that interconversion between different conformers in solution is typically slow on the NMR timescale. This leads to the observed inequivalency that is not present in the parent compound

65. Similar behaviour for other nickel(II)-dithiocarbamate complexes has been observed previously by our group.⁷

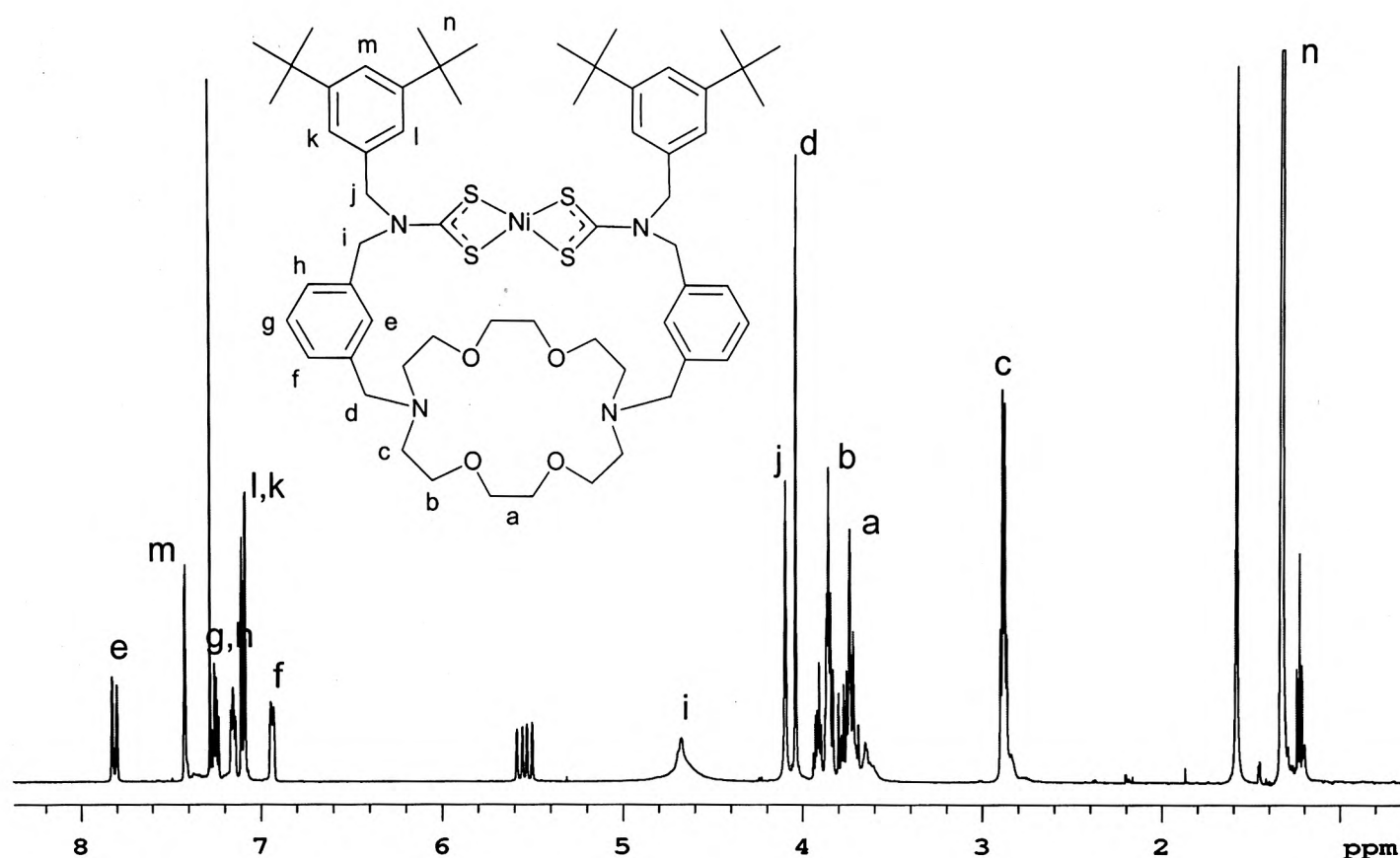


Figure 3.7: ^1H NMR spectrum (500 MHz) of receptor **66** in CDCl_3 .

The ^1H NMR spectrum of receptor **61** in d_6 -DMSO is likewise indicative of an unsymmetrical and rigidified structure. In addition, all the peaks are quite broad, perhaps indicating some distortion away from square-planar nickel(II)-dithiocarbamate coordination.

3.2.6 X-ray structural investigations of receptors **66** and **67**

The slow evaporation of a chloroform / methanol solution of receptor **66** yielded X-ray quality crystals (green platelets) of **66**· CH_3OH . The structure was solved by Dr. R. L. Paul (University of Oxford) and is shown in Figure 3.8; full data are given in Appendix F.5.

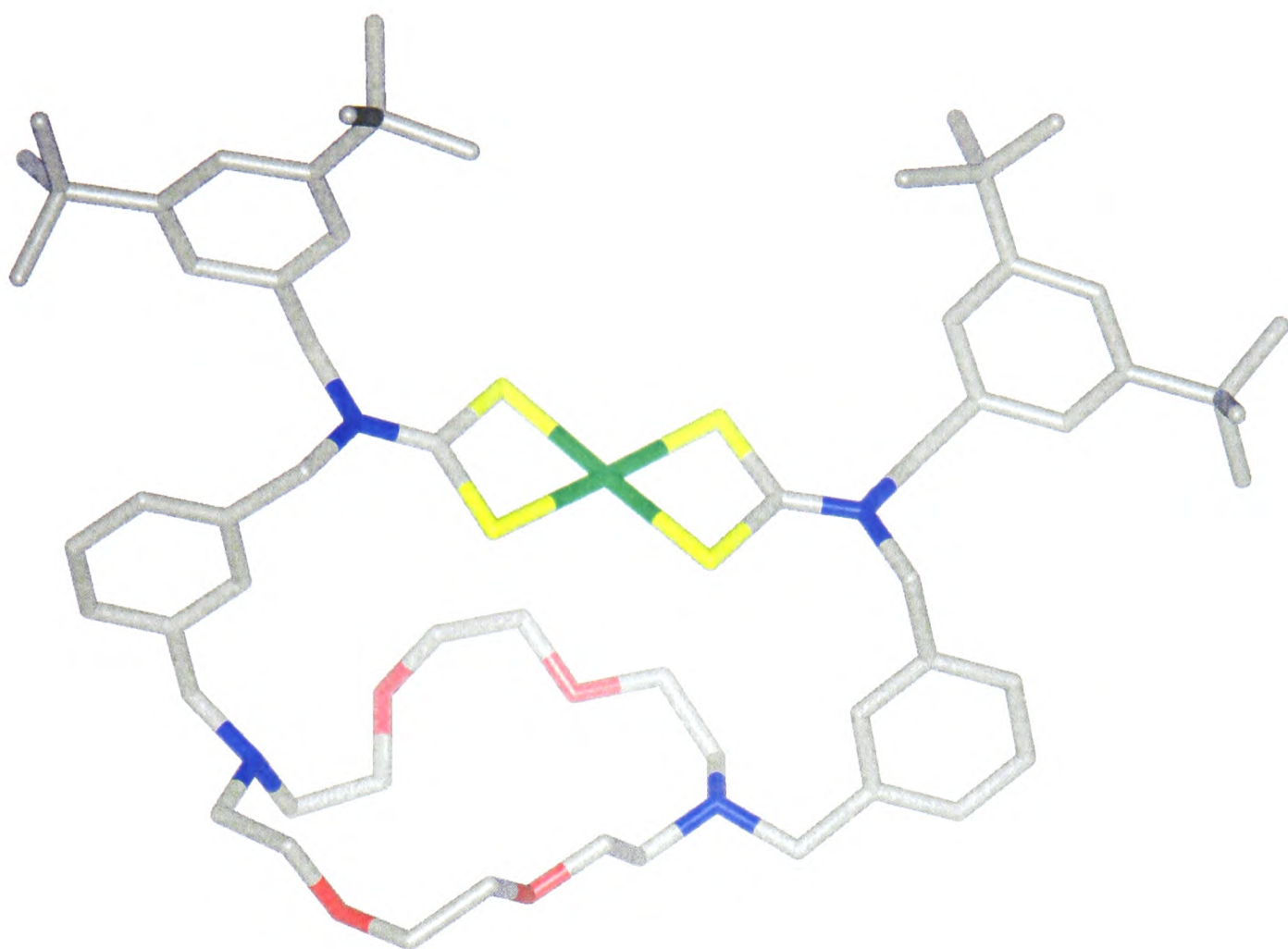


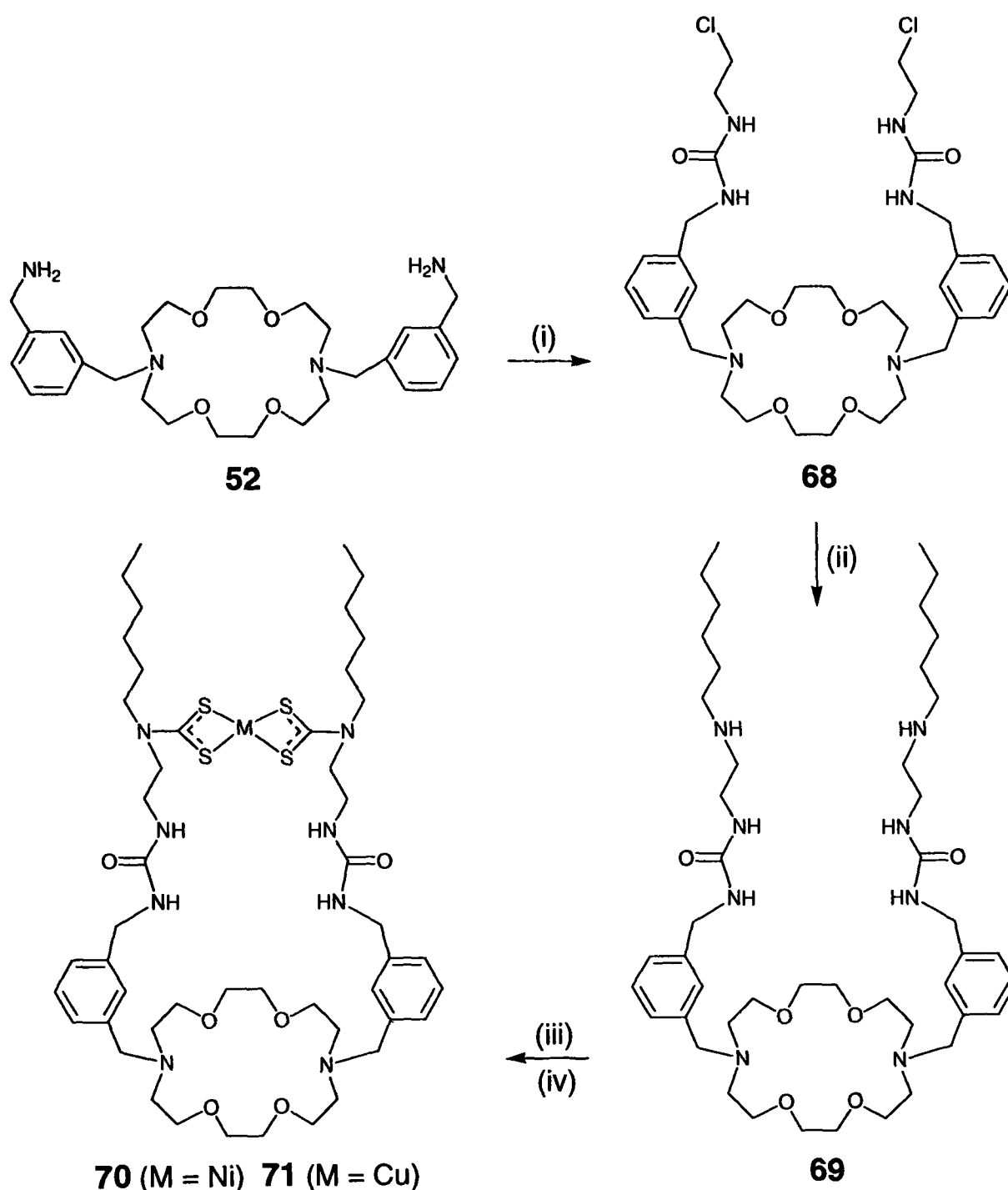
Figure 3.8: Crystal structure of receptor **66**
(the hydrogen atoms have been omitted for clarity).

The receptor is situated on a crystallographic twofold axis of rotation (monoclinic system, $P \bar{2}_1/c$ space group). As expected, the nickel(II)-dithiocarbamate group forms an almost perfect square planar linkage¹⁷ with the nickel atom lying only 3.7° out of the N–C–C–N plane. The Ni–S bond distances (Ni–S ~ 2.20 Å) and angles (S–Ni–S $\sim 80^\circ$) and C–S distances (C–S ~ 1.72 Å) are typical of a nickel(II)-dithiocarbamate complex. The N–C bond distance (N–C ~ 1.32 Å) is significantly less than that of a single carbon-nitrogen bond (~ 1.47 Å)¹⁸ but more than a double carbon-nitrogen bond (~ 1.30 Å),¹⁸ as might be expected due to the considerable double bond character between these two atoms.⁵ In addition, there is one molecule of methanol (not shown in Figure 3.8) associated with each receptor, hydrogen bonded to an oxygen atom in the azacrown ether ring (O(1)–O(100) = $2.773(5)$ Å).

The slow evaporation of a chloroform / methanol solution of receptor **67** yielded X-ray quality crystals (brown blocks) of **67**·CH₃OH. The structure was solved by Dr. R. L. Paul (University of Oxford) and is isostructural to that for **66** shown above; full data are given in Appendix F.6.

3.2.7 Attempted syntheses

The synthesis of two other macrobicyclic transition metal dithiocarbamate-bridged azacrown ion-pair receptors (**70** and **71**) was attempted. The structure of these receptors is similar to **61** and **62** except that they contain urea rather than amide linkages. The proposed synthetic method is shown in Scheme 3.11.



Scheme 3.11: (i) 2-chloroethyl isocyanate, CHCl_3 ; (ii) hexylamine, CHCl_3 , 50°C , 7 %; (iii) CS_2 , KOH, 9:1 thf / H_2O ; (iv) $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ or $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$.

The coupling reaction of 2-chloroethyl isocyanate and bis-amine-functionalised 1,10-bis-aza[18]crown-6 **52** proved to be problematic and several attempted reactions all resulted in mixtures which could not be purified. The use of mild conditions resulted in the reaction failing to go to completion, giving a mixture of the desired product **68** and starting material **52**. However, the use of more vigorous conditions encouraged the intramolecular cyclisation of **68**, whereby the terminal chloride groups reacted with the urea protons to form stable five-membered rings. ^1H NMR spectroscopy and mass spectrometry revealed that compound **72**

(Figure 3.9) was the major reaction product under these conditions. The resulting mixture of desired product **68** and intramolecular cyclisation product **72** could not be purified.

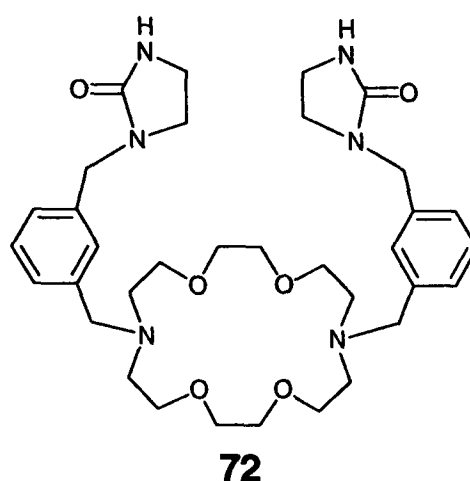


Figure 3.9: Intramolecular cyclisation product **72**.

Reaction of the impure mixture with excess hexylamine followed by column chromatography (silica, 20 % methanol in chloroform then pure methanol) gave the secondary amine **69** as a dark yellow oil in 7 % yield. Unfortunately, this very low yield meant that receptors **70** and **71** could not be synthesised in sufficient quantities for characterisation and further studies.

3.2.8 Summary

The condensation of primary amine-derivatised aza[15]crown-5 and 1,10-bis-aza[18]crown-6 compounds **48** and **52** with acid chloride synthons 3,4-dimethoxybenzoyl chloride, chlorocarbonyl ferrocene **9** and 1,1'-bis(chlorocarbonyl)ferrocene **55** produced four new azacrown ion-pair receptors (**49**, **50**, **53** and **58**). The exploitation of the metal-directed self-assembly properties of dithiocarbamate groups resulted in the synthesis of four new macrobicyclic transition metal dithiocarbamate-bridged azacrown ion-pair receptors (**61**, **62**, **66** and **67**). A diagrammatic summary of the receptors is provided in Appendix H. All these new compounds were characterised by ^1H NMR spectroscopy, mass spectrometry and elemental analysis, and by X-ray crystallography in the cases of **66** and **67**.

3.3 ^1H NMR Anion and Ion-Pair Binding Studies

As discussed previously (in Section 2.3.6 of Chapter Two), in order to undertake ^1H NMR ion-pair binding studies all species must remain soluble throughout the course of the titration. Consequently, 1:1 $\text{CD}_3\text{CN} / d_6\text{-DMSO}$ was chosen as the solvent system, as precipitation was often observed in systems with a lower proportion of $d_6\text{-DMSO}$.

The choice of alkali metal cation for these studies depended on the nature of the azacrown ether moiety in the receptor of interest. Based on the stability constant values discussed in Section 3.1, sodium cations were used in the case of ion-pair receptors containing an aza[15]crown-5 group, and potassium cations were used for those receptors containing the 1,10-bis-aza[18]crown-6 group. Addition of sodium perchlorate to solutions of receptors **49** and **50** and addition of potassium perchlorate to solutions of receptors **58** and **61** resulted in negligible changes in the respective ^1H NMR spectra. Consequently, no cation stability constants could be obtained by this technique.

^1H NMR titration experiments were carried out with **49**, **50**, **58** and **61** with benzoate anions in 1:1 $\text{CD}_3\text{CN} / d_6\text{-DMSO}$, both for the free receptors and in the presence of one equivalent of either sodium or potassium perchlorate. EQNMR¹⁹ analysis of the titration curves, monitoring the amide protons of the respective receptor, indicated 1:1 anion / receptor binding stoichiometries and gave the stability constant values shown in Table 3.1.

	49	50	58	61
benzoate	< 5	< 5	15	10
+ Na^+ / K^+	10^a	10^a	10^b	— ^{bc}

Table 3.1: Anion stability constants (K / M^{-1}) determined in 1:1 $\text{CD}_3\text{CN} / d_6\text{-DMSO}$ (errors $\leq 10\%$) for the free receptor and in the presence of one equivalent of cation (^a sodium perchlorate, ^b potassium perchlorate). ^c The amide peak became too broad to monitor.

Clearly, benzoate anions are bound very weakly in this competitive solvent system by all four receptors. Anion binding is so weak that it is difficult to comment on the effect of cation complexation on anion binding.

Following these discouraging results, some anion binding studies were performed in less competitive solvents (CDCl_3 and CD_3CN), in the hope of increasing the anion association constants. ^1H NMR titrations were carried out with receptors **50** and **58** with chloride, benzoate and dihydrogen phosphate anions. However addition of anions caused the amide proton peaks to shift and disappear under the aromatic peaks, thereby preventing the determination of binding constants.

After these setbacks it was decided to investigate other methods of studying ion-pair binding, namely electrochemistry, UV-VIS spectroscopy and solid/liquid extraction experiments.

3.4 Electrochemical Anion and Ion-Pair Sensing

3.4.1 Electrochemical sensing with receptors containing ferrocene groups

The electrochemical properties of the ferrocene-containing receptors **50**, **53** and **58** were investigated by CV (see Appendix B). Electrochemical studies of the receptors (5×10^{-4} M in electrolyte solution) were conducted in 0.1 M tetrabutylammonium tetrafluoroborate in 1:1 dichloromethane / acetonitrile and the relevant data are given in Table 3.2.

	50	53	58
E_{pa}	188	184	399
E_{pc}	122	104	311
ΔE^a	66	80	88
$E_{1/2}^b$	155	144	355
I_{pa} / I_{pc}	1.05	1.25	1.65

Table 3.2: Electrochemical data for the free receptors. CVs were recorded under the following conditions: 5×10^{-4} M solutions of receptor in 0.1 M Bu_4NBF_4 in 1:1 CH_2Cl_2 / CH_3CN , scan rate 100 mV.s^{-1} , platinum working electrode, Ag / $AgNO_3$ reference electrode. Electrochemical potentials are ± 5 mV and are quoted relative to ferrocene. ^a $\Delta E = E_{pa} - E_{pc}$ ^b $E_{1/2} = (E_{pa} + E_{pc}) / 2$

The $E_{1/2}$ values of **50** and **53** occur about 150 mV positive of ferrocene due to the electron withdrawing carbonyl group attached to one of the cyclopentadienyl rings. In the case of **58**, in which both rings are functionalised with a carbonyl group, the $E_{1/2}$ value occurs 355 mV positive of ferrocene.

The electrochemical response of the receptors at different scan rates was investigated, and all three receptors behaved in a similar manner. As the scan rate is increased the redox wave broadens (ΔE increases) and the plots of current ($I_{pa} - I_{pc}$) against the square root of scan rate are linear (R^2 values greater than 0.994). The data in Table 3.2 reveal that ΔE is greater than $59/n$ mV and I_{pa} / I_{pc} is greater than unity (although only just in the case of receptor **50**). Together these results indicate that these systems are best described as quasi-reversible (see Section 2.4.1 of Chapter Two).

Anion and ion-pair sensing studies were conducted on solutions of the receptors (5×10^{-4} M in electrolyte solution) in 0.1 M tetrabutylammonium tetrafluoroborate in 1:1 dichloromethane / acetonitrile. CVs and SWVs were recorded for the free receptors (**50**, **53**

and **58**) and upon addition of 0.5, 1, 2, 5 and 10 equivalents of tetrabutylammonium chloride, benzoate or dihydrogen phosphate. These studies were repeated in the presence of one equivalent of either sodium perchlorate (for receptor **50**) or potassium perchlorate (for receptors **53** and **58**). As mentioned in Section 3.3, the choice of cation for these studies was based on size complementarity with the azacrown group in the receptors.

CVs and SWVs recorded upon addition of anions to **53** show features common to all three receptors (Figures 3.10 – 3.12). Firstly, addition of anions results in significant cathodic shifts in the redox potentials of the receptors. As discussed previously (in Section 2.4 of Chapter Two), this anion-induced cathodic perturbation can be attributed to the complexation of an anionic guest by the amide protons in close proximity to the ferrocene redox centres, thereby facilitating their oxidation to ferrocenium.

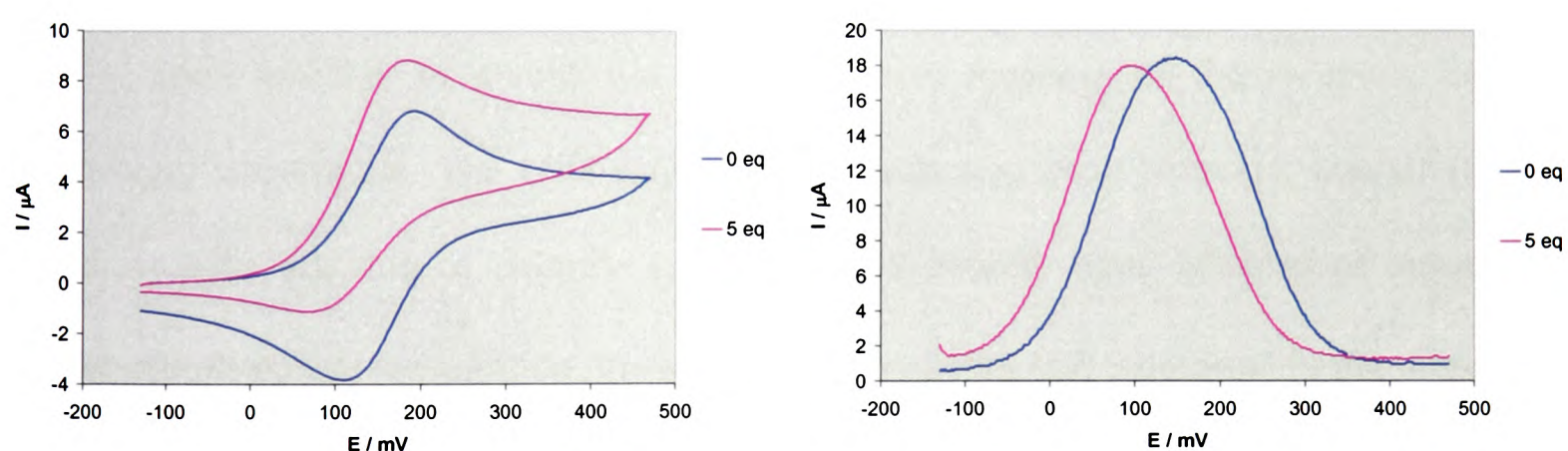


Figure 3.10: CVs and SWVs of **53** upon addition of tetrabutylammonium chloride.

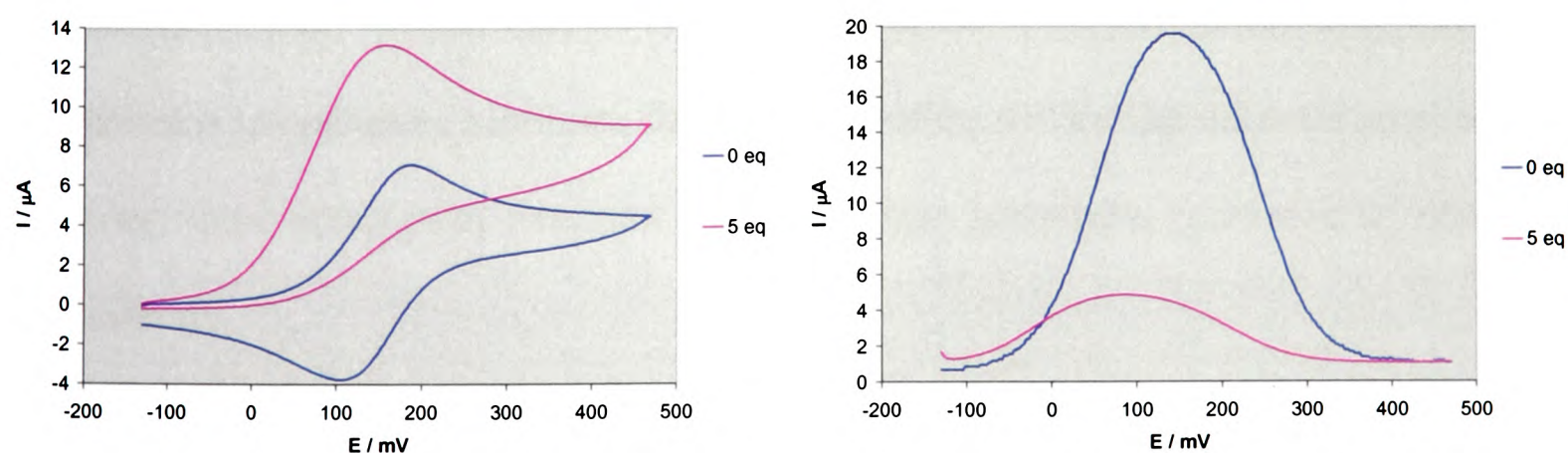


Figure 3.11: CVs and SWVs of **53** upon addition of tetrabutylammonium benzoate.

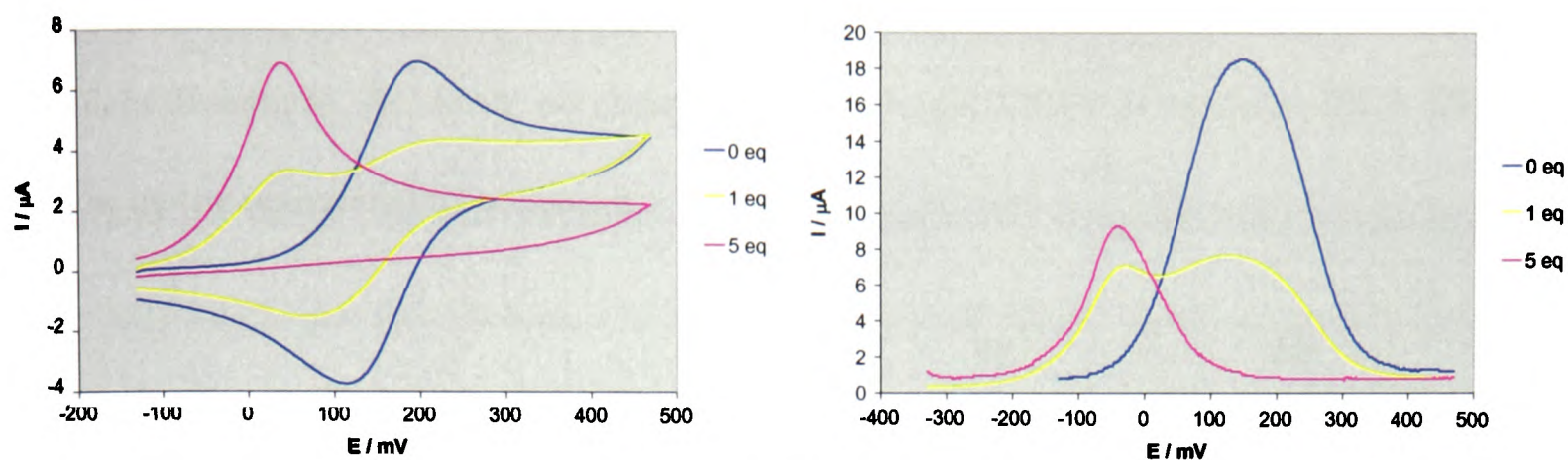


Figure 3.12: CVs and SWVs of **53** upon addition of tetrabutylammonium dihydrogen phosphate.

Secondly, the redox waves gradually shift in a cathodic direction upon addition of chloride or benzoate, whereas addition of dihydrogen phosphate results in the evolution of a new cathodically shifted peak and the concurrent disappearance of the initial one. This behaviour was observed for the calix[4]arene-based receptors investigated in Chapter Two, and suggests that the binding of dihydrogen phosphate is kinetically slow on the CV or SWV timescale.

Thirdly, upon addition of anions the electrochemical response of the receptors becomes increasingly irreversible. The CVs show that the reduction peak becomes smaller (I_{pa} / I_{pc} increases) upon addition of chloride and disappears entirely upon addition of benzoate or dihydrogen phosphate; in addition, the redox wave broadens (ΔE increases) in the presence of anions. Again, this behaviour has been described previously (in Section 2.4.2 of Chapter Two). The disappearance of the reduction wave on anion addition indicates that a bound anion / ferrocenium cation ion-pair may be disfavours reduction back to ferrocene or that an EC mechanism is in operation. Similarly, the intensities of the SWVs also decrease upon addition of anions, most notably for benzoate and dihydrogen phosphate, indicative of increasing irreversibility.

The magnitudes of the cathodic shifts in the redox potentials of the receptors upon addition of five equivalents of anion (as determined from SWV) are given in Table 3.3. It should be noted

that the redox wave of receptor **50** shifted 10 – 15 mV anodically upon addition of one equivalent of sodium. However, no change occurred in the SWVs of receptors **53** or **58** upon addition of one equivalent of potassium.

	50	53	58
chloride	35	55	115
+ Na ⁺ / K ⁺	30 ^a	45 ^b	80 ^b
benzoate	100	50	170
+ Na ⁺ / K ⁺	105 ^a	40 ^b	125 ^b
dihydrogen phosphate	110	190	230
+ Na ⁺ / K ⁺	100 ^a	185 ^b	240 ^b

Table 3.3: Cathodic shifts in the $E_{1/2}$ values of the receptors upon addition of 5 equivalents of anions, for the free receptor and in the presence of one equivalent of cation (^a sodium perchlorate, ^b potassium perchlorate) (errors ± 10 mV). SWVs were recorded under the following conditions: 5×10^{-4} M solutions of receptor in 0.1 M Bu₄NBF₄ in 1:1 CH₂Cl₂ / CH₃CN, frequency 25 Hz, scan increment 2 mV, platinum working electrode, Ag / AgNO₃ reference electrode.

The data reported in Table 3.3 show that the shift magnitudes are generally greatest for dihydrogen phosphate followed by benzoate then chloride. Receptor **58** displays the largest shifts for all three anions, and a notably large shift for chloride. Consideration of the macrobicyclic structure of **58** reveals that the two amide groups are preorganised for cooperative anion binding, which may explain the larger cathodic perturbations observed for this receptor upon addition of anions.

Unfortunately, in most cases, the observed anion-induced cathodic shifts were the same (within error) in the presence / absence of one equivalent of alkali metal cation. In the case of receptor **58** with chloride and benzoate, however, the presence of one equivalent of potassium perchlorate caused a reduction in the magnitude of the observed anion-induced cathodic

shifts. This result is in contrast to the ion-pair sensing behaviour of the calix[4]arene-based receptor described previously (in Section 2.4.3 of Chapter Two), which exhibited a significantly larger cathodic shift upon addition of benzoate in the presence of potassium cations.

Clearly, these results indicate that the processes leading to positive or negative cooperativity in electrochemical ion-pair sensing are complex. A smaller anion-induced cathodic shift in the presence of a cation might be explained by significant ion-pairing occurring outside the receptor. Alternatively, the presence of a closely bound cation (which competes for the attraction of the anion) may reduce the ability of the anion to stabilise the ferrocenium cation, resulting in smaller cathodic shift magnitudes.

3.4.2 Electrochemical sensing with receptors containing transition metal dithiocarbamate groups

The electrochemical properties of the macrobicyclic transition metal dithiocarbamate-bridged azacrown ion-pair receptors **61**, **66**, **62** and **67** were investigated by CV in the usual manner.

CVs of receptors **61** and **66** are typical of nickel(II)-dithiocarbamate complexes reported in the literature.²⁰ Both receptors exhibit three irreversible metal-centred electrochemical processes, namely a nickel(II) / nickel(IV) two electron oxidation, a nickel(IV) / nickel(III) one electron reduction, and a nickel(III) / nickel(II) one electron reduction. Table 3.4 displays the relevant data for **61** and **66**, together with comparative data for a simple complex, nickel(II) bis(*N,N*-diethyl-dithiocarbamate) (Ni(dtcEt₂)₂).²¹ Due to the irreversible nature of these redox processes, neither **61** nor **66** were suitable for electrochemical sensing studies.

	61	66	Ni(dtcEt ₂) ₂
E _{pa} (Ni(II) / Ni(IV))	355	375	475
E _{pc} (Ni(IV) / Ni(III))	-340	-180	-410
E _{pc} (Ni(III) / Ni(II))	-885	-775	-925

Table 3.4: Electrochemical data for nickel(II)-dithiocarbamate complexes. CVs were recorded under the following conditions: 5×10^{-4} M solutions of receptor in 0.1 M Bu₄NBF₄ in 1:1 CH₂Cl₂ / CH₃CN, scan rate 100 mV.s⁻¹, glassy carbon working electrode, Ag / AgNO₃ reference electrode. Electrochemical potentials are ± 5 mV and are quoted relative to ferrocene.

The electrochemical properties of copper(II)-dithiocarbamate complexes have been extensively studied.²⁰ The CVs of receptors **62** and **67** are typical of such complexes, with both receptors exhibiting two metal-centred electrochemical processes, namely a quasi-reversible copper(II) / copper(III) oxidation and an irreversible copper(II) / copper(I) reduction. Table 3.5 displays the relevant data for the copper(II) / copper(III) couple of **62** and **67**, together with comparative data for a simple complex, copper(II) bis(*N,N*-diethyl-dithiocarbamate) (Cu(dtcEt₂)₂).²¹ The copper(II) / copper(I) reduction occurs at negative potentials (E_{pc} = -935 for **62**, -1045 mV for **67** and -1205 mV for Cu(dtcEt₂)₂), and the irreversible nature of this couple may be attributable to the stereochemical change that occurs from square-planar copper(II) to tetrahedral copper(I). Sensing studies involved observing shifts in the potential of the copper(II) / copper(III) redox wave.

	62	67	Cu(dtcEt ₂) ₂
E _{pa}	151	147	105
E _{pc}	49	63	-20
ΔE ^a	102	84	125
E _{1/2} ^b	100	105	63
I _{pa} / I _{pc}	2.10	1.30	1.1

Table 3.5: Electrochemical data for the copper(II) / copper(III) redox couple of copper(II)-dithiocarbamate complexes. CVs were recorded under the following conditions: 5×10^{-4} M solutions of receptor in 0.1 M Bu₄NBF₄ in 1:1 CH₂Cl₂ / CH₃CN, scan rate 100 mV.s⁻¹, glassy carbon working electrode, Ag / AgNO₃ reference electrode. Electrochemical potentials are ± 5 mV and are quoted relative to ferrocene. ^a ΔE = E_{pa} - E_{pc} ^b E_{1/2} = (E_{pa} + E_{pc}) / 2

The electrochemical response of the receptors at different scan rates was investigated. For both **62** and **67**, the redox wave broadens (ΔE increases) as the scan rate is increased and the plots of current (I_{pa} - I_{pc}) against the square root of scan rate are linear (R² values greater than 0.993). The data in Table 3.5 reveal that ΔE is greater than 59/n mV and I_{pa} / I_{pc} is greater than unity, indicating that these are quasi-reversible systems.

Ion-pair electrochemical sensing studies were carried out as described above (in Section 3.4.1). The magnitudes of the cathodic shifts in the redox potentials of the copper(II) / copper(III) couples of the receptors upon addition of five equivalents of anion (as determined from SWV) are given in Table 3.6. No change occurred in the SWVs of receptors **62** or **67** upon addition of one equivalent of potassium perchlorate, presumably because the cation binding site is located too far away from the copper(II)-dithiocarbamate centre for effective cation sensing. As observed previously (in Section 3.4.1), upon addition of anions the electrochemical response of the receptors becomes increasingly irreversible.

	62	67	Cu(dtcEt ₂) ₂
chloride	35	25	5
+ K ⁺	30	30	— ^a
benzoate	90	60	15
+ K ⁺	100	65	— ^a
dihydrogen phosphate	85	20	10
+ K ⁺	85	20	— ^a

Table 3.6: Cathodic shifts in the $E_{1/2}$ values of the copper(II) / copper(III) couples of receptors **62** and **67** upon addition of 5 equivalents of anions, for the free receptor and in the presence of one equivalent of potassium perchlorate (errors ± 10 mV). ^a Studies were not performed. SWVs were recorded under the following conditions: 5×10^{-4} M solutions of receptor in 0.1 M Bu₄NBF₄ in 1:1 CH₂Cl₂ / CH₃CN, frequency 25 Hz, scan increment 2 mV, glassy carbon working electrode, Ag / AgNO₃ reference electrode.

The data in Table 3.6 reveal that receptor **62** exhibits the largest cathodic shift magnitudes upon addition of anions. These anion-induced cathodic shifts may be explained by the cooperative binding of an anion by the two amide groups of the receptor, whereby the close proximity of the bound anion to the metal centre stabilises the charged copper(III)-dithiocarbamate species. The magnitude of the shift reflects how effectively the anion stabilises the copper(III) oxidation state.

It should be noted that receptor **67** (unlike **62**) contains no amide functionalities for anion binding. Based on this, one might have predicted only small cathodic shifts for **67** in the presence of anions. However, surprisingly, **67** exhibits significantly larger cathodic shift magnitudes upon addition anions than those observed for the acyclic model complex Cu(dtcEt₂)₂.

Electrochemical sensing of anions by copper(II)-dithiocarbamate macrocycles with no amide hydrogen bonding sites has been reported previously.²² The dinuclear copper(II)-

dithiocarbamate receptor **3.6** (Figure 3.13) displays selective electrochemical recognition of perrhenate and dihydrogen phosphate over chloride, bromide and nitrate anions. The observed cathodic shifts are attributed to direct electrostatic interaction between the anion and the oxidised copper(III)-dithiocarbamate species. The selectivity is presumably due to the larger tetrahedral anions possessing a better size complementarity for the molecular cavity.

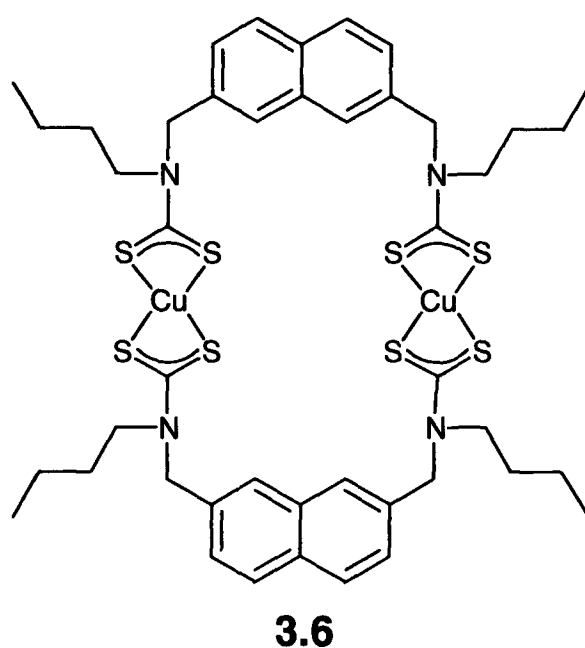


Figure 3.13: Copper(II)-dithiocarbamate macrocyclic receptor **3.6** capable of electrochemical anion recognition.

In light of this example, the observed anion-induced cathodic shifts for receptor **67** (and $\text{Cu}(\text{dtcEt}_2)_2$) may be ascribed to direct interaction between the anion and the oxidised receptor, whereby the anion stabilises the copper(III) oxidation state (in other words, ion-pair stabilisation). Clearly though, there must be other factors which result in the larger anion-induced cathodic shifts for **67** compared to $\text{Cu}(\text{dtcEt}_2)_2$. For example, the cathodic shift magnitude is five times larger upon addition of chloride to **67** than to $\text{Cu}(\text{dtcEt}_2)_2$, perhaps due to size complementarity between the anion and the charged cavity (as observed for tetrahedral anions in the above example). Upon addition of benzoate, the cathodic shift magnitude is four times larger for **67** than for $\text{Cu}(\text{dtcEt}_2)_2$, possibly indicating a significant contribution from aromatic π - π interactions in the binding of benzoate to receptor **67**.

Comparing the results for receptors **62** and **67** given in Table 3.6 reveals the following. The cathodic shift observed upon addition of chloride to **67** is comparable to that for **62**, perhaps demonstrating that a direct interaction with the oxidised copper(III)-dithiocarbamate centre is more important than hydrogen bonding interactions in the case of chloride. However, significantly larger cathodic shifts are observed upon addition of benzoate and dihydrogen phosphate to **62** compared to **67**, revealing that for these guests, anion recognition by the amide groups of receptor **62** results in enhanced electrochemical detection.

Unfortunately, neither **62** nor **67** demonstrate a significant cooperative ion-pair effect, as the cathodic shift magnitudes are the same (within error) in the presence / absence of potassium.

3.5 UV-VIS Spectroscopic Anion and Ion-Pair Binding Studies

3.5.1 Nickel(II)-dithiocarbamate receptors 61 and 66

Nickel(II)-dithiocarbamate complexes display characteristic absorptions in the UV-VIS region. Typically they undergo ligand centred (LC) π - π^* transitions at ~ 230 and 320 nm, metal to ligand charge transfer (MLCT) transitions at ~ 390 and 430 nm and weak nickel(II) d-d transitions at ~ 490 and 650 nm.²³

UV-VIS absorption spectra were recorded for solutions of receptors **61** and **66** (5×10^{-5} M) in 4:1 acetonitrile / DMSO. In the case of both receptors, the lower wavelength LC transition was hidden by absorption of the DMSO solvent, and the nickel(II) d-d transitions were too weak to be observed.²⁴ Table 3.7 displays the wavelengths, molar extinction coefficients and assignments for the absorption maxima of **61** and **66** in 4:1 acetonitrile / DMSO. In addition, absorption data for $\text{Ni}(\text{dtcEt}_2)_2$ are given for comparison.

61	66	Ni(dtcEt ₂) ₂	assignment
326 (25.6)	327 (34.6)	327 (36.9)	LC
367 (15.6)	400 (6.0)	399 (5.8)	MLCT
474 (12.0)	430 (1.6)	427 (1.6)	MLCT

Table 3.7: Wavelengths (λ / nm) and molar extinction coefficients (ϵ / $10^3 \text{ M}^{-1} \text{ cm}^{-1}$) of the absorption maxima of receptors **61** and **66** in 4:1 CH₃CN / DMSO.

Receptor **66** displays absorptions typical of a nickel(II)-dithiocarbamate complex. However, the position and intensity of the absorption bands observed for **61** are somewhat different. Perhaps this is an indication of significant distortion of the nickel(II)-dithiocarbamate centre, due to steric strain in the macrocycle or intramolecular hydrogen bonding.

UV-VIS anion titrations were undertaken with receptors **61** and **66** in 4:1 acetonitrile / DMSO (see Appendix C). In the case of **61**, addition of chloride resulted in essentially no changes to the spectrum beyond those due to simple dilution effects. However, the addition of benzoate or dihydrogen phosphate resulted in rather unexpected behaviour. Very large changes occurred in the spectrum and, more importantly, a time delay was observed for the absorption to reach a constant value.

To investigate this behaviour in more detail, ten equivalents of benzoate or dihydrogen phosphate were added to a solution of receptor **61** in 4:1 acetonitrile / DMSO and spectra recorded at two minute intervals until the absorption had reached a constant value. The equilibration time was approximately 14 minutes for benzoate and 18 minutes for dihydrogen phosphate. For example, Figure 3.14 shows the spectra recorded upon addition of dihydrogen phosphate to **61** and the change in absorbance at 367 nm over time.

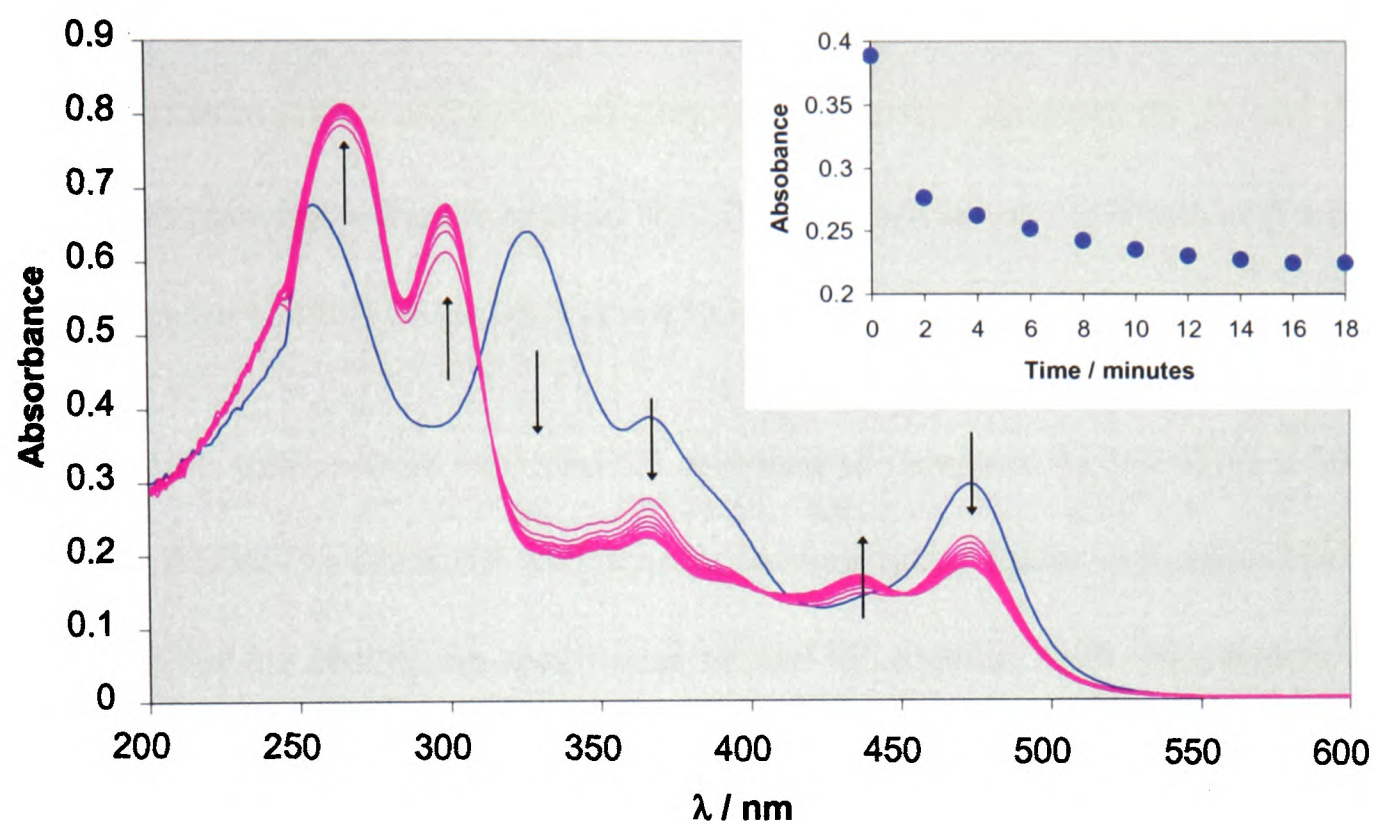


Figure 3.14: UV-VIS absorption spectra of receptor **61** in 4:1 CH_3CN / DMSO recorded at two minute intervals after the addition of ten equivalents of dihydrogen phosphate. (Inset) The change in absorbance at 367 nm over time.

Analogous titrations with receptor **66** showed only small changes in the UV-VIS spectrum upon addition of chloride, benzoate or dihydrogen phosphate anions, attributable to simple dilution effects.

These results indicate that more than just simple anion binding is occurring with **61** and benzoate or dihydrogen phosphate. Importantly, this time delay effect is not observed upon addition of anions to the model complex $\text{Ni}(\text{dtcEt}_2)_2$. In addition, anion complexation processes taking over 10 minutes to reach equilibrium have never been reported for comparable systems. Therefore, it seems most likely that the anion is initially bound by the amide groups of the receptor and then another process is occurring, either a conformational change in the molecule or possibly the formation of a new coordination complex *via* ligand exchange at the metal centre. One intriguing possibility is the anion-induced transformation from monomeric to dimeric species. Clearly such effects precluded the determination of anion binding constants for these nickel(II)-dithiocarbamate receptors.

3.5.2 Copper(II)-dithiocarbamate receptors **62** and **67**

Copper(II)-dithiocarbamate complexes display characteristic absorptions in the UV-VIS region, typically showing a ligand centred (LC) π - π^* transition at ~ 270 nm and a ligand to metal charge transfer (LMCT) transition at ~ 435 nm.²⁵

UV-VIS absorption spectra were recorded for solutions of receptors **62** and **67** (5×10^{-5} M) in 4:1 acetonitrile / DMSO. Table 3.8 displays the wavelengths, molar extinction coefficients and assignments for the absorption maxima of **62** and **67**, together with comparative data for $\text{Cu}(\text{dtcEt}_2)_2$.

62	67	$\text{Cu}(\text{dtcEt}_2)_2$	assignment
435 (9.5)	435 (11.4)	433 (11.8)	LC
270 (32.3)	275 (29.9)	269 (32.9)	LMCT

Table 3.8: Wavelengths (λ / nm) and molar extinction coefficients (ϵ / $10^3 \text{ M}^{-1} \text{ cm}^{-1}$) of the absorption maxima of receptors **62** and **67** in 4:1 CH_3CN / DMSO.

UV-VIS titrations with receptors **62** and **67** in 4:1 acetonitrile / DMSO resulted in only small changes to the original spectra upon addition of anions, and so titrations were repeated in a less competitive solvent mixture (1:1 dichloromethane / acetonitrile). UV-VIS absorption spectra were recorded for solutions of **62** and **67** upon addition of tetrabutylammonium chloride, benzoate or dihydrogen phosphate, and titrations were repeated for the receptors in the presence of one equivalent of potassium perchlorate. Importantly, the copper(II)-dithiocarbamate receptors showed no time delay effect, and in all cases a constant absorbance value was reached in less than one minute. The resulting spectra were analysed by the computer program Specfit[™],²⁶ yielding the stability constants (log K values) given in Table 3.9. Good agreement between experimental and calculated intensities was obtained using a

1:1 anion / receptor binding model in all cases. As an example, Figure 3.15 shows the results of the titration of **62** with dihydrogen phosphate.

	62	67
chloride	3.12	3.05
+ K ⁺	3.86	3.53
benzoate	3.53	3.46
+ K ⁺	4.13	3.86
dihydrogen phosphate	5.21	4.34
+ K ⁺	4.88	4.17

Table 3.9: Stability constants (log K values) determined from UV-VIS titrations of receptors **62** and **67** with anions (both in the absence and presence of potassium) in 1:1 CH₂Cl₂ / CH₃CN. Specfit™ determined errors < 2 %.

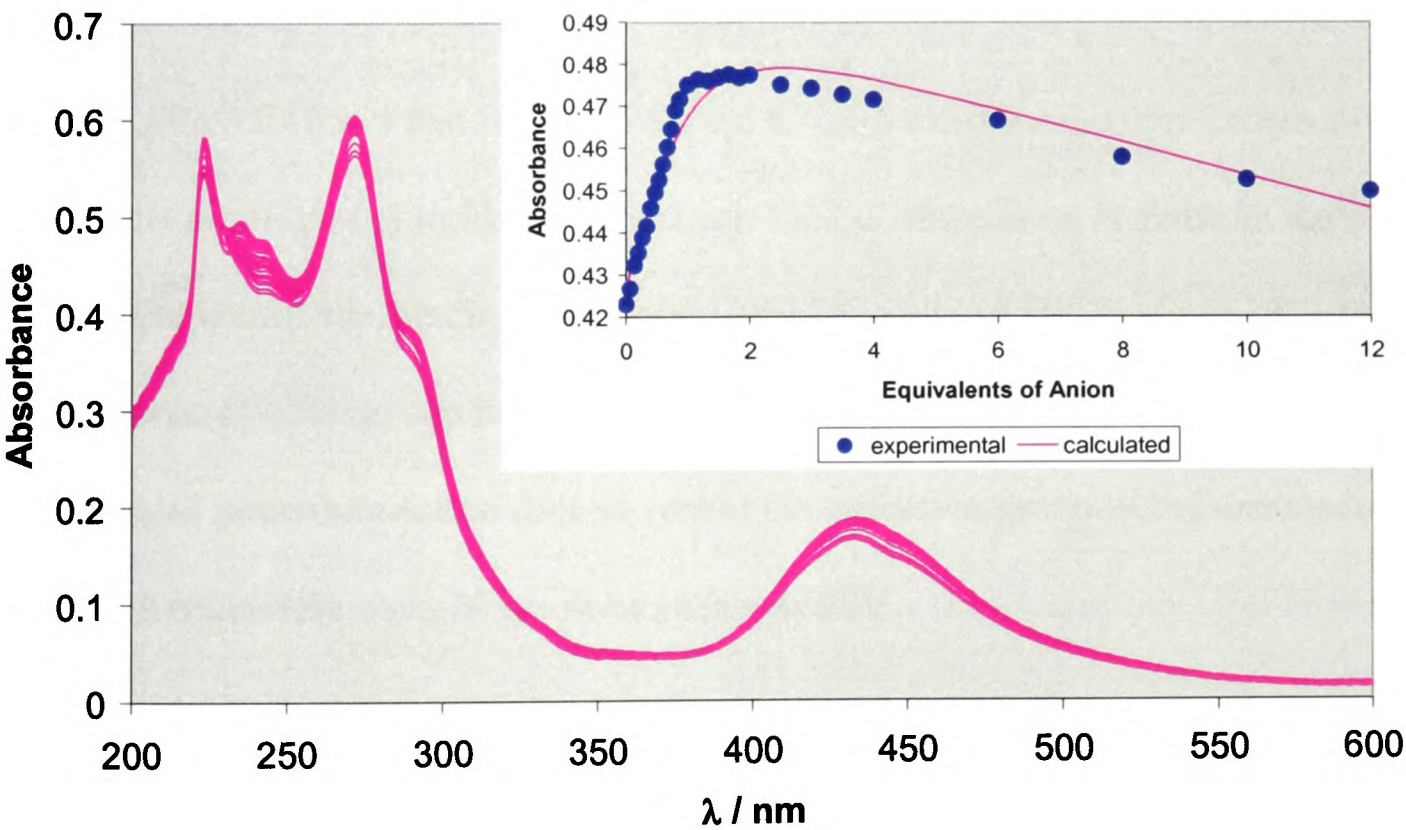


Figure 3.15: UV-VIS titration of receptor **62** with dihydrogen phosphate in 1:1 CH₂Cl₂ / CH₃CN. (Inset) The experimental and calculated change in absorbance at 243 nm.

Consideration of the data in Table 3.9 reveals the following points. Receptors **62** and **67** both bind dihydrogen phosphate most strongly, followed by benzoate then chloride. For all three anions, the stability constants for **62** are greater than those for **67**.

The most remarkable aspect of these results is the binding of anions by receptor **67**. It is surprising that the anion stability constants for **67** are so high, considering that **67** (unlike **62**) contains no amide functionalities capable of hydrogen bonding to anionic guests. In fact, previous studies of copper(II)-dithiocarbamate complexes with no hydrogen bonding sites (such as **3.6** (Figure 3.13) and $\text{Cu}(\text{dtcEt}_2)_2$) have shown no evidence for anion binding by UV-VIS titration experiments. Although macrocycle **3.6** was shown to electrochemically sense the presence of some anions, this was attributed to direct electrostatic interaction between the anion and the oxidised copper(III)-dithiocarbamate species, and no interaction between anions and the neutral complex was observed. Hence, the binding of anions by **67** is unexpected. It is not clear what anion / receptor interactions could account for the observed binding.

Importantly, Table 3.9 shows that receptors **62** and **67** both exhibit a positive cooperative ion-pair effect in the binding of chloride and benzoate. That is, there is an increase in the stability constant magnitudes for the binding of chloride and benzoate in the presence of potassium. This enhancement of binding can be understood by simple electrostatics, as the presence of a positively charged potassium cation (bound within the azacrown group of the receptor) makes the binding of a negatively charged anion more favourable.

However, surprisingly, the presence of potassium results in a decrease in the binding constants for dihydrogen phosphate. This highlights the effects of competing equilibria on the binding processes. This effect could be due to the formation of strong potassium cation / dihydrogen phosphate anion ion-pairs in solution, or precipitation of the KH_2PO_4 salt, competing with the binding of the ion-pair by the receptors.

3.6 Solid / Liquid Extraction Studies

The ability of receptor **58** to extract and solubilise potassium salts into non-polar organic solvents was investigated. In a typical experiment, the receptor was dissolved in CDCl_3 and stirred with excess solid KCl , KOAc or KH_2PO_4 for 24 hours. After filtration, the ^1H NMR spectra were recorded and compared to that of the free receptor. No changes were observed in the ^1H NMR spectra after stirring with KCl or KH_2PO_4 , however in the case of KOAc , the spectrum revealed a signal corresponding to the acetate anion at 1.99 ppm. Integration of this signal indicated that **58** extracts solid KOAc into chloroform solution with 100 % efficiency.

3.7 Summary

A range of new potential ion-pair receptors have been synthesised, containing aza[15]crown-5 or 1,10-bis-aza[18]crown-6 groups for alkali metal cation complexation together with amide functionalities for anion binding. In addition, ferrocene or transition metal dithiocarbamate groups were incorporated into the receptors to enable the electrochemical and/or optical sensing of guest binding. All receptors were characterised by ^1H NMR spectroscopy, mass spectrometry and elemental analysis, and by X-ray crystallography in the cases of **66** and **67**.

The anion and ion-pair binding properties of the receptors were investigated primarily by voltammetric techniques and UV-VIS spectroscopy. The ferrocene- and copper(II)-dithiocarbamate-containing receptors (**50**, **53**, **58**, **62** and **67**) were shown to electrochemically sense the binding of chloride, benzoate and dihydrogen phosphate anions by significant cathodic perturbations of the metallocene or copper(II) / copper(III) redox couples in 1:1 dichloromethane / acetonitrile. Unfortunately, in most cases, the presence of co-bound alkali metal cations had little effect on the magnitudes of the observed anion-induced shifts in the redox waves.

UV-VIS spectroscopic studies indicated a time delay effect for the addition of anions to solutions of nickel(II)-dithiocarbamate receptor **61** in 4:1 acetonitrile / DMSO, however no such effect was observed for the copper(II)-dithiocarbamate receptors. UV-VIS anion titrations were performed with receptors **62** and **67** in 1:1 dichloromethane / acetonitrile, both in the presence and absence of potassium cations. A positive cooperative ion-pair effect was observed in the binding of chloride and benzoate, whereby the presence of potassium cations caused an enhancement in the strength of anion binding, however a negative effect was observed in the binding of dihydrogen phosphate.

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Chapter Four

Self-Assembled Monolayers of Receptors on Gold Surfaces

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Chapter Four: Self-Assembled Monolayers of Receptors on Gold Surfaces

4.1 Introduction

The objective of the research presented in this chapter was the synthesis and investigation of disulphide-appended anion and ion-pair receptors, designed to form self-assembled monolayers (SAMs) on gold electrodes and gold nanoparticles for the electrochemical and/or optical sensing of guest binding.

4.1.1 SAMs on gold

The study of the chemical and physical properties of molecular adlayers on surfaces is an ever expanding field of research due to their potential use in applications such as corrosion prevention,¹ lubrication,¹ electrical conduction,² adhesion³ and catalysis.⁴ The area of most relevance to this thesis is the spontaneous formation of self-assembled monolayers by sulphur-containing compounds on clean gold surfaces.

In the early 1980s, Nuzzo & Allara reported the first sulphur-based SAMs,⁵ and since then a range of sulphur-containing molecules (such as thiols, sulphides, disulphides, thiophenes and xanthates) have been shown to form monolayers on gold.⁶ The most widely studied of these compounds have been organic thiols, in which strong gold-sulphur bonds ($\sim 185 \text{ kJ.mol}^{-1}$) tether the molecules to the surface (Figure 4.1).

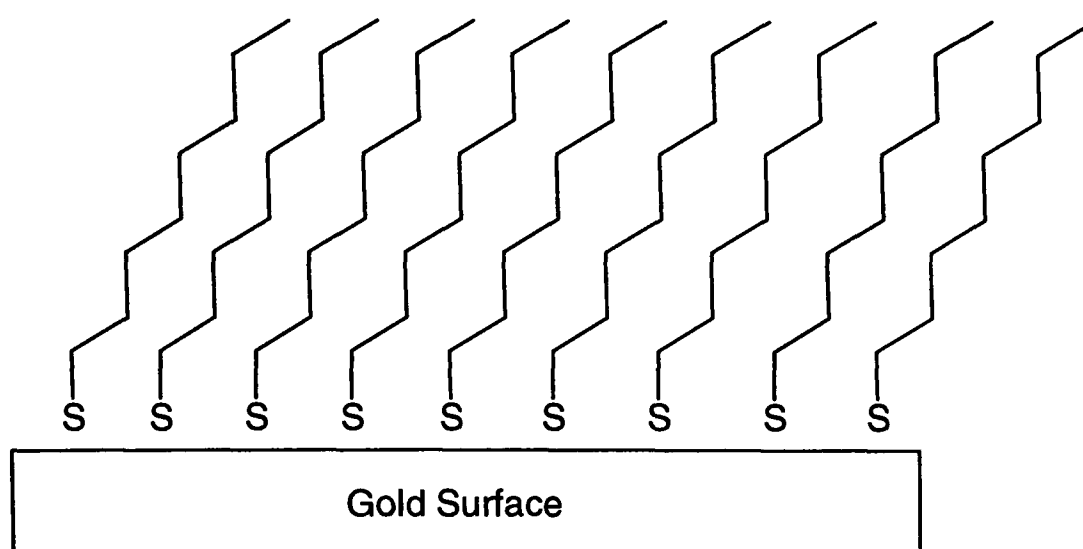


Figure 4.1: An octanethiol SAM on a gold surface.

The self-assembly process is initiated by strong chemical interactions between the sulphur head-groups and the gold surface leading to chemisorption of the molecules. The formation of a crystalline monolayer requires the ordering of the organic tail-groups *via* attractive lateral intermolecular forces which, in the case of alkanethiols, align the molecules in parallel.

The methodology for the formation of SAMs is relatively simple⁷ and the resultant films are densely packed, highly ordered and largely free of defects.⁸ In addition, the use of a wide variety of structurally diverse organosulphur adsorbates offers great versatility in monolayer design.⁹

4.1.2 Electrochemical sensing by SAMs on gold

The literature (and indeed this thesis) provides numerous examples of the exploitation of the redox-active ferrocene moiety in the selective electrochemical sensing of anions in organic and aqueous media. In particular acyclic, macrocyclic and calixarene amide-functionalised ferrocene derivatives have been shown to undergo substantial cathodic perturbations of the respective metallocene redox couple in the presence of a variety of anions of biological and environmental importance.

By functionalising a redox-active anion sensing unit (such as an amide- or urea-functionalised ferrocene derivative) with a sulphur-containing anchoring group, monolayers capable of electrochemically recognising anions can be developed. The spontaneous self-assembly of such compounds onto the surface of gold electrodes may lead to the development of new sensing devices.

Modified electrodes in which the sensor molecules are covalently tethered to the surface have a number of potential advantages. Firstly, the efficiency of the sensor is increased, as only a small amount of the sensor material is required. Secondly, the ease of use is improved because the sensor is more portable and robust than a comparable device in which the sensor unit is in solution. Finally, the highly preorganised nature of the SAM structure can increase the strength of the binding interaction, as demonstrated by the following example.

Beer and co-workers have recently reported the formation of robust SAMs of a disulphide-appended amide-functionalised ferrocene compound (Figure 4.2) which can electrochemically sense anions.¹⁰ Voltammetric studies in 2:1 dichloromethane / acetonitrile revealed reproducible cathodic shifts of the ferrocene redox couple upon addition of anions. For the free receptor, shifts of 40 mV with chloride and 210 mV with dihydrogen phosphate were observed, which increased to 100 mV and 300 mV (respectively) for SAMs of the receptor on gold. Importantly, the anchoring of the sensing unit to the electrode resulted in consistently larger anion-induced cathodic shifts than observed diffusively. This 'surface sensing amplification' highlights the significant advantages associated with preorganisation of the host on a surface.

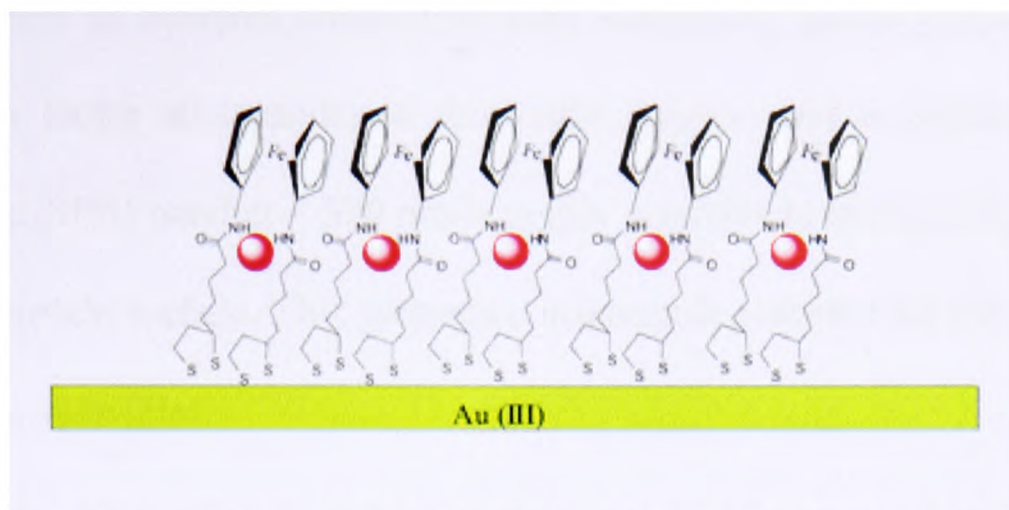


Figure 4.2: Schematic of anion binding within the surface-confined host.

4.1.3 Gold nanoparticles

Recent years have witnessed an explosive growth in studies focussing on the adsorption of molecular species onto colloidal particles of gold, silver, copper and platinum. These functionalised nanoparticles have found use in a wide range of technologies including the manufacture of microelectronics,¹¹ colloid-modified electrodes,¹² coloured labelling agents for electron and visible microscopy¹³ and quantum-confinement materials.¹⁴

The seminal work by Brust and co-workers on the two-phase synthesis of alkanethiol-protected gold nanoparticles¹⁵ has further advanced this area of research. Functionalised nanoparticles generated in this manner are typically 1 – 5 nm in diameter, and exist as dark brown-black solids that are easy to isolate, stable in air and soluble in a wide range of organic solvents. These features permit facile manipulation and characterisation using a variety of techniques such as TEM, XPS, and UV-VIS, NMR, Raman and FTIR spectroscopy.

Gold and silver nanoparticles have been of increasing interest in applications to biological and chemical nanosensors. In recent years, optical¹⁶ and electrochemical¹⁷ nanoprobe have been developed by modifying the surface of metal nanoparticles with various functional molecules. Gold nanoprobe capable of optically sensing biological macromolecules such as polynucleotides have been extensively studied,¹⁸ however there are few nanoparticle-type optical probes for smaller ions and molecules. The ability of functionalised gold nanoparticles

to detect the presence of analytes arises from their interesting optical properties. They have tremendously high molar absorptivity in the visible region, and in particular, the surface plasmon resonance (SPR) band at ~ 520 nm is highly sensitive to changes in the environment close to the nanoparticle surface. This presents considerable potential for the optical detection of various ions and molecules.

For example, the amide-functionalised gold nanoparticles shown in Figure 4.3 were synthesised by ligand exchange of hexanethiol-protected gold nanoparticles with an amide-containing thiol.¹⁹ Addition of anions to solutions of the derivatised nanoparticles in dichloromethane resulted in dramatic changes in the SPR band in the respective UV-VIS spectra.

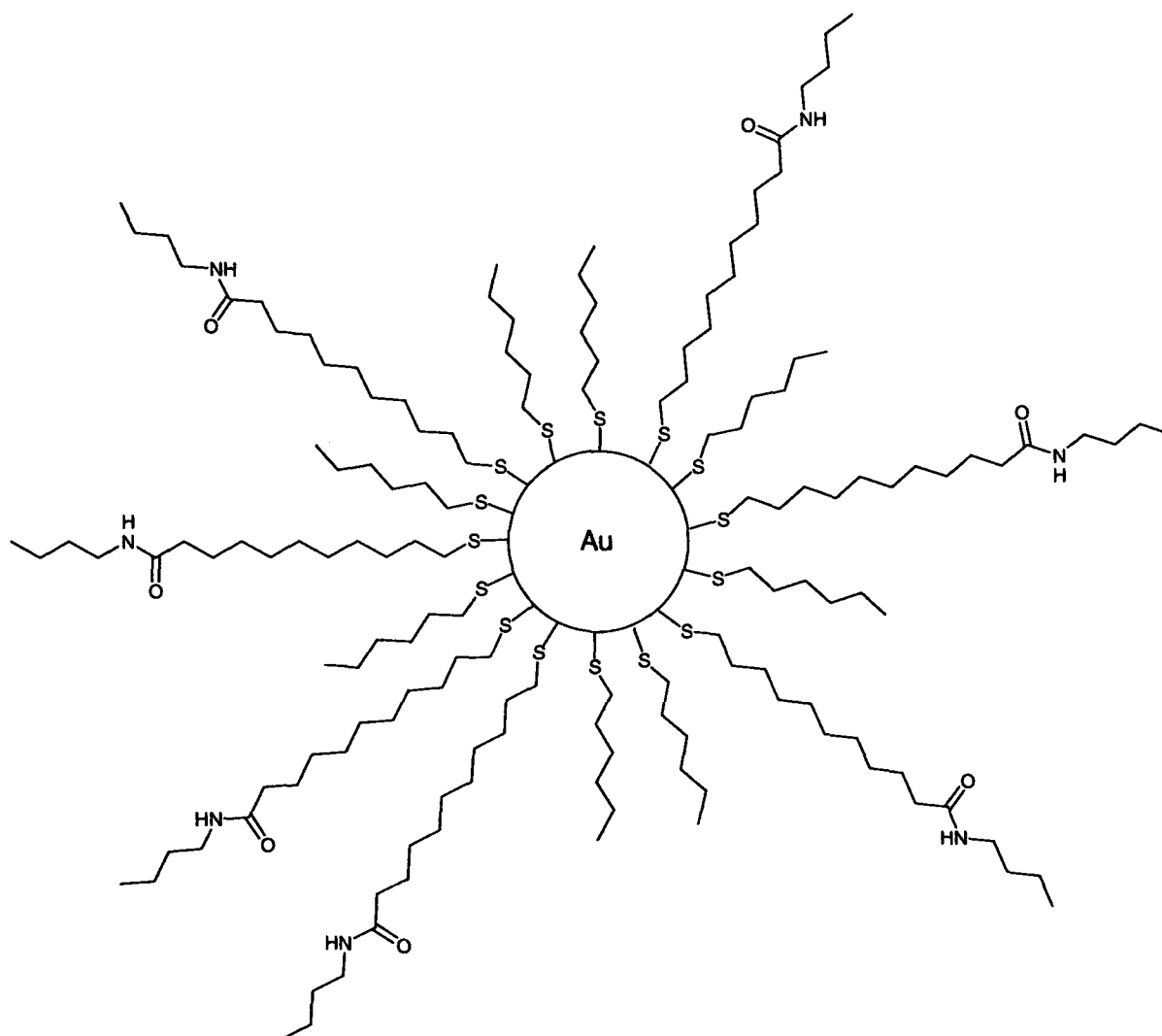


Figure 4.3: An amide-functionalised gold nanoparticle capable of optically detecting anions.

By adapting the synthetic methodology described in Section 2.2 of Chapter Two, the following section (Section 4.2) reports the synthesis and characterisation of novel upper-rim

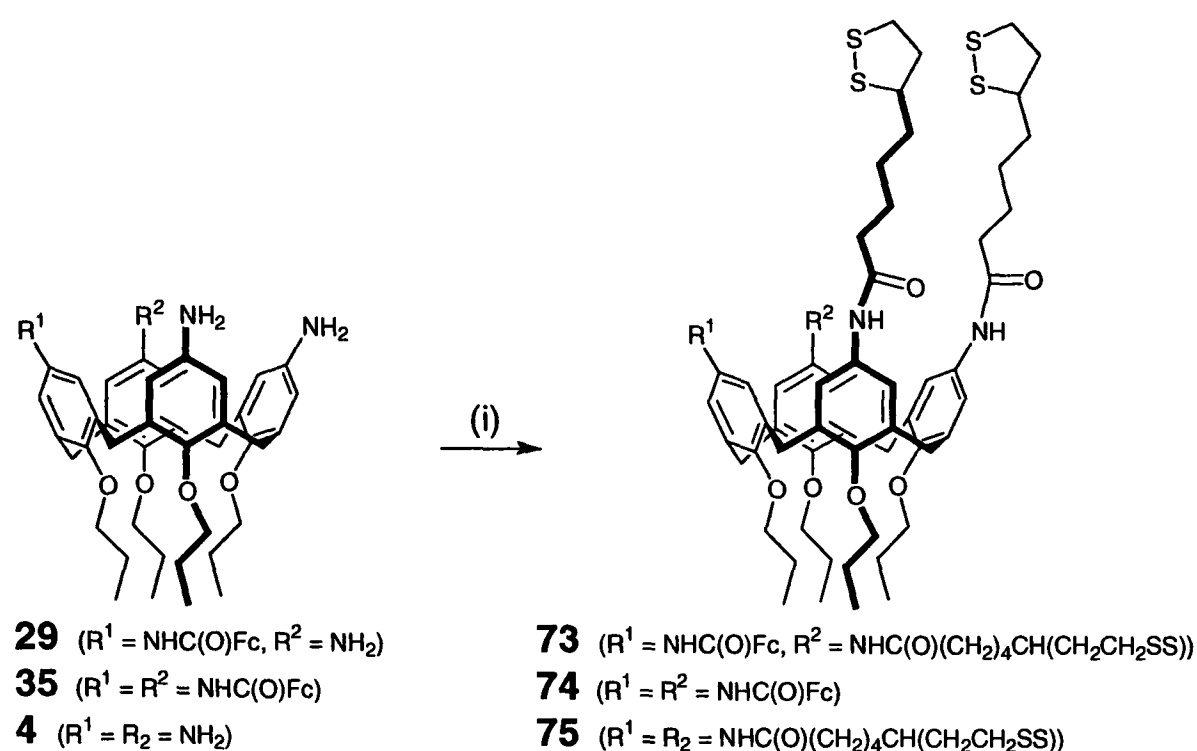
functionalised calix[4]arene anion receptors incorporating amide and/or urea functionalities for anion binding, disulphide groups for self-assembly onto gold electrodes, and ferrocene moieties for electrochemical sensing of guest binding. The anion binding properties of these receptors are studied initially by ^1H NMR spectroscopy (Section 4.3). The electrochemical anion sensing abilities of the ferrocene- and disulphide-appended calix[4]arene anion receptors are investigated, both diffusively (Section 4.4) and as SAMs on gold electrodes (Section 4.5).

Furthermore, the synthesis and characterisation of disulphide-appended ion-pair receptors containing 1,10-bis-aza[18]crown-6 or benzo[15]crown-5 groups for the complexation of alkali metal cations together with amide functionalities for anion binding is also reported (Section 4.6). The ion-pair binding properties of these receptors are investigated by ^1H NMR spectroscopy (Section 4.7), and attempts to self-assemble these receptors onto gold nanoparticles for the spectroscopic detection of anions are described (Section 4.8).

4.2 Synthesis and Characterisation of Disulphide-Appended Calix[4]arene Anion Receptors

This section outlines the synthesis and characterisation of ferrocene- and disulphide-appended calix[4]arene anion receptors, designed to form self-assembled monolayers on gold electrodes for the electrochemical sensing of anionic guests.

Condensation reactions of upper-rim amino-derivatised calix[4]arene compounds **29**, **35** and **4** (see Section 2.2 of Chapter Two) with thioctic acid afforded three new disulphide-appended calix[4]arene anion receptors (Scheme 4.1).

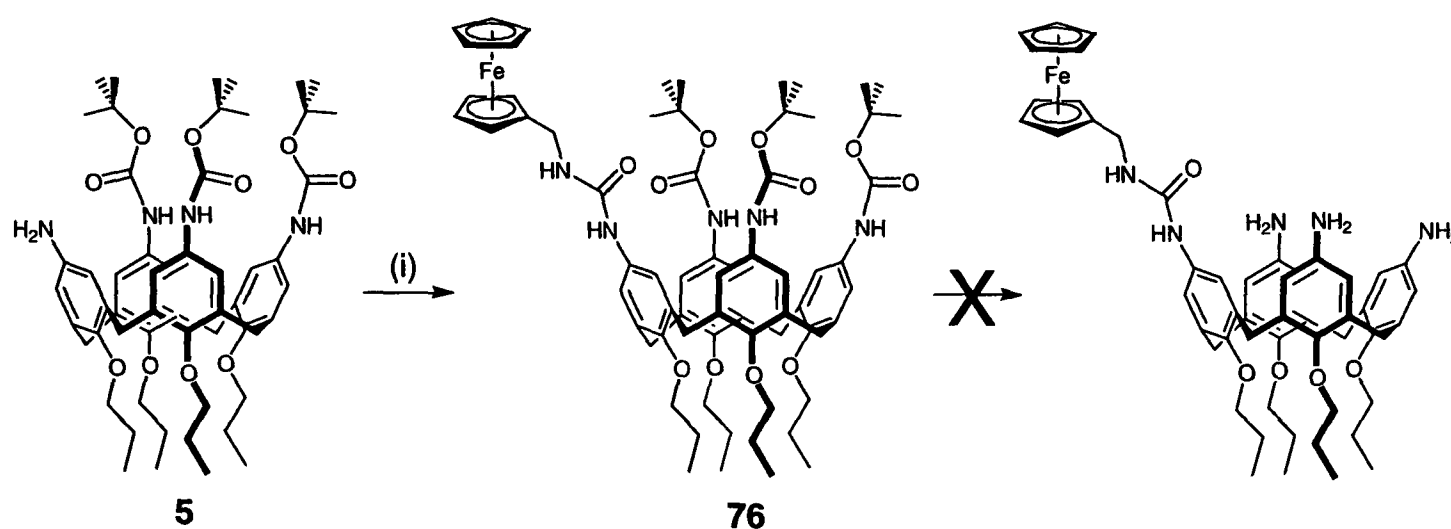


Scheme 4.1: (i) thioctic acid, EDC, CH_2Cl_2 ; **73** 47 %, **74** 53 %, **75** 36 %.

Mono-ferrocene tri-amino calix[4]arene **29** was reacted with an excess of both thioctic acid and the carbodiimide coupling agent (1-(3-(dimethylamino)propyl)-3-ethyl-carbodiimide hydrochloride or EDC) in dichloromethane. Purification by column chromatography (silica, 1:1 chloroform / ethylacetate) followed by precipitation from chloroform / hexane gave receptor **73** as a pale orange solid in 47 % yield. Similarly, reaction of bis-ferrocene bis-amino calix[4]arene **35** with thioctic acid afforded receptor **74** as an orange solid in 53 % yield, and reaction of tetra-amino calix[4]arene **4** with thioctic acid produced receptor **75** as a cream solid in 36 % yield.

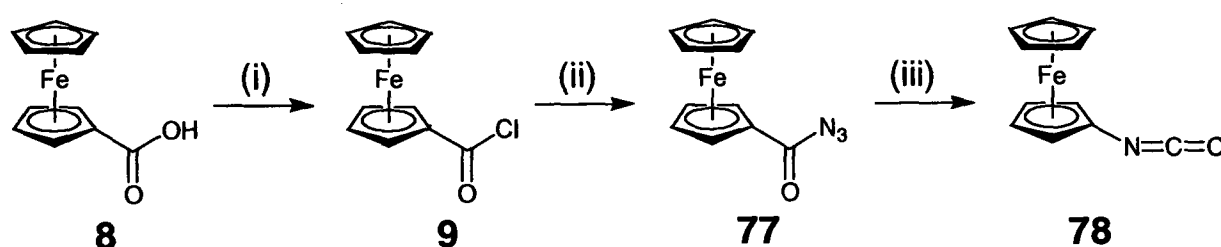
The synthesis of an analogous ferrocene-urea-appended receptor was attempted according to the methodology outlined previously (in Section 2.2.6 of Chapter Two), Scheme 4.2. Tri-BOC-protected calix[4]arene precursor **5** was reacted with one and a half equivalents of the protected isocyanate synthon **18** in the presence of ethyldiisopropylamine base and a catalytic amount of DMAP in dichloromethane. Column chromatography (silica, 1:1 ethylacetate / hexane) followed by precipitation from chloroform / hexane gave **76** as a pale yellow solid in 46 % yield. However, the attempted deprotection of **76** with trifluoroacetic acid in

dichloromethane resulted in the oxidative cleavage of the ferrocene group, rather than the desired product. Consequently, a different approach to a ferrocene-urea-functionalised receptor was attempted.



Scheme 4.2: (i) ferrocene mononitrophenolate **18**, $\text{Et}(\text{iPr})_2\text{N}$, DMAP, CH_2Cl_2 , 46 %.

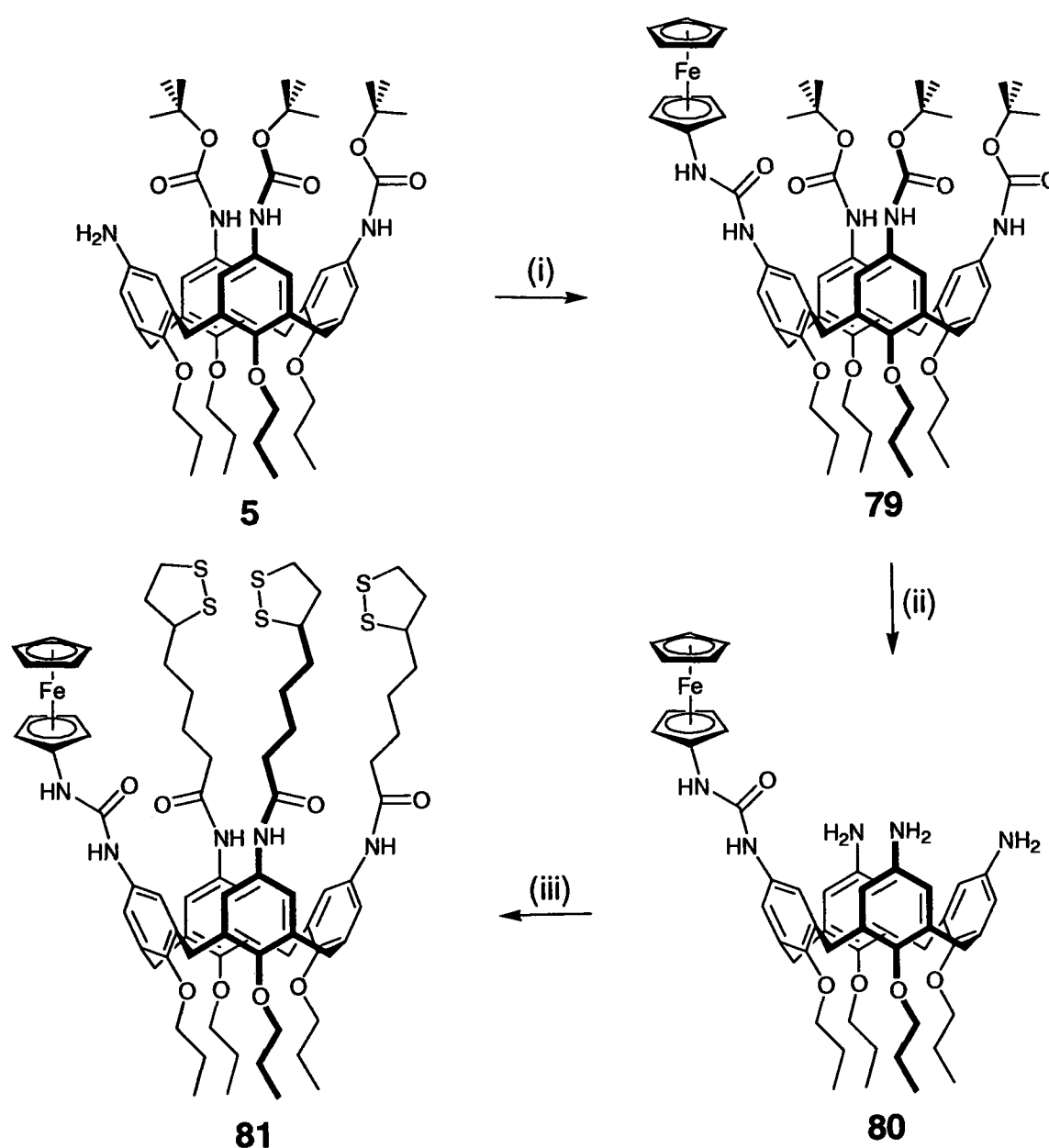
The ferrocene isocyanate synthon **78** was synthesised according to a modified literature method, Scheme 4.3.²⁰ Ferrocene carboxylic acid **8** was reacted with oxalyl chloride to give the acid chloride **9** which was reacted with sodium azide in acetone to produce the acyl azide **77** in 93 % yield. Heating **77** in toluene caused the rearrangement of the acyl azide (with the evolution of nitrogen) and extraction into hexane afforded orange crystals of isocyanatoferrocene **78** in 33 % yield.



Scheme 4.3: (i) oxalyl chloride, pyridine, CH_2Cl_2 , reflux;
(ii) $\text{NaN}_3(\text{aq})$, acetone, 93 %; (iii) toluene, 110 °C, 33 %.

The synthesis of ferrocene-urea- and disulphide-appended receptor **81** is outlined in Scheme 4.4. Tri-BOC-protected calix[4]arene precursor **5** was reacted with one and a half equivalents of isocyanatoferrocene **78** in chloroform. Purification by column chromatography (silica,

10 % ethylacetate in chloroform) followed by precipitation from dichloromethane / hexane gave **79** as a pale yellow powder in 60 % yield. Deprotection with trifluoroacetic acid in dichloromethane followed by washing with aqueous sodium hydroxide produced **80** in 76 % yield. This was reacted with four equivalents of both thioctic acid and EDC in dichloromethane. Column chromatography (silica, 1:1 chloroform / ethylacetate) followed by precipitation from chloroform / hexane afforded receptor **81** as a pale orange solid in 43 % yield. Figure 4.4 shows an assigned ^1H NMR spectrum for **81** in d_6 -DMSO. The assignments were confirmed by ^1H - ^1H correlation (COSY) NMR spectroscopy.



Scheme 4.4: (i) isocyanatoferrrocene **78**, CHCl_3 , 60 %; (ii) TFA, CH_2Cl_2 , 76 %; (iii) thioctic acid, EDC, CH_2Cl_2 , 43 %.

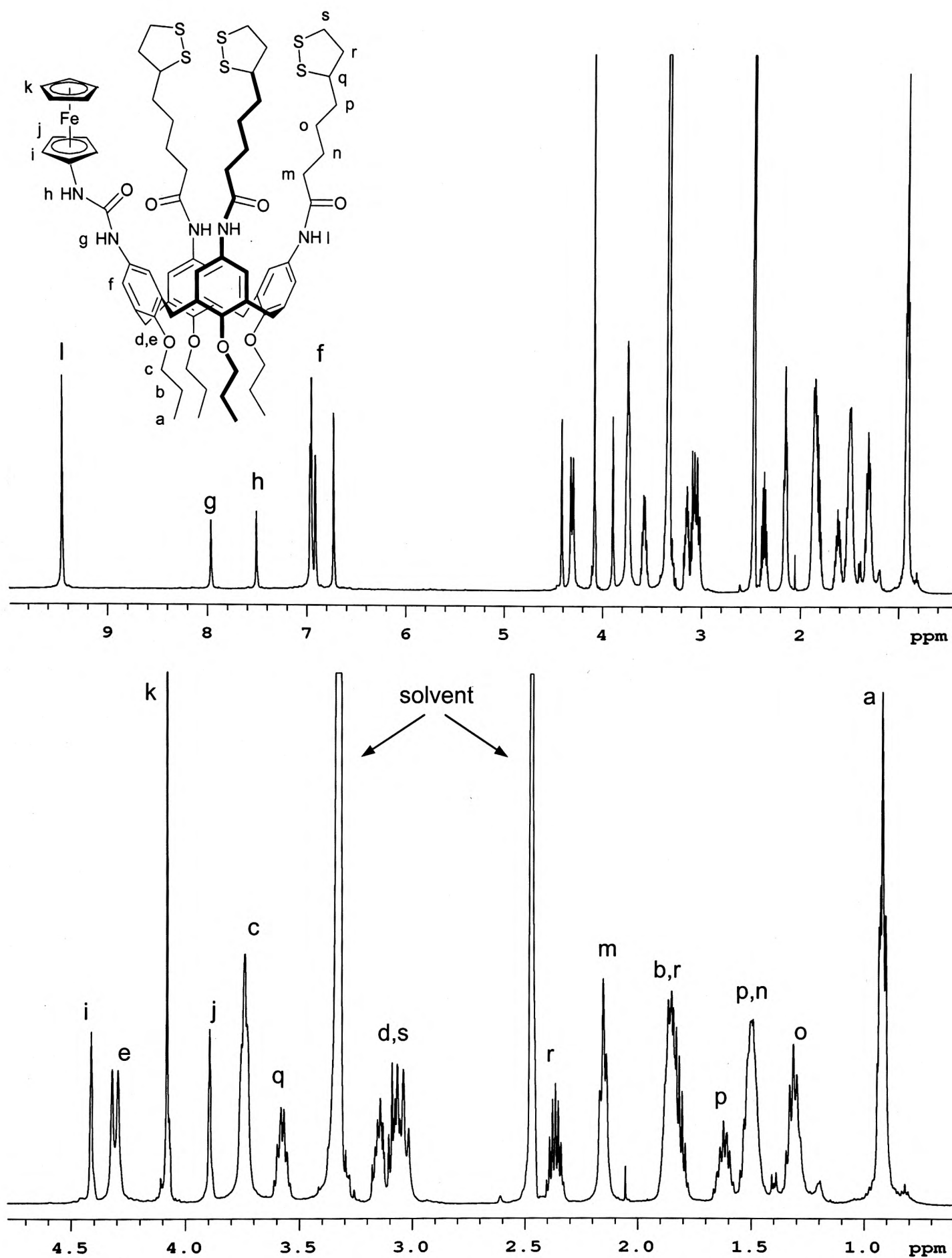


Figure 4.4: ^1H NMR spectrum (500 MHz) of receptor **81** in d_6 -DMSO, showing the full spectrum and an expansion between 0 and 5 ppm.

In summary, four new upper-rim functionalised ferrocene- and disulphide-appended calix[4]arene anion receptors (**73**, **74**, **75** and **81**) were synthesised by condensing various

amine-derivatised calix[4]arene compounds with thioctic acid. All new species were characterised by ^1H NMR spectroscopy, mass spectrometry and elemental analysis.

4.3 ^1H NMR Anion Binding Studies

The anion binding properties of the four upper-rim functionalised ferrocene- and disulphide-appended calix[4]arene receptors were investigated initially by ^1H NMR spectroscopy. ^1H NMR titrations were carried out with receptors **75**, **73**, **81** and **74** with chloride, benzoate and dihydrogen phosphate anions (added as their tetrabutylammonium salts) in 1:1 CD_3CN / d_6 -DMSO. In all cases, addition of anions resulted in significant downfield perturbations of the amide or urea signals, indicating that the anions are bound by the hydrogen bonding moieties of the receptors. Additional evidence for the binding of anions in the vicinity of the upper-rim was provided by the downfield shifts of the signals for the aromatic protons *ortho* to the point of substitution. EQNMR²¹ analysis of the titration data indicated 1:1 anion / receptor binding stoichiometries and gave the stability constant values shown in Table 4.1.

	75	73 ^a	81 ^a	74 ^a
chloride	< 5	10	10	10
benzoate	50	55	55	65
dihydrogen phosphate	155	95	85	70

Table 4.1: Anion stability constants (K / M^{-1}) determined in 1:1 CD_3CN / d_6 -DMSO (errors $\leq 10\%$). ^a The two or three different amide and/or urea peaks of these receptors gave the same stability constants (within error).

All four receptors show similar stability constant magnitudes for each anion, not surprising given that they all have four hydrogen bond donor groups arranged around the calix[4]arene upper-rim. The receptors display a preference for binding dihydrogen phosphate over benzoate; chloride is bound only weakly in this solvent system. Interestingly, the data seem to

show a trend whereby the strength of benzoate binding increases and the strength of dihydrogen phosphate binding decreases as the alkyl chain amides are replaced by ferrocenoyl-amide groups.

4.4 Electrochemical Anion Sensing – Diffusive Studies

4.4.1 Electrochemical data

The electrochemical properties of the ferrocene- and disulphide-appended calix[4]arene anion receptors **81**, **73** and **74** were investigated initially by CV (see Appendix B). Electrochemical studies of the receptors (5×10^{-4} M in electrolyte solution) were conducted in 0.1 M tetrabutylammonium tetrafluoroborate in 1:1 dichloromethane / acetonitrile and the relevant data are given in Table 4.2.

	81	73	74
E_{pa}	-129	218	211
E_{pc}	-200	138	134
ΔE^a	71	80	77
$E_{1/2}^b$	-165	178	173
I_{pa} / I_{pc}	1.05	1.15	1.20

Table 4.2: Electrochemical data for the free receptors. CVs were recorded under the following conditions: 5×10^{-4} M solutions of receptor in 0.1 M Bu₄NBF₄ in 1:1 CH₂Cl₂ / CH₃CN, scan rate 100 mV.s⁻¹, glassy carbon working electrode, Ag / AgNO₃ reference electrode. Electrochemical potentials are ± 5 mV and are quoted relative to ferrocene. ^a $\Delta E = E_{pa} - E_{pc}$ ^b $E_{1/2} = (E_{pa} + E_{pc}) / 2$

The $E_{1/2}$ values of receptors **73** and **74** both occur about 175 mV positive of ferrocene, due to the electron withdrawing nature of the carbonyl group attached directly to the cyclopentadienyl ring. The $E_{1/2}$ value of receptor **81** occurs 165 mV negative of ferrocene, due to the electron donating nature of the NH group. The more negative potential of the couple in

the ferrocene-urea-appended receptor **81** could well be a significant factor in the superior redox behaviour of this receptor in both diffusive and SAM electrochemical anion sensing experiments (see Sections 4.4.2 and 4.5.2).

The electrochemical response of the receptors at different scan rates was investigated. For all three receptors, the plot of current against the square root of scan rate is linear (R^2 values greater than 0.998). Figures 4.5 and 4.6 show the results for **81**. Once again, these receptors may be described as quasi-reversible systems (see Section 2.4.1 of Chapter Two).

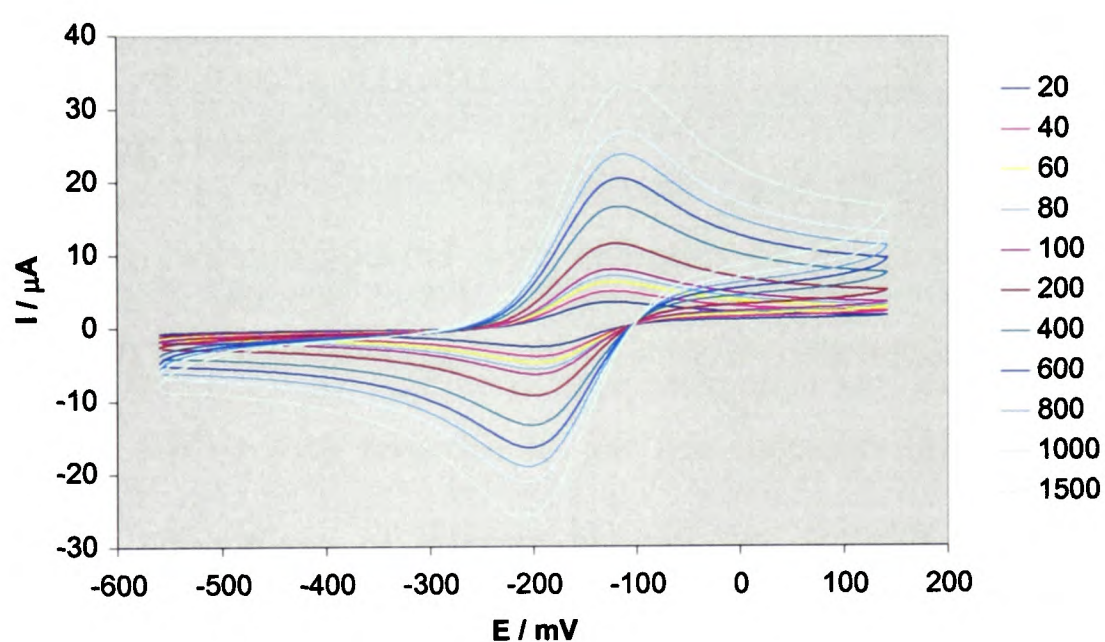


Figure 4.5: CVs of receptor **81** recorded at various scan rates. CVs were recorded under the following conditions: 5×10^{-4} M solutions of receptor in 0.1 M Bu_4NBF_4 in 1:1 CH_2Cl_2 / CH_3CN , glassy carbon working electrode, Ag / AgNO_3 reference electrode.

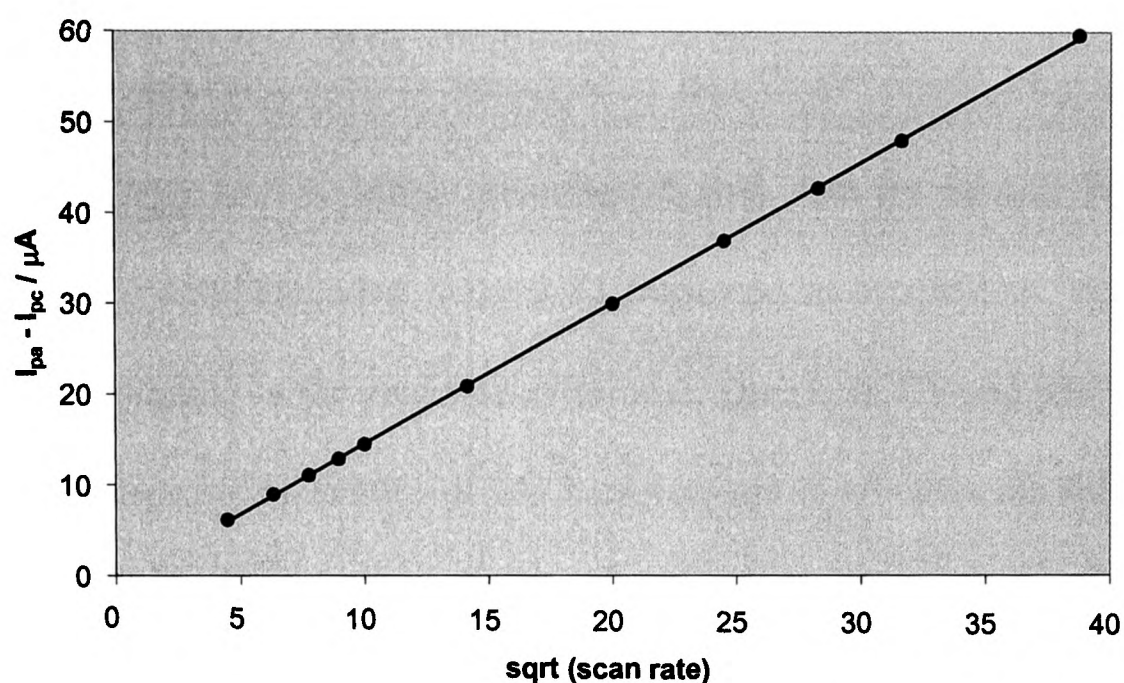


Figure 4.6: Plot of current against the square root of scan rate for receptor **81**.

4.4.2 Anion sensing studies

Anion sensing studies were conducted with solutions of the receptors (5×10^{-4} M in electrolyte solution) in 0.1 M tetrabutylammonium tetrafluoroborate in 1:1 dichloromethane / acetonitrile. CVs and SWVs were recorded for the free receptors (**81**, **73** and **74**) and upon addition of 0 – 20 equivalents of tetrabutylammonium chloride, benzoate, dihydrogen phosphate or perrhenate.

As noted previously (in Section 2.4.2 of Chapter Two), addition of anions typically results in significant cathodic shifts in the redox potentials of the receptors, attributable to the complexation of an anionic guest by the amide protons in close proximity to the ferrocene redox centres, thereby facilitating their oxidation to ferrocenium.

Furthermore, CVs reveal that upon addition of anions to receptors **73** and **74**, the reduction peak disappears entirely after the addition of between 2 and 10 equivalents of anion, thereby preventing the determination of $E_{1/2}$ values. This tendency toward increasing irreversibility in the presence of anions has been described previously for analogous ferrocene-amide-appended calix[4]arene receptors (in Section 2.4.2 of Chapter Two). The disappearance of the

reduction wave on anion addition indicates that a bound anion / ferrocenium cation ion-pair may be disfavoured reduction back to ferrocene or that an EC mechanism is in operation. Consequently, SWV was used to obtain quantitative shift data for **73** and **74**. Addition of anions to the ferrocene-urea-appended receptor **81** causes no such problems (although ΔE and I_{pa} / I_{pc} both increase slightly in the presence of anions). Thus both CV and SWV were used to investigate the anion sensing properties of this receptor, and in all cases the shifts determined by CV and SWV were identical.

The magnitudes of the cathodic shifts in the redox potentials of the receptors upon addition of 10 equivalents of anion are given in Table 4.3. CVs recorded before and after the addition of 10 equivalents of anions to receptor **81** are shown in Figures 4.7 – 4.9, together with ΔE and I_{pa} / I_{pc} values for the shifted waves.

	81 ^{a b}	73 ^b	74 ^b
chloride	60	50	70
benzoate	150	165	115
dihydrogen phosphate	200	240	260
perrhenate	< 5	< 5	< 5

Table 4.3: Cathodic shifts in the $E_{1/2}$ values of the receptors upon addition of 10 equivalents of anions (errors ± 10 mV). Voltammograms were recorded under the following conditions: 5×10^{-4} M solutions of receptor in 0.1 M Bu_4NBF_4 in 1:1 $\text{CH}_2\text{Cl}_2 / \text{CH}_3\text{CN}$, glassy carbon working electrode, Ag / AgNO_3 reference electrode.

^a CVs: scan rate 100 mV.s^{-1} . ^b SWVs: frequency 25 Hz, scan increment 2 mV.

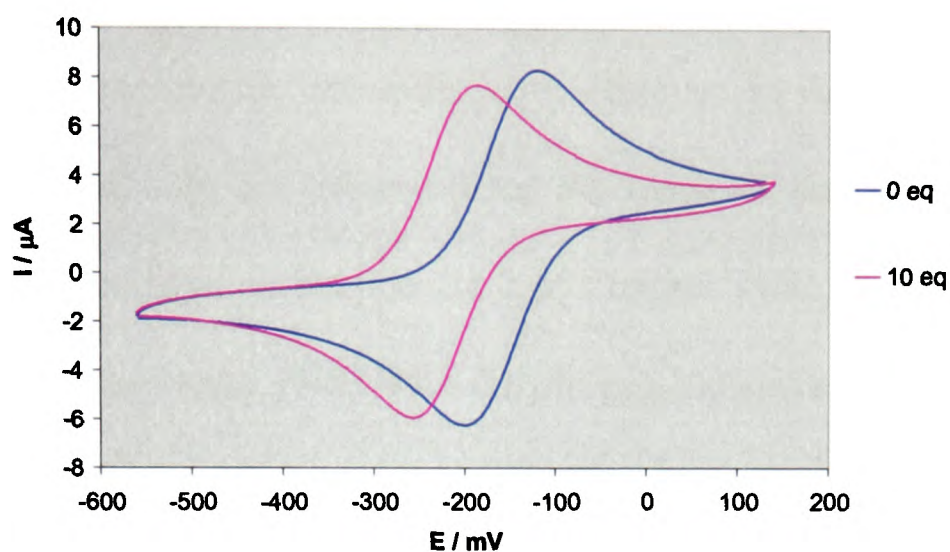


Figure 4.7: CVs of receptor **81** before and after the addition of 10 equivalents of tetrabutylammonium chloride ($\Delta E = 72$ mV and $I_{pa} / I_{pc} = 1.05$).

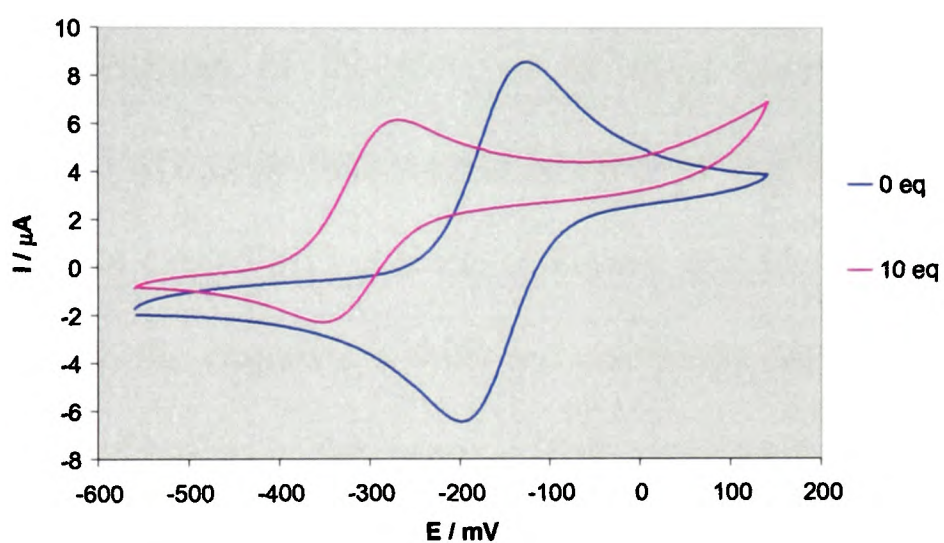


Figure 4.8: CVs of receptor **81** before and after the addition of 10 equivalents of tetrabutylammonium benzoate ($\Delta E = 84$ mV and $I_{pa} / I_{pc} = 1.30$).

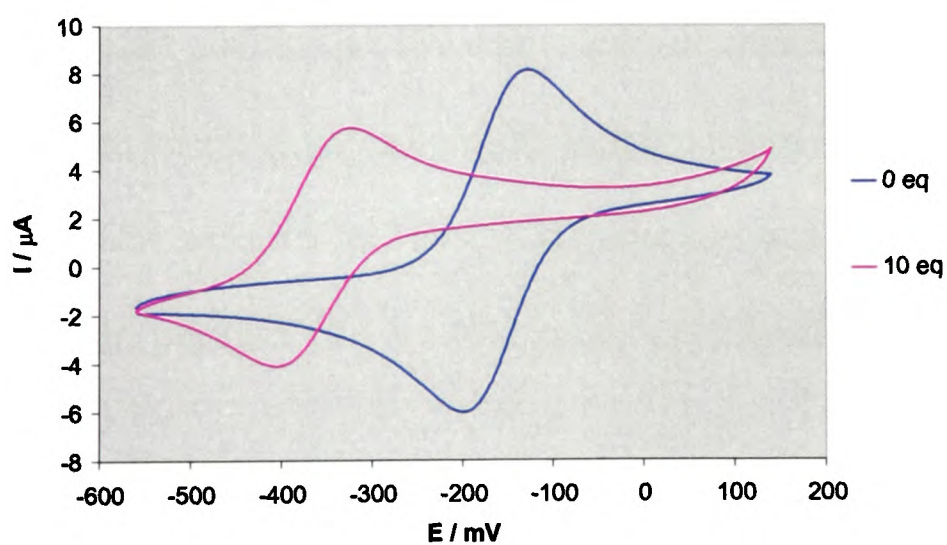


Figure 4.9: CVs of receptor **81** before and after the addition of 10 equivalents of tetrabutylammonium dihydrogen phosphate ($\Delta E = 84$ mV and $I_{pa} / I_{pc} = 1.30$).

For all three receptors, the largest shift magnitudes are observed for dihydrogen phosphate followed by benzoate then chloride; no shifts were observed in the presence of perrhenate anions. This general trend was also observed for the range of similar ferrocene-appended calix[4]arene receptors described in Section 2.4.2 of Chapter Two. The two ferrocene-amide receptors **73** and **74** display larger shifts with dihydrogen phosphate than the ferrocene-urea receptor **81**.

Anion competition experiments were conducted with receptor **81** under the same conditions described above. CVs were recorded for the free receptor and upon consecutive additions of 10 equivalents of tetrabutylammonium perrhenate, chloride, benzoate and dihydrogen phosphate. The redox potential of the receptor remained unchanged after addition of perrhenate then shifted 65 mV cathodically upon addition of chloride. Addition of benzoate then dihydrogen phosphate caused further shifts of 80 mV and 45 mV in the position of the redox couple. Importantly, the cumulative shifts are essentially those given in Table 4.3 for the independent addition of anions to the receptor. This experiment demonstrates that **81** can selectively sense dihydrogen phosphate in the presence of equimolar amounts of perrhenate, chloride and benzoate.

Another anion competition experiment was carried out with receptor **81**. CVs were recorded for the free receptor and after addition of 100 equivalents of chloride then 10 equivalents of dihydrogen phosphate. The resulting cathodic shifts in the position of the redox couple were essentially the same as those reported in Table 4.3, indicating that **81** can selectively sense dihydrogen phosphate in the presence of a ten-fold excess of chloride.

Importantly, the shifts quoted in Table 4.3 represent maximum shift values. Addition of another 10 equivalents of the anions results in minimal perturbations (of less than 5 mV) in

the position of the redox couples. This is particularly relevant for comparing the diffusive and SAM electrochemical anion sensing studies (see Section 4.5).

4.5 Electrochemical Anion Sensing – SAMs on Gold Electrodes

The upper-rim functionalised ferrocene- and disulphide-appended calix[4]arene anion receptors were designed to form SAMs on gold electrodes for the electrochemical recognition of anions. This section describes the formation and characterisation of monolayers of receptors **81**, **73** and **74** on gold electrodes, and discusses the electrochemical anion sensing properties of these monolayers in organic and aqueous solutions.

4.5.1 Formation and characterisation of SAMs of receptors on gold electrodes

4.5.1.1 Formation of SAMs

The successful formation of good monolayers requires ultra-clean gold surfaces. The gold electrodes were prepared according to the protocol detailed in Appendix E. The electrodes were immersed in aqua regia for five minutes, mechanically polished for one hour on a polishing wheel using an alumina slurry and then electropolished for 100 scans in 1M sulphuric acid. The clean electrodes were rinsed with water and alcohol, dried under argon and immersed in solutions of the receptor (1 – 3 mM in dichloromethane) overnight. After formation of the monolayers, the modified electrodes were washed with dichloromethane and alcohol and dried under argon.

4.5.1.2 Electrochemical characterisation of SAMs

The electrochemical properties of SAMs of receptors **81**, **73** and **74** on gold electrodes were investigated by CV (see Appendix E) in 0.1 M tetrabutylammonium tetrafluoroborate in 1:1 dichloromethane / acetonitrile; the relevant data are given in Table 4.4.

	81	73	74
E_{pa}	-149	197	198
E_{pc}	-175	153	146
ΔE^a	26	44	52
$E_{1/2}^b$	-162	175	172
I_{pa} / I_{pc}	1.00	1.05	1.10

Table 4.4: Electrochemical data for SAMs of the receptors on gold electrodes. CVs were recorded under the following conditions: 0.1 M Bu_4NBF_4 in 1:1 CH_2Cl_2 / CH_3CN , scan rate 100 mV.s^{-1} , Ag / $AgNO_3$ reference electrode. Electrochemical potentials are $\pm 5 \text{ mV}$ and are quoted relative to ferrocene. ^a $\Delta E = E_{pa} - E_{pc}$ ^b $E_{1/2} = (E_{pa} + E_{pc}) / 2$

Comparison of the electrochemical data obtained for the free (Table 4.2) and surface confined (Table 4.4) receptors reveals two important points. Firstly, the $E_{1/2}$ values for monolayers of the receptors are the same (within error) as those obtained by diffusive studies. Secondly, the peak separation (ΔE) is typically much smaller for monolayers of the receptors. Ideally there should be no peak separation ($\Delta E = 0$) for an adsorbed species.²² However, the SAMs investigated here all showed some peak separation, due to (i) non-ideality of the electrode surface and/or receptor, (ii) imperfections in the monolayer or (iii) slow electron transfer kinetics. It should also be noted that the peak separation varied significantly from one experiment to the next, and the ΔE values reported in Table 4.4 are the smallest that were observed. For example, for monolayers of receptor **81**, ΔE varied from 26 to 88 mV. This could be an indication of the quality of a given monolayer, or in other words a measure of the degree of imperfection in the monolayer structure.

Figure 4.10 shows CVs recorded for SAMs of receptors **81** and **73**. These CVs reveal features typical of the electrochemistry of redox-active monolayers, namely small peak separations, small faradaic currents and reduced capacitance compared to diffusive voltammetry.

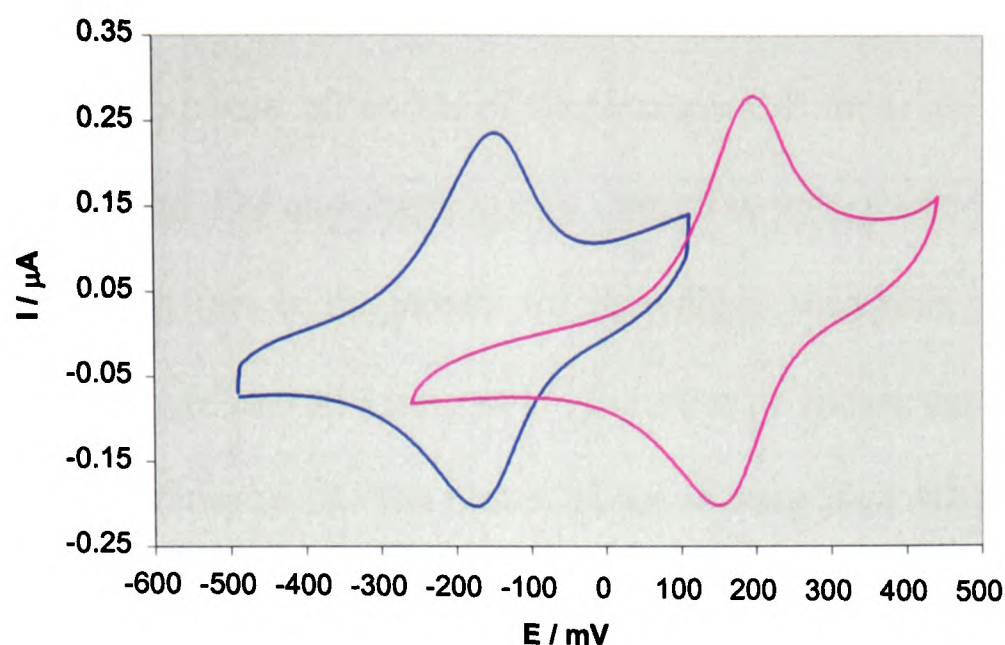


Figure 4.10: CVs of SAMs of receptors **81** and **73** on gold electrodes.

4.5.1.3 Stability

The stability of SAMs of the receptors on gold was probed by cycling the potential over a range ± 300 mV of the half wave potential, typically for 500 scans. The response to repeated cycling was variable. In some cases, this led to a large decrease in the faradaic currents and an increase in the peak separation (ΔE), and these monolayers were deemed to be of poor quality and were discarded. In other cases though, the monolayers were stable to such cycling (only small decreases in the faradaic currents were observed), and these were deemed to be of sufficiently good quality for further investigation.

The decrease in peak heights over time may be attributed to the slow decomposition of the ferrocene group in the receptors, as the oxidised forms of ferrocene-containing compounds can be unstable. It is well known that some ferrocenium species decompose in the presence of nucleophilic reagents such as anions.²³

Monolayers of the ferrocene-urea receptor **81** were more stable over time than monolayers of the ferrocene-amide receptors **73** and **74**. This may be related to the more negative redox potential of **81** compared to **73** and **74**.

4.5.1.4 Reversibility

The electrochemical response of SAMs of the receptors at different scan rates (20 – 1500 mV.s^{-1}) was investigated. For adsorbed species, current is proportional to scan rate and a plot of current against scan rate is diagnostic for monolayer formation (diffusively, current is proportional to the square root of scan rate).²² Figure 4.11 shows the plot of current against scan rate for SAMs of receptor **81**. The plot is linear, as were plots obtained for monolayers of **73** and **74** (R^2 values were greater than 0.999 in all cases).

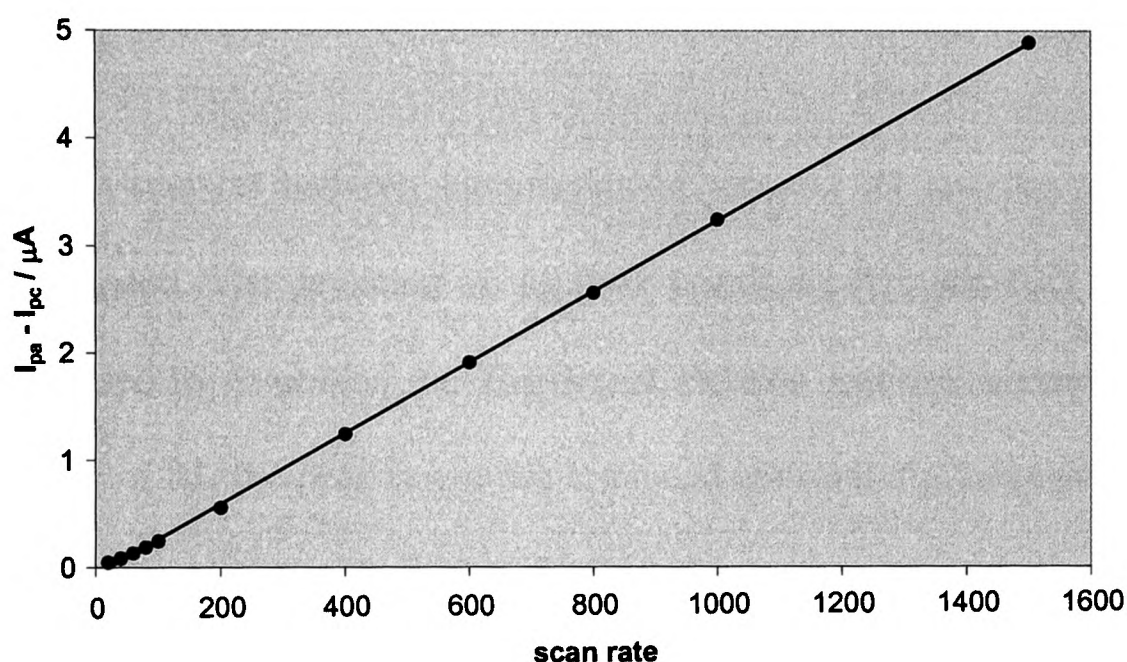


Figure 4.11: Plot of current against scan rate for SAMs of receptor **81**.

4.5.1.5 Coverage

The number of molecules of receptor bound to the gold surface of an electrode can be calculated from the area under the oxidation wave. The anodic peak area divided by the scan rate gives the charge transferred during the oxidation of the monolayer. As the number of electrons involved in the oxidation of each molecule of receptor is known (one for **81** and **73**, two for **74**), the total number of molecules in the monolayer may be calculated by dividing the charge transferred by the number of electrons (one or two) and the charge on the electron (1.602×10^{-19} C). In addition, as the surface area of the electrodes are known (1.6 mm diameter gold discs, 0.0201 cm^2), the coverage (molecules.cm^{-2}) can be determined.

For example, the anodic peak areas measured from CVs of monolayers of receptor **81** were typically 2.5×10^{-7} C which corresponds to 1.6×10^{12} molecules or 7.8×10^{13} molecules.cm⁻² (1.3×10^{-10} mol.cm⁻²). Based on the crystal structure data reported in Section 2.2.4 of Chapter Two for similar receptors, the ‘molecular footprint’ of **81** is estimated to be about 1×10^{-14} cm². These values are consistent with **81** forming good monolayers. However, the molecular packing is not as tight as typically observed with simple alkane thiols, not surprising considering the size of these calix[4]arene receptor molecules compared to simple alkane thiols. Receptors **73** and **74** formed monolayers with similar molecular coverages.

4.5.1.6 Kinetics

The rate of electron transfer between monolayers of receptor **81** and the underlying gold surface was investigated. The deviation of the peak potentials (E_{pa} and E_{pc}) with increasing scan rate may be used to determine the kinetics of electron transfer, according to Laviron theory.²⁴ In the case of **81**, the peak potentials remained constant until a scan rate of about 5 V.s⁻¹, indicating that electron transfer is fast. However, instrumental limitations prevented an accurate determination of this rate of electron transfer, as the step potentials required by the instrument were too large with respect to the shifts in the peak potentials to enable reliable analysis.

4.5.2 Anion sensing in organic solution

The anion sensing properties of SAMs of receptors **81**, **73** and **74** on gold electrodes were studied in 0.1 M tetrabutylammonium tetrafluoroborate in 1:1 dichloromethane / acetonitrile. CVs were recorded in blank electrolyte solution and upon addition of various anions (tetrabutylammonium chloride, benzoate, dihydrogen phosphate or perrhenate) such that their concentration varied from 0 – 20 mM.

Addition of anions to monolayers of **73** or **74** surprisingly resulted in the complete disappearance of the redox waves even at fairly low anion concentrations (1 mM). Clearly, these SAM-confined ferrocene-amide receptor molecules are very sensitive to oxidative decomposition of the ferrocene group, especially in the presence of chloride, benzoate and dihydrogen phosphate anions. Consequently, these monolayers were useless as anion sensors.

However, monolayers of ferrocene-urea-appended calix[4]arene receptor **81** were much more stable in the presence of anions. The magnitudes of the cathodic shifts in the redox potential of SAMs of **81** upon addition of anions are given in Table 4.5. The peak separation (ΔE) and I_{pa} / I_{pc} values for the shifted waves are also reported.

	$E_{1/2}$ shift	ΔE^a	I_{pa} / I_{pc}
chloride	115	32	1.00
benzoate	180	82	1.05
dihydrogen phosphate	250	83	1.05
perrhenate	< 5	–	–

Table 4.5: Cathodic shifts in the $E_{1/2}$ value of SAMs of receptor **81** upon addition of anions (errors ± 10 mV). CVs were recorded under the following conditions: 0.1 M Bu_4NBF_4 in 1:1 $\text{CH}_2\text{Cl}_2 / \text{CH}_3\text{CN}$, scan rate 100 mV.s^{-1} , Ag / AgNO_3 reference electrode. ^a $\Delta E = E_{pa} - E_{pc}$

Importantly, the shift magnitudes quoted in Table 4.5 are maximum shift values. Upon addition of chloride, benzoate or dihydrogen phosphate anions to monolayers of receptor **81**, the redox potential was observed to shift cathodically until a maximum value was reached, typically at an anion concentration of approximately 5 mM. Further increases in the anion concentration resulted in no further shifts in the redox wave.

Comparison of the anion-induced cathodic shifts reported for the free (Table 4.3) and surface confined (Table 4.5) receptor reveals a ‘surface sensing amplification’. In other words, the

shifts observed for monolayers of **81** are consistently greater than those observed diffusively. Specifically, in the presence of chloride, the redox potential of the surface bound receptor shifts almost twice as much as for the free receptor (115 mV compared to 60 mV). These results highlight the significant sensing advantages associated with the preorganisation of a receptor on a surface (Figure 4.12).

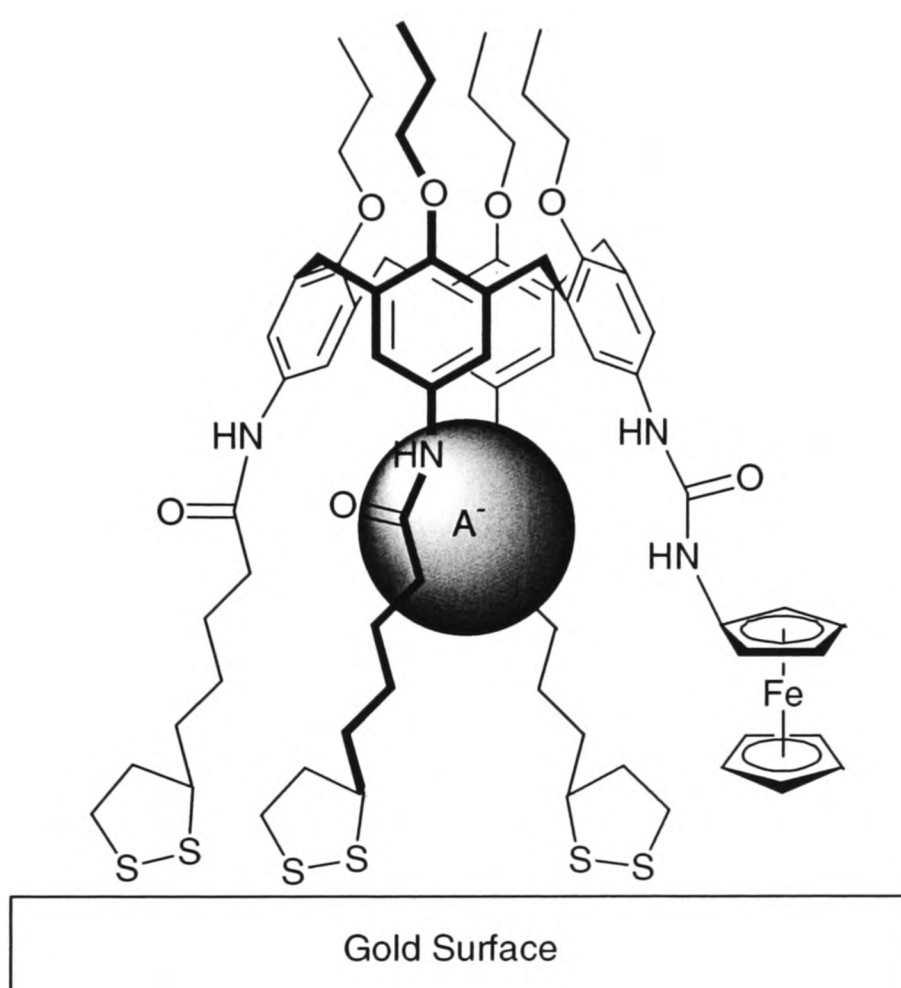


Figure 4.12: Schematic of receptor **81** attached to a gold electrode surface.

The CVs recorded before and after the addition of anions to monolayers of **81** are shown in Figures 4.12 – 4.14.

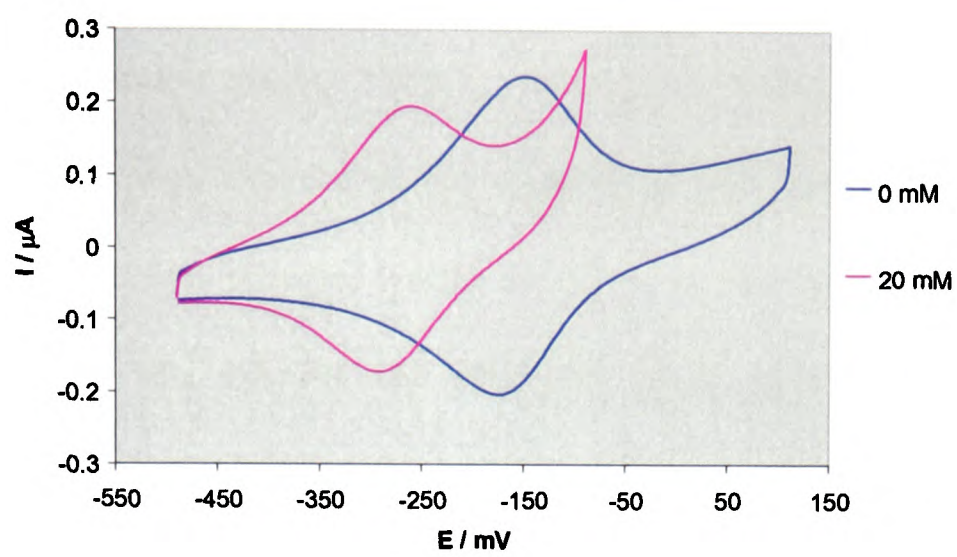


Figure 4.12: CVs of a SAM of receptor **81** in the absence and presence of 20 mM tetrabutylammonium chloride.

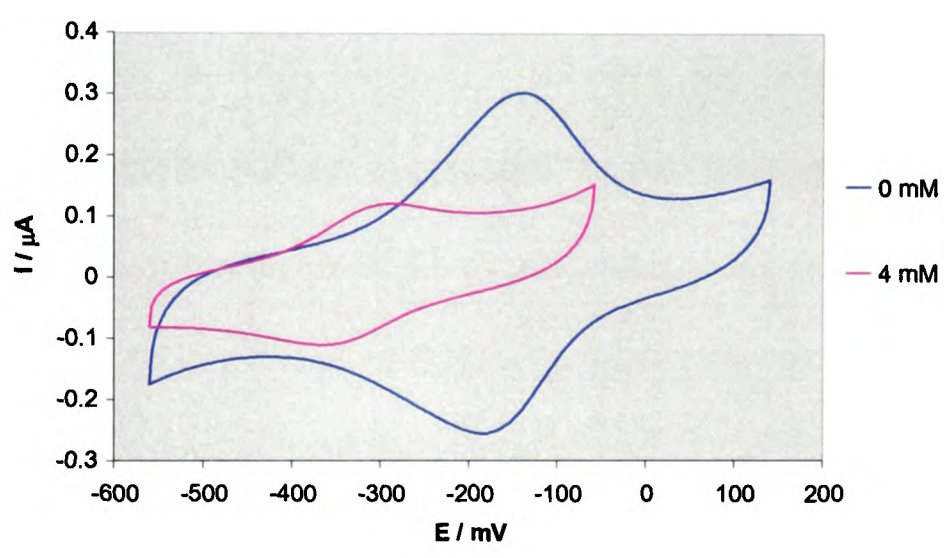


Figure 4.13: CVs of a SAM of receptor **81** in the absence and presence of 4 mM tetrabutylammonium benzoate.

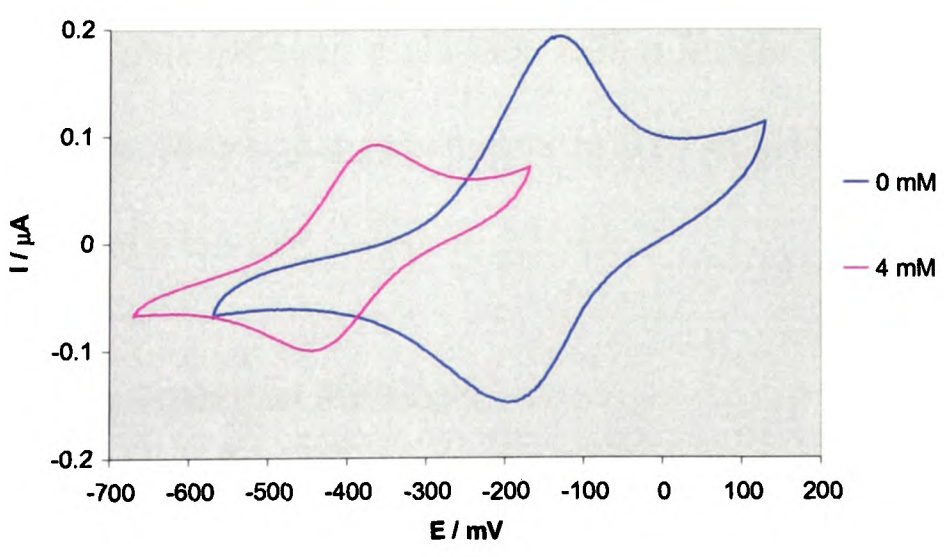


Figure 4.14: CVs of a SAM of receptor **81** in the absence and presence of 4 mM tetrabutylammonium dihydrogen phosphate.

The cathodically shifted waves were all characterised by a greater peak separation than that observed for the original redox couple. Such an increase in peak separation is indicative of both a slower rate of electron transfer to the underlying gold surface and possible anion coordination-induced structural changes within the film. In addition, a 30 – 70 % drop in faradaic current activity was consistently observed upon anion binding, due to slow decomposition of the ferrocene group.

SAMs of receptor **81** were sufficiently stable in the presence of chloride to allow the repetition of sensing studies with the same monolayer. After carrying out one sensing experiment with chloride, the modified electrode could be rinsed thoroughly and used for a second sensing experiment. In fresh electrolyte solution, the original wave was obtained again. This robustness of the monolayer is essential for the development of practical sensing devices. However, although monolayers of **81** were stable enough in the presence of benzoate and dihydrogen phosphate to determine shift data, generally the monolayer had decomposed after completing the sensing studies with these anions.

An anion competition experiment was conducted with monolayers of receptor **81**. CVs were recorded in blank electrolyte solution, in the presence of 20 mM chloride and then in the presence both 20 mM chloride and 2 mM dihydrogen phosphate. The redox couple of the receptor shifted 115 mV upon addition of chloride then a further 125 mV upon addition of dihydrogen phosphate. This shows that monolayers of **81** can selectively sense dihydrogen phosphate in the presence of a ten-fold excess of chloride.

4.5.3 Anion sensing in aqueous solution

Coordination-mediated anion detection in an aqueous medium is challenging due to the accompanying unfavourable energetic requirements of dehydration and the low binding constants of anions, particularly to neutral receptors.²⁵ The ability of SAMs of receptor **81** to

sense perrhenate (a comparatively poorly hydrated anion) in aqueous solution was investigated.

Before anion sensing studies were conducted, the electrochemical behaviour of monolayers of receptor **81** in aqueous solution was characterised. CVs were recorded in 0.1 M aqueous sodium perchlorate; the relevant data are given in Table 4.6. Potentials are quoted relative to the mercury sulphate reference electrode.

81	
E_{pa}	-78
E_{pc}	-257
ΔE^a	179
$E_{1/2}^b$	-168
I_{pa} / I_{pc}	1.10

Table 4.6: Electrochemical data for SAMs of receptor **81** in aqueous solution. CVs were recorded under the following conditions: 0.1 M aqueous sodium perchlorate, scan rate 100 mV.s⁻¹. Electrochemical potentials are ± 5 mV and are quoted relative to the HgSO₄ reference electrode. ^a $\Delta E = E_{pa} - E_{pc}$ ^b $E_{1/2} = (E_{pa} + E_{pc}) / 2$

The peak separation (ΔE) is much greater for the monolayer in aqueous solution (compared to organic solution), possibly indicating slower electron transfer kinetics in water. One might expect solvent mediated electron transfer to be slower for a hydrophobic monolayer in an aqueous environment.

Analogous methods to those employed in the characterisation of monolayers in organic solvents reveal that SAMs of **81** are likewise stable and reversible (the plot of current against scan rate is linear, $R^2 = 0.996$) in aqueous media. CVs recorded at different scan rates reveal

that the peak separation increases rapidly as the scan rate increases, again indicative of slower electron transfer kinetics in aqueous solution.

The ability of SAMs of receptor **81** to sense perrehnate and dihydrogen phosphate anions in aqueous solution was investigated. The magnitudes of the cathodic shifts in the redox potential of SAMs of **81** upon addition of perrehnate or dihydrogen phosphate (such that the concentration of anions was 20 mM) are given in Table 4.7. The peak separation (ΔE) and I_{pa} / I_{pc} values for the shifted waves are also reported. CVs recorded before and after the addition of perrhenate to a SAM of **81** are shown in Figure 4.15.

	$E_{1/2}$ shift	ΔE^a	I_{pa} / I_{pc}
dihydrogen phosphate	< 5	–	–
perrhenate	25	224	1.15

Table 4.7: Cathodic shifts in the $E_{1/2}$ value of SAMs of receptor **81** upon addition of anions (errors ± 10 mV). CVs were recorded under the following conditions: 0.1 M aqueous sodium perchlorate, scan rate 100 mV.s⁻¹, HgSO₄ reference electrode. ^a $\Delta E = E_{pa} - E_{pc}$

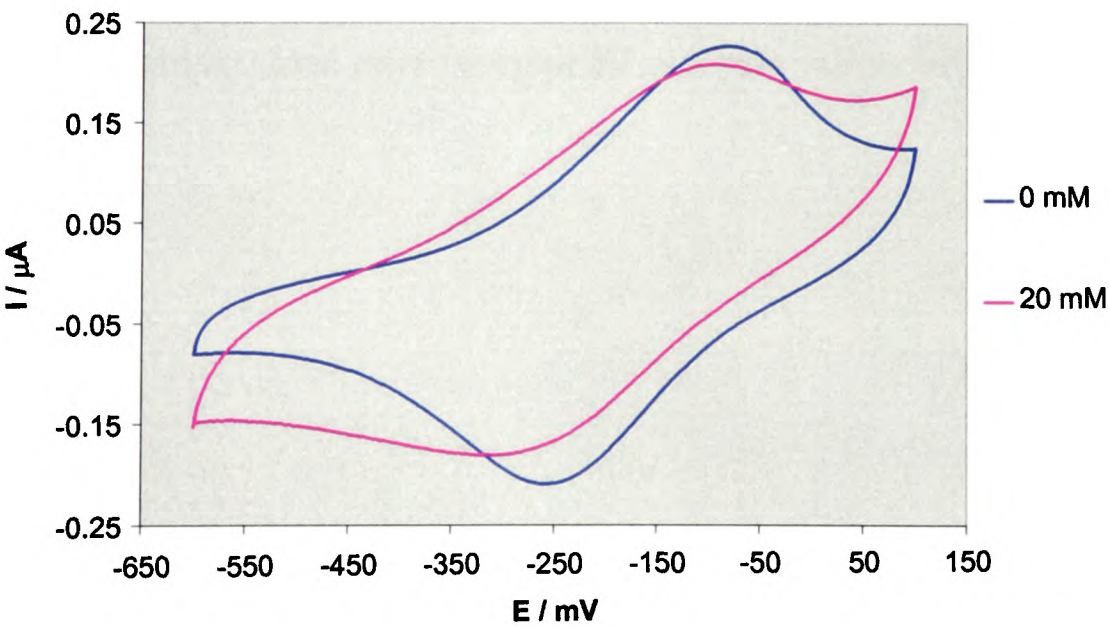


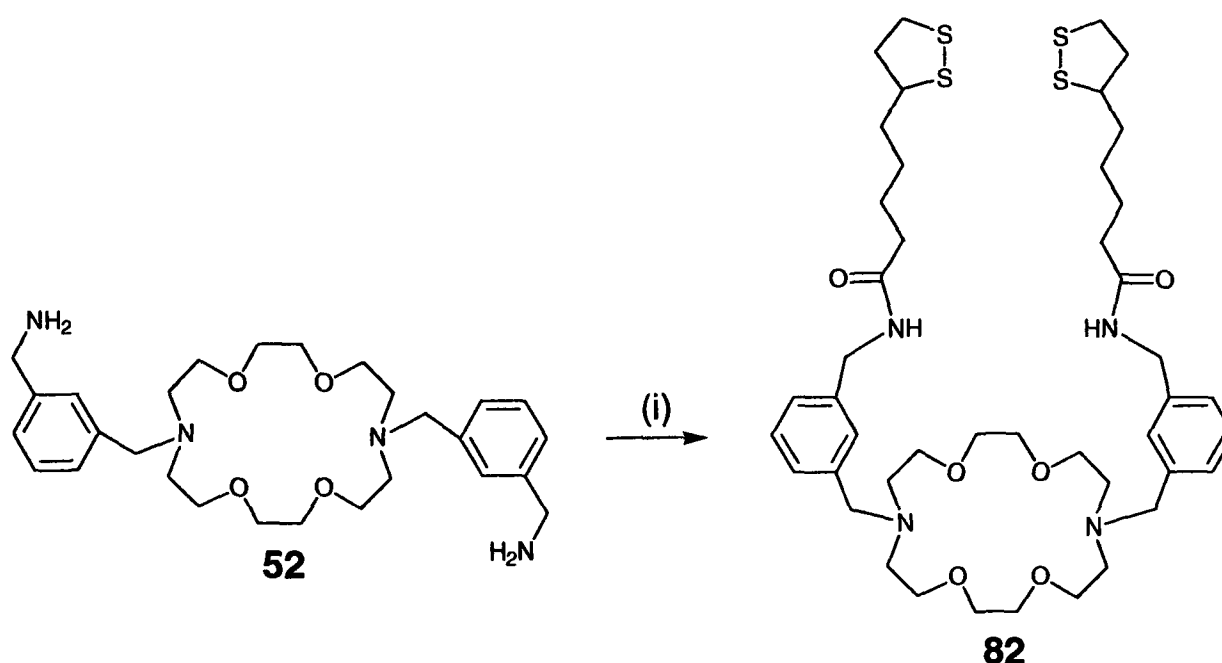
Figure 4.15: CVs of a SAM of receptor **81** in the absence and presence of 20 mM tetrabutylammonium perrhenate in aqueous solution.

Reproducible shifts of 20 – 30 mV were observed with perrhenate anions, whereas no shifts were seen with dihydrogen phosphate. Anion competition experiments show that monolayers of receptor **81** can selectively sense perrhenate in the presence of equimolar dihydrogen phosphate. This behaviour, the selective sensing of perrhenate over dihydrogen phosphate, is a complete reversal of the sensing experienced in organic solvent, and may be attributed to the much more highly hydrated nature of dihydrogen phosphate (compared to perrhenate) in aqueous solution.

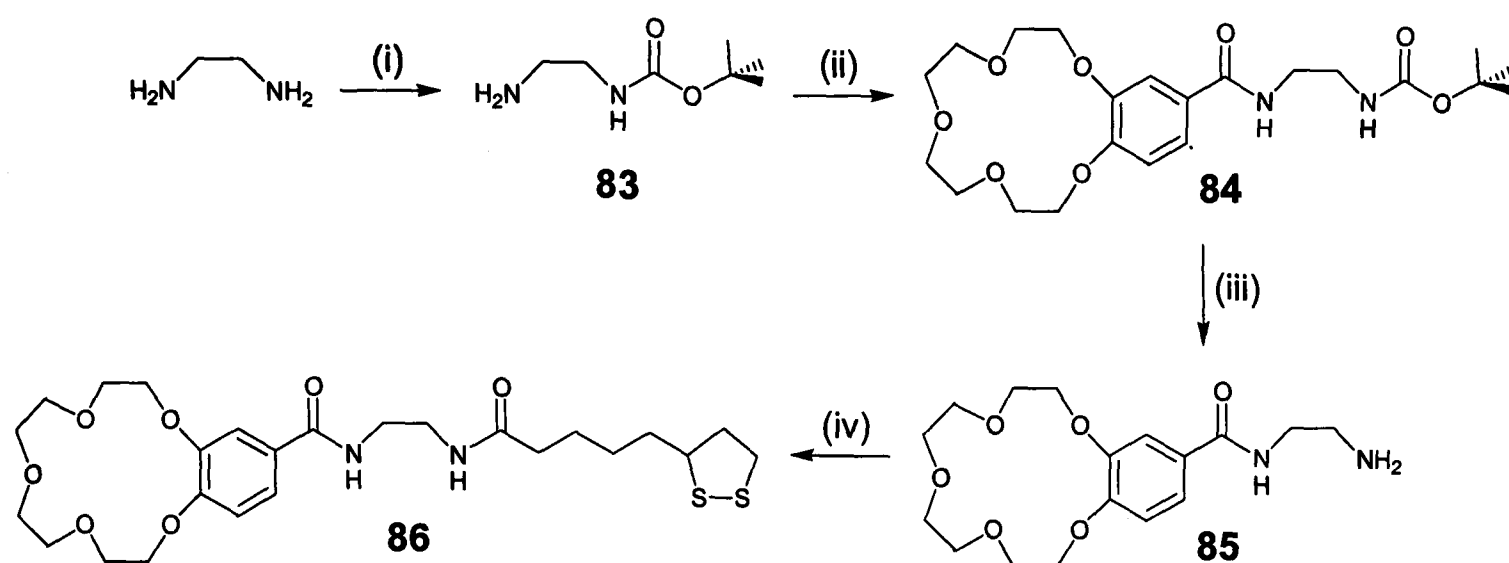
4.6 Synthesis and Characterisation of Disulphide-Appended Ion-Pair Receptors

This section outlines the synthesis and characterisation of disulphide-appended ion-pair receptors, designed to self-assemble onto gold nanoparticles for the spectroscopic sensing of anions and alkali metal cation-anion ion-pairs.

Bis-amine-functionalised 1,10-bis-aza[18]crown-6 **52** (see Section 3.2 of Chapter Three) was reacted with three equivalents of both thiocetic acid and EDC in dichloromethane (Scheme 4.5). The organic layer was washed with aqueous lithium hydroxide to remove the excess starting materials. Solvent removal gave receptor **82** as a pale yellow oil in 93 % yield.

Scheme 4.5: (i) thioctic acid, EDC, CH₂Cl₂, 93 %.

The synthesis of benzo[15]crown-5 disulphide-appended ion-pair receptor **86** is shown in Scheme 4.6. Mono-BOC-protection of ethylenediamine gave **83**²⁶ as a colourless oil in 91 % yield. This was reacted with 4-(chlorocarboxy)benzo[15]crown-5 **15** in the presence of triethylamine base in dichloromethane, and precipitation from dichloromethane / hexane produced **84** as a white powder in 91 % yield. Deprotection of **84** with trifluoroacetic acid in dichloromethane gave the TFA salt of **85** in quantitative yield. This was reacted with one and a half equivalents of both thioctic acid and EDC in dichloromethane in the presence of excess triethylamine base. The organic layer was washed with aqueous lithium hydroxide to remove the excess starting materials and any inorganic impurities. Precipitation from chloroform / hexane afforded receptor **86** as a cream solid in 54 % yield. Figure 4.16 shows an assigned ¹H NMR spectrum for **86** in CDCl₃.



Scheme 4.6: (i) BOC-anhydride, 1,4-dioxane, 91 %;
(ii) 4-(chlorocarboxy)benzo[15]crown-5 **15**, Et₃N, CH₂Cl₂, 91 %;
(iii) TFA, CH₂Cl₂, 99 %; (iv) thioctic acid, EDC, Et₃N, CH₂Cl₂, 54 %.

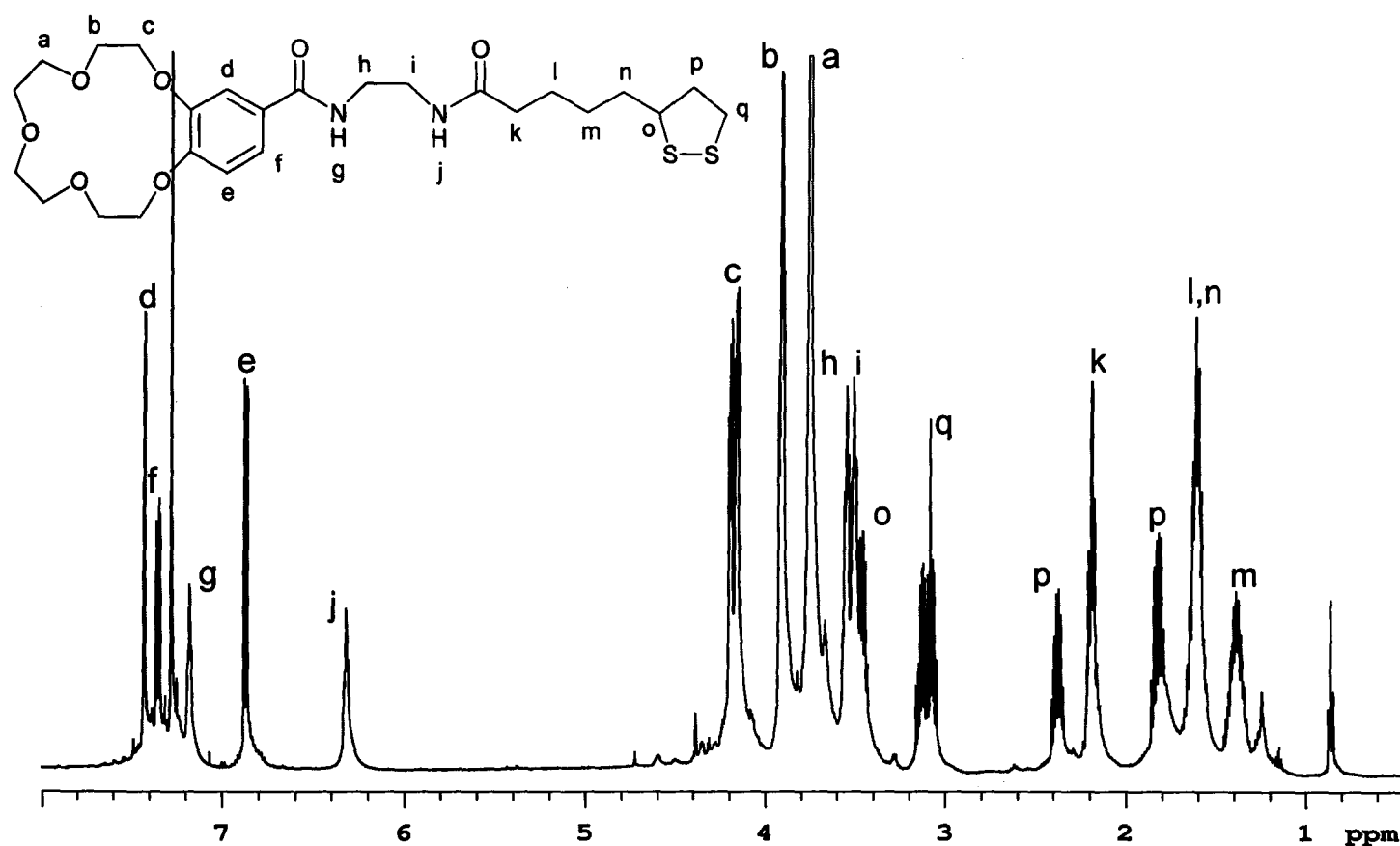


Figure 4.16: ¹H NMR spectrum (500 MHz) of receptor **86** in CDCl₃.

In summary, two new disulphide-appended ion-pair receptors **82** and **86** were synthesised by condensing either amine-derivatised 1,10-bisaza[18]crown-6 or benzo[15]crown-5 compounds with thioctic acid. Both receptors were characterised by ¹H NMR spectroscopy, mass spectrometry and elemental analysis.

4.7 ^1H NMR Ion-Pair Binding Studies

The ion-pair binding properties of the disulphide-appended ion-pair receptors **82** and **86** were investigated initially by ^1H NMR spectroscopy. These heteroditopic receptors were designed for the simultaneous complexation of both cations and anions (ion-pair recognition). As discussed in Section 2.3.6 of Chapter Two, the choice of solvent for these experiments was limited by the solubilities of the various species present in the titrations. Receptor **82** was sufficiently soluble only in d_6 -DMSO solution. However, ^1H NMR titration experiments with chloride, benzoate and dihydrogen phosphate in d_6 -DMSO resulted in no observable binding of anions.

Receptor **86** was found to be soluble in 1:1 CD_3CN / d_6 -DMSO, so some preliminary ^1H NMR titration experiments were carried out with benzoate anions in the absence / presence of 0.5 equivalents of potassium perchlorate. It was envisaged that the formation of a potassium cation sandwich complex between the benzo[15]crown-5 ether moieties of two receptor molecules would arrange the amide groups to create an anion binding environment more favourable than for the free receptor alone. EQNMR analysis of the titration curves, monitoring the amide protons of the receptor, indicated a 1:1 benzoate / receptor binding stoichiometry. Stability constants of $K = 50 \pm 5 \text{ M}^{-1}$ were obtained both in the absence and presence of potassium cations, indicating no cation-induced enhancement of anion binding. Possibly, the anion binding site is too flexible for cooperative ion-pair recognition.

Of course, the anion binding ability of receptor **86** was expected to be fairly weak in such a competitive solvent system. However, the reason that disulphide functionalities were incorporated into the design of these receptors was to enable their attachment to gold surfaces. Confining **86** to a surface would reduce the flexibility inherent in the receptor, thereby creating a more preorganised ion-pair receptor (Figure 4.17). Unfortunately, repeated attempts

to synthesise gold nanoparticles functionalised with ion-pair receptors proved problematic (see Section 4.8).

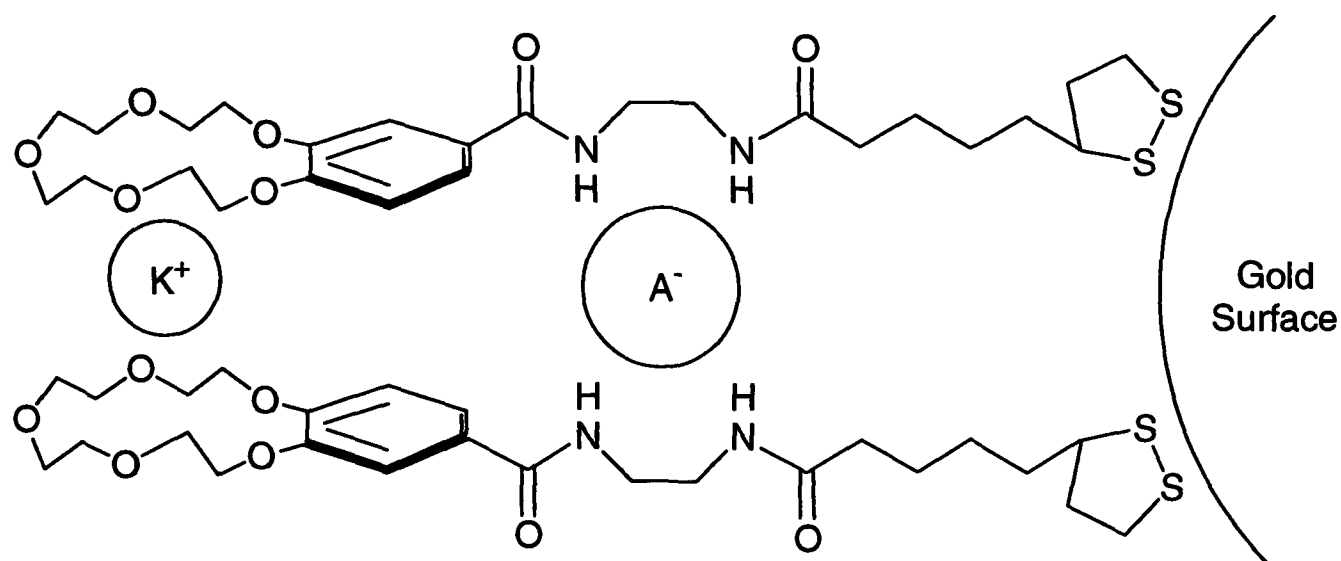


Figure 4.17: Ion-pair recognition by receptor **86** tethered to a gold surface.

4.8 Attempted Synthesis of Functionalised Gold Nanoparticles

Several attempts were made to self-assemble the disulphide-appended receptors **75**, **82** and **86** onto gold nanoparticles. These receptor-functionalised nanoparticles were conceived as potential spectroscopic sensors for anion and ion-pair recognition, whereby the binding processes would be reported *via* perturbations in the surface plasmon resonance (SPR) band of the nanoparticles.

4.8.1 Attempted synthesis by ligand displacement

There are several recent reports in the literature whereby functionalised gold nanoparticles have been synthesised by the displacement of the thiol ligands from dodecanethiol-protected nanoparticles.²⁷ This methodology was followed in an attempt to self-assemble the disulphide-appended receptors onto gold nanoparticles.

Dodecanethiol-protected gold nanoparticles were synthesised according to the Brust methodology.²⁸ This technique involves growing nanometre-sized (typically 1 – 5 nm in

diameter) clusters of gold atoms by the reduction of tetrachloroaurate in a two-phase system. The development of the nanoparticles is controlled by the simultaneous attachment of thiol monolayers to the growing nuclei.

An aqueous solution of hydrogen tetrachloroaurate was transferred into toluene solution with the use of a phase-transfer reagent (aliquat[®] 336). Dodecanethiol was added and the tetrachloroaurate reduced with aqueous sodium borohydride to give a dark purple organic phase from which the dodecanethiol-protected gold nanoparticles were isolated as a black waxy solid in 96 % yield. Elemental analysis showed that these nanoparticles consisted of about 78 % gold and 22 % dodecanethiol. The ¹H NMR spectrum of these nanoparticles in CDCl₃ is very broad, as expected for such species.²⁹

Displacement of the dodecanethiol ligands with receptor molecules **75**, **82** or **86** was attempted in the following way. A solution of receptor in dichloromethane was added to a solution of dodecanethiol-protected gold nanoparticles in dichloromethane and the mixture stirred for 48 hours. The stoichiometry was such that there was one equivalent of receptor per dodecanethiol ligand. Solvent removal followed by addition of methanol gave black solid products in all cases.

Unfortunately, ¹H NMR spectroscopy and elemental analysis of these products showed that no displacement had occurred. The nanoparticles remained intact and surrounded by dodecanethiol ligands, but there was no evidence for the presence of the receptor molecules. It is possible that the dodecanethiol-protected nanoparticles are too stable to readily undergo displacement by the disulphide-appended receptors. Thus, direct synthesis of the nanoparticles in the presence of the receptors was attempted.

4.8.2 Attempted direct synthesis

A similar method to that outlined above for the Brust synthesis of the dodecanethiol-functionalised nanoparticles was followed, with the following exception. Instead of adding dodecanethiol to the organic layer, a 1:1 mixture of dodecanethiol / receptor or just receptor was added. However in all cases, this direct synthesis in the presence of receptors **75**, **82** or **86** resulted in the formation of insoluble black products. Elemental analysis revealed the presence of the receptors, however this material was possibly polymeric and unsuitable for any further studies.

4.9 Summary

A range of new disulphide-appended anion and ion-pair receptors have been synthesised *via* the condensation of various amine-derivatised compounds with thioctic acid, and characterised by ^1H NMR spectroscopy, mass spectrometry and elemental analysis. These receptors were designed to form self-assembled monolayers on gold electrodes and gold nanoparticles for the electrochemical and/or optical sensing of guest binding.

The anion binding properties of the upper-rim functionalised ferrocene- and disulphide-appended calix[4]arene receptors were investigated by ^1H NMR spectroscopy in 1:1 CD_3CN / d_6 -DMSO. Typically, addition of chloride, benzoate and dihydrogen phosphate anions to solutions of the receptors caused downfield shifts in the amide or urea resonances, indicating that the anions were bound by the hydrogen bonding moieties. EQNMR analyses of the resulting titration curves revealed 1:1 binding stoichiometries and modest stability constants in all cases, with a selectivity trend dihydrogen phosphate > benzoate > chloride. ^1H NMR ion-pair binding studies with receptors **82** and **86** were hampered by solubility problems.

The electrochemical anion sensing abilities of receptors **81**, **73** and **74** were investigated by diffusive voltammetry in 1:1 dichloromethane / acetonitrile. All three redox-active receptors were shown to electrochemically recognise anionic guest species. SAMs of these upper-rim functionalised ferrocene- and disulphide-appended calix[4]arene receptors were prepared on gold electrodes, and all exhibited stable and reversible ferrocene / ferrocenium electrochemical responses in organic electrolyte. Disappointingly, the addition of anions to SAMs of ferrocene-amide linked receptors **73** and **74** resulted in decomposition of the monolayers. However, SAMs of ferrocene-urea-appended calix[4]arene receptor **81** were stable and the magnitudes of the anion-induced cathodic shifts observed were all significantly larger than those observed diffusively. For example, redox responses were more cathodically shifted by 55 mV for chloride ($\Delta E_{1/2}$ monolayer = 115 mV, $\Delta E_{1/2}$ diffusive = 60 mV) and 50 mV for H_2PO_4^- ($\Delta E_{1/2}$ monolayer = 250 mV, $\Delta E_{1/2}$ diffusive = 200 mV). This surface sensing amplification result highlights the significant advantages associated with preorganisation of the redox-active calix[4]arene receptor on a gold electrode surface. Furthermore, SAMs of **81** were shown to selectively sense perrhenate in the presence of equimolar amounts of dihydrogen phosphate in aqueous solution.

Attempts to assemble disulphide-appended receptors onto gold nanoparticles either by ligand displacement reactions with dodecanethiol-functionalised nanoparticles or by direct synthesis using an adapted Brust methodology were unfortunately unsuccessful.

4.10 Future Research

The development of electrochemical and UV-VIS spectroscopic sensing devices *via* the self-assembly of anion and ion-pair receptors onto gold electrode and gold nanoparticle surfaces is a new and promising area of research.

The results presented in this chapter show that ferrocene- and disulphide-appended calix[4]arene receptor **81** forms SAMs on gold electrode surfaces which exhibit a surface sensing amplification in the electrochemical recognition of anions in organic solvents. In addition, SAMs of receptor **81** can sense perrhenate anions in aqueous solution. In the future, the incorporation of charged groups into receptor design may enable the detection of more highly hydrated anions (such as dihydrogen phosphate) in aqueous media. The investigation of such surface-modified electrodes is ongoing, with the aim of developing practical sensing devices for anions of biological, medical and environmental importance.

The attempts described in this chapter to self-assemble disulphide-appended ion-pair receptors onto the surfaces of gold nanoparticles were unfortunately unsuccessful. However, the study of such receptor-functionalised nanoparticles is a relatively new area of research, and there is a great deal of potential for the UV-VIS spectroscopic detection of anions and ion-pairs by these species. In the future, the development of a reliable synthetic methodology for the functionalisation of gold nanoparticles may lead to interesting optical sensing devices.

Furthermore, in the future, the availability of a new SPR (surface plasmon resonance) instrument may enable the determination of stability constants for the binding of guest species to anion and ion-pair receptors attached to gold surfaces.

4.11 References

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Chapter Five

Experimental

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Chapter Five: Experimental

5.1 Solvent and Reagent Pre-Treatment

Unless otherwise stated, commercial grade solvents and other chemicals were used without further purification. Dry solvents were used for some syntheses and all spectroscopic and electrochemical studies. Dichloromethane and acetonitrile were pre-dried and purified by distillation over calcium hydride. Triethylamine was distilled from potassium hydroxide. Thionyl chloride was distilled from triphenyl phosphite and used immediately in subsequent reactions. Deionised water was used in all cases. Tetrabutylammonium salts of chloride, benzoate, acetate, dihydrogen phosphate and perrhenate were stored in a desiccator under vacuum containing self-indicating silica.

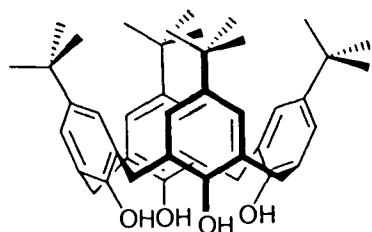
The 1,3-bis(amino) calix[4]arene derivative **24** was synthesised by Dr. S. E. Matthews according to a literature procedure.¹

5.2 Instrumentation and Services

NMR spectra were recorded on a Varian Mercury 300 or a Varian Unity Plus 500 instrument. Elemental analyses² and electrospray mass spectrometry were performed by in-house services at the Inorganic Chemistry Laboratory, University of Oxford. FAB mass spectrometry was performed by the EPSRC mass spectrometry service, University of Wales, Swansea. X-ray crystallography was undertaken by Dr. A. R. Cowley and Dr. R. L. Paul at the Chemical Crystallography Laboratory, University of Oxford.

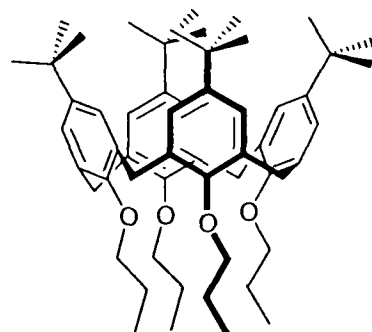
5.3 Experimental for Chapter Two

Tetra-*t*-butylcalix[4]arene **1**³



p-*t*-Butylphenol (200 g, 1.33 mol) and sodium hydroxide pellets (2.40 g, 0.06 mol) were placed into a 2 L, 3 neck round bottom flask fitted with a mechanical stirrer. Formaldehyde (37 % w/v, 130 mL, 1.60 mmol) was added and the system stirred at 120 °C for 3 hours, at which stage the reaction mixture had changed to a deep yellow viscous material. The heat was removed and the material frothed and filled the entire flask. Diphenylether (1 L) was added and heated gently with stirring to dissolve the product. A nitrogen inlet and condenser were fitted to the flask and the temperature increased to azeotrope off the water. Distillation was continued for 2 hours at which stage 90 mL of water / diphenylether had been distilled off. The condenser was fitted to reflux and the temperature increased to 250 °C for 3 hours to afford a clear dark liquid. When the liquid had cooled to 100 °C, ethylacetate (1 L) was added and the solution allowed to stir for 30 minutes. The precipitate was isolated by filtration and washed with ethylacetate (2 × 250 mL), glacial acetic acid (2 × 100 mL) and finally water (250 mL). The creamy microcrystalline product was allowed to air dry for 2 hours then further dried in the oven overnight (117 g, 54 %). ¹H NMR (300 MHz, CDCl₃): δ 10.34 (s, OH, 4H), 7.05 (s, ArH, 8H), 4.25 (d, *J* = 12.6 Hz, ArCH_{ax}H_{eq}Ar, 4H), 3.49 (d, *J* = 12.6 Hz, ArCH_{ax}H_{eq}Ar, 4H), 1.20 (s, CH₃, 36H).

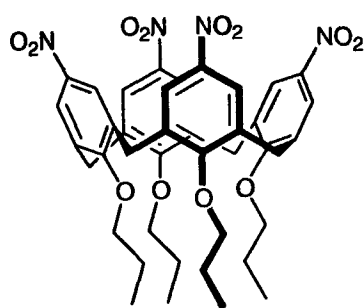
5,11,17,23-Tetra-*t*-butyl-25,26,27,28-tetra-propoxy-calix[4]arene **2**⁴



Compound **1** (20.40 g, 31.4 mmol) and sodium hydride (6.30 g, excess) were suspended in dry dimethylformamide (400 mL) in a 2 L, 3 neck round bottom flask and stirred under nitrogen for 1 hour. *n*-Propyl iodide (28 mL, excess) was added slowly from a dropping

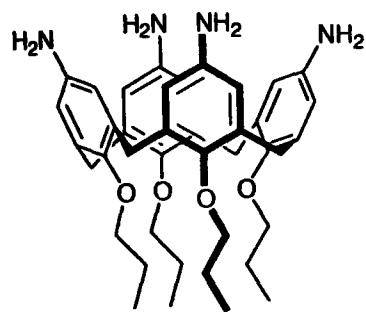
funnel and the system stirred at room temperature overnight. Water (100 mL) was added and the precipitate formed collected by filtration. The solid was dissolved in chloroform (300 mL) and washed with hydrochloric acid (15 %, 2×100 mL) and water (2×100 mL). The organic layer was dried over potassium carbonate and the solvent evaporated to give an orange oil. Dissolution in chloroform (100 mL) and addition of methanol (400 mL) yielded the product as a white solid (17.40 g, 68 %). ^1H NMR (300 MHz, CDCl_3): δ 6.77 (s, ArH, 8H), 4.41 (d, $J = 12.6$ Hz, $\text{ArCH}_{\text{ax}}\text{H}_{\text{eq}}\text{Ar}$, 4H), 3.81 (t, $J = 7.5$ Hz, $\text{OCH}_2\text{CH}_2\text{CH}_3$, 8H), 3.11 (d, $J = 12.6$ Hz, $\text{ArCH}_{\text{ax}}\text{H}_{\text{eq}}\text{Ar}$, 4H), 2.03 (sext, $J = 7.5$ Hz, $\text{OCH}_2\text{CH}_2\text{CH}_3$, 8H), 1.09 (s, CH_3 , 36H), 1.01 (t, $J = 7.5$ Hz, $\text{OCH}_2\text{CH}_2\text{CH}_3$, 12H).

5,11,17,23-Tetra-nitro-25,26,27,28-tetra-propoxy-calix[4]arene **3⁵**



A mixture of glacial acetic acid (75 mL) and fuming nitric acid (75 mL) was added to a stirred solution of **2** (12.15 g, 14.9 mmol) in dichloromethane (450 mL). After 90 minutes the solution had changed colour from deep black to orange. Water (200 mL) was added and

stirring continued for 10 minutes. The water was decanted and the organic layer washed with water (6×150 mL), dried over anhydrous magnesium sulphate, filtered, and the solvent removed under vacuum. Precipitation from chloroform / methanol gave the product as a pale yellow solid (9.18 g, 80 %). ^1H NMR (300 MHz, CDCl_3): δ 7.57 (s, ArH, 8H), 4.52 (d, $J = 14.1$ Hz, $\text{ArCH}_{\text{ax}}\text{H}_{\text{eq}}\text{Ar}$, 4H), 3.96 (t, $J = 7.5$ Hz, $\text{OCH}_2\text{CH}_2\text{CH}_3$, 8H), 3.41 (d, $J = 14.1$ Hz, $\text{ArCH}_{\text{ax}}\text{H}_{\text{eq}}\text{Ar}$, 4H), 1.92 (sext, $J = 7.5$ Hz, $\text{OCH}_2\text{CH}_2\text{CH}_3$, 8H), 1.03 (t, $J = 7.5$ Hz, $\text{OCH}_2\text{CH}_2\text{CH}_3$, 12H).

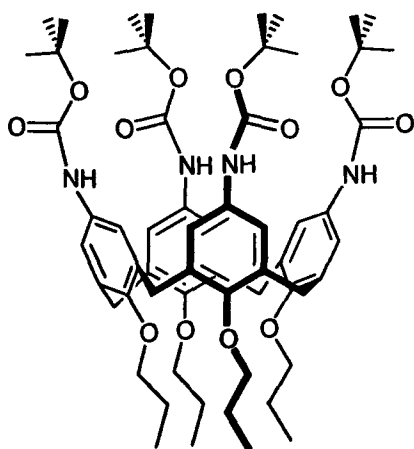
5,11,17,23-Tetra-amino-25,26,27,28-tetra-propoxy-calix[4]arene 4⁶

Hydrazine hydrate (40 mL) was added to a suspension of **3** (9.05 g, 11.7 mmol) and Raney nickel (catalytic) in methanol (400 mL). The mixture was heated at reflux for 4 hours to give an almost colourless solution which was filtered while hot through Celite®. The filtrate was

diluted with water (350 mL) to give a cloudy solution which was extracted with dichloromethane (3 × 200 mL). The organic layer was dried over anhydrous magnesium sulphate, filtered, and the solvent removed under vacuum. Precipitation from dichloromethane / hexane gave a buff coloured product (6.80 g, 89 %). ¹H NMR (300 MHz, CDCl₃): δ 6.05 (s, ArH, 8H), 4.31 (d, *J* = 13.2 Hz, ArCH_{ax}H_{eq}Ar, 4H), 3.72 (t, *J* = 7.5 Hz, OCH₂CH₂CH₃, 8H), 2.92 (d, *J* = 13.2 Hz, ArCH_{ax}H_{eq}Ar, 4H), 1.87 (sext, *J* = 7.5 Hz, OCH₂CH₂CH₃, 8H), 0.96 (t, *J* = 7.5 Hz, OCH₂CH₂CH₃, 12H).

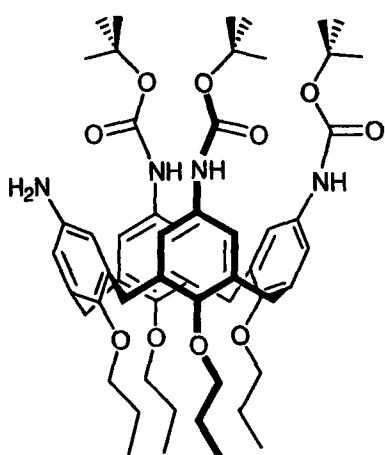
5,11,17,23-Tetra-*N*-*t*-butoxycarbonyl-25,26,27,28-tetra-propoxy-calix[4]arene 38, 5-amino-11,17,23-tri-*N*-*t*-butoxycarbonyl-25,26,27,28-tetra-propoxy-calix[4]arene 6 and 5,11-di-amino-17,23-di-*N*-*t*-butoxycarbonyl-25,26,27,28-tetra-propoxy-calix[4]arene 7⁷

Di-*t*-butyl-dicarbonate (BOC-anhydride, 6.04 g, 27.7 mmol) in dichloromethane (100 mL) was added dropwise to a stirred solution of **4** (6.69 g, 10.2 mmol) in dichloromethane (200 mL) and the mixture was stirred under nitrogen overnight. The solvent was removed leaving a brown residue. Three products were isolated by column chromatography (silica, hexane / ethylacetate 2:1 then 1:1 then 1:2).



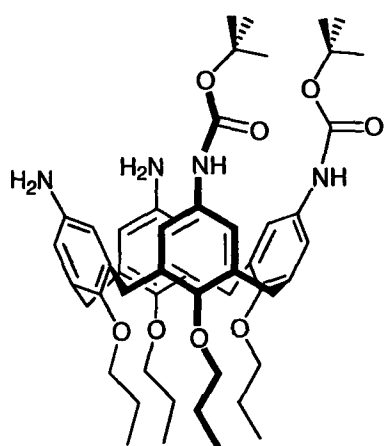
Tetra-BOC-protected calix[4]arene **38** was the first product eluted from the column; evaporation of the solvent yielded a cream solid (0.46 g, 4 %). ¹H NMR (300 MHz, *d*₆-DMSO): δ 8.73 (s, NH, 4H), 6.75 (s, ArH, 8H), 4.28 (d, *J* = 12.9 Hz, ArCH_{ax}H_{eq}Ar, 4H), 3.72 (t, *J* = 7.5 Hz, OCH₂CH₂CH₃, 8H), 2.98 (d, *J* = 12.9 Hz,

$\text{ArCH}_{\text{ax}}\text{H}_{\text{eq}}\text{Ar}$, 4H), 1.87 (sext, $J = 7.5$ Hz, $\text{OCH}_2\text{CH}_2\text{CH}_3$, 8H), 1.39 (s, CH_3 , 36H), 0.94 (t, $J = 7.5$ Hz, $\text{OCH}_2\text{CH}_2\text{CH}_3$, 12H).



Tri-BOC-protected calix[4]arene **5** was the second product eluted from the column; evaporation of the solvent yielded a yellow solid (4.63 g, 47 %). ^1H NMR (300 MHz, d_6 -DMSO): δ 8.93 (s, NH, 2H), 8.71 (s, NH, 1H), 6.98 & 6.96 & 6.46 & 5.70 (all s, ArH, $4 \times 2\text{H}$), 4.28 & 4.21 (both d, $J = 12.9$ Hz, $\text{ArCH}_{\text{ax}}\text{H}_{\text{eq}}\text{Ar}$, $2 \times 2\text{H}$), 4.17 (s,

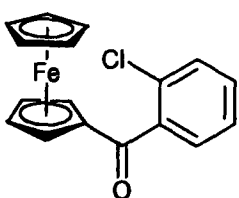
NH_2 , 2H), 3.79 (t, $J = 7.8$ Hz, $\text{OCH}_2\text{CH}_2\text{CH}_3$, 4H), 3.63 & 3.55 (both t, $J = 7.2$ Hz, $\text{OCH}_2\text{CH}_2\text{CH}_3$, $2 \times 2\text{H}$), 2.98 & 2.89 (both d, $J = 12.9$ Hz, $\text{ArCH}_{\text{ax}}\text{H}_{\text{eq}}\text{Ar}$, $2 \times 2\text{H}$), 1.91 – 1.77 (m, $\text{OCH}_2\text{CH}_2\text{CH}_3$, 8H), 1.44 (s, CH_3 , 18H), 1.35 (s, CH_3 , 9H), 0.99 & 0.98 (both t, $J = 7.5$ Hz, $\text{OCH}_2\text{CH}_2\text{CH}_3$, $2 \times 3\text{H}$), 0.88 (t, $J = 7.5$ Hz, $\text{OCH}_2\text{CH}_2\text{CH}_3$, 6H).



Di-BOC-protected calix[4]arene **6** was the third product eluted from the column; evaporation of the solvent yielded an orange solid (2.02 g, 23 %). ^1H NMR (300 MHz, d_6 -DMSO): δ 8.86 (s, NH, 2H), 6.74 & 6.67 & 5.93 & 5.90 (all s, ArH, $4 \times 2\text{H}$), 4.30 (s, NH_2 , 4H), 4.28 & 4.14 (both d, $J = 12.9$ Hz, $\text{ArCH}_{\text{ax}}\text{H}_{\text{eq}}\text{Ar}$, $2 \times 1\text{H}$), 4.21 (d, $J = 12.9$

Hz, $\text{ArCH}_{\text{ax}}\text{H}_{\text{eq}}\text{Ar}$, 2H), 3.70 & 3.62 (both t, $J = 7.2$ Hz, $\text{OCH}_2\text{CH}_2\text{CH}_3$, $2 \times 4\text{H}$), 2.97 & 2.79 (both d, $J = 12.9$ Hz, $\text{ArCH}_{\text{ax}}\text{H}_{\text{eq}}\text{Ar}$, $2 \times 1\text{H}$), 2.88 (d, $J = 12.9$ Hz, $\text{ArCH}_{\text{ax}}\text{H}_{\text{eq}}\text{Ar}$, 2H), 1.83 (sext, $J = 7.5$ Hz, $\text{OCH}_2\text{CH}_2\text{CH}_3$, 8H), 1.40 (s, CH_3 , 18H), 0.93 & 0.92 (both t, $J = 7.5$ Hz, $\text{OCH}_2\text{CH}_2\text{CH}_3$, $2 \times 6\text{H}$).

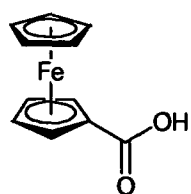
(2-Chlorobenzoyl)ferrocene **7**⁸



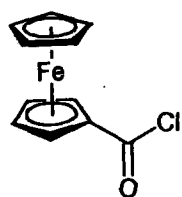
2-Chlorobenzoyl chloride (6.40 mL, 50.5 mmol) was added to a stirred solution of recrystallised ferrocene (9.31 g, 50.0 mmol) in dry

dichloromethane (200 mL) in a 2 L, 3 neck round bottom flask. The reaction vessel was cooled in an ice-bath and aluminium(III) chloride (7.01 g, 52.6 mmol) was added portion-wise over 1 hour maintaining the temperature of the reaction mixture below 5 °C. The ice-bath was removed and the resulting deep blue solution stirred for a further 90 minutes before again being cooled in ice. Water (200 mL) was carefully added and the cooled mixture stirred for 1 hour. The organic fraction was collected and the aqueous layer extracted with dichloromethane (2 × 50 mL). The combined organic phases were washed with water (1 × 50 mL) and sodium hydroxide solution (10 % w/v, 2 × 50 mL), dried over anhydrous magnesium sulphate, filtered and evaporated to dryness to leave a red oil which gradually solidified under high vacuum. Soxhlet extraction into hexane yielded red needle crystals of the product (7.50 g, 46 %).

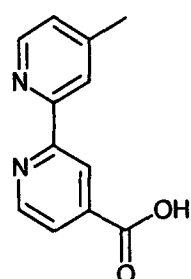
Carboxyferrocene **8**⁸



A 500 mL, 3 neck round bottom flask was charged with potassium *t*-butoxide (14.18 g, excess) in dry 1,2-dimethoxyethane (100 mL) and the mixture stirred under nitrogen. Water (0.7 mL, 38.9 mmol) and **7** (7.40 g, 22.8 mmol) were added and the mixture heated at reflux for 3 hours after which time the colour had changed from red to light tan. The mixture was cooled and poured into water (250 mL), which was washed with diethylether (3 × 40 mL) and the ether washings back extracted with sodium hydroxide solution (10 % w/v, 2 × 25 mL). The combined aqueous phases were acidified with hydrochloric acid to afford an orange-brown precipitate which was collected by filtration, dried under high vacuum and recrystallised from dry toluene (4.55 g, 40 %). ¹H NMR (300 MHz, *d*₆-DMSO): δ 12.14 (br s, OH, 1H), 4.71 (s, C₅H₄, 2H), 4.46 (s, C₅H₄, 2H), 4.21 (s, C₅H₅, 5H).

Chlorocarbonyl ferrocene 9⁸

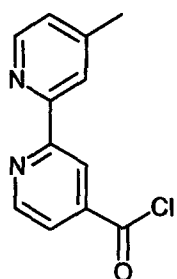
Compound **8** (3.97 g, 17.3 mmol) was suspended in dry dichloromethane (200 mL) and oxalyl chloride (10 mL, excess) in dry dichloromethane (100 mL) was added dropwise under a nitrogen atmosphere giving a dark red solution. The reaction mixture was heated to reflux for 2 hours then left to stir under nitrogen at room temperature overnight. The solution was filtered and the solvent removed under vacuum. The resulting dark red-brown oily residue was dissolved in dry dichloromethane (50 mL), Celite® was added and the solvent removed under vacuum. The resulting powder was Soxhlet extracted into dry hexane. The hexane solution was evaporated to leave a red oil which solidified under high vacuum to give a red solid (2.84 g, 66 %). The product was not characterised but used immediately for subsequent reactions.

4-Carboxy-4'-methyl-2,2'-bipyridine 10⁹

4,4'-Dimethyl-2,2'-bipyridine (11.80 g, 64.0 mmol) and selenium dioxide (8.34 g, 75.1 mmol) were suspended in 1,4-dioxane (500 mL) and heated to reflux for 24 hours. The mixture was filtered while hot through Celite® to remove elemental selenium, the residue washed with hot 1,4-dioxane (3 × 50 mL) and the solvent removed under reduced pressure. The yellow-orange residue was stirred in ethanol (250 mL) and a solution of silver nitrate (11.92 g, 70.2 mmol) in water (80 mL) added dropwise. The suspension was stirred rapidly as aqueous sodium hydroxide (1 M, 200 mL) was added dropwise over 20 minutes to form silver oxide. The dark brown / black mixture was stirred rapidly for 18 hours, freed of ethanol and filtered through Celite®. The solid residue was washed with aqueous sodium hydroxide (1 M, 100 mL) and water (60 mL) and the combined alkaline filtrates washed with dichloromethane (3 × 100 mL) to remove any unreacted starting material. Acidification of the aqueous layer to pH 3 with aqueous acetic acid / hydrochloric acid (3 M, 1:1 v/v) produced a white precipitate. The mixture was left in a

refrigerator (4 °C) overnight, then the solid was collected by filtration, dried and Soxhlet extracted with acetone (1 L) for 5 days. The solvent was removed under reduced pressure to yield the product as a white powder (4.14 g, 30 %). ^1H NMR (300 MHz, d_6 -DMSO): δ 8.83 (d, $J = 5.1$ Hz, bipy H^6 , 1H), 8.78 (s, bipy H^3 , 1H), 8.54 (d, $J = 5.1$, bipy $H^{6'}$, 1H), 8.24 (s, bipy $H^{3'}$, 1H), 7.83 (d, $J = 5.1$ Hz, bipy H^5 , 1H), 7.30 (d, $J = 5.1$ Hz, bipy $H^{5'}$, 1H), 2.42 (s, CH_3 , 3H).

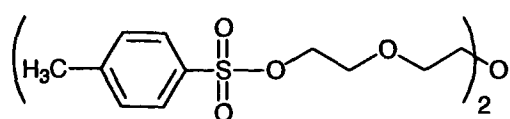
4-Chlorocarbonyl-4'-methyl-2,2'-bipyridine 11



Compound **10** (0.22 g, 1.0 mmol) was suspended in thionyl chloride (10 mL) and heated to reflux overnight under nitrogen to give a clear golden yellow solution.

The excess liquid was removed under vacuum and the solid product dried under vacuum for several hours. The product was not characterised but used immediately for subsequent reactions.

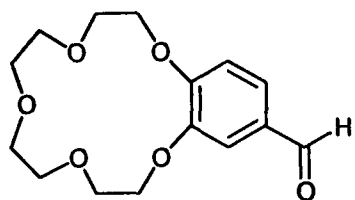
Tetraethyleneglycol ditosylate 12¹⁰



A solution of *p*-toluenesulfonyl chloride (25.09 g, 131.6 mmol) in tetrahydrofuran (35 mL) was added dropwise over 30 minutes to a stirred and cooled (5 °C) biphasic mixture of tetraethyleneglycol (11.67 g, 60.1 mmol) in tetrahydrofuran (35 mL) and sodium hydroxide (14.06 g, 351.5 mmol) in water (35 mL). The mixture was stirred at 0 °C for a further 2 hours then quenched by pouring into ice-water (100 mL). The product was extracted with dichloromethane (4 × 50 mL) and washed with water (2 × 100 mL) and saturated aqueous sodium chloride (100 mL). The organic layer was dried over anhydrous magnesium sulphate, filtered and the solvent removed under vacuum to give the product as a colourless oil (27.34 g, 91 %). ^1H NMR (300 MHz, CDCl_3): δ 7.77 (d, $J = 7.5$ Hz, Ar H , 4H), 7.32 (d, $J = 7.5$ Hz, Ar H , 4H), 4.15 (t, $J = 4.8$ Hz,

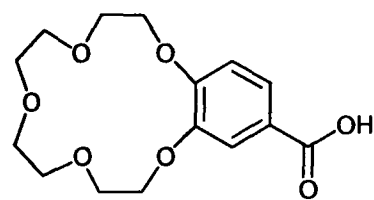
TsOCH₂CH₂O, 4H), 3.67 (t, $J = 4.8$ Hz, TsOCH₂CH₂O, 4H), 3.56 (s, OCH₂CH₂O, 8H), 2.44 (s, ArCH₃, 6H).

4-Formylbenzo[15]crown-5 **13**¹¹



A solution of **12** (10.12 g, 20.1 mmol) in dry acetonitrile (400 mL) was added dropwise to a stirred solution of 3,4-dihydroxybenzaldehyde (2.79 g, 20.2 mmol) and caesium fluoride (25g, 8-fold excess) in dry acetonitrile (200 mL) under a nitrogen atmosphere. The mixture was heated to reflux for 20 hours, cooled to room temperature, filtered and the solvent removed under vacuum. The resulting yellow oil was dissolved in chloroform (100 mL), extracted with aqueous sodium hydroxide (10 %, 100 mL), water (100 mL) and saturated aqueous sodium chloride (100 mL), dried over anhydrous magnesium sulphate and the solvent evaporated to give a pale yellow oil. The product was extracted with hot diisopropylether from which the pure product crystallised on standing for several days as a pale yellow solid (4.26 g, 71 %). ¹H NMR (300 MHz, *d*₆-DMSO): δ 9.79 (s, CHO, 1H), 7.52 (d, $J = 8.1$ Hz, ArH, 1H), 7.35 (s, ArH, 1H), 7.12 (d, $J = 8.1$ Hz, ArH, 1H), 4.14 & 4.09 (m, ArOCH₂CH₂O, 2 $\times$ 2H), 3.77 (m, ArOCH₂CH₂O, 4H), 3.60 (s, OCH₂CH₂O, 8H).

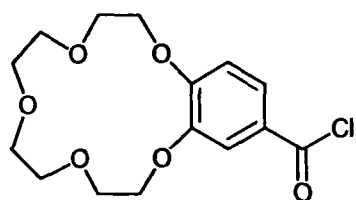
4-Carboxybenzo[15]crown-5 **14**¹²



Compound **13** (2.05 g, 6.9 mmol) was added to a solution of sodium carbonate (0.73 g, 6.9 mmol) in water (10 mL) maintained at 0 °C by an ice bath. Potassium permanganate (1.85 g, 11.7 mmol) in water (60 mL) was added dropwise to the solution over 1 hour and the brown-purple mixture stirred at room temperature overnight. The precipitated solid was removed by filtration through Celite® and the filtrate acidified to pH 1 with aqueous sulphuric acid (1 M). The solution was washed with dichloromethane (4 $\times$ 100 mL) and the organic extracts dried over anhydrous magnesium sulphate, filtered and evaporated to dryness to yield a white solid (1.55 g, 72 %). ¹H NMR

(300 MHz, d_6 -DMSO): δ 12.62 (s, OH, 1H), 7.52 (d, J = 8.4 Hz, ArH, 1H), 7.39 (s, ArH, 1H), 6.99 (d, J = 8.4 Hz, ArH, 1H), 4.07 (m, ArOCH₂CH₂O, 4H), 3.76 (m, ArOCH₂CH₂O, 4H), 3.60 (s, OCH₂CH₂O, 8H).

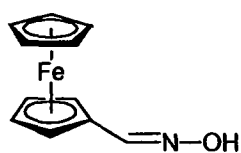
4-(Chlorocarboxy)benzo[15]crown-5 **15**



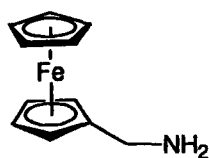
A drop of pyridine was added to a suspension of **14** (1.47 g, 4.7 mmol) in dry dichloromethane (25 mL) and the reaction mixture cooled in an ice bath. Oxalyl chloride (5 mL, excess) was added and the mixture

allowed to regain room temperature while stirring under nitrogen overnight. The clear solution was evaporated, dry dichloromethane was twice added and removed to ensure the complete removal of oxalyl chloride and the solid dried under high vacuum for several hours. The product was not characterised but used immediately for subsequent reactions.

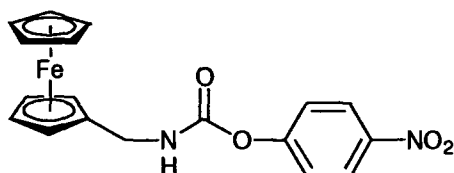
Ferrocene carboxaldehyde oxime **16**¹³



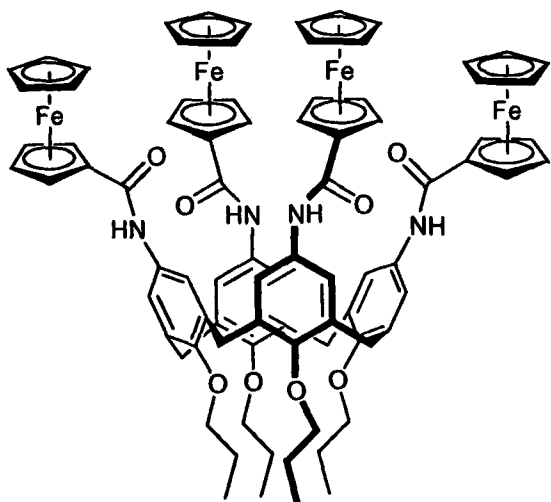
A solution of hydroxylamine hydrochloride (2.82 g, 40.6 mmol) in water (6 mL) was added to a solution of ferrocene carboxaldehyde (6.03 g, 28.2 mmol) in absolute ethanol (30 mL). Finely powdered sodium hydroxide (2.60 g, 65.0 mmol) was added portion-wise with care and the mixture heated to reflux for 4 hours, cooled to room temperature and water (150 mL) added. The mixture was filtered and the alkaline filtrate neutralised by bubbling a slow stream of carbon dioxide through it for 2 hours. The orange crystalline precipitate was isolated by filtration, washed with water and dried rigorously under vacuum (4.62 g, 72 %). ¹H NMR (300 MHz, CDCl₃): δ 7.96 (s, N=CH, 1H), 7.56 (s, OH, 1H), 4.51 & 4.34 (both s, C₅H₄, 2 × 2H), 4.21 (s, C₅H₅, 5H).

Ferrocene methylamine 17¹³

Compound **16** (2.25 g, 9.8 mmol) was dissolved in dry tetrahydrofuran (80 mL), lithium aluminium hydride (1.70 g, excess) was added portion-wise and the mixture stirred under nitrogen for 6 hours. Toluene (80 mL) then ethylacetate (15 mL) were added (with care) followed by a few drops of aqueous sodium hydroxide (5 M) to complete the precipitation of the inorganics. The mixture was filtered and the gummy residue washed with copious amounts of 4:1 toluene / methanol. The orange filtrate was evaporated to dryness then redissolved in dichloromethane and the solution filtered and evaporated. Column chromatography (silica, methanol then 95:5 methanol / aqueous ammonia) afforded the product as a yellow solid (1.71 g, 81 %). ¹H NMR (300 MHz, CDCl₃): δ 4.13 (m, C₅H₄ & C₅H₅, 9H), 3.54 (s, CH₂, 2H).

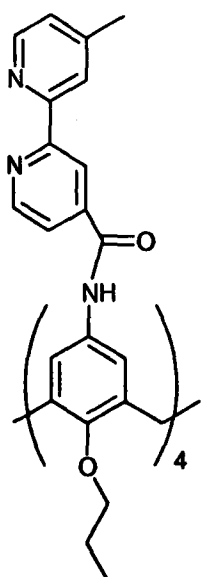
Ferrocene mononitrophenolate 18

p-Nitrophenol chloroformate (1.13 g, 5.6 mmol) was added to a solution of **17** (1.20 g, 5.6 mmol) and ethyldiisopropylamine (1 mL, excess) in dichloromethane (50 mL) and the resulting mixture stirred under nitrogen overnight. The solvent was removed under vacuum and the residue purified by column chromatography (silica, 4:1 ethylacetate / hexane) to yield the product as an orange solid (1.85 g, 87 %). ¹H NMR (300 MHz, CDCl₃): δ 8.25 (d, *J* = 9.3 Hz, ArH, 2H), 7.32 (d, *J* = 9.3 Hz, ArH, 2H), 5.31 (br, NH, 1H), 4.25 - 4.10 (m, C₅H₄ & C₅H₅ & CH₂, 11H).

Tetra(Fcamide)calix 19

A solution of **4** (500 mg, 0.77 mmol) in dry dichloromethane (50 mL) was added dropwise to a stirred solution of **9** (1150 mg, 4.63 mmol) and triethylamine (5 mL, excess) in dry dichloromethane (50 mL) and the mixture was stirred for 48 hours under a nitrogen atmosphere. Water (100 mL) was added and the mixture

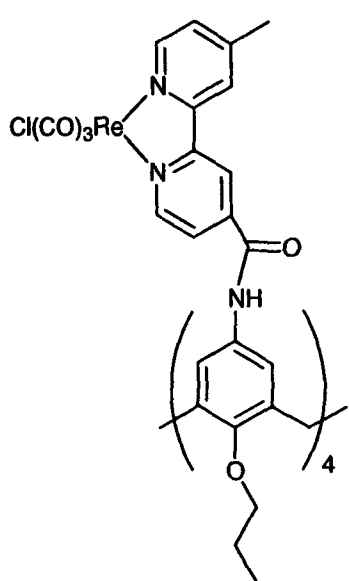
stirred for 30 minutes. The organic fraction was separated, washed with water (100 mL), dried over anhydrous magnesium sulphate, filtered, and the solvent removed under vacuum. The product was obtained as a pale yellow-orange powder after precipitation from a chloroform / hexane solution, followed by filtration and washing with hexane (1040 mg, 90 %). (Found: C, 66.5; H, 5.1; N, 3.7 %. $C_{84}H_{84}Fe_4N_4O_8$ requires C, 67.2; H, 5.6; N, 3.7 %.) FAB-MS m/z : 1501.5 (M^+), 1524.5 (MNa^+). 1H NMR (300 MHz, d_6 -DMSO): δ 9.18 (s, NH, 4H), 7.18 (s, ArH, 8H), 4.86 (s, C_5H_4 , 8H), 4.43 (d, $J = 12.6$ Hz, $ArCH_{ax}H_{eq}Ar$, 4H), 4.31 (s, C_5H_4 , 8H), 4.14 (s, C_5H_5 , 20H), 3.85 (t, $J = 7.5$ Hz, $OCH_2CH_2CH_3$, 8H), 3.20 (d, $J = 12.6$ Hz, $ArCH_{ax}H_{eq}Ar$, 4H), 1.98 (sext, $J = 7.5$ Hz, $OCH_2CH_2CH_3$, 8H), 1.00 (t, $J = 7.5$ Hz, $OCH_2CH_2CH_3$, 12H). X-ray quality orange crystals of **19**·3CH₃OH·3CHCl₃ were obtained from a chloroform solution of the compound exposed to methanol (see Appendix F.2).

Compound 20

Procedure was the same as that for **19**, except **4** (300 mg, 0.46 mmol) and **11** (600 mg, 2.58 mmol) were used. The product was obtained as a light brown solid after precipitation from chloroform / hexane (480 mg, 73 %). (Found: C, 73.3; H, 6.1; N, 11.5 %. $C_{88}H_{84}N_{12}O_8$ requires C, 73.5; H, 5.9; N, 11.7 %.) FAB-MS m/z : 1438.3 (MH^+). 1H NMR (300 MHz, d_6 -DMSO): δ 10.35 (s, NH,

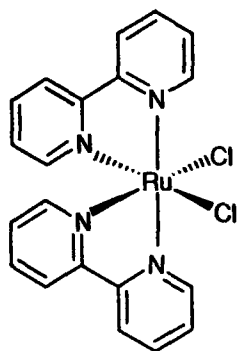
4H), 8.70 (s, $\text{bipy}H^3$, 4H), 8.65 (d, $J = 5.1$ Hz, $\text{bipy}H^6$, 4H), 8.32 (d, $J = 5.1$ Hz, $\text{bipy}H^{6'}$, 4H), 8.17 (s, $\text{bipy}H^{3'}$, 4H), 7.75 (d, $J = 5.1$ Hz, $\text{bipy}H^5$, 4H), 7.29 (s, ArH, 8H), 7.19 (d, $J = 5.1$ Hz, $\text{bipy}H^{5'}$, 4H), 4.46 (d, $J = 12.9$ Hz, $\text{ArCH}_{\text{ax}}\text{H}_{\text{eq}}\text{Ar}$, 4H), 3.87 (t, $J = 7.2$ Hz, $\text{OCH}_2\text{CH}_2\text{CH}_3$, 8H), 3.23 (d, $J = 12.9$ Hz, $\text{ArCH}_{\text{ax}}\text{H}_{\text{eq}}\text{Ar}$, 4H), 2.38 (s, CH_3 , 12H), 1.97 (sext, $J = 7.2$ Hz, $\text{OCH}_2\text{CH}_2\text{CH}_3$, 8H), 1.00 (t, $J = 7.2$ Hz, $\text{OCH}_2\text{CH}_2\text{CH}_3$, 12H).

Tetra(Rebpy)calix 21



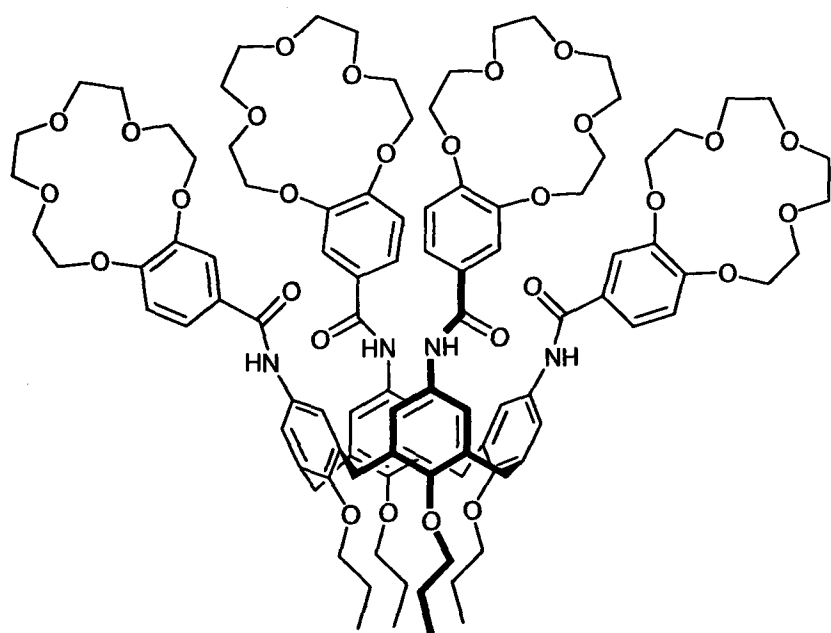
A solution of rhenium pentacarbonyl chloride (310 mg, 0.86 mmol) in dry tetrahydrofuran (40 mL) was heated to reflux for 30 minutes. A solution of **20** (220 mg, 0.15 mmol) in dry tetrahydrofuran (20 mL) was added dropwise with stirring and the mixture heated to reflux under nitrogen overnight. The solvent was removed under vacuum and the residue purified by column chromatography (silica, 30:1 dichloromethane / methanol). Precipitation from dichloromethane /

hexane afforded the product as a yellow-brown solid (180 mg, 44 %). (Found: C, 44.3; H, 3.4; N, 6.0 %. $\text{C}_{100}\text{H}_{84}\text{Cl}_4\text{N}_{12}\text{O}_{20}\text{Re}_4$ requires C, 45.1; H, 3.2; N, 6.3 %.) FAB-MS m/z : 2624.7 (M^+Cl^-). ^1H NMR (300 MHz, d_6 -DMSO): δ 10.64 (s, NH, 4H), 9.09 (d, $J = 5.1$ Hz, $\text{bipy}H^6$, 4H), 8.98 (s, $\text{bipy}H^3$, 4H), 8.81 (d, $J = 5.1$ Hz, $\text{bipy}H^{6'}$, 4H), 8.60 (s, $\text{bipy}H^{3'}$, 4H), 7.99 (d, $J = 5.1$ Hz, $\text{bipy}H^5$, 4H), 7.50 (d, $J = 5.1$ Hz, $\text{bipy}H^{5'}$, 4H), 7.41 (s, ArH, 8H), 4.52 (d, $J = 11.7$ Hz, $\text{ArCH}_{\text{ax}}\text{H}_{\text{eq}}\text{Ar}$, 4H), 3.91 (t, $\text{OCH}_2\text{CH}_2\text{CH}_3$, 8H), 3.31 (d, $J = 11.7$ Hz, $\text{ArCH}_{\text{ax}}\text{H}_{\text{eq}}\text{Ar}$, 4H), 2.31 (s, CH_3 , 12H), 2.02 (sext, $J = 7.2$ Hz, $\text{OCH}_2\text{CH}_2\text{CH}_3$, 8H), 1.02 (t, $J = 7.2$ Hz, $\text{OCH}_2\text{CH}_2\text{CH}_3$, 12H).

Cis-bis(2,2'-bipyridyl)dichlororuthenium(II) 39¹⁴

Ruthenium(III) chloride (3.02 g, 14.6 mmol) and anhydrous lithium chloride (3.37 g, 79.5 mmol) were dissolved in dimethylformamide (40 mL). 2,2'-Bipyridine (3.58 g, 22.9 mmol) was added and the mixture brought to reflux for 8 hours, cooled to room temperature, poured into rapidly stirred acetone

(200 mL) and stored in a freezer (-18 °C) overnight. The precipitate was isolated by filtration and washed with water (3 × 10 mL) and diethylether (3 × 10 mL). The crude product was purified by heating to reflux in methanol (50 mL) for 5 minutes to dissolve any soluble impurities, mainly tris(2,2'-bipyridyl)dichlororuthenium(III). The solution was filtered to yield the pure product as a fine black powder (3.23 g, 43 %). ¹H NMR (300 MHz, *d*₆-DMSO): δ 9.96 (d, *J* = 5.5 Hz, bipy $H^{6'}$, 2H), 8.63 (d, *J* = 8.5 Hz, bipy $H^{3'}$, 2H), 8.47 (d, *J* = 8.5 Hz, bipy H^3 , 2H), 8.05 (t, *J* = 7.5 Hz, bipy $H^{4'}$, 2H), 7.76 (t, *J* = 6.5 Hz, bipy H^5 , 2H), 7.67 (t, *J* = 7.5 Hz, bipy H^4 , 2H), 7.50 (d, *J* = 5.5 Hz, bipy H^6 , 2H), 7.09 (t, *J* = 6.5 Hz, bipy H^5 , 2H).

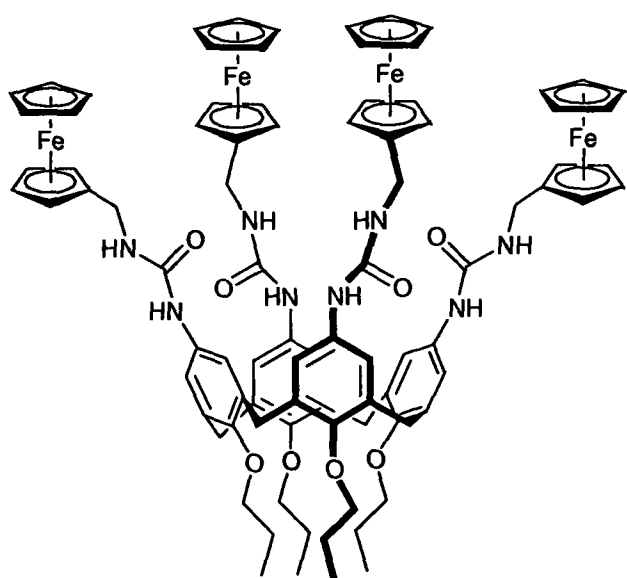
Tetra(crown)calix 22

A solution of **4** (300 mg, 0.46 mmol) in dry chloroform (50 mL) was added dropwise to a stirred solution of **15** (910 mg, 2.75 mmol) and triethylamine (2 mL, excess) in dry chloroform (50 mL) and the mixture heated to reflux under nitrogen overnight. The heat was removed and

aqueous lithium hydroxide (1M, 50 mL) added and the solution stirred at room temperature overnight. The organic layer was separated, washed with water (50 mL), dried over anhydrous magnesium sulphate, filtered and the solvent removed under vacuum. The product was obtained as a white solid after precipitation from chloroform / hexane (480 mg, 57 %).

(Found: C, 65.1; H, 7.0; N, 3.1 %. $C_{100}H_{124}N_4O_{28}$ requires C, 65.6; H, 6.8; N, 3.1 %.) ES-MS m/z : 633.1 (MNa_3^{3+}), 638.4 (MNa_2K^{3+}), 938.1 (MNa_2^{2+}), 946.1 ($MNaK^{2+}$), 1853.2 (MNa^+), 1869.2 (MK^+). 1H NMR (500 MHz, d_6 -DMSO): δ 9.74 (s, NH, 4H), 7.48 (d, $J = 8.5$ Hz, benzoArH, 4H), 7.43 (s, benzoArH, 4H), 7.20 (s, ArH, 8H), 6.89 (d, $J = 8.5$ Hz, benzoArH, 4H), 4.43 (d, $J = 12.5$ Hz, $ArCH_{ax}H_{eq}Ar$, 4H), 4.05 & 4.00 (both s, $ArOCH_2CH_2O$, $2 \times 8H$), 3.84 (t, $J = 7.0$ Hz, $OCH_2CH_2CH_3$, 8H), 3.75 & 3.71 (both s, $ArOCH_2CH_2O$, $2 \times 8H$), 3.59 (s, OCH_2CH_2O , 32H), 3.16 (d, $J = 12.5$ Hz, $ArCH_{ax}H_{eq}Ar$, 4H), 1.93 (sext, $J = 7.0$ Hz, $OCH_2CH_2CH_3$, 8H), 0.96 (t, $J = 7.0$ Hz, $OCH_2CH_2CH_3$, 12H).

Tetra(Fcurea)calix 23

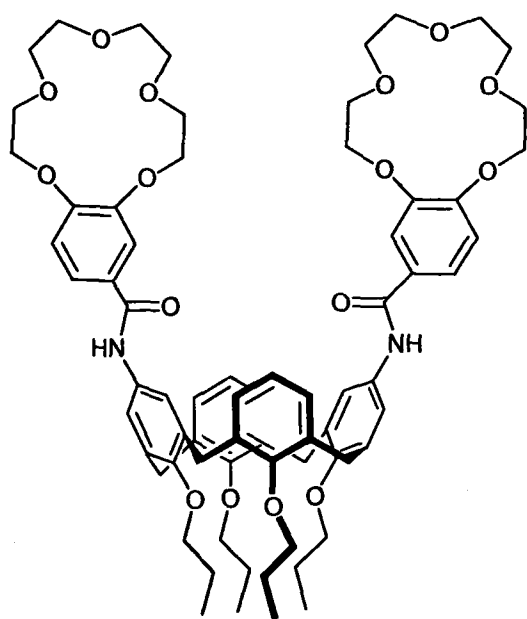


A solution of **4** (500 mg, 0.77 mmol) in dry dichloromethane (20 mL) was added dropwise to a stirred solution of **18** (1750 mg, 4.61 mmol), ethyldiisopropylamine (2 mL, excess) and 4-dimethylaminopyridine (DMAP, catalytic) in dry dichloromethane (20 mL) and the mixture was stirred for 24 hours under a nitrogen atmosphere. The

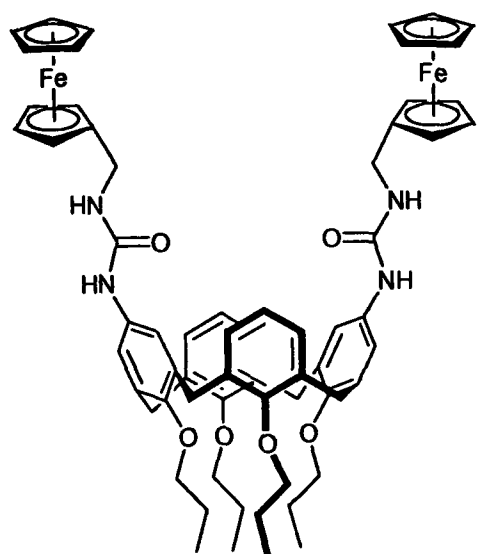
reaction mixture was washed repeatedly with sodium carbonate solution (10 %, 4×50 mL) then the organic fraction was dried over anhydrous magnesium sulphate, filtered, and the solvent removed under vacuum. The residue was purified by column chromatography (silica, 10 % methanol in chloroform). The product was obtained as a pale yellow powder after precipitation from a chloroform / hexane solution, followed by filtration and washing with hexane (590 mg, 48 %). (Found: C, 63.5; H, 5.8; N, 6.8 %. $C_{88}H_{96}Fe_4N_8O_8 \cdot \frac{1}{2}CHCl_3$ requires C, 63.4; H, 5.8; N, 6.7 %.) ES-MS m/z : 1617.5 (MH^+), 1656.4 (MK^+). 1H NMR (500 MHz, d_6 -DMSO): δ 8.19 (s, ArNH, 4H), 6.77 (s, ArH, 8H), 5.90 (t, $J = 5.5$ Hz, CH_2NH , 4H), 4.30 (d, $J = 13.0$ Hz, $ArCH_{ax}H_{eq}Ar$, 4H), 4.16 (s, C_5H_5 , 20H), 4.13 (s, C_5H_4 , 8H), 4.07 (s, C_5H_4 ,

8H), 3.93 (d, $J = 5.5$ Hz, CH_2NH , 8H), 3.74 (t, $J = 7.5$ Hz, $\text{OCH}_2\text{CH}_2\text{CH}_3$, 8H), 3.02 (d, $J = 13.0$ Hz, $\text{ArCH}_{\text{ax}}\text{H}_{\text{eq}}\text{Ar}$, 4H), 1.89 (sext, $J = 7.5$ Hz, $\text{OCH}_2\text{CH}_2\text{CH}_3$, 8H), 0.93 (t, $J = 7.5$ Hz, $\text{OCH}_2\text{CH}_2\text{CH}_3$, 12H). ^1H NMR (500 MHz, C_6D_6): δ 8.18 (d, $J = 2.5$ Hz, ArH , 4H), 8.04 (s, ArNH , 4H), 7.46 (t, $J = 5.5$ Hz, CH_2NH , 4H), 6.69 (d, $J = 2.5$ Hz, ArH , 4H), 4.76 (d, $J = 12.0$ Hz, $\text{ArCH}_{\text{ax}}\text{H}_{\text{eq}}\text{Ar}$, 4H), 4.51 & 4.45 (both dd, $J = 14.5$ & 5.5 Hz, CH_2NH , $2 \times 4\text{H}$), 4.41 (s, C_5H_4 , 4H), 4.22 (s, C_5H_4 , 4H), 4.11 (s, C_5H_5 , 20H), 3.93 (s, C_5H_4 , 4H), 3.89 (t, $J = 7.5$ Hz, $\text{OCH}_2\text{CH}_2\text{CH}_3$, 8H), 3.85 (s, C_5H_4 , 4H), 3.43 (d, $J = 12.0$ Hz, $\text{ArCH}_{\text{ax}}\text{H}_{\text{eq}}\text{Ar}$, 4H), 2.07 (sext, $J = 7.5$ Hz, $\text{OCH}_2\text{CH}_2\text{CH}_3$, 8H), 0.89 (t, $J = 7.5$ Hz, $\text{OCH}_2\text{CH}_2\text{CH}_3$, 12H). X-ray quality crystals (orange-yellow blocks) of $23 \cdot 3\text{CH}_3\text{OH} \cdot 3\text{CHCl}_3$ were obtained from a chloroform solution of the compound exposed to methanol (see Appendix F.3).

Bis(crown)calix 25



Procedure was the same as that for **22**, except **24** (220 mg, 0.35 mmol) and **15** (350 mg, 1.06 mmol) were used. The product was obtained as a white solid after precipitation from chloroform / hexane (270 mg, 63 %). (Found: C, 68.2; H, 6.8; N, 2.3 %. $\text{C}_{70}\text{H}_{86}\text{N}_2\text{O}_{16}$ requires C, 69.4; H, 7.2; N, 2.3 %.) ES-MS m/z : 1249.8 (MK^+). ^1H NMR (500 MHz, d_6 -DMSO): δ 9.85 (s, NH , 2H), 7.58 (d, $J = 8.5$ Hz, benzoArH, 2H), 7.54 (s, benzoArH, 2H), 7.40 (s, ArH, 4H), 7.02 (d, $J = 8.5$ Hz, benzoArH, 2H), 6.38 (m, ArH, 6H), 4.36 (d, $J = 13.0$ Hz, $\text{ArCH}_{\text{ax}}\text{H}_{\text{eq}}\text{Ar}$, 4H), 4.10 (s, $\text{ArOCH}_2\text{CH}_2\text{O}$, 8H), 3.90 (t, $J = 7.5$ Hz, $\text{OCH}_2\text{CH}_2\text{CH}_3$, 4H), 3.78 (s, $\text{ArOCH}_2\text{CH}_2\text{O}$, 8H), 3.67 (t, $J = 7.5$ Hz, $\text{OCH}_2\text{CH}_2\text{CH}_3$, 4H), 3.61 (s, $\text{OCH}_2\text{CH}_2\text{O}$, 16H), 3.12 (d, $J = 13.0$ Hz, $\text{ArCH}_{\text{ax}}\text{H}_{\text{eq}}\text{Ar}$, 4H), 1.94 & 1.86 (both sext, $J = 7.5$ Hz, $\text{OCH}_2\text{CH}_2\text{CH}_3$, $2 \times 4\text{H}$), 1.03 & 0.89 (both t, $J = 7.5$ Hz, $\text{OCH}_2\text{CH}_2\text{CH}_3$, $2 \times 6\text{H}$).

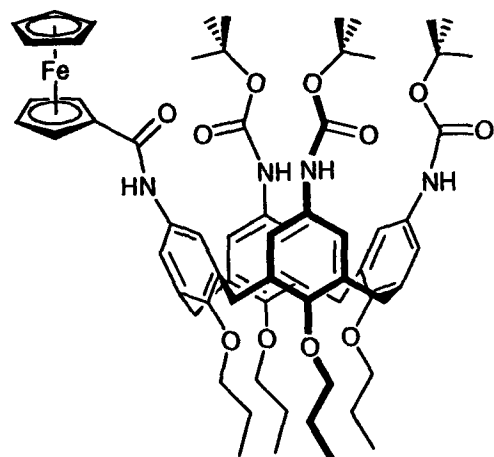
Bis(Fcurea)calix 26

Procedure was the same as that for **23**, except **24** (300 mg, 0.48 mmol) and **18** (400 mg, 1.05 mmol) were used. The product was obtained as an orange solid after column chromatography and solvent removal (360 mg, 68 %). (Found: C, 68.7; H, 6.4; N, 4.7 %. $C_{64}H_{72}Fe_2N_4O_6$ requires C, 69.6; H, 6.6; N, 5.1 %.)

ES-MS m/z : 1105.6 (MH^+). 1H NMR (500 MHz, d_6 -DMSO): δ

8.23 (s, ArNH, 2H), 6.96 (s, ArH, 4H), 6.41 (m, ArH, 6H), 6.02 (t, $J = 5.5$ Hz, CH_2NH , 2H), 4.30 (d, $J = 13.0$ Hz, $ArCH_{ax}H_{eq}Ar$, 4H), 4.17 (m, C_5H_4 & C_5H_5 , 14H), 4.09 (s, C_5H_4 , 4H), 3.97 (d, $J = 5.5$ Hz, CH_2NH , 4H), 3.80 & 3.68 (both t, $J = 7.5$ Hz, $OCH_2CH_2CH_3$, $2 \times 4H$), 3.06 (d, $J = 13.0$ Hz, $ArCH_{ax}H_{eq}Ar$, 4H), 1.88 & 1.84 (both sext, $J = 7.5$ Hz, $OCH_2CH_2CH_3$, $2 \times 4H$), 0.99 & 0.88 (both t, $J = 7.5$ Hz, $OCH_2CH_2CH_3$, $2 \times 6H$). 1H NMR (300 MHz, C_6D_6): δ 7.10 (d, $J = 7.5$ Hz, ArH, 4H), 6.95 (t, $J = 7.5$ Hz, ArH, 2H), 6.70 (s, ArNH, 2H), 6.34 (s, ArH, 4H), 5.47 (t, CH_2NH , 2H), 4.47 (d, $J = 13.5$ Hz, $ArCH_{ax}H_{eq}Ar$, 4H), 4.16 (d, $J = 5.0$ Hz, CH_2NH , 4H), 4.13 (s, C_5H_4 , 4H), 4.00 (s, C_5H_5 , 10H), 3.93 (s, C_5H_4 , 4H), 4.00 & 3.55 (both t, $J = 7.5$ Hz, $OCH_2CH_2CH_3$, $2 \times 4H$), 3.09 (d, $J = 13.5$ Hz, $ArCH_{ax}H_{eq}Ar$, 4H), 1.90 & 1.66 (both sext, $J = 7.5$ Hz, $OCH_2CH_2CH_3$, $2 \times 4H$), 0.91 & 0.77 (both t, $J = 7.5$ Hz, $OCH_2CH_2CH_3$, $2 \times 6H$). X-ray quality crystals (pale orange blocks) of $26 \cdot 2[N(C_4H_9)_4][C_6H_5CO_2]$ were obtained from a 1:1 CD_3CN / d_6 -DMSO solution of the compound containing a ten-fold excess of tetrabutylammonium benzoate (see Appendix F.4).

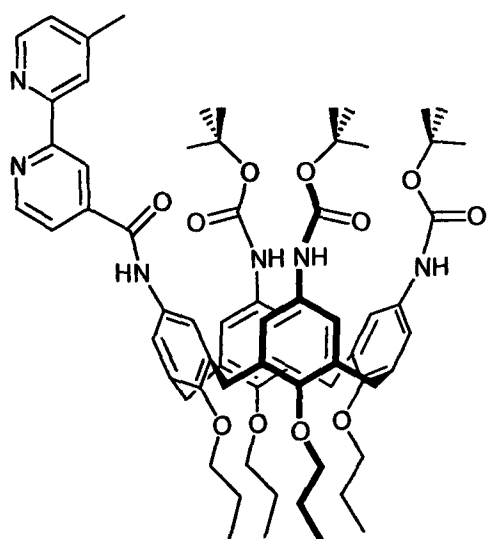
Compound 27



Procedure was the same as that for **19**, except **5** (980 mg, 1.03 mmol) and **9** (390 mg, 1.57 mmol) were used. The product was obtained as a pale orange powder after precipitation from a chloroform / hexane solution, followed by filtration and washing with hexane (810 mg, 68 %). (Found: C, 67.9; H, 7.0; N, 4.9 %. $C_{66}H_{84}FeN_4O_{11}$ requires C, 68.0; H, 7.3; N, 4.8 %.)

FAB-MS m/z : 865.5 ($M-3(BOC)H^+$), 965.5 ($M-2(BOC)H^+$), 1065.4 ($M-(BOC)H^+$), 1165.5 (MH^+), 1187.5 (MNa^+). 1H NMR (300 MHz, d_6 -DMSO): δ 9.07 (s, FcNH, 1H), 8.86 (s, BOCNH, 2H), 8.65 (s, BOCNH, 1H), 6.93 (s, ArH, 2H), 6.89 (s, ArH, 4H), 6.66 (s, ArH, 2H), 4.89 (s, C_5H_4 , 2H), 4.34 (s, C_5H_4 , 2H), 4.32 (d, $ArCH_{ax}H_{eq}Ar$, 4H), 4.13 (s, C_5H_5 , 5H), 3.79 (m, $OCH_2CH_2CH_3$, 8H), 3.07 & 3.00 (both d, $J = 12.9$ Hz, $ArCH_{ax}H_{eq}Ar$, $2 \times 2H$), 1.88 (sext, $J = 7.2$ Hz, $OCH_2CH_2CH_3$, 8H), 1.39 (s, CH_3 , 18H), 1.35 (s, CH_3 , 9H), 0.93 (m, $OCH_2CH_2CH_3$, 12H).

Compound 28

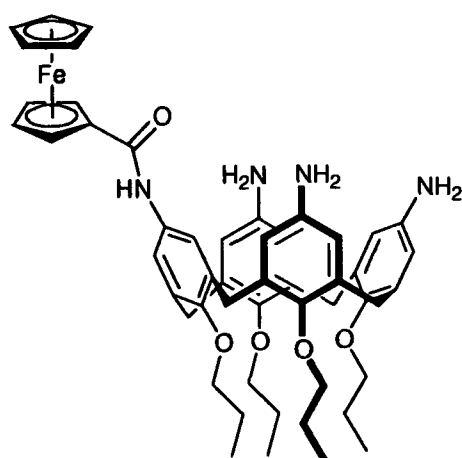


Procedure was the same as that for **19**, except **5** (450 mg, 0.47 mmol) and **11** (150 mg, 0.64 mmol) were used. The product was obtained as cream solid upon precipitation from chloroform / hexane (300 mg, 55 %). (Found: C, 69.3; H, 7.5; N, 7.1 %. $C_{67}H_{84}N_6O_{11}$ requires C, 70.0; H, 7.4; N, 7.3 %.)

FAB-MS m/z : 1049.3 ($M-(BOC)H^+$), 1149.5 (MH^+), 1171.4 (MNa^+). 1H NMR (300 MHz, d_6 -DMSO): δ 10.23 (s, bipyNH, 1H), 8.89 (s, BOCNH, 2H), 8.78 (d, $J = 4.8$ Hz, bipy H^6 , 1H), 8.75 (s, bipy H^3 , 1H), 8.56 (d, $J = 4.8$ Hz, bipy $H^{6'}$, 1H), 8.25 (s, bipy $H^{3'}$, 1H), 7.84 (d, $J = 4.8$ Hz, bipy H^5 , 1H), 7.32 (d, $J = 4.8$ Hz, bipy $H^{5'}$, 1H), 7.04 (s, ArH, 2H), 6.93 (s, ArH, 4H), 6.61 (s, ArH, 2H), 4.35 & 4.30 (both d, $J = 13.2$ Hz,

ArCH_{ax}H_{eq}Ar, 2 × 2H), 3.80 (m, OCH₂CH₂CH₃, 8H), 3.09 & 3.00 (both d, *J* = 13.2 Hz, ArCH_{ax}H_{eq}Ar, 2 × 2H), 2.42 (s, CH₃, 3H), 1.88 (sext, *J* = 7.2 Hz, OCH₂CH₂CH₃, 8H), 1.40 (s, CH₃, 18H), 1.26 (s, CH₃, 9H), 0.92 (m, OCH₂CH₂CH₃, 12H).

Compound 29

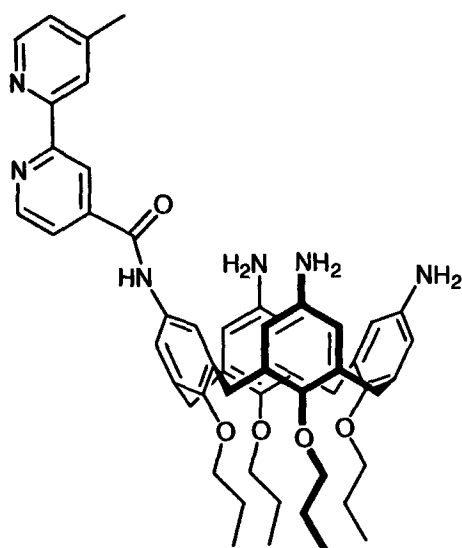


Trifluoroacetic acid (10 mL, excess) was added to a solution of **27** (700 mg, 0.60 mmol) in dichloromethane (50 mL) and the mixture stirred for 2 hours. The solvent was removed under vacuum and the residue dried under high vacuum for several hours to yield the product as its TFA salt (650 mg, 99 %).

(Found: C, 59.8; H, 5.7; N, 4.9 %. C₅₁H₆₀FeN₄O₅·2C₂HF₃O₂ requires C, 60.4; H, 5.7; N, 5.1 %.) ES-MS *m/z*: 865.7 (MH⁺). ¹H NMR (300 MHz, *d*₆-DMSO): δ 9.32 (s, FcNH, 1H), 7.39 & 6.92 & 6.34 & 6.25 (all s, ArH, 4 × 2H), 4.96 (s, C₅H₄, 2H), 4.43 (s, C₅H₄, 2H), 4.35 & 4.34 (both d, *J* = 13.2 Hz, ArCH_{ax}H_{eq}Ar, 2 × 2H), 4.21 (s, C₅H₅, 5H), 3.87 (t, *J* = 7.2 Hz, OCH₂CH₂CH₃, 4H), 3.72 & 3.70 (both t, *J* = 7.2 Hz, OCH₂CH₂CH₃, 2 × 2H), 3.28 & 3.19 (both d, *J* = 13.2 Hz, ArCH_{ax}H_{eq}Ar, 2 × 2H), 1.85 (sext, *J* = 7.2 Hz, OCH₂CH₂CH₃, 8H), 1.02 (t, *J* = 7.2 Hz, OCH₂CH₂CH₃, 6H), 0.89 & 0.88 (both t, *J* = 7.2 Hz, OCH₂CH₂CH₃, 2 × 3H).

To convert the product to its pure amine form, the TFA salt was dissolved in dichloromethane (100 mL) and the organic layer washed with aqueous sodium hydroxide (1M, 100 mL) and water (100 mL), dried over anhydrous magnesium sulphate, filtered, the solvent removed under vacuum and the product dried under high vacuum for several hours.

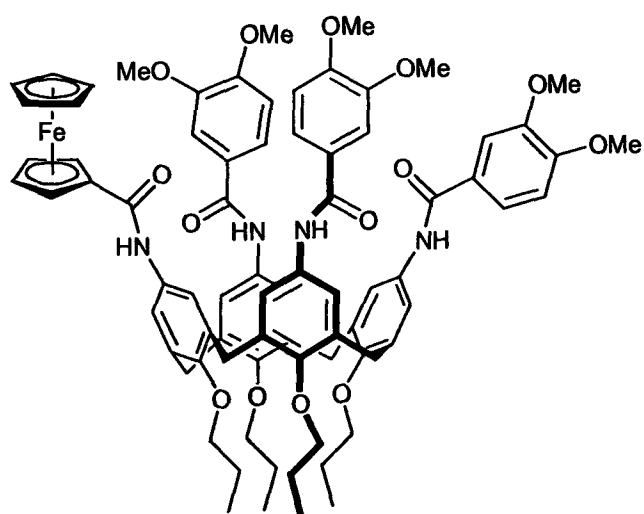
Compound 30



Procedure was the same as that for **29**, except **28** (110 mg, 0.10 mmol) was used. The solvent was removed under vacuum and the residue dried under high vacuum for several hours to yield the product as its TFA salt (80 mg, 78 %). (Found: C, 61.2; H, 6.0; N, 7.5 %. $C_{52}H_{60}N_6O_5 \cdot 2C_2HF_3O_2$ requires C, 62.4; H, 5.8; N, 7.8 %.) ES-MS m/z : 425.5 (MH_2^{2+}), 849.9 (MH^+). 1H NMR

(500 MHz, d_6 -DMSO): δ 10.53 (s, bipyNH, 1H), 8.90 (d, $J = 5.0$ Hz, bipyH⁶, 1H), 8.86 (s, bipyH³, 1H), 8.63 (d, $J = 5.0$ Hz, bipyH^{6'}, 1H), 8.34 (s, bipyH^{3'}, 1H), 7.90 (d, $J = 5.0$ Hz, bipyH⁵, 1H), 7.41 (d, $J = 5.0$ Hz, bipyH^{5'}, 1H), 7.50 & 6.92 & 6.38 & 6.28 (all s, ArH, 4 × 2H), 4.37 & 4.34 (both d, $J = 13.5$ Hz, ArCH_{ax}H_{eq}Ar, 2 × 2H), 3.89 (t, $J = 7.0$ Hz, OCH₂CH₂CH₃, 4H), 3.74 & 3.72 (both t, $J = 7.0$ Hz, OCH₂CH₂CH₃, 2 × 2H), 3.30 & 3.23 (both d, $J = 13.5$ Hz, ArCH_{ax}H_{eq}Ar, 2 × 2H), 2.44 (s, CH₃, 3H), 1.83 (sext, $J = 7.0$ Hz, OCH₂CH₂CH₃, 8H), 1.00 (t, $J = 7.0$ Hz, OCH₂CH₂CH₃, 6H), 0.88 & 0.87 (both t, $J = 7.0$ Hz, OCH₂CH₂CH₃, 2 × 3H).

Fctri(benzo)calix 31

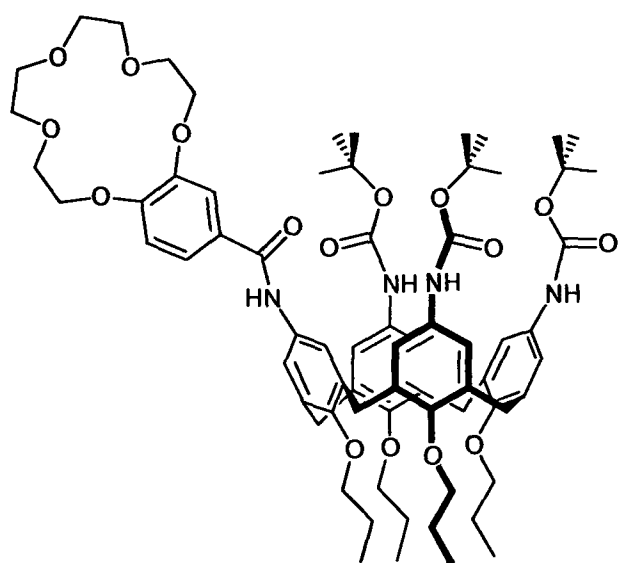


A solution of **29** (160 mg, 0.18 mmol) and triethylamine (2 mL, excess) in chloroform (30 mL) was stirred under nitrogen for 10 minutes. A solution of 3,4-dimethoxybenzoyl chloride (130 mg, 0.65 mmol) and triethylamine (2 mL, excess) in chloroform (30 mL) was stirred under nitrogen for 10

minutes. The amine solution was added dropwise to the stirred acid chloride solution and the mixture heated to reflux under nitrogen for 48 hours. The heat was removed, water (50 mL) was added and the mixture stirred for 30 minutes. The organic fraction was separated, washed

with water (50 mL), dried over anhydrous magnesium sulphate, filtered, and the solvent removed under vacuum. The residue was purified by column chromatography (silica, 30:1 chloroform / methanol) and the product obtained as a pale yellow solid after precipitation from chloroform / hexane (120 mg, 48 %). (Found: C, 68.9; H, 6.0; N, 4.2 %. $C_{78}H_{84}FeN_4O_{14}$ requires C, 69.0; H, 6.2; N, 4.1 %.) FAB-MS m/z : 1357.6 (MH^+), 1379.6 (MNa^+). 1H NMR (300 MHz, d_6 -DMSO): δ 9.78 (s, benzoNH, 1H), 9.72 (s, benzoNH, 2H), 9.17 (s, FcNH, 1H), 7.45 (m, benzoArH, 6H), 7.25 (s, ArH, 2H), 7.20 (s, ArH, 4H), 7.15 (s, ArH, 2H), 6.96 (d, benzoArH, 1H), 6.88 (d, $J = 8.4$ Hz, benzoArH, 2H), 4.88 (s, C_5H_4 , 2H), 4.44 (d, $J = 12.0$ Hz, $ArCH_{ax}H_{eq}Ar$, 4H), 4.32 (s, C_5H_4 , 2H), 4.15 (s, C_5H_5 , 5H), 3.75 (s, OCH_3 , 18H), 3.70 (m, $OCH_2CH_2CH_3$, 8H), 3.19 (d, $J = 12.0$ Hz, $ArCH_{ax}H_{eq}Ar$, 4H), 1.97 (m, $OCH_2CH_2CH_3$, 8H), 1.00 (m, $OCH_2CH_2CH_3$, 12H).

Compound 32

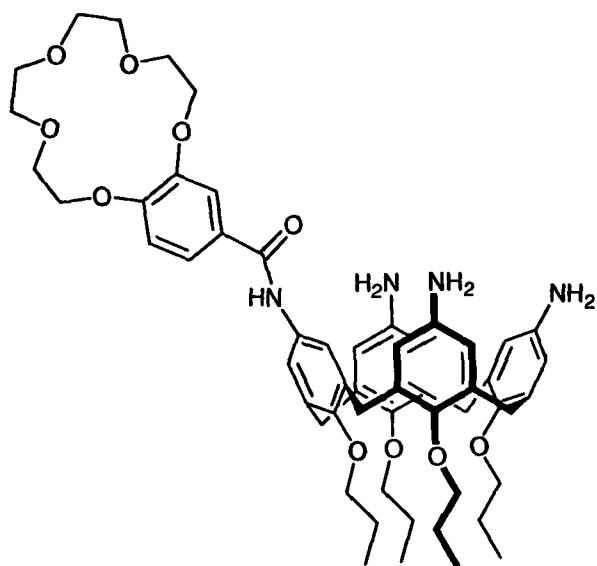


Procedure was the same as that for **22**, except **5** (990 mg, 1.04 mmol) and **15** (520 mg, 1.57 mmol) were used. The product was obtained as a white solid after precipitation from chloroform / hexane (860 mg, 66 %). (Found: C, 66.9; H, 7.4; N, 4.4 %. $C_{70}H_{94}N_4O_{16}$ requires C, 67.4; H, 7.6; N, 4.5 %.) FAB-MS m/z :

1147.2 ($M-(BOC)H^+$), 1247.2 (M^+), 1270.3 (MNa^+), 1286.4 (MK^+). 1H NMR (300 MHz, d_6 -DMSO): δ 9.68 (s, benzoNH, 1H), 8.84 (s, BOCNH, 2H), 8.68 (s, BOCNH, 1H), 7.51 (d, $J = 8.7$ Hz, benzoArH, 1H), 7.47 (s, benzoArH, 1H), 6.97 (d, $J = 8.7$ Hz, benzoArH, 1H), 7.03 & 6.90 & 6.86 & 6.71 (all s, ArH, $4 \times 2H$), 4.34 & 4.30 (both d, $J = 12.6$ Hz, $ArCH_{ax}H_{eq}Ar$, $2 \times 2H$), 4.07 (s, $ArOCH_2CH_2O$, 4H), 3.76 (m, $ArOCH_2CH_2O$ & $OCH_2CH_2CH_3$, 12H), 3.60 (s, OCH_2CH_2O , 8H), 3.06 & 3.01 (both d, $J = 12.6$ Hz, $ArCH_{ax}H_{eq}Ar$, $2 \times 2H$), 1.88 (sext, $J =$

7.5 Hz, $\text{OCH}_2\text{CH}_2\text{CH}_3$, 8H), 1.40 (s, CH_3 , 18H), 1.33 (s, CH_3 , 9H), 0.94 (m, $\text{OCH}_2\text{CH}_2\text{CH}_3$, 12H).

Compound 33



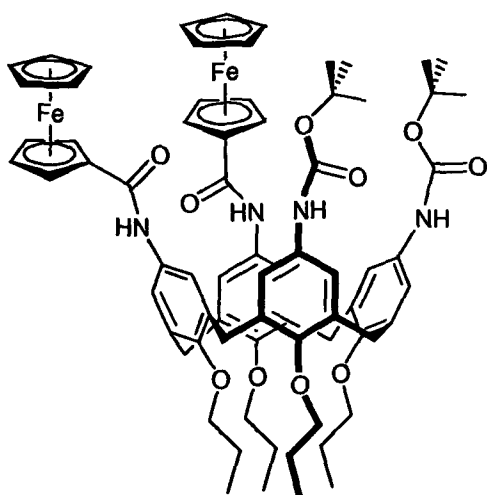
Procedure was the same as that for **29**, except **32** (740 mg, 0.59 mmol) was used. The product was obtained as its TFA salt after precipitation from chloroform / hexane (510 mg, 73 %). (Found: C, 59.8; H, 6.3; N, 4.6 %.

$\text{C}_{55}\text{H}_{70}\text{N}_4\text{O}_{10} \cdot 2\text{C}_2\text{HO}_2\text{F}_3$ requires C, 60.3; H, 6.2; N, 4.8

%. ES-MS m/z : 485.5 (MHNa^{2+}), 948.0 (MH^+), 970.0

(MNa^+). ^1H NMR (300 MHz, d_6 -DMSO): δ 9.87 (s, benzoNH, 1H), 7.55 (d, $J = 8.7$ Hz, benzoArH, 1H), 7.48 (s, benzoArH, 1H), 7.03 (d, $J = 8.7$ Hz, benzoArH, 1H), 7.35 & 6.87 & 6.46 & 6.37 (all s, ArH, $4 \times 2\text{H}$), 4.36 & 4.35 (both d, $J = 13.2$ Hz, $\text{ArCH}_{ax}\text{H}_{eq}\text{Ar}$, $2 \times 2\text{H}$), 4.10 (s, $\text{ArOCH}_2\text{CH}_2\text{O}$, 4H), 3.79 (m, $\text{ArOCH}_2\text{CH}_2\text{O}$ & $\text{OCH}_2\text{CH}_2\text{CH}_3$, 12H), 3.62 (s, $\text{OCH}_2\text{CH}_2\text{O}$, 8H), 3.32 & 3.22 (both d, $J = 13.2$ Hz, $\text{ArCH}_{ax}\text{H}_{eq}\text{Ar}$, $2 \times 2\text{H}$), 1.87 (sext, $J = 7.2$ Hz, $\text{OCH}_2\text{CH}_2\text{CH}_3$, 8H), 1.02 (t, $J = 7.2$ Hz, $\text{OCH}_2\text{CH}_2\text{CH}_3$, 6H), 0.92 & 0.91 (both t, $J = 7.2$ Hz, $\text{OCH}_2\text{CH}_2\text{CH}_3$, $2 \times 3\text{H}$).

Compound 34



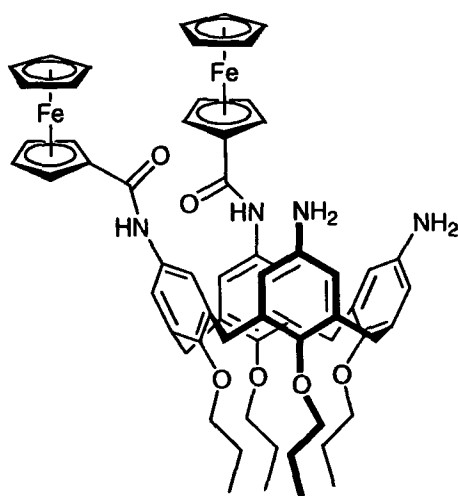
Procedure was the same as that for **19**, except **6** (990 mg, 1.16mmol) and **9** (870 mg, 3.50 mmol) were used. The product was obtained as a pale orange powder after precipitation from chloroform / hexane, followed by filtration and washing with hexane (1200 mg, 81 %). (Found: C, 67.2; H, 6.6; N, 4.4 %.

$\text{C}_{72}\text{H}_{84}\text{Fe}_2\text{N}_4\text{O}_{10}$ requires C, 67.7; H, 6.6; N, 4.4 %.) FAB-MS

m/z : 1078.3 ($\text{M}-2(\text{BOC})\text{H}^+$), 1178.3 ($\text{M}-(\text{BOC})\text{H}^+$), 1278.3 (MH^+), 1300.5 (MNa^+). ^1H NMR

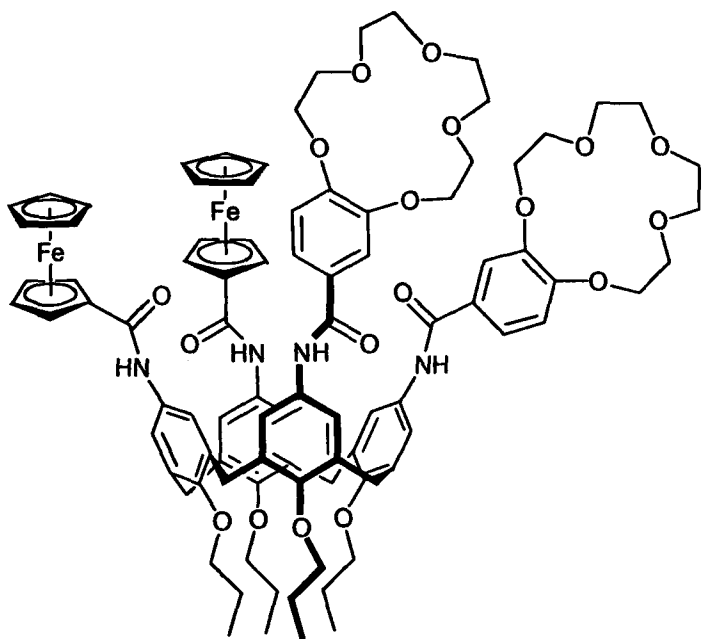
(300 MHz, d_6 -DMSO): δ 9.14 (s, FcNH, 2H), 8.77 (s, BOCNH, 2H), 7.09 & 7.04 & 6.85 & 6.81 (all s, ArH, 4×2 H), 4.90 (s, C_5H_4 , 4H), 4.34 (m, C_5H_4 & $ArCH_{ax}H_{eq}Ar$, 8H), 4.14 (s, C_5H_5 , 10H), 3.81 & 3.76 (both t, $J = 7.2$ Hz, $OCH_2CH_2CH_3$, 2×4 H), 3.16 & 3.03 (both d, $J = 12.9$ Hz, $ArCH_{ax}H_{eq}Ar$, 2×1 H), 3.09 (d, $J = 12.9$ Hz, $ArCH_{ax}H_{eq}Ar$, 2H), 1.93 & 1.91 (both sext, $J = 7.2$ Hz, $OCH_2CH_2CH_3$, 2×4 H), 1.35 (s, CH_3 , 18H), 0.97 (t, $J = 7.2$ Hz, $OCH_2CH_2CH_3$, 12H).

Compound 35



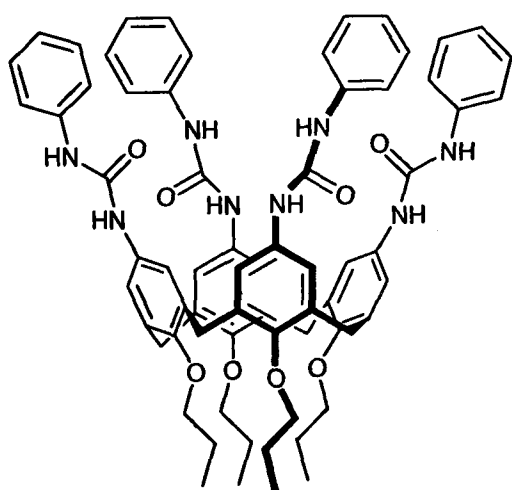
Procedure was the same as that for **29**, except **34** (1010 mg, 0.79 mmol) was used. The solvent was removed under vacuum and the residue dried under high vacuum for several hours to yield the product as its TFA salt (1020 mg, 99 %). (Found: C, 61.0; H, 5.5; N, 4.1 %. $C_{62}H_{68}Fe_2N_4O_6 \cdot 2C_2HF_3O_2$ requires C, 60.7; H, 5.4; N, 4.3 %.) ES-MS m/z : 539.3 (MH_2^{2+}), 1077.7 (MH^+). 1H

NMR (300 MHz, d_6 -DMSO): δ 9.23 (s, FcNH, 2H), 7.23 & 7.13 & 6.82 & 6.75 (all s, ArH, 4×2 H), 4.92 & 4.89 (both s, C_5H_4 , 2×2 H), 4.38 (m, C_5H_4 & $ArCH_{ax}H_{eq}Ar$, 8H), 4.17 (s, C_5H_5 , 10H), 3.84 & 3.82 (both t, $J = 7.2$ Hz, $OCH_2CH_2CH_3$, 2×4 H), 3.37 & 3.18 (both d, $J = 12.9$ Hz, $ArCH_{ax}H_{eq}Ar$, 2×1 H), 3.27 (d, $J = 12.9$ Hz, $ArCH_{ax}H_{eq}Ar$, 2H), 1.91 (sext, $J = 7.2$ Hz, $OCH_2CH_2CH_3$, 8H), 0.97 (t, $J = 7.2$ Hz, $OCH_2CH_2CH_3$, 12H). Procedure to convert the product to its pure amine form was the same as that for **29**.

BisFc-bis(crown)calix 36

Procedure was the same as that for **22**, except **35** (510 mg, 0.47 mmol) and **15** (480 mg, 1.45 mmol) were used. The product was obtained as a pale orange solid after precipitation from chloroform / hexane (390 mg, 49 %). (Found: C, 65.0; H, 6.0; N, 3.5 %. $C_{92}H_{104}Fe_2N_4O_{18}$ requires C, 66.3; H, 6.3; N, 3.4 %.) ES-MS m/z : 856.0

(MNa_2^{2+}), 864.0 ($MNaK^{2+}$), 1689.1 (MNa^+), 1705.0 (MK^+). 1H NMR (500 MHz, d_6 -DMSO): δ 9.77 (s, benzoNH, 2H), 9.19 (s, FcNH, 2H), 7.49 (d, $J = 8.5$ Hz, benzoArH, 2H), 7.43 (s, benzoArH, 2H), 7.28 (s, ArH, 2H), 7.20 (s, ArH, 4H), 7.17 (s, ArH, 2H), 6.93 (d, $J = 8.5$ Hz, benzoArH, 2H), 4.86 (s, C_5H_4 , 4H), 4.43 (d, $ArCH_{ax}H_{eq}Ar$, $J = 12.0$ Hz, 4H), 4.31 (s, C_5H_4 , 4H), 4.14 (s, C_5H_5 , 10H), 4.05 & 3.98 (both s, $ArOCH_2CH_2O$, $2 \times 4H$), 3.85 (t, $J = 7.5$ Hz, $OCH_2CH_2CH_3$, 8H), 3.74 & 3.68 (both s, $ArOCH_2CH_2O$, $2 \times 4H$), 3.58 (s, OCH_2CH_2O , 16H), 3.18 (d, $J = 12.0$ Hz, $ArCH_{ax}H_{eq}Ar$, 4H), 1.96 & 1.94 (both sext, $J = 7.5$ Hz, $OCH_2CH_2CH_3$, $2 \times 4H$), 0.97 (t, $J = 7.5$ Hz, $OCH_2CH_2CH_3$, 12H).

Compound 37¹⁵

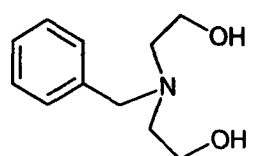
Phenylisocyanate (330 mg, 2.77 mmol) was added dropwise to a stirred solution of **4** (300 mg, 0.46 mmol) in dry dichloromethane (20 mL) and the mixture was stirred for 2 hours under a nitrogen atmosphere. Filtration of the solution yielded the product as a cream coloured solid (300 mg, 58 %). 1H NMR (300 MHz, d_6 -DMSO): δ 8.32 (s, PhNH, 4H),

8.18 (s, ArNH, 4H), 7.31 (d, $J = 8.4$ Hz, *o*-PhH, 8H), 7.19 (t, $J = 8.1$ Hz, *m*-PhH, 8H), 6.89 (t, $J = 7.8$ Hz, *p*-PhH, 4H), 6.80 (s, ArH, 8H), 4.34 (d, $J = 12.6$ Hz, $ArCH_{ax}H_{eq}Ar$, 4H), 3.77 (t, J

= 7.5 Hz, $\text{OCH}_2\text{CH}_2\text{CH}_3$, 8H), 3.11 (d, $J = 12.6$ Hz, $\text{ArCH}_{\text{ax}}\text{H}_{\text{eq}}\text{Ar}$, 4H), 1.92 (sext, $J = 7.5$ Hz, $\text{OCH}_2\text{CH}_2\text{CH}_3$, 8H), 0.98 (t, $J = 7.5$ Hz, $\text{OCH}_2\text{CH}_2\text{CH}_3$, 12H). ^1H NMR (500 MHz, C_6D_6): δ 9.95 (s, PhNH , 4H), 8.13 (d, $J = 8.0$ Hz, $o\text{-PhH}$, 8H), 8.05 (d, $J = 2.5$ Hz, ArH , 4H), 7.28 (s, ArNH , 4H), 7.11 (t, $J = 8.0$ Hz, $m\text{-PhH}$, 8H), 6.77 (t, $J = 8.0$ Hz, $p\text{-PhH}$, 4H), 6.27 (d, $J = 2.5$ Hz, ArH , 4H), 4.51 (d, $J = 12.0$ Hz, $\text{ArCH}_{\text{ax}}\text{H}_{\text{eq}}\text{Ar}$, 4H), 3.64 (t, $J = 7.5$ Hz, $\text{OCH}_2\text{CH}_2\text{CH}_3$, 8H), 3.17 (d, $J = 12.0$ Hz, $\text{ArCH}_{\text{ax}}\text{H}_{\text{eq}}\text{Ar}$, 4H), 1.93 (sext, $J = 7.5$ Hz, $\text{OCH}_2\text{CH}_2\text{CH}_3$, 8H), 0.79 (t, $J = 7.5$ Hz, $\text{OCH}_2\text{CH}_2\text{CH}_3$, 12H).

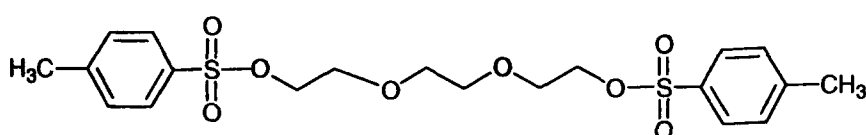
5.4 Experimental for Chapter Three

N-Benzyldiethanolamine **40**¹⁶



Diethanolamine (42 g, 0.40 mol) and anhydrous sodium carbonate (24 g, 0.23 mol) were placed in a 500 mL, 3 neck round bottom flask and the mixture heated to 80 °C with stirring under nitrogen. Benzyl chloride (56 g, 0.44 mol) was added dropwise over 2 hours and the mixture stirred vigorously at 80 °C for 20 hours. The mixture was cooled to room temperature, dichloromethane (100 mL) was added, and the salts filtered and washed with further dichloromethane. The solvent was removed under vacuum and the crude product purified by vacuum distillation (Kugelrohr, 144 °C (0.1 torr)) to yield a colourless oil (60 g, 77 %). ^1H NMR (300 MHz, CDCl_3): δ 7.31 (m, ArH , 5H), 3.70 (s, ArCH_2 , 2H), 3.61 (t, $J = 5.4$ Hz, CH_2OH , 4H), 3.18 (br s, OH , 2H), 2.70 (t, $J = 5.4$ Hz, NCH_2 , 4H).

Triethyleneglycol ditosylate **41**¹⁰

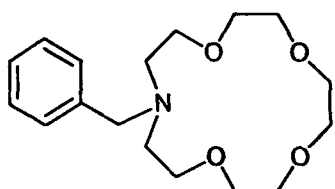


Procedure was the same as that for **12**, except *p*-toluenesulfonyl chloride (31.05

g, 162.9 mmol) and triethyleneglycol (11.16 g, 74.3 mmol) were used. The product was obtained as a white solid after solvent removal and recrystallisation from ethanol (32.85 g, 96

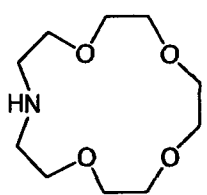
%). ^1H NMR (300 MHz, CDCl_3): δ 7.78 (d, $J = 7.2$ Hz, ArH, 4H), 7.34 (d, $J = 7.2$ Hz, ArH, 4H), 4.13 (t, $J = 4.8$ Hz, $\text{TsOCH}_2\text{CH}_2\text{O}$, 4H), 3.64 (t, $J = 4.8$ Hz, $\text{TsOCH}_2\text{CH}_2\text{O}$, 4H), 3.52 (s, $\text{OCH}_2\text{CH}_2\text{O}$, 4H), 2.44 (s, ArCH_3 , 6H).

N*-Benzylaza[15]crown-5 **42*

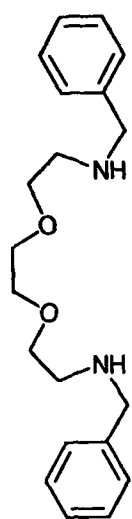


A suspension of sodium hydride (2.46 g, 102.5 mmol) in tetrahydrofuran (150 mL) was heated to reflux under nitrogen in a 3 neck round bottom flask. A solution of **40** (9.75 g, 49.9 mmol) and **41** (22.93 g, 50.0 mmol) in tetrahydrofuran (50 mL) was added dropwise with vigorous stirring. Reflux was continued for 20 hours then the reaction mixture allowed to cool to room temperature, quenched with water (200 mL) and the solvent removed under vacuum. The residue was dissolved in water (200 mL), extracted with dichloromethane (3×100 mL) and the combined organic fractions dried over anhydrous magnesium sulphate, filtered and the solvent removed under vacuum. Column chromatography (silica, 5 % methanol in chloroform) followed by vacuum distillation (Kugelrohr, 125°C (0.1 torr)) gave the product as a colourless oil (6.48 g, 42 %). ^1H NMR (300 MHz, CDCl_3): δ 7.30 (s, ArH, 5H), 3.67 (m, ArCH_2N & $\text{NCH}_2\text{CH}_2\text{O}$ & $\text{OCH}_2\text{CH}_2\text{O}$, 18H), 2.77 (t, $\text{NCH}_2\text{CH}_2\text{O}$, 4H).

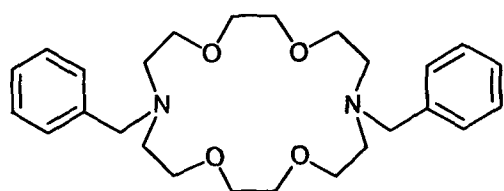
Aza[15]crown-5 **43**



A solution of **42** (6.10 g, 19.7 mmol) in absolute ethanol (40 mL) was added to 10 % Pd-C catalyst (0.80 g) in a Parr hydrogenation apparatus and the mixture stirred under hydrogen (4 atm) at room temperature for 24 hours. The reaction mixture was filtered through a bed of Celite® and the solvent evaporated to give a colourless oil which solidified under high vacuum to give the product as a soft, white, hygroscopic solid (4.14 g, 96 %). ^1H NMR (500 MHz, CDCl_3): δ 3.65 (m, $\text{NCH}_2\text{CH}_2\text{O}$ & $\text{OCH}_2\text{CH}_2\text{O}$, 16H), 2.85 (t, $J = 5.5$ Hz, $\text{NCH}_2\text{CH}_2\text{O}$, 4H).

***N,N'*-Dibenzyl-4,7-dioxa-1,10-diazadecane 44**¹⁸

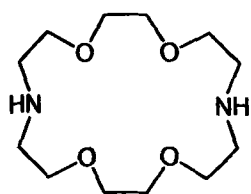
Benzylamine (200 mL, excess) and 1,2-bis(2-chloroethoxy)ethane (22.70 g, 121.4 mmol) were stirred together under nitrogen at 120 °C for 48 hours. The mixture was allowed to cool to room temperature, sodium hydroxide (8.05 g, 201.3 mmol) was added and the mixture returned to 120 °C and stirred for 1 hour. The excess benzylamine was distilled off under high vacuum (45 °C (0.2 torr)) and the residue dissolved in chloroform (200 mL), washed with water (2 × 150 mL), dried over anhydrous magnesium sulphate, filtered, and the solvent removed under vacuum. Any remaining traces of benzylamine were removed by heating under vacuum (60 °C (0.05 torr)). Vacuum distillation (Kugelrohr, 175 °C (0.2 torr)) gave the product as a pale yellow, viscous oil (37.17 g, 93 %). ¹H NMR (300 MHz, CDCl₃): δ 7.30 (m, ArH, 10H), 3.79 (s, ArCH₂, 4H), 3.60 (t, *J* = 5.1 Hz, NCH₂CH₂O, 4H), 3.59 (s, OCH₂CH₂O, 4H), 2.79 (t, *J* = 5.1 Hz, NCH₂CH₂O, 4H).

***N,N'*-Dibenzyl-1,10-bis-aza[18]crown-6 45**¹⁸

Compound **44** (12.08 g, 36.8 mmol), 1,2-bis(2-iodoethoxy)ethane (16.25 g, 43.9 mmol), anhydrous sodium carbonate (18.60 g, 175.5 mmol), anhydrous sodium iodide (2.78 g, 18.5 mmol) and dry acetonitrile (500 mL) were stirred and heated to reflux under nitrogen for 48 hours. The mixture was allowed to cool, the inorganics filtered off and washed with hot acetonitrile (2 × 50 mL) and the solvent removed under vacuum. The residue was dissolved with warming in 1:1 dioxane / acetone (80 mL) and the solution left in the freezer overnight. The colourless crystals that formed were filtered off and dissolved in chloroform (200 mL). The organic layer was washed with water (2 × 150 mL) which was then back extracted with chloroform (2 × 100 mL). The combined organic layers were dried over anhydrous magnesium sulphate, filtered, and the solvent removed under vacuum. The residue

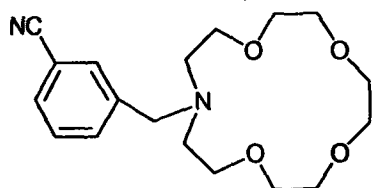
was recrystallised from boiling hexane to yield the product as a pale yellow solid (8.44 g, 52 %). ^1H NMR (300 MHz, CDCl_3): δ 7.40 – 7.20 (m, ArH, 10H), 3.69 (s, ArCH₂N, 4H), 3.63 (t, J = 6.0 Hz, NCH₂CH₂O, 8H), 3.62 (s, OCH₂CH₂O, 8H), 2.83 (t, J = 6.0 Hz, NCH₂CH₂O, 8H).

1,10-Bis-aza[18]crown-6 **46**¹⁸

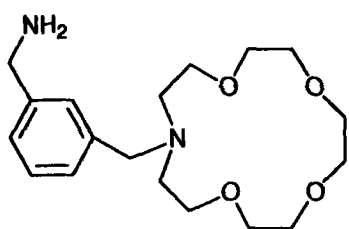


A solution of **45** (6.04 g, 13.6 mmol) in absolute ethanol (60 mL) was added to Pearlman's catalyst ($\text{Pd}(\text{OH})_2\text{-C}$, 0.60 g) in a Parr hydrogenation apparatus and the mixture stirred under hydrogen (3 atm) at room temperature for 72 hours. The reaction mixture was filtered through a bed of Celite® and the solvent removed under vacuum. Recrystallisation of the residue from hot hexane afforded the product as a cream microcrystalline solid (2.07 g, 58 %). ^1H NMR (500 MHz, CDCl_3): δ 3.60 (t, J = 4.5 Hz, NCH₂CH₂O, 8H), 3.58 (s, OCH₂CH₂O, 8H), 2.79 (t, J = 4.5 Hz, NCH₂CH₂O, 8H).

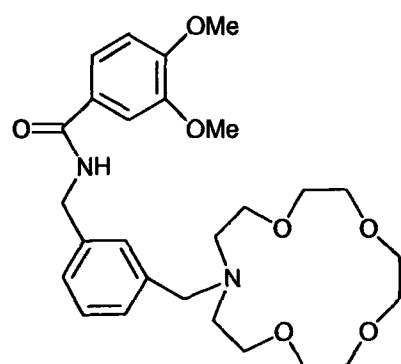
N-(*m*-Cyanobenzyl)aza[15]crown-5 **47**¹⁹



Compound **43** (345 mg, 1.57 mmol), α -bromo-*m*-tolunitrile (310 mg, 1.58 mmol) and anhydrous potassium carbonate (220 mg, 1.59 mmol) were suspended in acetone (20 mL) and the mixture heated to reflux for 16 hours. The solution was allowed to cool to room temperature, the inorganics filtered off, the solvent removed under vacuum and the resulting material further purified by column chromatography (silica, 3 % methanol in chloroform) to yield the product as a yellow oil (470 mg, 89 %). ^1H NMR (300 MHz, CDCl_3): δ 7.80 – 7.30 (m, ArH, 4H), 3.80 – 3.60 (m, NCH₂CH₂O & OCH₂CH₂O, 16H), 3.60 (s, ArCH₂N, 2H), 2.80 (t, NCH₂CH₂O, 4H).

***N*-(α -Amino-*m*-xylylyl)aza[15]crown-5 **48**¹⁹**

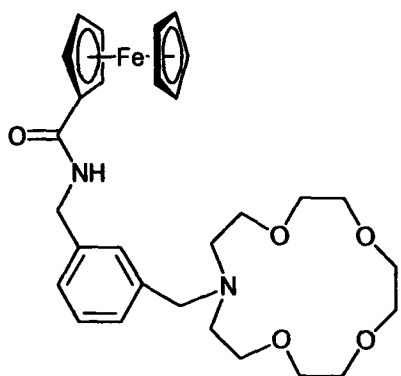
A solution of **47** (450 mg, 1.35 mmol) in dry tetrahydrofuran (20 mL) was added dropwise to a stirred suspension of lithium aluminium hydride (80 mg, 2.11 mmol) in dry tetrahydrofuran (20 mL) under a nitrogen atmosphere. The reaction mixture was heated at reflux for 3 hours then stirred at room temperature for a further 16 hours. Aqueous ammonium chloride (1M, 40 mL) was added and the solvent removed under vacuum. Water (50 mL) was added, the mixture extracted with dichloromethane (2 $\times$ 50 mL) and the combined organic fractions washed with brine (50 mL), dried over anhydrous magnesium sulphate, filtered and the solvent removed under vacuum to give the oily product (360 mg, 79 %). ¹H NMR (300 MHz, CDCl₃): δ 7.40 – 7.10 (m, ArH, 4H), 3.86 (s, ArCH₂NH₂, 2H), 3.80 – 3.60 (m, NCH₂CH₂O & OCH₂CH₂O & ArCH₂N, 18H), 2.80 (t, NCH₂CH₂O, 4H).

Receptor 49

A solution of **48** (180 mg, 0.53 mmol) in chloroform (20 mL) was added dropwise to a stirred solution of 3,4-dimethoxybenzoyl chloride (110 mg, 0.55 mmol) and triethylamine (2 mL, excess) in chloroform (30 mL) and the mixture heated to reflux under nitrogen overnight. The heat was removed, water (50 mL) was added and the mixture stirred for 30 minutes. The organic fraction was separated, washed with water (50 mL), dried over anhydrous magnesium sulphate, filtered, and the solvent removed under vacuum. The resulting material was purified by preparative thin layer chromatography (silica, 20 % methanol in chloroform) and dried under high vacuum to yield the product as a pale yellow oil (150 mg, 56 %). (Found: C, 64.2; H, 7.8; N, 5.5 %. C₂₇H₃₈N₂O₇ requires C, 64.5; H, 7.6; N, 5.6 %.) ES-MS *m/z*: 503.4 (MH⁺), 525.4 (MNa⁺). ¹H NMR (300 MHz, *d*₆-DMSO): δ 8.90 (t, *J* = 5.7 Hz, NH, 1H), 7.51 (d, *J* = 8.4 Hz, benzoArH, 1H), 7.47 (s, benzoArH, 1H), 7.30 –

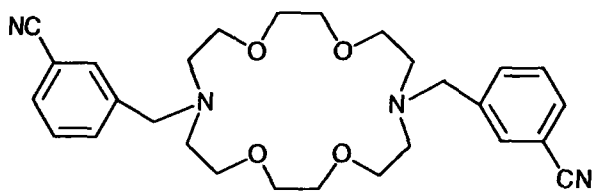
7.10 (m, ArH, 4H), 7.00 (d, $J = 8.4$ Hz, benzoArH, 1H), 4.43 (d, $J = 5.7$ Hz, ArCH₂NH, 2H), 3.77 (s, OCH₃, 6H), 3.56 (s, ArCH₂N, 2H), 3.50 (m, NCH₂CH₂O & OCH₂CH₂O, 16H), 2.60 (t, $J = 6.0$ Hz, NCH₂CH₂O, 4H).

Receptor 50

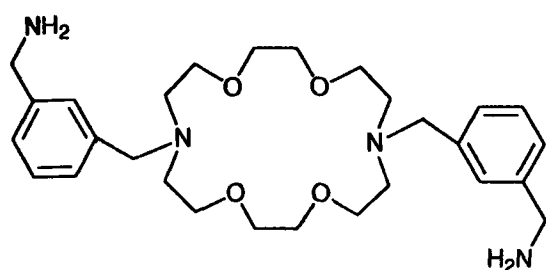


Procedure was the same as that for **49**, except **48** (170 mg, 0.50 mmol) and **9** (125 mg, 0.50 mmol) were used. The product was purified by preparative thin layer chromatography (silica, 10 % methanol in chloroform) and dried under high vacuum to yield a dark orange oil (170 mg, 61 %). (Found: C, 60.7; H, 6.3; N, 5.0 %. C₂₉H₃₈FeN₂O₅· $\frac{1}{4}$ CHCl₃ requires C, 60.5; H, 6.6; N, 4.8 %.) ES-MS m/z : 551.3 (MH⁺), 573.3 (MNa⁺). ¹H NMR (300 MHz, *d*₆-DMSO): δ 8.35 (t, $J = 5.7$ Hz, NH, 1H), 7.30 – 7.10 (m, ArH, 4H), 4.80 (s, C₅H₄, 2H), 4.36 (d, ArCH₂NH, 2H), 4.33 (s, C₅H₄, 2H), 4.11 (s, C₅H₅, 5H), 3.58 (s, ArCH₂N, 2H), 3.50 (m, NCH₂CH₂O & OCH₂CH₂O, 16H), 2.62 (t, $J = 6.0$ Hz, NCH₂CH₂O, 4H).

N,N'-Bis(*m*-cyanobenzyl)-1,10-bis-aza[18]crown-6 **51**¹⁹

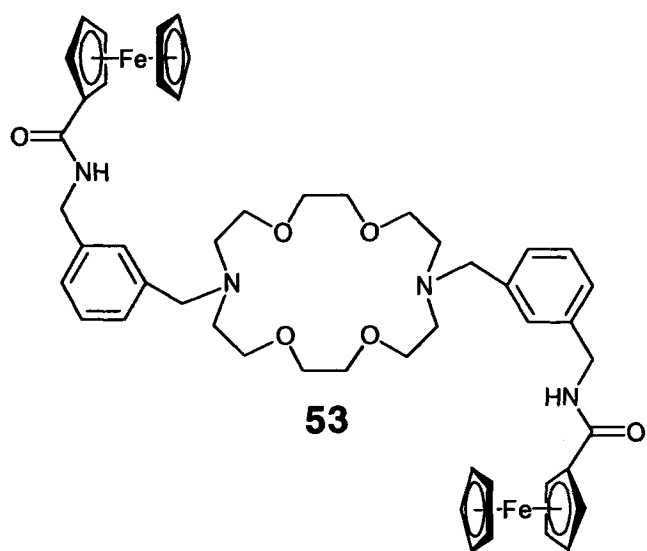


Procedure was the same as that for **47**, except **46** (800 mg, 3.05 mmol), α -bromo-*m*-tolunitrile (1200 mg, 6.12 mmol) and anhydrous potassium carbonate (840 mg, 6.08 mmol) in acetone (40 mL) were used. The pure product was obtained (without column chromatography) after solvent removal as a yellow powder (1490 mg, 99 %). ¹H NMR (300 MHz, CDCl₃): δ 7.72 (s, ArH, 2H), 7.57 (d, $J = 7.8$ Hz, ArH, 2H), 7.49 (d, $J = 7.8$ Hz, ArH, 2H), 7.37 (t, $J = 7.8$ Hz, ArH, 2H), 3.74 (s, ArCH₂N, 4H), 3.64 (t, $J = 5.7$ Hz, NCH₂CH₂O, 8H), 3.62 (s, OCH₂CH₂O, 8H), 2.81 (t, $J = 5.7$ Hz, NCH₂CH₂O, 8H).

N,N'*-Bis(α -amino-*m*-xylylyl)-1,10-bis-aza[18]crown-6 **52*¹⁹

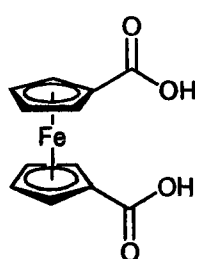
Procedure was the same as that for **48**, except that **51** (640 mg, 1.30 mmol) in tetrahydrofuran (80 mL) and lithium

aluminium hydride (200 mg, 5.28 mmol) in tetrahydrofuran (40 mL) were used. The aqueous layer was basified (pH 14) with sodium hydroxide solution (1M) prior to the dichloromethane extraction. The product was obtained as a yellow oil (550 mg, 85 %). ¹H NMR (300 MHz, CDCl₃): δ 7.30 – 7.10 (m, ArH, 8H), 3.85 (s, ArCH₂NH₂, 4H), 3.68 (s, ArCH₂N, 4H), 3.63 (t, J = 6.0 Hz, NCH₂CH₂O, 8H), 3.61 (s, OCH₂CH₂O, 8H), 2.82 (t, J = 6.0 Hz, NCH₂CH₂O, 8H).

Receptor 53

Procedure was the same as that for **49**, except **52** (160 mg, 0.32 mmol) and **9** (160 mg, 0.64 mmol) were used. The product was purified by preparative thin layer chromatography (silica, 20 % methanol in chloroform) and dried under high vacuum to yield a red oil (190 mg, 64 %). (Found: C, 62.3; H, 6.9; N, 5.6 %.

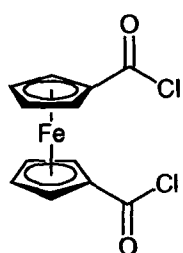
$C_{50}H_{60}Fe_2N_4O_6 \cdot 2CH_3OH$ requires C, 63.2; H, 6.9; N, 5.7 %.) ES-MS m/z : 463.3 (MH₂⁺), 925.5 (MH⁺), 947.5 (MNa⁺), 963.4 (MK⁺). ¹H NMR (300 MHz, *d*₆-DMSO): δ 8.36 (t, J = 6.0 Hz, NH, 2H), 7.30 – 7.10 (m, ArH, 8H), 4.81 (s, C₅H₄, 4H), 4.35 (d, ArCH₂NH, 4H), 4.33 (s, C₅H₄, 4H), 4.11 (s, C₅H₅, 10H), 3.59 (s, ArCH₂N, 4H), 3.48 (t, J = 5.7 Hz, NCH₂CH₂O, 8H), 3.43 (s, OCH₂CH₂O, 8H), 2.65 (t, J = 5.7 Hz, NCH₂CH₂O, 8H).

1,1'-Bis(carboxy)ferrocene **54**²⁰

A 1 L, 3 neck round bottom flask was charged with dry hexane (10 mL), *N,N,N',N'*-tetramethylethylenediamine (TMEDA, 17.54 g, 150.9 mmol) and *n*-

butyl lithium (2.5 M in hexane, 100 mL, 250.0 mmol) and the mixture stirred under nitrogen for 10 minutes. A solution of ferrocene (12.52 g, 67.3 mmol) in dry hexane (370 mL) was added dropwise over a period of 40 minutes, and the mixture left stirring under nitrogen overnight. The mixture was poured into a 3 L flask containing dry ether (200 mL) and dry ice (excess) and the resulting solution stirred overnight. Filtration yielded the ferrocene bis-lithiate, which was dissolved in water (200 mL) and acidified with hydrochloric acid to afford a tan precipitate. The product was collected by filtration, dried under high vacuum and recrystallised from dry toluene to give an orange solid (12.54 g, 68 %). ^1H NMR (300 MHz, d_6 -DMSO): δ 4.67 (s, C_5H_4 , 4H), 4.43 (s, C_5H_4 , 4H).

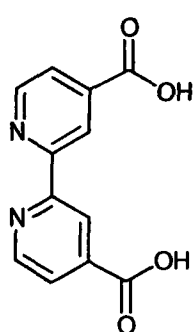
1,1'-Bis(chlorocarbonyl)ferrocene **55**



A mixture of **54** (2.87 g, 10.5 mmol) and oxalyl chloride (10 mL, excess) was heated to reflux under nitrogen for 1 hour. The volatiles were removed under vacuum and the residue dissolved in dry dichloromethane. The solution was

filtered, the solvent removed and the product left under high vacuum for several hours to give a deep red residue. The product was not characterised but used immediately for subsequent reactions.

4,4'-Bis(carboxy)-2,2'-bipyridine **56**²¹



Concentrated sulphuric acid (150 mL) was stirred and cooled in an ice-bath.

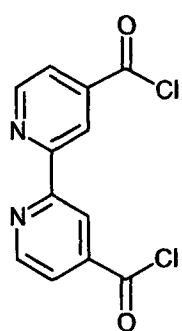
4,4'-Dimethyl-2,2'-bipyridine (10.09 g, 54.8 mmol) was added portion-wise to the acid while maintaining the temperature of the reaction mixture below 10 °C.

Finely ground chromium(VI) oxide (32.75 g, excess) was added with care over 1

hour and the mixture stirred at 5 °C for a further 30 minutes. The dark green-blue solution was stirred at 75 °C for 4 hours, at room temperature for 18 hours then poured into a rapidly stirred ice / water mixture (1 L) and allowed to stand for 12 hours. The solution was decanted

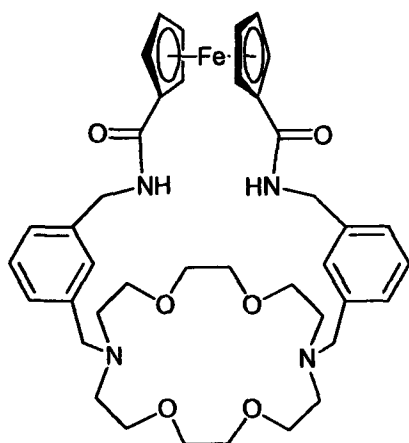
and a slurry of Celite® (25 g) in water (50 mL) added. The solids were isolated by filtration through Celite® and washed with water (250 mL). The residue was suspended in water (750 mL) and the pH adjusted to 9 with aqueous sodium hydroxide (10%) at which point the blue-green chromium(III) salts precipitated out. The mixture was heated to 50 °C then filtered to afford a bright yellow solution. Acidification of the filtrate to pH 2 with hydrochloric acid (3 M) caused the product to precipitate from solution. It was filtered off and washed with water (3 × 100 mL), acetone (3 × 100 mL) and diethylether (3 × 100 mL) and dried under vacuum to afford a white solid (11.57 g, 87 %). ¹H NMR (300 MHz, *d*₆-DMSO): δ 8.88 (d, *J* = 4.8 Hz, bipy*H*⁶, 2H), 8.81 (s, bipy*H*³, 2H), 7.89 (d, *J* = 4.8 Hz, bipy*H*⁵, 2H).

4,4'-Bis(chlorocarbonyl)-2,2'-bipyridine **57**



Procedure was the same as that for **11**, except that **56** (500 mg, 2.05 mmol) was used. The product was not characterised but used immediately for subsequent reactions.

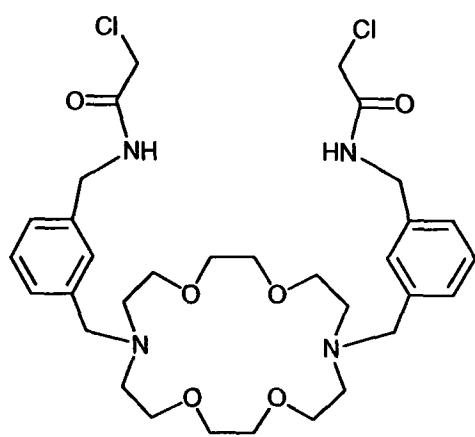
Receptor **58**



Solutions of **52** (500 mg, 1.00 mmol) in chloroform (200 mL) and **55** (310 mg, 1.00 mmol) in chloroform (200 mL) were simultaneously added dropwise over 2 hours to a stirred solution of triethylamine (5 mL, excess) in chloroform (200 mL) and the mixture heated to reflux under nitrogen overnight. The solvent was removed under vacuum and the residue dissolved in chloroform (50 mL). Water (50 mL) was added and the mixture stirred for 30 minutes. The organic fraction was separated, washed with water (50 mL), dried over anhydrous magnesium sulphate, filtered, and the solvent removed under vacuum. The resulting material was purified by preparative thin layer

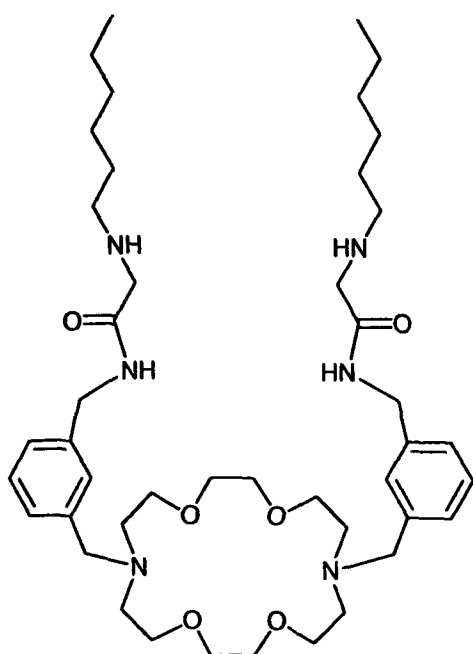
chromatography (silica, 20 % methanol in chloroform). Precipitation from chloroform / diethylether afforded the product as an orange solid (90 mg, 12 %). (Found: C, 64.0; H, 7.1; N, 6.9 %. $C_{40}H_{50}FeN_4O_6$ requires C, 65.0; H, 6.8; N, 7.6 %.) ES-MS m/z : 739.4 (MH^+), 761.3 (MNa^+), 777.3 (MK^+). 1H NMR (300 MHz, d_6 -DMSO): δ 8.41 (t, $J = 6.0$ Hz, NH, 2H), 7.39 (s, ArH, 2H), 7.30 – 7.00 (m, ArH, 6H), 4.83 (s, C_5H_4 , 4H), 4.41 (d, ArCH₂NH, 4H), 4.34 (s, C_5H_4 , 4H), 3.58 (s, ArCH₂N, 4H), 3.39 (m, NCH₂CH₂O & OCH₂CH₂O, 16H), 2.60 (t, $J = 5.7$ Hz, NCH₂CH₂O, 8H).

Compound 59



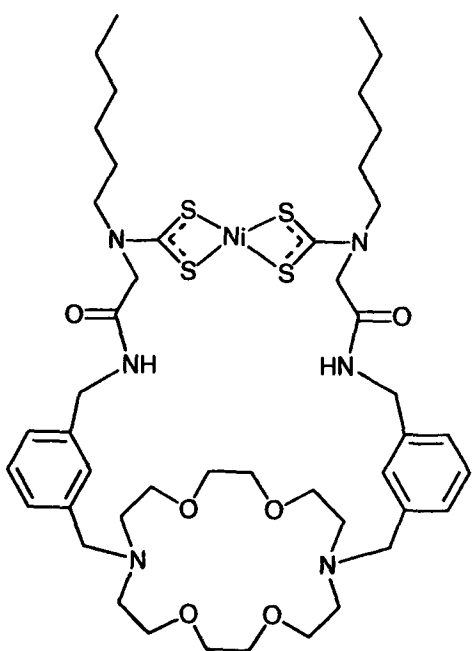
A solution of chloroacetyl chloride (250 mg, 2.21 mmol) in chloroform (50 mL) was added dropwise to a stirred biphasic mixture of **52** (500 mg, 1.00 mmol) in chloroform (50 mL) and sodium hydroxide (200 mg, excess) in water (20 mL). The mixture was stirred for 1 hour, the organic layer separated and

the aqueous layer extracted with chloroform (2 × 50 mL). The combined organic fractions were dried over anhydrous magnesium sulphate, filtered, and the solvent removed under vacuum to give the product as a dark orange oil (640 mg, 98 %). ES-MS m/z : 653.3 (MH^+), 675.3 (MNa^+), 691.3 (MK^+). 1H NMR (300 MHz, $CDCl_3$): δ 7.30 – 7.10 (m, ArH, 8H), 6.95 (br t, NH, 2H), 4.47 (d, $J = 6.0$ Hz, ArCH₂NH, 4H), 4.10 (s, COCH₂Cl, 4H), 3.68 (s, ArCH₂N, 4H), 3.63 (t, $J = 6.0$ Hz, NCH₂CH₂O, 8H), 3.61 (s, OCH₂CH₂O, 8H), 2.82 (t, $J = 6.0$ Hz, NCH₂CH₂O, 8H).

Compound 60

A solution of **59** (620 mg, 0.95 mmol) in chloroform (20 mL) was added dropwise with stirring to hexylamine (20 mL, excess) and the mixture stirred overnight at 50 °C. The mixture was allowed to cool to room temperature, chloroform (100 mL) was added and the mixture washed with water (4 × 100 mL). The organic layer was dried over anhydrous magnesium sulphate, filtered, and the solvent removed under vacuum. The

residue was dried under high vacuum with heating (to remove all traces of hexylamine) to afford the product as an orange oil (690 mg, 93 %). ES-MS m/z : 783.6 (MH^+), 805.6 (MNa^+), 821.6 (MK^+). 1H NMR (300 MHz, $CDCl_3$): δ 7.60 (br t, NH, 2H), 7.30 – 7.10 (m, ArH, 8H), 4.46 (d, J = 6.0 Hz, ArCH₂NH, 4H), 3.68 (s, ArCH₂N, 4H), 3.63 (t, J = 6.0 Hz, NCH₂CH₂O, 8H), 3.61 (s, OCH₂CH₂O, 8H), 3.32 (s, COCH₂NH, 4H), 2.83 (t, J = 6.0 Hz, NCH₂CH₂O, 8H), 2.59 (t, J = 6.6 Hz, NCH₂CH₂(CH₂)₃CH₃, 4H), 1.44 (quint, J = 6.6 Hz, NCH₂CH₂(CH₂)₃CH₃, 4H), 1.27 (m, NCH₂CH₂(CH₂)₃CH₃, 12H), 0.88 (t, J = 6.6 Hz, NCH₂CH₂(CH₂)₃CH₃, 6H).

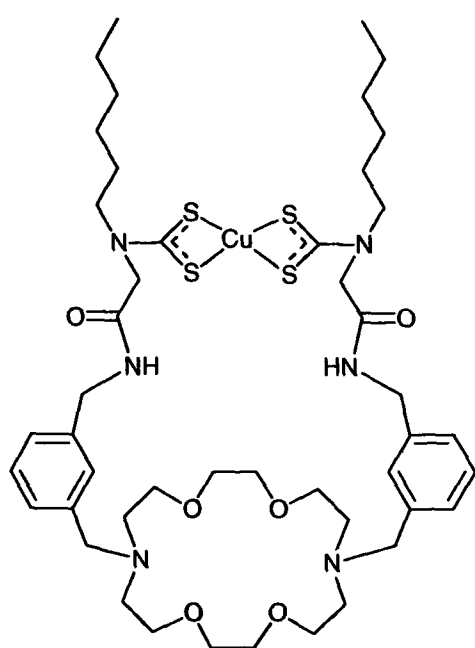
Receptor 61

Potassium hydroxide (80 mg, 1.43 mmol) and carbon disulphide (80 mg, 1.05 mmol) were added to a solution of **60** (330 mg, 0.42 mmol) in 9:1 tetrahydrofuran / water (100 mL) and the mixture stirred for 30 minutes. A solution of nickel acetate tetrahydrate (120 mg, 0.48 mmol) in water (5 mL) was added dropwise and the resulting solution stirred overnight. The solvent was removed under vacuum, water was added (50

mL) and the mixture extracted with dichloromethane (2 × 50 mL). The organic layer was

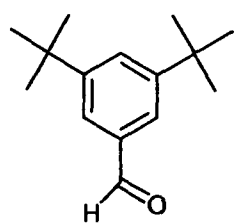
washed with aqueous lithium hydroxide (1M, 50 mL), dried over anhydrous magnesium sulphate, filtered, and the solvent removed under vacuum. Precipitation from chloroform / methanol gave the product as a tan solid (200 mg, 48 %). (Found: C, 55.6; H, 7.2; N, 8.3 %. $C_{46}H_{72}N_6NiO_6S_4$ requires C, 55.7; H, 7.3; N, 8.5 %.) ES-MS m/z : 991.4 (MH^+), 1013.4 (MNa^+), 1029.3 (MK^+). 1H NMR (300 MHz, d_6 -DMSO): δ 8.65 & 8.59 (both br s, NH, $2 \times 1H$), 7.30 – 7.10 (m, ArH, 8H), 4.27 (d, $J = 6.0$ Hz, $ArCH_2NH$, 4H), 3.48 (m, $COCH_2N$ & $ArCH_2N$ & $NCH_2CH_2(CH_2)_3CH_3$ & NCH_2CH_2O & OCH_2CH_2O , 28H), 2.64 (t, NCH_2CH_2O , 8H), 1.53 (br s, $NCH_2CH_2(CH_2)_3CH_3$, 4H), 1.20 (br s, $NCH_2CH_2(CH_2)_3CH_3$, 12H), 0.82 (br s, $NCH_2CH_2(CH_2)_3CH_3$, 6H).

Receptor 62



Procedure was the same as that for **61**, except copper acetate monohydrate (100 mg, 0.50 mmol) was used. Precipitation from chloroform / methanol gave the product as a dark brown solid (180 mg, 43 %). (Found: C, 55.4; H, 7.5; N, 8.4 %. $C_{46}H_{72}CuN_6O_6S_4$ requires C, 55.4; H, 7.3; N, 8.4 %.) ES-MS m/z : 996.8 (MH^+), 1034.7 (MK^+).

3,5-Di-*t*-butylbenzaldehyde **64**²²

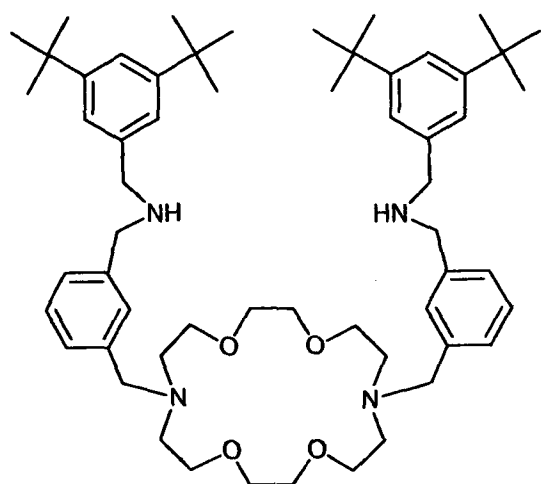


A mixture of 3,5-di-*t*-butyltoluene (25.02 g, 122.4 mmol), *N*-bromosuccinimide (31.84 g, 178.9 mmol) and 1,1'-azobis(cyclohexanecarbonitrile) (0.13 g, catalytic) in 1,2-dichloroethane (100

mL) was heated at reflux for 4 hours, filtered and the solvent removed under vacuum. Hexamethylenetetramine (47.02 g, 335.4 mmol), water (35 mL) and ethanol (35 mL) were added and the mixture heated to reflux for 4 hours. Hydrochloric acid (32 %, 33 mL) was

added and the mixture heated to reflux for an additional 30 minutes. The mixture was allowed to cool to room temperature, poured into diethylether (200 mL) and washed with water (2 × 200 mL) and brine (2 × 200 mL). The organic fraction was dried over anhydrous magnesium sulphate, filtered, and the solvent removed under vacuum to yield the product as a yellow crystalline solid (24.33 g, 91 %). ¹H NMR (300 MHz, CDCl₃): δ 10.01 (s, CHO, 1H), 7.72 (d, *J* = 0.7 Hz, ArH, 2H), 7.70 (t, *J* = 0.7 Hz, ArH, 1H), 1.36 (s, CH₃, 18H).

Compound 65

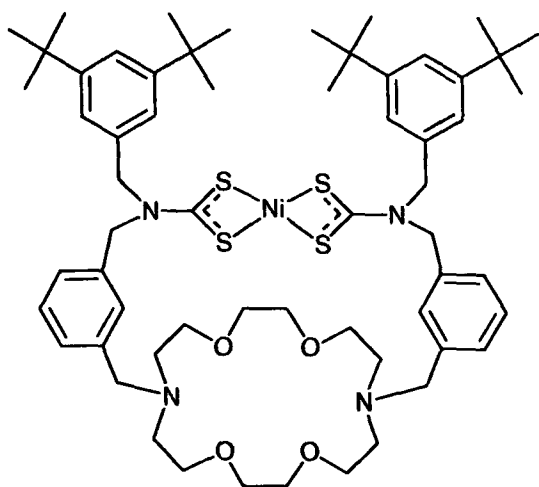


A solution of **52** (750 mg, 1.50 mmol) and **64** (720 mg, 3.30 mmol) in toluene (100 mL) was heated at reflux using a Dean-Stark apparatus (whereby the reaction is driven by the azeotropic distillation of water) to form the imine. The solvent was removed under vacuum, the residue dissolved in methanol (50 mL) and sodium borohydride (600 mg,

excess) added. The mixture was stirred for 2 hours then acidified to pH 1 with hydrochloric acid (2M) and basified to pH 14 with aqueous sodium hydroxide (2 M). Water (100 mL) was added and the mixture extracted with dichloromethane (2 × 100 mL). The organic layer was dried over anhydrous magnesium sulphate, filtered, and the solvent removed under vacuum to give the product as a pale yellow oil (1290 mg, 95 %). The hydrogen chloride salt of the amine was formed by bubbling hydrogen chloride gas through a solution of the amine (100 mg, 0.11 mmol) in dichloromethane (100 mL) to give a white solid which was filtered off and used for the elemental analysis. (Found: C, 56.5; H, 7.9; N, 4.7 %. C₅₈H₈₈N₄O₄·9HCl requires C, 56.5; H, 7.9; N, 4.5 %.) Both the amine and the hydrochloride salt of the amine gave essentially the same mass and NMR spectra. ES-MS *m/z*: 453.3 (MH₂⁺), 905.7 (MH⁺), 927.7 (MNa⁺), 943.7 (MK⁺). ¹H NMR (500 MHz, CDCl₃): δ 7.34 (t, *J* = 2.0 Hz, tBuArH, 2H), 7.32 (s, ArH, 2H), 7.30 – 7.20 (m, ArH, 6H), 7.19 (d, *J* = 2.0 Hz, tBuArH, 4H), 3.82 & 3.80 (both

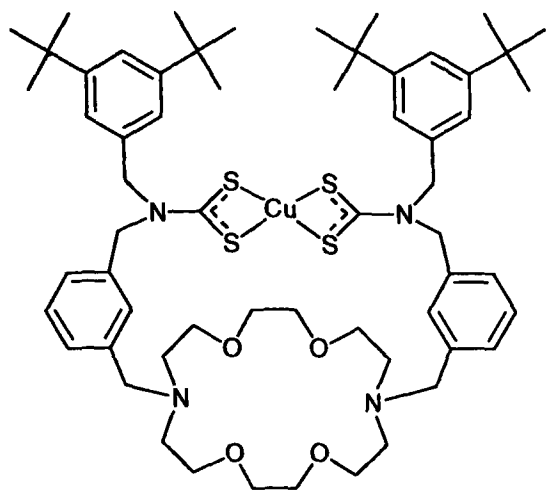
s, ArCH_2NH & $\text{tBuArCH}_2\text{NH}$, $2 \times 4\text{H}$), 3.68 (s, ArCH_2N , 4H), 3.62 (t, $J = 6.0$ Hz, $\text{NCH}_2\text{CH}_2\text{O}$, 8H), 3.59 (s, $\text{OCH}_2\text{CH}_2\text{O}$, 8H), 2.82 (t, $J = 6.0$ Hz, $\text{NCH}_2\text{CH}_2\text{O}$, 8H), 1.32 (s, CH_3 , 36H).

Receptor 66



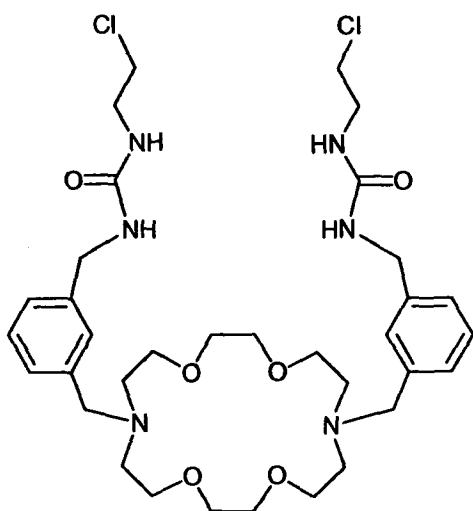
Procedure was the same as that for **61**, except **65** (580 mg, 0.64 mmol), potassium hydroxide (80 mg, 1.43 mmol), carbon disulphide (110 mg, 1.44 mmol) and nickel acetate tetrahydrate (180 mg, 0.72 mmol) were used. After solvent removal, the residue was dissolved in dichloromethane, methanol was added and the solution left to stand overnight

to afford the product as a green solid (380 mg, 53 %). (Found: C, 64.6; H, 7.7; N, 4.9; Ni, 5.0 %. $\text{C}_{60}\text{H}_{86}\text{N}_4\text{NiO}_4\text{S}_4$ requires C, 64.7; H, 7.8; N, 5.0; Ni, 5.3 %.) ES-MS m/z : 1113.5 (MH^+), 1135.5 (MNa^+), 1151.5 (MK^+). ^1H NMR (500 MHz, CDCl_3): δ 7.83 & 7.81 (both s, ArH , $2 \times 1\text{H}$), 7.43 (m, $J = 1.2$ Hz, tBuArH , 2H), 7.26 & 7.25 (both t, $J = 7.5$ Hz, ArH , $2 \times 1\text{H}$), 7.16 & 7.15 (both d, $J = 7.5$ Hz, ArH , $2 \times 1\text{H}$), 7.11 & 7.09 (both d, $J = 1.2$ Hz, tBuArH , $2 \times 2\text{H}$), 6.94 (d, $J = 7.5$ Hz, ArH , 2H), 4.67 (br s, ArCH_2N , 4H), 4.11 (s, $\text{tBuArCH}_2\text{N}$, 4H), 4.05 (s, ArCH_2N , 4H), 3.86 (m, $\text{NCH}_2\text{CH}_2\text{O}$, 8H), 3.74 (m, $\text{OCH}_2\text{CH}_2\text{O}$, 8H), 2.89 & 2.88 (both t, $J = 6.0$ Hz, $\text{NCH}_2\text{CH}_2\text{O}$, $2 \times 4\text{H}$), 1.33 (s, CH_3 , 36H). X-ray quality crystals (green platelets) of **66**· CH_3OH were obtained by slow evaporation of a chloroform / methanol solution of the receptor (see Appendix F.5).

Receptor 67

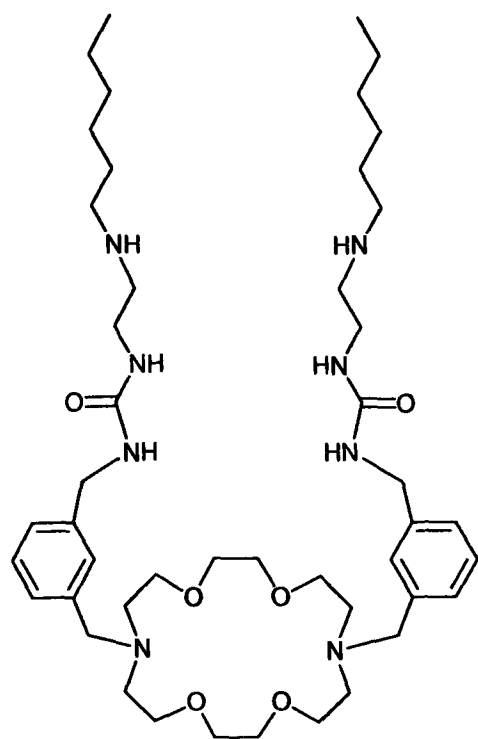
Procedure was the same as that for **66**, except copper acetate monohydrate (140 mg, 0.70 mmol) was used. The product was obtained as a dark brown microcrystalline solid (330 mg, 46 %). (Found: C, 64.0; H, 7.7; N, 4.9; Cu, 5.5 %. $C_{60}H_{86}CuN_4O_4S_4$ requires C, 64.4; H, 7.8; N, 5.0; Cu, 5.7 %.) ES-MS m/z : 1118.5 (MH^+), 1140.5 (MNa^+),

1156.5 (MK^+). X-ray quality crystals (brown blocks) of **67**·CH₃OH were obtained by slow evaporation of a chloroform / methanol solution of the receptor (see Appendix F.6).

Compound 68

A solution of 2-chloroethyl isocyanate (220 mg, 2.08 mmol) in chloroform (50 mL) was added dropwise to a stirred solution of **52** (500 mg, 1.00 mmol) in chloroform (100 mL). The mixture was stirred under nitrogen overnight and the solvent removed under vacuum to give the impure and oily product. ¹H NMR (500 MHz, CDCl₃): δ 7.36 (s, ArH, 2H), 7.23 (t, $J = 7.0$ Hz, ArH, 2H), 7.16 & 7.15 (both d, $J = 7.0$ Hz, ArH, $2 \times 2H$), 6.00 (t, ArCH₂NH, 2H), 5.94 (t, NHCH₂CH₂Cl, 2H), 4.22 (d, $J = 5.0$ Hz, ArCH₂NH, 4H), 3.58 (m, ArCH₂N & NCH₂CH₂O & OCH₂CH₂O, 20H), 3.54 (t, $J = 6.0$ Hz, NHCH₂CH₂Cl, 4H), 3.47 (q, $J = 6.0$ Hz, NHCH₂CH₂Cl, 4H), 2.72 (t, $J = 6.0$ Hz, NCH₂CH₂O, 8H).

Compound 69

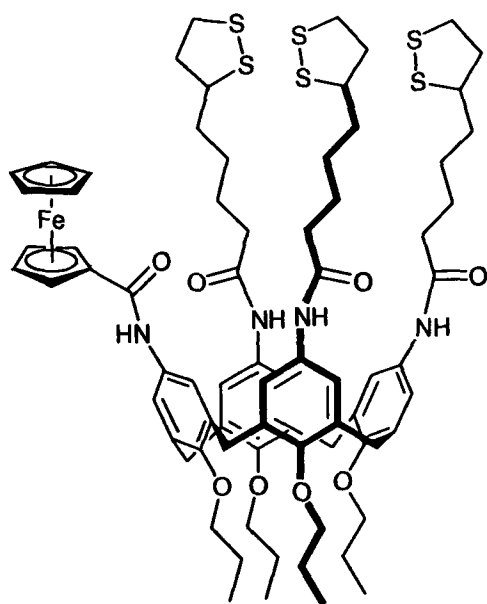


Procedure was the same as that for **60**, except impure **68** (600 mg, 0.84 mmol) was used. Column chromatography (silica, 20 % methanol in chloroform then pure methanol) gave the product as a dark yellow oil (50 mg, 7 %). ^1H NMR (500 MHz, d_6 -DMSO): δ 7.30 – 7.00 (m, ArH, 8H), 6.43 (t, ArCH₂NH, 2H), 5.93 (t, J = 5.5 Hz, NHCH₂CH₂NH, 2H), 4.16 (d, J = 5.5 Hz, ArCH₂NH, 4H), 3.57 (s, ArCH₂N, 4H), 3.50 (t, J = 6.0 Hz, NCH₂CH₂O, 8H), 3.47 (s, OCH₂CH₂O, 8H), 3.05 (q, J = 6.0

Hz, NHCH₂CH₂NH, 4H), 2.65 (t, J = 6.0 Hz, NCH₂CH₂O, 8H), 2.47 (m, NHCH₂CH₂NH & NCH₂CH₂(CH₂)₃CH₃, 8H), 1.34 (quint, J = 6.5 Hz, NCH₂CH₂(CH₂)₃CH₃, 4H), 1.21 (m, NCH₂CH₂(CH₂)₃CH₃, 12H), 0.82 (t, J = 6.5 Hz, NCH₂CH₂(CH₂)₃CH₃, 6H).

5.5 Experimental for Chapter Four

Receptor 73



Thioctic acid (375 mg, 1.82 mmol) and 1-(3-(dimethylamino)propyl)-3-ethyl-carbodiimide hydrochloride (EDC, 350 mg, 1.83 mmol) were added to a solution of **29** (390 mg, 0.45 mmol) in dry dichloromethane (100 mL) and the mixture stirred under nitrogen overnight. The solvent was removed under vacuum and the residue dissolved in dichloromethane (100 mL). The organic layer was washed

with sodium hydroxide solution (1M, 2 × 50 mL) and water (50 mL), dried over anhydrous magnesium sulphate, filtered, and the solvent removed under vacuum. The residue was further purified by column chromatography (silica, 1:1 chloroform / ethylacetate). Precipitation from

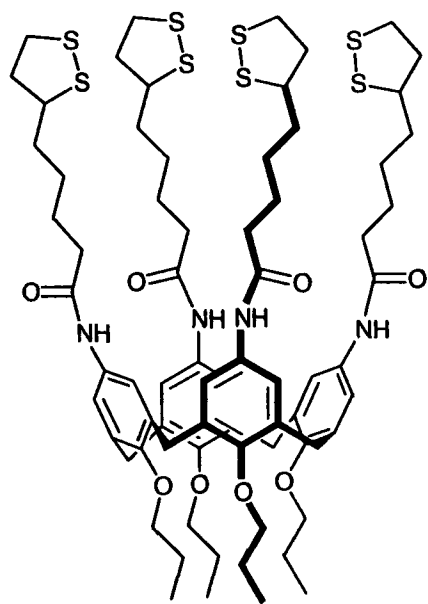
The chemical structure shows a macrocyclic ligand with a central cavity. The macrocycle is composed of four phenyl rings linked by four amide bonds (NH-C=O). Each amide group is part of a ferrocene moiety, where the amide nitrogen is attached to a cyclopentadienyl ring, which is in turn sandwiched between two iron (Fe) atoms. The four ferrocene arms are oriented outwards from the macrocycle. Additionally, there are two long, flexible side chains attached to the macrocycle, each consisting of a propyl chain followed by a 1,2,3-dithiolane ring (a five-membered ring with two adjacent sulfur atoms).

Procedure was the same as that for **73**, except **35** (440 mg, 0.41 mmol), thioctic acid (250 mg, 1.21 mmol) and EDC (235 mg, 1.23mmol) were used. Column chromatography (silica, 1:1 chloroform / ethylacetate) followed by precipitation from chloroform / hexane gave the product as an orange solid (340 mg, 57 %). (Found: C, 63.0; H, 6.0; N, 3.5 %. $C_{78}H_{92}Fe_2N_4O_8S_4$ requires C, 64.5; H, 6.4 N, 3.9 %.) ES-MS

m/z: 1475.3 (MNa⁺), 1491.2 (MK⁺). ¹H NMR (500 MHz, *d*₆-DMSO): δ 9.44 (s, NH, 2H), 9.20 (s, FcNH, 2H), 7.17 & 7.13 & 7.00 & 6.96 (all s, ArH, 4 × 2H), 4.92 (s, C₅H₄, 4H), 4.36 (m, C₅H₄ & ArCH_{ax}H_{eq}Ar, 8H), 4.16 (s, C₅H₅, 10H), 3.81 & 3.79 (both t, *J* = 7.5 Hz, OCH₂CH₂CH₃, 2 × 4H), 3.56 (m, COCH₂CH₂CH₂CH₂CH-CH₂CH₂SS, 2H), 3.11 (m, ArCH_{ax}H_{eq}Ar & COCH₂CH₂CH₂CH₂CH-CH₂CH₂SS, 8H), 2.35 (m, COCH₂CH₂CH₂CH₂CH-

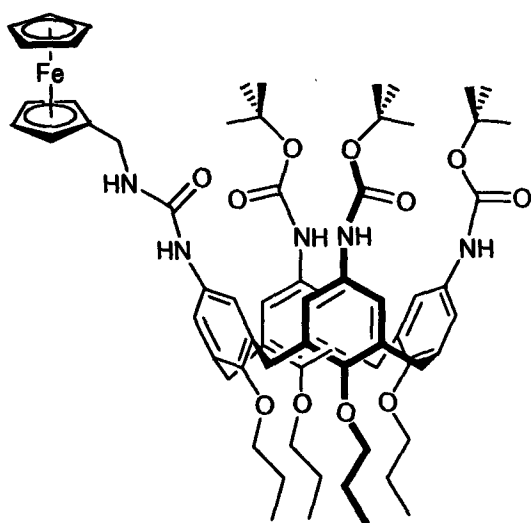
$\text{CH}_2\text{CH}_2\text{SS}$, 2H), 2.08 (t, $J = 7.5$ Hz, $\text{COCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}-\text{CH}_2\text{CH}_2\text{SS}$, 4H), 1.92 & 1.90 (both sext, $J = 7.5$ Hz, $\text{OCH}_2\text{CH}_2\text{CH}_3$, $2 \times 4\text{H}$), 1.81 (m, $\text{COCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}-\text{CH}_2\text{CH}_2\text{SS}$, 2H), 1.58 (m, $\text{COCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}-\text{CH}_2\text{CH}_2\text{SS}$, 2H), 1.46 (m, $\text{COCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}-\text{CH}_2\text{CH}_2\text{SS}$ & $\text{COCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}-\text{CH}_2\text{CH}_2\text{SS}$, 6H), 1.27 (m, $\text{COCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}-\text{CH}_2\text{CH}_2\text{SS}$, 4H), 0.95 & 0.94 (both t, $J = 7.5$ Hz, $\text{OCH}_2\text{CH}_2\text{CH}_3$, $2 \times 6\text{H}$).

Receptor 75



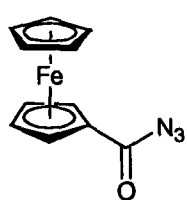
Procedure was the same as that for **73**, except **4** (400 mg, 0.61 mmol), thiocetic acid (760 mg, 3.68 mmol) and EDC (700 mg, 3.65 mg) were used. Column chromatography (silica, 1:1 chloroform / ethylacetate) followed by precipitation from chloroform / hexane gave the product as a cream solid (310 mg, 36 %). (Found: C, 61.2; H, 6.8; N, 4.2 %. $\text{C}_{72}\text{H}_{100}\text{N}_4\text{O}_8\text{S}_8$ requires C, 61.5; H, 7.2 N, 4.0 %.) ES-MS m/z : 1405.5 (MH^+), 1427.4 (MNa^+), 1443.4

(MK^+). ^1H NMR (500 MHz, d_6 -DMSO): δ 9.45 (s, NH, 4H), 6.93 (s, ArH, 8H), 4.32 (d, $J = 13.0$ Hz, $\text{ArCH}_{\text{ax}}\text{H}_{\text{eq}}\text{Ar}$, 4H), 3.75 (t, $J = 7.5$ Hz, $\text{OCH}_2\text{CH}_2\text{CH}_3$, 8H), 3.59 (m, $\text{COCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}-\text{CH}_2\text{CH}_2\text{SS}$, 4H), 3.16 & 3.11 (both m, $\text{COCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}-\text{CH}_2\text{CH}_2\text{SS}$, $2 \times 4\text{H}$), 3.04 (d, $J = 13.0$ Hz, $\text{ArCH}_{\text{ax}}\text{H}_{\text{eq}}\text{Ar}$, 4H), 2.39 (m, $\text{COCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}-\text{CH}_2\text{CH}_2\text{SS}$, 4H), 2.16 (t, $J = 7.5$ Hz, $\text{COCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}-\text{CH}_2\text{CH}_2\text{SS}$, 8H), 1.86 (sext, $J = 7.5$ Hz, $\text{OCH}_2\text{CH}_2\text{CH}_3$, 8H), 1.84 (m, $\text{COCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}-\text{CH}_2\text{CH}_2\text{SS}$, 4H), 1.63 (m, $\text{COCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}-\text{CH}_2\text{CH}_2\text{SS}$, 4H), 1.51 (m, $\text{COCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}-\text{CH}_2\text{CH}_2\text{SS}$ & $\text{COCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}-\text{CH}_2\text{CH}_2\text{SS}$, 12H), 1.32 (m, $\text{COCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}-\text{CH}_2\text{CH}_2\text{SS}$, 8H), 0.92 (t, $J = 7.5$ Hz, $\text{OCH}_2\text{CH}_2\text{CH}_3$, 12H).

Compound 76

Procedure was the same as that for **23**, except **5** (1000 mg, 1.05 mmol) and **18** (600 mg, 1.58 mmol) were used. Column chromatography (silica, 1:1 ethylacetate / hexane) followed by precipitation from chloroform / hexane gave the product as a pale yellow solid (580 mg, 46 %). (Found: C, 66.4; H, 6.0; N, 5.8 %. $C_{67}H_{87}FeN_5O_{11}$ requires C, 67.4; H, 7.3; N, 5.9 %.)

ES-MS m/z : 1194.6 (MH^+), 1216.6 (MNa^+), 1232.6 (MK^+). 1H NMR (300 MHz, d_6 -DMSO): δ 8.88 (s, BOCNH, 2H), 8.67 (s, BOCNH, 1H), 8.01 (s, ArNH, 1H), 6.91 (s, ArH, 4H), 6.65 (s, ArH, 2H), 6.55 (s, ArH, 2H), 5.76 (t, $J = 5.7$ Hz, CH_2NH , 1H), 4.28 (d, $J = 12.6$ Hz, $ArCH_{ax}H_{eq}Ar$, 4H), 4.13 (s, C_5H_5 , 5H), 4.10 (s, C_5H_4 , 2H), 4.05 (s, C_5H_4 , 2H), 3.89 (d, $J = 5.7$ Hz, CH_2NH , 2H), 3.78 & 3.65 (both t, $J = 7.5$ Hz, $OCH_2CH_2CH_3$, $2 \times 4H$), 3.00 & 2.98 (both d, $J = 12.6$ Hz, $ArCH_{ax}H_{eq}Ar$, $2 \times 2H$), 1.86 (sext, $J = 7.5$ Hz, $OCH_2CH_2CH_3$, 8H), 1.41 (s, CH_3 , 18H), 1.35 (s, CH_3 , 9H), 0.96 & 0.90 (both t, $J = 7.5$ Hz, $OCH_2CH_2CH_3$, $2 \times 6H$).

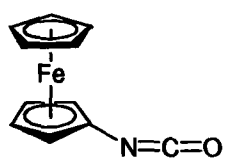
Ferroceneacetyl azide **77²³**

Oxalyl chloride (5 mL, excess) and pyridine (5 drops) were added to a suspension of **8** (3.39 g, 14.7 mmol) in dichloromethane (100 mL) and the mixture stirred at room temperature for 4 hours then heated to reflux overnight.

The volatiles were removed under vacuum and the solid residue dried under high vacuum for several hours. The residue was dissolved in acetone (75 mL) and a solution of sodium azide (1.44 g, 22.3 mmol) in water (7 mL) was added in one portion. The mixture was stirred for 30 minutes then poured into water (700 mL) precipitating a brown solid which was collected by filtration, washed with aqueous sodium hydrogen carbonate (1 M, 50 mL) and water (50 mL) and dried under vacuum (in the presence of phosphorus pentoxide) yielding the product as a

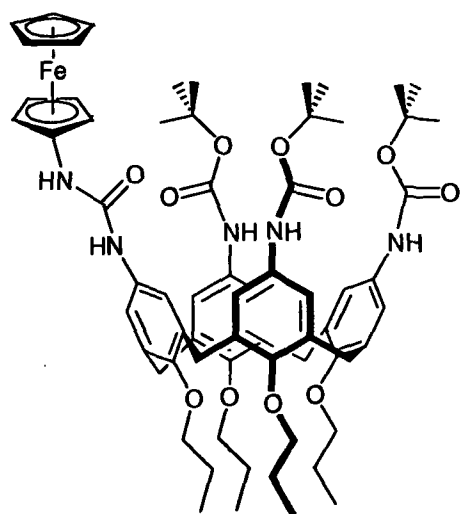
brown solid (3.50 g, 93 %). The product was not characterised but used immediately for subsequent reactions.

Isocyanatoferrocene **78**²³



A solution of **77** (3.45 g, 13.5 mmol) in dry toluene (100 mL) was heated at 110 °C for 30 minutes and the progress of the decomposition followed by thin layer chromatography. The solvent was removed under vacuum and the residue extracted with hexane (3 × 20 mL). The combined extracts were filtered through Celite®, the solvent removed under vacuum and the residue dried under high vacuum yielding the product as orange crystals (1.01 g, 33 %). The product was not characterised but used immediately for subsequent reactions.

Compound **79**

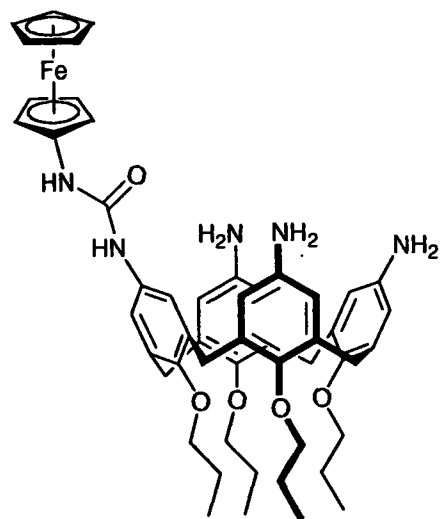


A solution of **5** (990 mg, 1.04 mmol) in chloroform (50 mL) was added dropwise to a stirred solution of **78** (360 mg, 1.59 mmol) in chloroform (50 mL) and the mixture stirred under nitrogen overnight. The solvent was removed under vacuum and the residue purified by column chromatography (silica, 10 % ethylacetate in chloroform). The product was obtained as a pale

yellow powder after precipitation from dichloromethane / hexane, followed by filtration and washing with hexane (730 mg, 60 %). (Found: C, 67.0; H, 7.4; N, 5.8 %. $C_{66}H_{85}FeN_5O_{11}$ requires C, 67.2; H, 7.3; N, 5.9 %.) ES-MS m/z : 1181.1 (MH^+). 1H NMR (500 MHz, d_6 -DMSO): δ 8.87 (s, BOCNH, 2H), 8.75 (s, BOCNH, 1H), 7.96 (s, ArNH, 1H), 7.37 (s, FcNH, 1H), 6.90 (s, ArH, 4H), 6.75 (s, ArH, 2H), 6.65 (s, ArH, 2H), 4.41 (s, C_5H_4 , 2H), 4.30 & 4.29 (both d, $J = 13.0$ Hz, $ArCH_{ax}H_{eq}Ar$, $2 \times 2H$), 4.08 (s, C_5H_5 , 5H), 3.89 (s, C_5H_4 , 2H), 3.77 (t, $J = 7.5$ Hz, $OCH_2CH_2CH_3$, 4H), 3.70 & 3.69 (both t, $J = 7.5$ Hz, $OCH_2CH_2CH_3$, $2 \times 2H$), 3.03

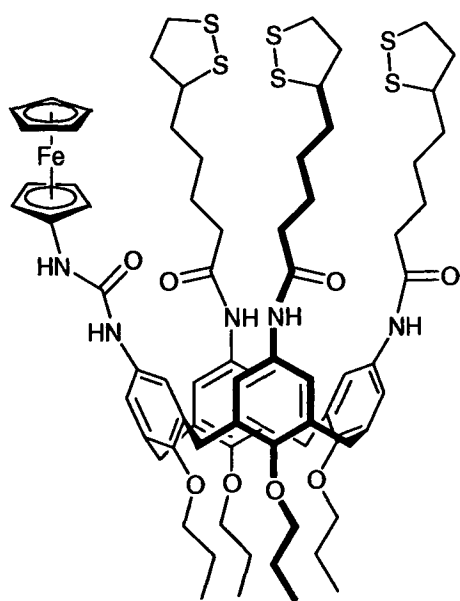
& 2.99 (both d, $J = 13.0$ Hz, $\text{ArCH}_{\text{ax}}\text{H}_{\text{eq}}\text{Ar}$, $2 \times 2\text{H}$), 1.87 (m, $\text{OCH}_2\text{CH}_2\text{CH}_3$, 8H), 1.39 (s, CH_3 , 18H), 1.34 (s, CH_3 , 9H), 0.91 (m, $\text{OCH}_2\text{CH}_2\text{CH}_3$, 12H).

Compound 80



Trifluoroacetic acid (5 mL, excess) was added to a solution of **79** (300 mg, 0.25 mmol) in dichloromethane (100 mL) and the mixture stirred for 1 hour. The mixture was washed with water (50 mL) and aqueous sodium hydroxide (1 M, 50 mL), dried over anhydrous magnesium sulphate, filtered, and the solvent removed under vacuum. The residue was dried under high vacuum for several hours to yield the product as a red solid (170 mg, 76 %). The product was not characterised but used immediately for subsequent reactions.

Receptor 81

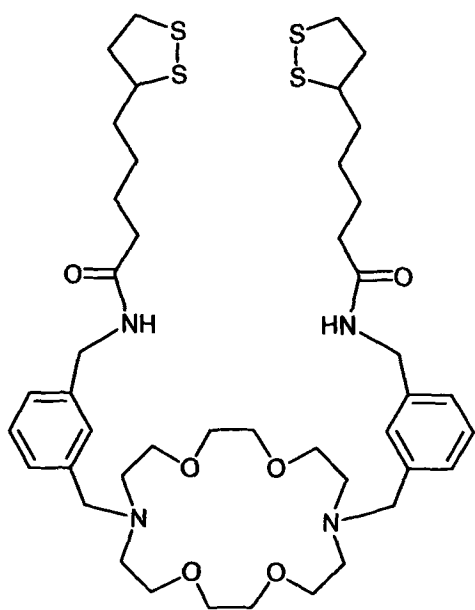


Procedure was the same as that for **73**, except **80** (170 mg, 0.19 mmol), thiocetic acid (170 mg, 0.82 mmol) and EDC (160 mg, 0.83 mmol) were used. Column chromatography (silica, 1:1 chloroform / ethylacetate) followed by precipitation from chloroform / hexane gave the product as a pale orange solid (120 mg, 43 %). (Found: C, 62.1; H, 6.7; N, 4.9 %. $\text{C}_{75}\text{H}_{97}\text{FeN}_5\text{O}_8\text{S}_6$ requires C, 62.3; H, 6.8 N, 4.8 %.) ES-MS m/z : 1444.7 (MH^+).

^1H NMR (500 MHz, d_6 -DMSO): δ 9.46 (s, NH, 3H), 7.97 (s, ArNH, 1H), 7.51 (s, FcNH, 1H), 6.97 & 6.96 & 6.92 & 6.73 (all s, ArH, $4 \times 2\text{H}$), 4.42 (s, C_5H_4 , 2H), 4.31 (d, $J = 12.5$ Hz, $\text{ArCH}_{\text{ax}}\text{H}_{\text{eq}}\text{Ar}$, 4H), 4.09 (s, C_5H_5 , 5H), 3.90 (s, C_5H_4 , 2H), 3.74 (m, $\text{OCH}_2\text{CH}_2\text{CH}_3$, 8H), 3.58 (m, $\text{COCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}-\text{CH}_2\text{CH}_2\text{SS}$, 3H), 3.08 (m, $\text{ArCH}_{\text{ax}}\text{H}_{\text{eq}}\text{Ar}$ & $\text{COCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}-\text{CH}_2\text{CH}_2\text{SS}$, 10H), 2.37 (m, $\text{COCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}-\text{CH}_2\text{CH}_2\text{SS}$,

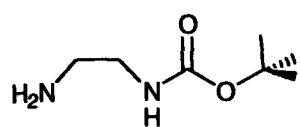
3H), 2.16 (m, $\text{COCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}-\text{CH}_2\text{CH}_2\text{SS}$, 6H), 1.84 (m, $\text{OCH}_2\text{CH}_2\text{CH}_3$ & $\text{COCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}-\text{CH}_2\text{CH}_2\text{SS}$, 11H), 1.62 (m, $\text{COCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}-\text{CH}_2\text{CH}_2\text{SS}$, 3H), 1.49 (m, $\text{COCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}-\text{CH}_2\text{CH}_2\text{SS}$ & $\text{COCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}-\text{CH}_2\text{CH}_2\text{SS}$, 9H), 1.31 (m, $\text{COCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}-\text{CH}_2\text{CH}_2\text{SS}$, 6H), 0.92 (m, $\text{OCH}_2\text{CH}_2\text{CH}_3$, 12H).

Receptor 82

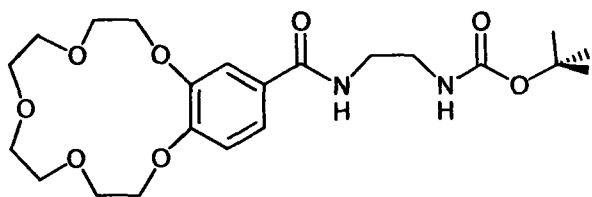


Thioctic acid (680 mg, 3.30 mmol) and EDC (630 mg, 3.29 mmol) were added to a solution of **52** (550 mg, 1.10 mmol) in dry dichloromethane (100 mL) and the mixture stirred under nitrogen overnight. The solvent was removed under vacuum and the residue dissolved in dichloromethane (100 mL). The organic layer was washed with aqueous lithium hydroxide (1M, 2×50 mL) and water (50 mL), dried over anhydrous

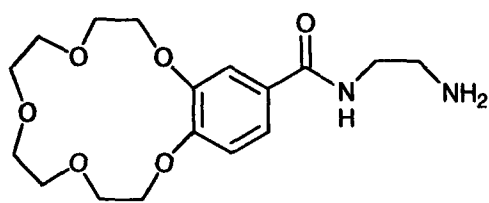
magnesium sulphate, filtered, and the solvent removed under vacuum to give the product as a pale yellow oil (900 mg, 93 %). (Found: C, 60.8; H, 7.6; N, 6.3 %. $\text{C}_{44}\text{H}_{68}\text{N}_4\text{O}_6\text{S}_4$ requires C, 60.2; H, 7.8 N, 6.4 %.) ES-MS m/z : 439.2 (MH_2^+), 877.4 (MH^+), 899.4 (MNa^+), 915.4 (MK^+). ^1H NMR (300 MHz, d_6 -DMSO): δ 8.27 (t, $J = 6.0$ Hz, NH, 2H), 7.30 – 7.00 (m, ArH, 8H), 4.22 (d, $J = 6.0$ Hz, ArCH_2NH , 4H), 3.58 (s, ArCH_2N , 4H), 3.50 (t, $J = 5.7$ Hz, $\text{NCH}_2\text{CH}_2\text{O}$, 8H), 3.47 (s, $\text{OCH}_2\text{CH}_2\text{O}$, 8H), 3.31 (obscured m, $\text{COCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}-\text{CH}_2\text{CH}_2\text{SS}$, 2H), 3.10 (m, $\text{COCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}-\text{CH}_2\text{CH}_2\text{SS}$, 4H), 2.66 (t, $J = 5.7$ Hz, $\text{NCH}_2\text{CH}_2\text{O}$, 8H), 2.37 (m, $\text{COCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}-\text{CH}_2\text{CH}_2\text{SS}$, 2H), 2.11 (m, $\text{COCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}-\text{CH}_2\text{CH}_2\text{SS}$, 4H), 1.83 (m, $\text{COCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}-\text{CH}_2\text{CH}_2\text{SS}$, 2H), 1.64 (m, $\text{COCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}-\text{CH}_2\text{CH}_2\text{SS}$, 2H), 1.53 (m, $\text{COCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}-\text{CH}_2\text{CH}_2\text{SS}$ & $\text{COCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}-\text{CH}_2\text{CH}_2\text{SS}$, 6H), 1.34 (m, $\text{COCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}-\text{CH}_2\text{CH}_2\text{SS}$, 4H).

***N*-*t*-Butoxycarbonyl-1,2-diaminoethane **83**²⁴**

A solution of di-*t*-butyl-dicarbonate (2.43 g, 11.1 mmol) in 1,4-dioxane (30 mL) was added dropwise over 30 minutes to a stirred solution of ethylenediamine (5.33 g, excess) in 1,4-dioxane (30 mL) under a nitrogen atmosphere. The mixture was stirred at room temperature overnight, filtered and the solvent removed under vacuum to afford a colourless oil. Water (50 mL) was added and the white precipitate that formed removed by filtration. The aqueous layer was extracted with dichloromethane (3 × 100 mL) and the combined organic fractions dried over anhydrous magnesium sulphate, filtered and the solvent removed under vacuum to yield the product as a colourless oil (1.63 g, 91 %). ¹H NMR (300 MHz, CDCl₃): δ 4.90 (br t, NH, 1H), 3.15 (q, *J* = 5.7 Hz, CH₂NH, 2H), 2.78 (t, *J* = 5.7 Hz, NH₂CH₂, 2H), 1.43 (s, CH₃, 9H), 1.15 (s, NH₂, 2H).

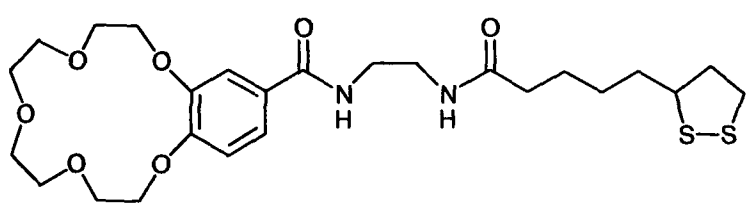
4'-(2-*t*-Butoxycarbonylaminoethyl)benzo[15]crown-5 **84**

A solution of **15** (1080 mg, 3.27 mmol) in anhydrous dichloromethane was added dropwise to a rapidly stirred solution of **83** (630 mg, 3.93 mmol) and triethylamine (2 mL, excess) in anhydrous dichloromethane under a nitrogen atmosphere. The mixture was stirred overnight, filtered, washed with aqueous sodium hydrogen carbonate (1M, 2 × 100mL) and water (2 × 100mL), dried over anhydrous magnesium sulphate, filtered and the solvent removed under vacuum. The residue was recrystallised from dichloromethane / hexane to give the product as a white powder (1350 mg, 91 %). ¹H NMR (500 MHz, CDCl₃): δ 7.45 (s, ArH, 1H), 7.37 (d, *J* = 8.5 Hz, ArH, 1H), 7.18 (br t, crownNH, 1H), 6.85 (d, *J* = 8.5 Hz, ArH, 1H), 5.01 (br t, NHBOC, 1H), 4.20 & 4.16 (both t, *J* = 4.5 Hz, ArOCH₂CH₂O, 2 × 2H), 3.92 & 3.91 (both t, *J* = 4.5 Hz, ArOCH₂CH₂O, 2 × 2H), 3.76 (s, OCH₂CH₂O, 8H), 3.53 (q, *J* = 5.5 Hz, crownNHCH₂, 2H), 3.39 (q, *J* = 5.5 Hz, CH₂NHBOC, 2H), 1.40 (s, CH₃, 9H).

Compound 85

Trifluoroacetic acid (10 mL, excess) was added to a solution of **84** (580 mg, 1.28 mmol) in dichloromethane (50 mL) and the mixture stirred for 2 hours. The solvent was removed under

vacuum and the residue dried under high vacuum for several hours to yield the product as its TFA salt (590 mg, 99 %). ^1H NMR (500 MHz, CDCl_3): δ 8.45 (s, NH, 1H), 7.51 (d, $J = 8.5$ Hz, ArH, 1H), 7.41 (s, NH_2 , 2H), 7.09 (s, ArH, 1H), 6.85 (d, $J = 8.5$ Hz, ArH, 1H), 4.22 & 4.04 (both s, $\text{ArOCH}_2\text{CH}_2\text{O}$, $2 \times 2\text{H}$), 3.79 & 3.63 (both s, $\text{ArOCH}_2\text{CH}_2\text{O}$, $2 \times 2\text{H}$), 3.74 (s, $\text{OCH}_2\text{CH}_2\text{O}$, 8H), 3.68 (s, NHCH_2 , 2H), 3.37 (s, CH_2NH_2 , 2H).

Receptor 86

Thioctic acid (400 mg, 1.94 mmol) and EDC (370 mg, 1.93 mg) were added to a solution of **85** (TFA salt, 590 mg, 1.26 mmol) and

triethylamine (5 mL, excess) in dry dichloromethane (100 mL) and the mixture stirred under nitrogen overnight. The solvent was removed under vacuum and the residue dissolved in dichloromethane (100 mL). The organic layer was washed with aqueous lithium hydroxide (1M, 2×50 mL) and water (50 mL), dried over anhydrous magnesium sulphate, filtered, and the solvent removed under vacuum. Precipitation from chloroform / hexane gave the product as a cream solid (370 mg, 54 %). (Found: C, 54.3; H, 7.3; N, 5.5 %. $\text{C}_{25}\text{H}_{38}\text{N}_2\text{O}_7\text{S}_2$ requires C, 55.3; H, 7.1 N, 5.2 %.) ES-MS m/z : 543.1 (MH^+), 565.0 (MNa^+). ^1H NMR (500 MHz, CDCl_3): δ 7.43 (s, ArH, 1H), 7.36 (d, $J = 8.5$ Hz, ArH, 1H), 7.18 (t, $J = 4.0$ Hz, crownNH, 1H), 6.87 (d, $J = 8.5$ Hz, ArH, 1H), 6.32 (t, $J = 5.5$ Hz, NH, 1H), 4.20 & 4.16 (both t, $J = 4.5$ Hz, $\text{ArOCH}_2\text{CH}_2\text{O}$, $2 \times 2\text{H}$), 3.92 & 3.91 (both t, $J = 4.5$ Hz, $\text{ArOCH}_2\text{CH}_2\text{O}$, $2 \times 2\text{H}$), 3.76 (s, $\text{OCH}_2\text{CH}_2\text{O}$, 8H), 3.55 (m, crownNHCH₂, 2H), 3.51 (m, CH₂NH, 2H), 3.46 (m, COCH₂CH₂CH₂CH₂CH-CH₂CH₂SS, 1H), 3.09 (m, COCH₂CH₂CH₂CH₂CH-CH₂CH₂SS, 2H),

2.38 (m, $\text{COCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}-\text{CH}_2\text{CH}_2\text{SS}$, 1H), 2.19 (t, $\text{COCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}-\text{CH}_2\text{CH}_2\text{SS}$, 2H), 1.82 (m, $\text{COCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}-\text{CH}_2\text{CH}_2\text{SS}$, 1H), 1.61 (m, $\text{COCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}-\text{CH}_2\text{CH}_2\text{SS}$ & $\text{COCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}-\text{CH}_2\text{CH}_2\text{SS}$, 4H), 1.39 (m, $\text{COCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}-\text{CH}_2\text{CH}_2\text{SS}$, 2H).

Dodecanethiol-protected gold nanoparticles²⁵

A yellow solution of hydrogen tetrachloroaurate (9.54 g of a solution comprising 41.66 % gold, 20.17 mmol) in water (120 mL) was added to a colourless solution of tricaprilmethylammonium chloride (aliquat®336, 10.12 g, 25.04 mmol) in toluene (200 mL). The two-phase mixture was stirred vigorously for 30 minutes after which time the tetrachloroaurate had been transferred into the organic layer. The organic phase was separated and dodecanethiol (1.70 g, 8.40 mmol) added. The mixture was stirred for 10 minutes, cooled in an ice-bath and a solution of sodium borohydride (3.18 g, 84.13 mmol) in water (100 mL) was slowly added. Stirring was continued for 3 hours, the dark purple organic phase was separated and the solvent reduced to 10 mL under vacuum. Ethanol (400 mL) was added and the mixture stored in a freezer (-18 °C) overnight. Filtration followed by washing with ethanol gave the product as a black waxy solid (4.88 g, 96 % based on gold elemental analysis). (Found: Au, 77.8; C, 15.8; H, 2.8; S, 3.6 %. The C:H:S ratio is that of dodecanethiol.) ¹H NMR (300 MHz, CDCl_3): δ 1.24 (br, CH_2 , 22H), 0.86 (br, CH_3 , 3H).

Tetrabutylammonium tetrafluoroborate

Tetrafluoroboric acid (48 %, 25 mL, 0.14 mol) was added dropwise to a stirred solution of tetrabutylammonium hydroxide (40 %, 75 mL, 0.12 mol) in water (150 mL). The white precipitate that formed was collected by filtration, washed with water (2 × 30 mL) and dissolved in dichloromethane (50 mL). The organic layer was separated and filtered. Diethylether (300 mL) was added with stirring to give a white solid which was collected by

filtration, washed with diethylether (2×30 mL) and dried under vacuum (35.2 g, 89 %). ^1H NMR (300 MHz, CDCl_3): δ 3.19 (t, $J = 8.5$ Hz, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$, 8H), 1.61 (m, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$, 8H), 1.41 (sext, $J = 7.2$ Hz, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$, 8H), 0.99 (t, $J = 7.2$ Hz, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$, 12H).

5.6 References

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Chapter Six

Appendices

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Chapter Six: Appendices

Appendix A: ^1H NMR Titrations

^1H NMR spectra were recorded on a Varian Mercury 300 instrument. In a typical anion titration experiment, aliquots of an anion (tetrabutylammonium chloride, acetate, benzoate or dihydrogen phosphate, 0.5 M, 2.5×10^{-4} moles in 0.5 mL deuterated solvent) were added to a 0.5 mL solution of a receptor (0.01 M, 5×10^{-6} moles in 0.5 mL deuterated solvent). Fifteen aliquots were added ($10 \times 2 \mu\text{L}$, $3 \times 10 \mu\text{L}$, $1 \times 20 \mu\text{L}$ and $1 \times 30 \mu\text{L}$) corresponding to 0, 0.2, 0.4, 0.6, 0.8, 1, 1.2, 1.4, 1.6, 1.8, 2, 3, 4, 5, 7 and 10 equivalents of anion. The chemical shift of a specific proton on the receptor was monitored as it moved downfield upon addition of anions. The resulting titration data was analysed by the computer program EQNMR¹ to yield stability constants for the anion / receptor binding processes.

For titrations in the presence of cations, the above procedure was repeated for addition of anions to a mixture of a receptor (5×10^{-6} moles in 0.4 mL deuterated solvent) and potassium or sodium perchlorate (0.1 mL of a 0.025, 0.05, 0.1 or 0.2 M solution in deuterated solvent depending on the required receptor / cation stoichiometry).

Job Plots² were obtained according to the following method. Solutions of a receptor (0.02 M, 6×10^{-5} moles in 3ml of deuterated solvent) and an anion (0.02 M, 6×10^{-5} moles in 3ml of deuterated solvent) were prepared and mixed in host / guest ratios of 10:0, 9:1, 8:2, 7:3, 6:4, 5:5, 4:6, 3:7, 2:8 and 1:9 to give ten samples each containing 0.5 mL of solution. The ^1H NMR spectrum of each sample was recorded and the chemical shift of a specific proton on the receptor was monitored to give a set of values for δ_{obs} . The free receptor chemical shift ($\delta_{\text{R}} = \delta_{\text{obs}}$ for the 10:0 sample) was subtracted from δ_{obs} to give $\Delta\delta$. The molefraction of receptor (x_{R}) was plotted against the product of $\Delta\delta$ and x_{R} to produce the Job Plot.

¹ M. J. Hynes, *J. Chem. Soc. Dalton Trans.*, 1993, 311.

² M. W. Likussar, D. F. Boltz, *Anal. Chem.*, 1971, **43**, 1265; K. A. Connors, *Binding Constants, The Measurement of Complex Stability*, Wiley, 1987; T. Blanda, J. H. Horner, M. J. Newcomb, *J. Org. Chem.*, 1989, **54**, 4626.

Appendix B: Electrochemical Studies

Cyclic voltammetry (CV) and square wave voltammetry (SWV) were performed on a EG & G Princeton Applied Research Potentiostat / Galvanostat model 273 linked to a computer using a National Instruments GPIB-PCII/IIA interface and controlled by EG & G Princeton Applied Research Model 270/250 Research Electrochemistry Software. A standard one-compartment three-electrode electrochemical cell was used with either a platinum or glassy carbon solid disc working electrode, a platinum wire auxiliary electrode and a silver / silver nitrate reference electrode (silver wire in 10 mM silver nitrate in electrolyte solution). In all experiments, the electrolyte solution was 0.1 M tetrabutylammonium tetrafluoroborate in 1:1 dichloromethane / acetonitrile. Ferrocene was employed as an internal standard; all electrochemical potentials are quoted relative to the ferrocene / ferrocenium couple ($E_{1/2} = 55 \pm 5$ mV wrt the silver / silver nitrate reference electrode). CVs were typically recorded with a 5 s equilibration time, a scan increment of 2 mV and a scan rate of 100 mV.s⁻¹; two cycles were recorded and the second one used for analysis. SWVs were typically recorded with a 5 s equilibration time, a scan increment of 2 mV and a frequency of 25 Hz. The working electrode was cleaned between scans by polishing on a solvent-soaked cloth.

Initial electrochemical studies of a receptor (5×10^{-4} M in electrolyte solution) involved recording a CV and SWV and recording CVs at various scan rates (20, 40 60, 80, 100, 200, 400, 600, 800, 1000 and 1500 mV.s⁻¹). Anion sensing studies were performed by recording a CV and SWV after the addition of 0, 0.5, 1, 2, 5, 10 and 20 equivalents of anion (tetrabutylammonium chloride, benzoate, dihydrogen phosphate or perrhenate, 0.125 M in

electrolyte solution, 20 μL is 1 equivalent) to a 5 mL aliquot of the receptor solution. Ion-pair sensing studies involved the addition of 1 equivalent of cation (potassium or sodium perchlorate, 0.125 M in DMSO, 20 μL is 1 equivalent) to a 5 mL aliquot of the receptor solution prior to performing the anion sensing studies.

Appendix C: UV-VIS Spectroscopic Studies

UV-VIS absorption spectra were acquired on a Perkin Elmer Lambda 6 Spectrometer using Perkin Elmer Computerised Spectroscopy Software. Spectra were recorded at 293 K between 190 and 900 nm with the following settings: Ordinate Mode A, Slit 4, Speed 960. Background corrections were made with neat solvent (3 mL) in the reference cell and an empty sample cell.

UV-VIS absorption spectra were recorded for solutions of the receptors in dry solvent. In a typical anion titration experiment, aliquots of an anion (tetrabutylammonium chloride, benzoate or dihydrogen phosphate, 5×10^{-3} M in dry solvent) were added to a 3 mL solution of a receptor (5×10^{-5} M in dry solvent). Twenty eight aliquots were added ($13 \times 2 \mu\text{L}$, $1 \times 4 \mu\text{L}$, $6 \times 5 \mu\text{L}$, $4 \times 15 \mu\text{L}$ and $4 \times 60 \mu\text{L}$) corresponding to 0, 0.07, 0.13, 0.2, 0.27, 0.33, 0.4, 0.47, 0.53, 0.6, 0.67, 0.73, 0.8, 0.87, 1, 1.17, 1.33, 1.5, 1.67, 1.83, 2, 2.5, 3, 3.5, 4, 6, 8, 10 and 12 equivalents of anion. Spectra were recorded and analysed by the computer program Specfit^{TM 1} to yield stability constants for the anion / receptor binding processes.

For titrations in the presence of one equivalent of potassium, a 3 μL aliquot of potassium perchlorate (0.05 M, 1.25×10^{-4} moles in 2.5 mL DMSO) was added to the 3 mL solution of receptor prior to the addition of anions.

¹ R. A. Binstead, A. D. Zuberbuhler, B. Jung, *Specfit 3.30.*, Spectrum Software Associates, 2002.

Appendix D: Luminescence Titrations

Emission spectra were acquired on a Perkin Elmer LS 50 B fluorescence spectrometer. Spectra were recorded at 298 K between 500 and 700 nm for solutions of the receptor (2×10^{-5} M) in dry acetonitrile. In a typical anion titration experiment, aliquots of an anion (tetrabutylammonium chloride, acetate, benzoate or dihydrogen phosphate, 6×10^{-3} M in dry acetonitrile) were added to a 3 mL solution of the receptor (2×10^{-5} M in dry acetonitrile). Twenty nine aliquots were added ($15 \times 2 \mu\text{L}$, $14 \times 5 \mu\text{L}$) corresponding to 0, 0.2, 0.4, 0.6, 0.8, 1, 1.2, 1.4, 1.6, 1.8, 2, 2.2, 2.4, 2.6, 2.8, 3, 3.5, 4, 4.5, 5, 5.5, 6, 6.5, 7, 7.5, 8, 8.5, 9, 9.5 and 10 equivalents of anion. Spectra were recorded and analysed by the computer program SpecfitTM to yield stability constants for the anion / receptor binding processes.

Appendix E: Preparation and Electrochemical Studies of SAMs on Gold Electrodes

E.1 Instrumentation

Electrochemistry experiments were carried out using a PG-STAT 12 Autolab instrument controlled with General Purpose Electrochemical System (GPES) software (version 4.8). A two-compartment three-electrode electrochemical cell was used, designed and made in-house. The cell consisted of a working compartment (containing the working electrode and platinum gauze auxiliary electrode) and a reference compartment (containing the reference electrode) connected by a Luggin capillary (to allow conduction between the two compartments without permitting mass transport). The cell was situated in a Faraday cage to minimise external noise.

E.2 Diffusive anion sensing

CV and SWV experiments were conducted as described in Appendix B but using the above instrumentation. A glassy carbon solid disc working electrode (commercial BAS electrode, 3 mm diameter) and a silver / silver nitrate reference electrode (silver wire in 10 mM silver nitrate in electrolyte solution) were used. The supporting electrolyte was 0.1 M tetrabutylammonium tetrafluoroborate in 1:1 dichloromethane / acetonitrile. Initial electrochemical studies of a receptor (5×10^{-4} M in electrolyte solution) involved recording a CV and SWV and recording CVs at various scan rates (20, 40, 60, 80, 100, 200, 400, 600, 800, 1000 and 1500 mV.s^{-1}). Anion sensing studies were performed by recording a CV and SWV after the addition of 0, 0.5, 1, 2, 5, 10 and 20 equivalents of anion (tetrabutylammonium chloride, benzoate, dihydrogen phosphate or perrhenate, 0.05 M in electrolyte solution, 10 μL is 1 equivalent) to a 1 mL aliquot of the receptor solution.

E.3 Electrode preparation and monolayer formation

Commercial BAS polycrystalline gold disc electrodes (1.6 mm diameter) were cleaned according to the following protocol. They were immersed in aqua regia (4:3:1 water / hydrochloric acid / nitric acid) for five minutes and rinsed thoroughly with deionised water. The electrodes were mechanically polished on a polishing wheel (Buehler variable speed grinder-polisher, Ecomet3 and Automet 2) using an alumina / water slurry (alumina particle size 0.015 μm) on a polishing cloth (Buehler microcloth). Typically, manual polishing was continued for an hour before sonication in deionised water for three minutes. The electrodes were then electrochemically polished in 1M sulphuric acid by cycling the potential for 100 scans between -700 mV and 1100 mV (wrt the mercury sulphate reference electrode). They were rinsed thoroughly with deionised water and alcohol, dried under argon and immersed in solutions of the receptor (1 – 3 mM in dichloromethane) overnight at 5 °C in the dark. After

formation of the monolayers, the modified electrodes were washed with dichloromethane and alcohol and dried under argon.

E.4 Monolayer characterisation and anion sensing

Initial electrochemical studies of SAMs on gold electrodes involved recording a CV in 0.1 M tetrabutylammonium tetrafluoroborate in 1:1 dichloromethane / acetonitrile. CVs were typically recorded with a 5 s equilibration time, a scan increment of 2 mV and a scan rate of 100 mV.s⁻¹; two cycles were recorded and the second one used for analysis. To readily enable comparison with the diffusive data, all electrochemical potentials are quoted relative to the internal standard ferrocene ($E_{1/2} = 55 \pm 5$ mV wrt the silver / silver nitrate reference electrode). The stability of the monolayers was probed by cycling the potential for 500 scans. The reversibility of the monolayer systems was investigated by recording CVs at various scan rates (20, 40 60, 80, 100, 200, 400, 600, 800, 1000 and 1500 mV.s⁻¹). Anion sensing studies were performed by recording CVs after the addition of aliquots of tetrabutylammonium chloride, benzoate, dihydrogen phosphate or perrhenate. Aliquots of the anion solutions (10 mM or 100 mM in electrolyte solution) were added to 1 mL of electrolyte solution in the working compartment such that the concentration of anion varied from 0 – 20 mM.

The above studies in organic media were repeated in aqueous solution in the presence of 0.1 M sodium perchlorate supporting electrolyte. A mercury sulphate reference electrode was used. Anion sensing studies were performed with sodium perrhenate and sodium dihydrogen phosphate as described above.

E.5 Reagents

Analytical grade reagents were used. Organic solvents were freshly distilled immediately prior to use. Tetrabutylammonium salts were stored under vacuum in a dessicator. All water used for polishing, washing or as a solvent was purified by a Millipore machine (to a

resistivity of $18 \text{ M}\Omega\cdot\text{cm}^{-1}$). All glassware was cleaned in Decon detergent and rinsed thoroughly with water prior to use.

Appendix F: Crystallographic Data

F.1 Introduction

Crystal structure determinations were carried out by either Dr. A. R. Cowley (denoted §) or Dr. R. L. Paul (denoted #) at the Chemical Crystallography Laboratory, University of Oxford. Typically a single crystal was mounted on a glass fibre using perfluoropolyether oil and cooled rapidly to 150 K in a stream of cold N_2 using an Oxford Cryosystems CRYOSTREAM unit. Diffraction data were measured using an Enraf-Nonius KappaCCD diffractometer (graphite-monochromated MoK_α radiation, $\lambda = 0.71073 \text{ \AA}$). Intensity data were processed using the DENZO-SMN package.¹ The structure was solved using the direct-methods program SIR92,² which located all non-hydrogen atoms. Subsequent full-matrix least-squares refinement was carried out using the CRYSTALS program suite.³ Coordinates and anisotropic thermal parameters of all non-hydrogen atoms were refined. All hydrogen atoms were positioned geometrically after each cycle of refinement. A 3- or 4-term Chebychev polynomial weighting scheme was applied.

F.2 Crystal data for $19\cdot 3\text{CH}_3\text{OH}\cdot 3\text{CHCl}_3$ §

X-ray quality orange crystals of $19\cdot 3\text{CH}_3\text{OH}\cdot 3\text{CHCl}_3$ were obtained from a chloroform solution of the compound exposed to methanol. The non-hydrogen atom numbering system is outlined in the schematic structure shown in Figure F.2.1.

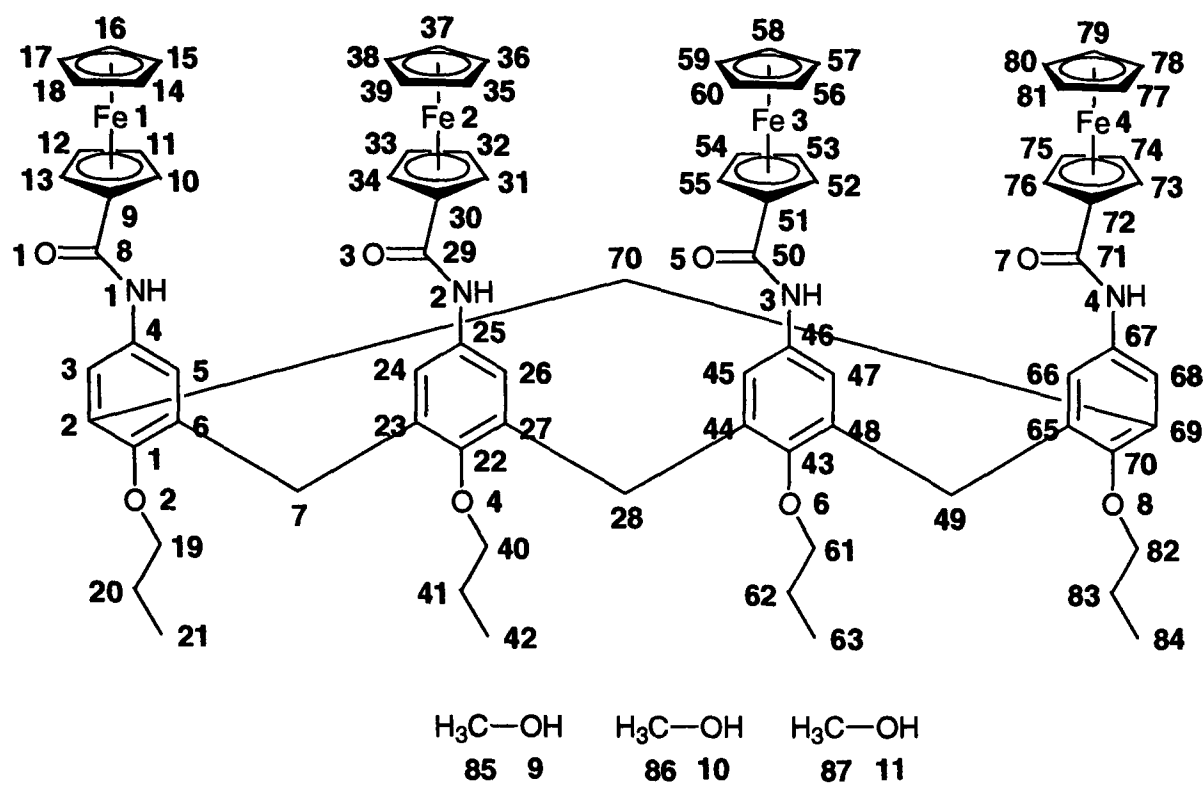


Figure F.2.1: Atom numbering system.

Table F.2.1: Crystal data and refinement details

Crystal identification	ARC142
Chemical formula	$\text{C}_{90}\text{H}_{99}\text{Cl}_9\text{Fe}_4\text{N}_4\text{O}_{11}$
Formula weight	1954.26
Temperature (K)	150
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	$P \bar{1}$
a (Å)	14.1072(1)
b (Å)	17.9519(1)
c (Å)	20.8413(2)
α (°)	70.9519(4)
β (°)	82.2956(4)
γ (°)	68.8153(4)
Cell volume (Å ³)	4533.4
Z	2
Calculated density (Mg/m ³)	1.432
Absorption coefficient (mm ⁻¹)	0.953
F_{000}	2027.10
Crystal size (mm)	0.3 x 0.3 x 0.3
Description of crystal	Orange fragment
Absorption correction	Semi-empirical from equivalent reflections
Transmission coefficients (min,max)	0.75, 0.75
θ range for data collection (°)	$5.0 \leq \theta \leq 27.5$
Index ranges	$-18 \leq h \leq 18, -21 \leq k \leq 22, 0 \leq l \leq 27$
Reflections measured	85895
Unique reflections	20463
R_{int}	0.047
Observed reflections ($I > 3\sigma(I)$)	13754

Refinement method	Full-matrix least-squares on F
Parameters refined	1091
Weighting scheme	Chebyshev 4-term polynomial
Goodness of fit	1.0504
R	0.0611
wR	0.0704
Residual electron density (min,max) ($\text{e}\text{\AA}^{-3}$)	-1.38, 1.63

Table F.2.2: Atomic coordinates, equivalent isotropic thermal parameters ($\text{\AA}^2$) and site occupancies (where not unity) of non-hydrogen atoms

Atom	x	y	z	U_{equiv}	Occupancy
Fe(1)	0.08648(4)	0.37791(3)	0.43135(3)	0.0270	
O(1)	-0.0032(2)	0.26256(16)	0.34346(12)	0.0298	
O(2)	0.27479(18)	-0.10572(15)	0.32615(12)	0.0236	
N(1)	0.0849(2)	0.16463(17)	0.43670(14)	0.0230	
C(1)	0.2298(2)	-0.0383(2)	0.35303(16)	0.0182	
C(2)	0.2326(2)	0.0435(2)	0.31689(15)	0.0184	
C(3)	0.1848(2)	0.1106(2)	0.34486(16)	0.0204	
C(4)	0.1327(2)	0.0971(2)	0.40646(16)	0.0213	
C(5)	0.1259(2)	0.0160(2)	0.44032(15)	0.0204	
C(6)	0.1731(2)	-0.0527(2)	0.41368(16)	0.0193	
C(7)	0.1571(2)	-0.1383(2)	0.44653(15)	0.0202	
C(8)	0.0253(2)	0.2443(2)	0.40231(16)	0.0213	
C(9)	-0.0050(2)	0.3090(2)	0.43847(16)	0.0208	
C(10)	-0.0588(3)	0.3984(2)	0.40735(19)	0.0283	
C(11)	-0.0617(3)	0.4427(2)	0.4544(2)	0.0309	
C(12)	-0.0102(3)	0.3826(2)	0.51382(19)	0.0287	
C(13)	0.0252(3)	0.2996(2)	0.50453(18)	0.0253	
C(14)	0.2046(3)	0.3365(3)	0.3697(2)	0.0456	
C(15)	0.1599(4)	0.4264(4)	0.3454(3)	0.0569	
C(16)	0.1677(5)	0.4597(4)	0.3965(4)	0.0703	
C(17)	0.2158(4)	0.3904(5)	0.4529(3)	0.0666	
C(18)	0.2394(3)	0.3141(4)	0.4360(3)	0.0567	
C(19)	0.3819(3)	-0.1464(3)	0.3346(2)	0.0400	
C(20)	0.4143(3)	-0.1872(3)	0.4069(3)	0.0436	
C(21)	0.5291(4)	-0.2300(4)	0.4119(3)	0.0644	
Fe(2)	-0.42966(4)	0.08902(3)	0.36270(3)	0.0277	
O(3)	-0.21078(19)	-0.09891(19)	0.45219(12)	0.0351	
O(4)	0.24379(16)	-0.27040(14)	0.38028(11)	0.0198	
N(2)	-0.16824(19)	-0.07657(17)	0.33976(13)	0.0198	
C(22)	0.1435(2)	-0.21762(19)	0.36690(15)	0.0164	
C(23)	0.0977(2)	-0.15580(19)	0.40101(15)	0.0181	
C(24)	-0.0054(2)	-0.1076(2)	0.39107(15)	0.0185	
C(25)	-0.0616(2)	-0.1208(2)	0.34806(15)	0.0188	
C(26)	-0.0124(2)	-0.1776(2)	0.31087(15)	0.0176	
C(27)	0.0907(2)	-0.22567(19)	0.31906(15)	0.0175	
C(28)	0.1436(2)	-0.2839(2)	0.27440(15)	0.0194	
C(29)	-0.2356(2)	-0.0730(2)	0.39291(17)	0.0222	

C(30)	-0.3443(3)	-0.0358(2)	0.37449(18)	0.0254
C(31)	-0.3889(3)	0.0033(3)	0.3090(2)	0.0338
C(32)	-0.4961(3)	0.0325(3)	0.3188(3)	0.0443
C(33)	-0.5189(3)	0.0125(3)	0.3896(3)	0.0425
C(34)	-0.4251(3)	-0.0304(3)	0.4247(2)	0.0337
C(35)	-0.3448(4)	0.1676(3)	0.3314(3)	0.0566
C(36)	-0.4404(4)	0.2104(3)	0.3023(3)	0.0557
C(37)	-0.5117(4)	0.2137(3)	0.3574(4)	0.0613
C(38)	-0.4579(6)	0.1721(4)	0.4179(3)	0.0684
C(39)	-0.3538(5)	0.1439(3)	0.4000(4)	0.0632
C(40)	0.2509(3)	-0.3541(2)	0.42648(18)	0.0274
C(41)	0.3601(3)	-0.4074(3)	0.4392(3)	0.0562
C(42)	0.3714(5)	-0.4970(3)	0.4868(5)	0.0904
Fe(3)	-0.19525(4)	-0.32692(3)	0.05613(3)	0.0247
O(5)	-0.17733(18)	-0.18019(16)	0.15074(12)	0.0259
O(6)	0.25891(17)	-0.17858(15)	0.19837(12)	0.0221
N(3)	-0.0572(2)	-0.18278(18)	0.06547(13)	0.0195
C(43)	0.1798(2)	-0.17794(19)	0.16563(15)	0.0177
C(44)	0.1243(2)	-0.23242(19)	0.20034(15)	0.0177
C(45)	0.0459(2)	-0.23310(19)	0.16692(15)	0.0179
C(46)	0.0200(2)	-0.1789(2)	0.10147(15)	0.0180
C(47)	0.0715(2)	-0.1219(2)	0.06947(15)	0.0187
C(48)	0.1509(2)	-0.11924(19)	0.10113(15)	0.0178
C(49)	0.1979(2)	-0.0492(2)	0.06958(15)	0.0196
C(50)	-0.1472(2)	-0.18907(19)	0.09369(16)	0.0194
C(51)	-0.2112(2)	-0.2058(2)	0.05294(17)	0.0232
C(52)	-0.3030(3)	-0.2238(2)	0.0786(2)	0.0302
C(53)	-0.3394(3)	-0.2436(3)	0.0278(2)	0.0382
C(54)	-0.2713(4)	-0.2388(3)	-0.0285(2)	0.0397
C(55)	-0.1913(3)	-0.2156(2)	-0.01409(17)	0.0284
C(56)	-0.0772(4)	-0.4073(3)	0.1189(3)	0.0466
C(57)	-0.1650(4)	-0.4289(3)	0.1426(2)	0.0475
C(58)	-0.1972(4)	-0.4503(3)	0.0917(3)	0.0507
C(59)	-0.1269(5)	-0.4419(3)	0.0359(3)	0.0556
C(60)	-0.0543(4)	-0.4145(3)	0.0532(3)	0.0543
C(61)	0.3595(3)	-0.2208(3)	0.1747(2)	0.0311
C(62)	0.3957(3)	-0.3172(3)	0.2054(2)	0.0419
C(63)	0.5036(4)	-0.3564(3)	0.1794(3)	0.0581
Fe(4)	-0.34221(4)	0.30016(4)	0.07792(3)	0.0308
O(7)	-0.0693(2)	0.24448(18)	0.03372(12)	0.0343
O(8)	0.33878(17)	-0.03258(15)	0.14832(12)	0.0235
N(4)	-0.0644(2)	0.18463(18)	0.14846(13)	0.0210
C(64)	0.2369(2)	0.0166(2)	0.15115(16)	0.0181
C(65)	0.1676(2)	0.0142(2)	0.11048(15)	0.0182
C(66)	0.0671(2)	0.0689(2)	0.11072(15)	0.0183
C(67)	0.0368(2)	0.1249(2)	0.14978(15)	0.0185
C(68)	0.1054(2)	0.1214(2)	0.19344(15)	0.0180
C(69)	0.2057(2)	0.0671(2)	0.19488(15)	0.0177
C(70)	0.2779(2)	0.0620(2)	0.24538(16)	0.0212
C(71)	-0.1084(3)	0.2427(2)	0.09030(17)	0.0239

C(72)	-0.2091(3)	0.3066(2)	0.09789(18)	0.0275	
C(73)	-0.2597(3)	0.3805(3)	0.0438(2)	0.0365	
C(74)	-0.3554(3)	0.4241(3)	0.0689(2)	0.0415	
C(75)	-0.3654(3)	0.3783(3)	0.1378(2)	0.0426	
C(76)	-0.2751(3)	0.3055(3)	0.1565(2)	0.0367	
C(77)	-0.3064(4)	0.1951(3)	0.0450(3)	0.0486	
C(78)	-0.3655(4)	0.1841(3)	0.1057(3)	0.0600	
C(79)	-0.4602(4)	0.2526(4)	0.0939(4)	0.0628	
C(80)	-0.4589(4)	0.3054(3)	0.0277(3)	0.0595	
C(81)	-0.3613(5)	0.2689(4)	-0.0040(3)	0.0617	
C(82)	0.3982(3)	0.0181(3)	0.1062(2)	0.0335	
C(83)	0.5081(3)	-0.0384(3)	0.1093(3)	0.0544	
C(84)	0.5786(5)	0.0094(5)	0.0772(5)	0.0856	
O(9)	-0.10905(19)	0.19434(16)	0.28668(12)	0.0289	
C(85)	-0.0774(3)	0.1052(3)	0.3246(2)	0.0354	
O(10)	-0.20347(19)	-0.04366(17)	0.19838(12)	0.0289	
C(86)	-0.1293(3)	-0.0049(3)	0.1658(2)	0.0352	
O(11)	0.0897(5)	0.3494(5)	0.2280(2)	0.1255	
C(87)	0.0366(8)	0.3580(4)	0.1710(3)	0.0937	
Cl(1)	-0.21493(15)	-0.26380(16)	0.35302(13)	0.1098	
Cl(2)	-0.07592(11)	-0.38914(9)	0.29586(7)	0.0621	
Cl(3)	-0.28826(14)	-0.36641(15)	0.30219(11)	0.0920	
C(88)	-0.1986(4)	-0.3138(3)	0.2899(3)	0.0493	
Cl(4)	-0.44848(18)	-0.58426(19)	0.33262(19)	0.1487	
Cl(5)	-0.25669(14)	-0.57788(9)	0.27206(8)	0.0725	
Cl(6)	-0.26343(13)	-0.68739(11)	0.40804(7)	0.0727	
C(89)	-0.3220(5)	-0.6406(3)	0.3303(3)	0.0606	
Cl(7)	-0.80419(11)	-0.4337(1)	0.15924(8)	0.0712	
Cl(8)	-0.63804(15)	-0.5838(2)	0.22374(12)	0.0756	0.659(5)
Cl(9)	-0.7158(2)	-0.57675(13)	0.0996(1)	0.0681	0.659(5)
C(90)	-0.7481(4)	-0.5477(4)	0.1760(3)	0.0447	0.659(5)
Cl(10)	-0.6264(4)	-0.5367(5)	0.2468(4)	0.0950	0.341(5)
Cl(11)	-0.6296(7)	-0.5349(8)	0.1099(4)	0.1843	0.341(5)
C(91)	-0.7036(7)	-0.5311(7)	0.1837(5)	0.0971	0.341(5)

Table F.2.3: Atomic coordinates, isotropic thermal parameters ($\text{\AA}^2$) and site occupancies (where not unity) of hydrogen atoms

Atom	x	y	z	U_{iso}	Occupancy
H(1)	0.0963	0.1523	0.4859	0.0278	
H(2)	-0.1948	-0.0467	0.2927	0.0232	
H(3)	-0.0437	-0.1807	0.0167	0.0257	
H(4)	-0.1040	0.1835	0.1921	0.0251	

H(31)	0.1882	0.1691	0.3202	0.0249
H(51)	0.0867	0.0069	0.4842	0.0249
H(71)	0.1187	-0.1374	0.4904	0.0249
H(72)	0.2248	-0.1851	0.4555	0.0249
H(101)	-0.0887	0.4248	0.3611	0.0334
H(111)	-0.0948	0.5060	0.4468	0.0380
H(121)	-0.0003	0.3960	0.5550	0.0386
H(131)	0.0641	0.2445	0.5381	0.0323
H(141)	0.2108	0.2954	0.3442	0.0618
H(151)	0.1283	0.4604	0.3001	0.0679
H(161)	0.1433	0.5219	0.3936	0.0967
H(171)	0.2304	0.3949	0.4969	0.0949
H(181)	0.2745	0.2546	0.4656	0.0704
H(191)	0.4150	-0.1021	0.3126	0.0482
H(192)	0.4059	-0.1919	0.3113	0.0482
H(201)	0.3920	-0.1420	0.4306	0.0549
H(202)	0.3814	-0.2315	0.4295	0.0549
H(211)	0.5483	-0.2567	0.4607	0.0772
H(212)	0.5625	-0.1861	0.3896	0.0772
H(213)	0.5519	-0.2756	0.3885	0.0772
H(241)	-0.0392	-0.0633	0.4150	0.0224
H(261)	-0.0517	-0.1841	0.2776	0.0216
H(281)	0.2184	-0.3077	0.2825	0.0225
H(282)	0.1162	-0.3322	0.2860	0.0225
H(311)	-0.3515	0.0090	0.2644	0.0427
H(321)	-0.5472	0.0623	0.2819	0.0569
H(331)	-0.5884	0.0262	0.4109	0.0555
H(341)	-0.4170	-0.0526	0.4751	0.0422
H(351)	-0.2789	0.1560	0.3054	0.0672
H(361)	-0.4558	0.2340	0.2528	0.0632
H(371)	-0.5872	0.2410	0.3535	0.0710
H(381)	-0.4876	0.1639	0.4649	0.0898
H(391)	-0.2964	0.1119	0.4325	0.0813
H(401)	0.2154	-0.3479	0.4703	0.0317
H(402)	0.2182	-0.3827	0.4061	0.0317
H(411)	0.3920	-0.3788	0.4601	0.0611
H(412)	0.3953	-0.4122	0.3950	0.0611
H(421)	0.4451	-0.5313	0.4944	0.0998
H(422)	0.3365	-0.4926	0.5311	0.0998
H(423)	0.3398	-0.5259	0.4660	0.0998
H(451)	0.0076	-0.2731	0.1903	0.0215
H(471)	0.0513	-0.0820	0.0229	0.0234
H(491)	0.2736	-0.0760	0.0689	0.0251
H(492)	0.1735	-0.0179	0.0221	0.0251
H(521)	-0.3355	-0.2226	0.1241	0.0380
H(531)	-0.4025	-0.2584	0.0313	0.0480
H(541)	-0.2782	-0.2499	-0.0715	0.0517
H(551)	-0.1325	-0.2077	-0.0447	0.0369
H(561)	-0.0379	-0.3897	0.1445	0.0533
H(571)	-0.1989	-0.4290	0.1879	0.0540

H(581)	-0.2577	-0.4682	0.0942	0.0645	
H(591)	-0.1291	-0.4533	-0.0078	0.0658	
H(601)	0.0038	-0.4023	0.0236	0.0602	
H(611)	0.4084	-0.1983	0.1867	0.0383	
H(612)	0.3584	-0.2069	0.1242	0.0383	
H(621)	0.3957	-0.3319	0.2560	0.0452	
H(622)	0.3489	-0.3408	0.1923	0.0452	
H(631)	0.5272	-0.4203	0.1999	0.0576	
H(632)	0.5504	-0.3329	0.1926	0.0576	
H(633)	0.5036	-0.3417	0.1289	0.0576	
H(661)	0.0161	0.0679	0.0823	0.0231	
H(681)	0.0824	0.1585	0.2242	0.0225	
H(701)	0.2901	0.1180	0.2329	0.0280	
H(702)	0.3439	0.0149	0.2439	0.0280	
H(731)	-0.2323	0.3981	-0.0034	0.0418	
H(741)	-0.4071	0.4782	0.0424	0.0494	
H(751)	-0.4256	0.3943	0.1682	0.0530	
H(761)	-0.2605	0.2616	0.2022	0.0425	
H(771)	-0.2364	0.1560	0.0383	0.0639	
H(781)	-0.3443	0.1366	0.1491	0.0750	
H(791)	-0.5178	0.2613	0.1275	0.0818	
H(801)	-0.5151	0.3591	0.0056	0.0745	
H(811)	-0.3384	0.2924	-0.0515	0.0794	
H(821)	0.3901	0.0674	0.1233	0.0417	
H(822)	0.3749	0.0407	0.0582	0.0417	
H(831)	0.5265	-0.0685	0.1581	0.0673	
H(832)	0.5165	-0.0818	0.0856	0.0673	
H(841)	0.6535	-0.0221	0.0765	0.1097	
H(842)	0.5513	0.0732	0.0563	0.1097	
H(5)	-0.0710	0.2189	0.3071	0.0347	
H(851)	-0.1122	0.0754	0.3073	0.0406	
H(852)	-0.0956	0.0990	0.3736	0.0406	
H(853)	-0.0021	0.0789	0.3194	0.0406	
H(6)	-0.1940	-0.0930	0.1812	0.0369	
H(861)	-0.1375	0.0448	0.1824	0.0426	
H(862)	-0.0596	-0.0481	0.1766	0.0426	
H(863)	-0.1387	0.0159	0.1156	0.0426	
H(7)	0.0569	0.3187	0.2688	0.1530	
H(871)	0.0662	0.3885	0.1283	0.1045	
H(872)	-0.0369	0.3919	0.1752	0.1045	
H(873)	0.0434	0.2997	0.1695	0.1045	
H(881)	-0.2085	-0.2699	0.2441	0.0590	
H(891)	-0.3182	-0.6899	0.3146	0.0727	
H(901)	-0.7986	-0.5750	0.2016	0.0497	0.659

H(911)	-0.7309	-0.5795	0.2036	0.1034	0.341
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Table F.2.4: Anisotropic thermal parameters (Å²)

Atom	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂
Fe(1)	0.0283(3)	0.0286(3)	0.0322(3)	-0.0172(2)	0.0094(2)	-0.0153(2)
O(1)	0.0370(14)	0.0271(12)	0.0229(12)	-0.010(1)	-0.012(1)	-0.002(1)
O(2)	0.0283(12)	0.0235(11)	0.0247(12)	-0.0146(9)	0.0015(9)	-0.009(1)
N(1)	0.0311(15)	0.0184(13)	0.0199(13)	-0.0101(11)	-0.0020(11)	-0.0047(11)
C(1)	0.0163(14)	0.0207(15)	0.0216(15)	-0.0124(12)	-0.0043(11)	-0.0040(11)
C(2)	0.0129(13)	0.0265(15)	0.0183(14)	-0.0086(12)	-0.0061(11)	-0.0060(12)
C(3)	0.0245(15)	0.0206(15)	0.0173(14)	-0.0059(12)	-0.0052(12)	-0.0072(12)
C(4)	0.0241(15)	0.0214(15)	0.0190(15)	-0.0112(12)	-0.0055(12)	-0.0022(12)
C(5)	0.0220(15)	0.0241(15)	0.0161(14)	-0.0089(12)	-0.0030(11)	-0.0057(12)
C(6)	0.0205(15)	0.0210(15)	0.0190(14)	-0.0071(12)	-0.0074(12)	-0.0066(12)
C(7)	0.0246(16)	0.0220(15)	0.0157(14)	-0.0074(12)	-0.0035(12)	-0.0073(12)
C(8)	0.0225(15)	0.0223(15)	0.0217(15)	-0.0101(13)	0.0006(12)	-0.0077(12)
C(9)	0.0221(15)	0.0198(15)	0.0218(15)	-0.0073(12)	0.0004(12)	-0.0078(12)
C(10)	0.0304(18)	0.0217(16)	0.0315(18)	-0.0076(14)	0.0029(14)	-0.0090(14)
C(11)	0.0309(18)	0.0232(17)	0.041(2)	-0.0163(15)	0.0079(16)	-0.0091(14)
C(12)	0.0313(18)	0.0319(18)	0.0333(19)	-0.0205(15)	0.0101(15)	-0.0168(15)
C(13)	0.0289(17)	0.0255(16)	0.0264(17)	-0.0133(14)	0.0022(13)	-0.0110(14)
C(14)	0.039(2)	0.062(3)	0.053(3)	-0.040(2)	0.022(2)	-0.026(2)
C(15)	0.054(3)	0.062(3)	0.053(3)	-0.018(2)	0.026(2)	-0.028(2)
C(16)	0.069(4)	0.063(3)	0.109(5)	-0.054(4)	0.058(4)	-0.054(3)
C(17)	0.051(3)	0.109(5)	0.078(4)	-0.058(4)	0.023(3)	-0.052(3)
C(18)	0.0199(19)	0.082(4)	0.074(3)	-0.036(3)	0.008(2)	-0.016(2)
C(19)	0.0292(19)	0.036(2)	0.055(3)	-0.0264(19)	0.0073(18)	-0.0029(16)
C(20)	0.0275(19)	0.047(2)	0.063(3)	-0.030(2)	-0.0046(19)	-0.0067(18)
C(21)	0.037(2)	0.061(3)	0.095(4)	-0.041(3)	-0.008(3)	0.002(2)
Fe(2)	0.0156(2)	0.0322(3)	0.0360(3)	-0.0154(2)	-0.00049(19)	-0.00425(19)
O(3)	0.0264(13)	0.0531(17)	0.0180(12)	-0.0107(11)	-0.000(1)	-0.0045(12)
O(4)	0.016(1)	0.018(1)	0.0237(11)	-0.0044(9)	-0.0059(8)	-0.0028(8)
N(2)	0.0163(12)	0.0236(13)	0.0182(12)	-0.0092(11)	-0.003(1)	-0.002(1)
C(22)	0.0155(13)	0.0163(13)	0.0170(14)	-0.0029(11)	-0.0014(11)	-0.0063(11)
C(23)	0.0205(14)	0.0193(14)	0.0152(14)	-0.0053(11)	-0.0028(11)	-0.0066(12)
C(24)	0.0191(14)	0.0215(15)	0.0153(14)	-0.0066(11)	0.0005(11)	-0.0068(12)
C(25)	0.0182(14)	0.0211(14)	0.0157(14)	-0.0048(12)	-0.0017(11)	-0.0054(12)
C(26)	0.0165(14)	0.0218(14)	0.0158(14)	-0.0067(12)	-0.0022(11)	-0.0063(11)
C(27)	0.0216(15)	0.0192(14)	0.0133(13)	-0.0056(11)	-0.0004(11)	-0.0081(12)
C(28)	0.0201(14)	0.0197(14)	0.0164(14)	-0.0068(12)	-0.0029(11)	-0.0024(12)
C(29)	0.0191(15)	0.0234(15)	0.0235(16)	-0.0116(13)	0.0006(12)	-0.0027(12)
C(30)	0.0206(16)	0.0318(17)	0.0279(17)	-0.0158(14)	0.0027(13)	-0.0085(13)
C(31)	0.0203(16)	0.051(2)	0.036(2)	-0.0239(18)	-0.0052(14)	-0.0070(16)
C(32)	0.0241(19)	0.058(3)	0.060(3)	-0.033(2)	-0.0117(18)	-0.0077(18)
C(33)	0.0210(18)	0.050(2)	0.068(3)	-0.032(2)	0.0079(18)	-0.0150(17)
C(34)	0.0256(18)	0.037(2)	0.043(2)	-0.0181(17)	0.0092(16)	-0.0138(15)
C(35)	0.036(2)	0.039(2)	0.093(4)	-0.015(3)	0.001(2)	-0.0152(19)
C(36)	0.062(3)	0.042(3)	0.055(3)	-0.003(2)	-0.006(2)	-0.015(2)

C(37)	0.030(2)	0.040(2)	0.108(5)	-0.030(3)	0.007(3)	-0.0004(19)
C(38)	0.122(6)	0.050(3)	0.052(3)	-0.028(3)	0.012(3)	-0.045(3)
C(39)	0.068(4)	0.046(3)	0.088(4)	-0.018(3)	-0.028(3)	-0.028(3)
C(40)	0.0267(17)	0.0221(16)	0.0305(18)	0.0032(13)	-0.0120(14)	-0.0106(14)
C(41)	0.033(2)	0.026(2)	0.094(4)	0.005(2)	-0.029(2)	-0.0031(17)
C(42)	0.057(3)	0.033(3)	0.160(7)	0.024(3)	-0.067(4)	-0.014(2)
Fe(3)	0.0314(3)	0.0225(2)	0.0254(3)	-0.00975(19)	0.0007(2)	-0.0133(2)
O(5)	0.0254(12)	0.0316(13)	0.0259(12)	-0.015(1)	0.0051(9)	-0.012(1)
O(6)	0.0194(11)	0.0268(12)	0.0243(11)	-0.0119(9)	-0.0037(9)	-0.0078(9)
N(3)	0.0209(13)	0.0274(14)	0.0159(12)	-0.009(1)	-0.002(1)	-0.0121(11)
C(43)	0.0185(14)	0.0200(14)	0.0188(14)	-0.0116(12)	0.0000(11)	-0.0062(12)
C(44)	0.0170(14)	0.0183(14)	0.0177(14)	-0.0095(11)	-0.0001(11)	-0.0023(11)
C(45)	0.0188(14)	0.0170(14)	0.0180(14)	-0.0070(11)	0.0003(11)	-0.0048(11)
C(46)	0.0183(14)	0.0205(14)	0.0177(14)	-0.0091(12)	-0.0011(11)	-0.0061(12)
C(47)	0.0229(15)	0.0210(14)	0.0145(13)	-0.0077(11)	-0.0003(11)	-0.0080(12)
C(48)	0.0191(14)	0.0197(14)	0.0189(14)	-0.0108(12)	0.0029(11)	-0.0079(12)
C(49)	0.0231(15)	0.0247(15)	0.0149(14)	-0.0081(12)	0.0034(11)	-0.0120(13)
C(50)	0.0207(15)	0.0167(14)	0.0220(15)	-0.0056(12)	-0.0028(12)	-0.0071(12)
C(51)	0.0222(15)	0.0196(15)	0.0287(17)	-0.0077(13)	-0.0039(13)	-0.0066(12)
C(52)	0.0234(17)	0.0277(17)	0.044(2)	-0.0121(15)	-0.0025(15)	-0.0119(14)
C(53)	0.0303(19)	0.033(2)	0.057(3)	-0.0121(18)	-0.0097(18)	-0.0151(16)
C(54)	0.053(3)	0.039(2)	0.037(2)	-0.0067(17)	-0.0184(19)	-0.0252(19)
C(55)	0.0383(19)	0.0316(18)	0.0224(16)	-0.0024(14)	-0.0086(14)	-0.0223(16)
C(56)	0.053(3)	0.0243(19)	0.056(3)	-0.0093(18)	-0.018(2)	-0.0022(18)
C(57)	0.072(3)	0.0238(19)	0.039(2)	-0.0035(17)	-0.003(2)	-0.012(2)
C(58)	0.072(3)	0.028(2)	0.061(3)	-0.013(2)	-0.003(2)	-0.027(2)
C(59)	0.087(4)	0.029(2)	0.048(3)	-0.022(2)	0.001(3)	-0.008(2)
C(60)	0.045(3)	0.030(2)	0.075(3)	-0.017(2)	0.014(2)	-0.0030(19)
C(61)	0.0223(17)	0.0360(19)	0.037(2)	-0.0161(16)	-0.0028(14)	-0.0076(15)
C(62)	0.031(2)	0.037(2)	0.045(2)	-0.0046(18)	-0.0016(17)	-0.0033(17)
C(63)	0.032(2)	0.050(3)	0.061(3)	-0.002(2)	0.006(2)	0.006(2)
Fe(4)	0.0238(3)	0.0328(3)	0.0365(3)	-0.0175(2)	-0.0093(2)	-0.0009(2)
O(7)	0.0311(13)	0.0400(15)	0.0199(12)	-0.0076(11)	-0.002(1)	0.0007(11)
O(8)	0.016(1)	0.0270(12)	0.0313(12)	-0.014(1)	0.0011(9)	-0.0080(9)
N(4)	0.0179(13)	0.0267(14)	0.0182(13)	-0.0101(11)	-0.001(1)	-0.0039(11)
C(64)	0.0157(14)	0.0206(14)	0.0195(14)	-0.0082(12)	0.0028(11)	-0.0072(11)
C(65)	0.0202(14)	0.0233(15)	0.0156(14)	-0.0072(12)	0.0035(11)	-0.0126(12)
C(66)	0.0196(14)	0.0245(15)	0.0137(13)	-0.0050(12)	-0.0019(11)	-0.0109(12)
C(67)	0.0178(14)	0.0215(15)	0.0145(14)	-0.0030(12)	0.0006(11)	-0.0071(12)
C(68)	0.0181(14)	0.0210(14)	0.0170(14)	-0.0079(12)	0.0014(11)	-0.0077(12)
C(69)	0.0177(14)	0.0232(15)	0.0165(14)	-0.0077(12)	0.0029(11)	-0.0113(12)
C(70)	0.0183(14)	0.0286(16)	0.0230(16)	-0.0121(13)	-0.0011(12)	-0.0113(13)
C(71)	0.0254(16)	0.0283(17)	0.0202(15)	-0.0089(13)	-0.0029(13)	-0.0091(13)
C(72)	0.0236(16)	0.0298(17)	0.0263(17)	-0.0101(14)	-0.0042(13)	-0.0030(14)
C(73)	0.037(2)	0.0286(19)	0.039(2)	-0.0076(16)	-0.0079(17)	-0.0051(16)
C(74)	0.034(2)	0.031(2)	0.059(3)	-0.0207(19)	-0.0120(19)	0.0004(16)
C(75)	0.0256(18)	0.055(3)	0.052(3)	-0.037(2)	-0.0056(17)	0.0011(18)
C(76)	0.0244(17)	0.052(2)	0.0295(19)	-0.0205(18)	-0.0026(15)	-0.0004(17)
C(77)	0.045(2)	0.043(2)	0.072(3)	-0.036(2)	-0.004(2)	-0.014(2)
C(78)	0.052(3)	0.049(3)	0.087(4)	-0.022(3)	-0.009(3)	-0.022(2)

C(79)	0.039(3)	0.069(3)	0.097(5)	-0.039(3)	-0.006(3)	-0.022(2)
C(80)	0.050(3)	0.051(3)	0.084(4)	-0.034(3)	-0.033(3)	-0.003(2)
C(81)	0.080(4)	0.063(3)	0.056(3)	-0.030(3)	-0.022(3)	-0.021(3)
C(82)	0.0223(17)	0.037(2)	0.045(2)	-0.0168(17)	0.0115(15)	-0.0147(15)
C(83)	0.025(2)	0.054(3)	0.090(4)	-0.034(3)	0.015(2)	-0.0139(19)
C(84)	0.050(3)	0.090(5)	0.134(7)	-0.056(5)	0.027(4)	-0.034(3)
O(9)	0.0341(13)	0.0309(13)	0.0217(12)	-0.006(1)	-0.006(1)	-0.0110(11)
C(85)	0.0299(19)	0.039(2)	0.032(2)	-0.0011(16)	-0.0051(15)	-0.0133(16)
O(10)	0.0319(13)	0.0354(13)	0.0251(12)	-0.014(1)	0.002(1)	-0.0143(11)
C(86)	0.042(2)	0.0313(19)	0.033(2)	-0.0090(16)	0.0065(16)	-0.0165(17)
O(11)	0.148(5)	0.192(7)	0.042(2)	0.010(3)	-0.010(3)	-0.102(5)
C(87)	0.163(8)	0.042(3)	0.057(4)	0.000(3)	-0.004(4)	-0.025(4)
Cl(1)	0.0888(12)	0.1502(18)	0.172(2)	-0.1311(18)	0.0677(13)	-0.0847(13)
Cl(2)	0.0625(8)	0.0505(7)	0.0566(7)	0.0002(6)	0.0019(6)	-0.0157(6)
Cl(3)	0.0810(11)	0.1431(17)	0.1144(14)	-0.0970(14)	0.042(1)	-0.0730(12)
C(88)	0.052(3)	0.050(3)	0.045(3)	-0.012(2)	0.011(2)	-0.023(2)
Cl(4)	0.0737(13)	0.118(2)	0.198(3)	0.015(2)	-0.0198(16)	-0.0177(13)
Cl(5)	0.1073(12)	0.0546(8)	0.0554(8)	-0.0005(6)	-0.0165(8)	-0.0361(8)
Cl(6)	0.088(1)	0.088(1)	0.0411(7)	-0.0010(7)	-0.0206(7)	-0.0392(9)
C(89)	0.086(4)	0.043(3)	0.053(3)	0.004(2)	-0.034(3)	-0.027(3)
Cl(7)	0.0550(8)	0.0561(7)	0.0773(9)	-0.0153(7)	0.0028(7)	0.0046(6)
Cl(8)	0.0317(9)	0.105(2)	0.0505(12)	0.0034(13)	-0.0034(8)	-0.0013(11)
Cl(9)	0.0945(19)	0.0491(11)	0.0465(11)	-0.0186(8)	0.0171(11)	-0.0108(11)
C(90)	0.036(3)	0.0532(13)	0.035(3)	-0.010(3)	0.004(2)	-0.009(3)
Cl(10)	0.075(3)	0.092(4)	0.090(4)	0.005(3)	-0.000(3)	-0.025(3)
Cl(11)	0.116(7)	0.216(11)	0.097(5)	-0.051(6)	0.005(4)	0.086(7)
C(91)	0.061(12)	0.090(14)	0.11(1)	-0.057(9)	0.002(5)	0.035(9)

Table F.2.5: Bond lengths (Å)
(H atoms have been excluded)

Fe(1) - C(9)	2.024(3)	Fe(3) - C(51)	2.029(3)
Fe(1) - C(10)	2.050(4)	Fe(3) - C(52)	2.040(4)
Fe(1) - C(11)	2.064(4)	Fe(3) - C(53)	2.056(4)
Fe(1) - C(12)	2.050(3)	Fe(3) - C(54)	2.044(4)
Fe(1) - C(13)	2.023(4)	Fe(3) - C(55)	2.033(3)
Fe(1) - C(14)	2.029(4)	Fe(3) - C(56)	2.037(4)
Fe(1) - C(15)	2.036(5)	Fe(3) - C(57)	2.042(4)
Fe(1) - C(16)	2.042(4)	Fe(3) - C(58)	2.051(4)
Fe(1) - C(17)	2.036(5)	Fe(3) - C(59)	2.048(4)
Fe(1) - C(18)	2.038(4)	Fe(3) - C(60)	2.033(5)
O(1) - C(8)	1.246(4)	O(5) - C(50)	1.247(4)
O(2) - C(1)	1.380(4)	O(6) - C(43)	1.379(4)

O(2) - C(19)	1.426(5)	O(6) - C(61)	1.448(4)
N(1) - C(4)	1.430(4)	N(3) - C(46)	1.435(4)
N(1) - C(8)	1.352(4)	N(3) - C(50)	1.352(4)
C(1) - C(2)	1.395(5)	C(43) - C(44)	1.408(4)
C(1) - C(6)	1.403(5)	C(43) - C(48)	1.404(4)
C(2) - C(3)	1.393(4)	C(44) - C(45)	1.389(4)
C(3) - C(4)	1.386(5)	C(45) - C(46)	1.390(4)
C(4) - C(5)	1.394(5)	C(46) - C(47)	1.388(4)
C(5) - C(6)	1.398(4)	C(47) - C(48)	1.396(4)
C(6) - C(7)	1.516(4)	C(48) - C(49)	1.523(4)
C(7) - C(23)	1.512(4)	C(49) - C(65)	1.521(4)
C(8) - C(9)	1.468(4)	C(50) - C(51)	1.476(4)
C(9) - C(10)	1.433(5)	C(51) - C(52)	1.436(5)
C(9) - C(13)	1.436(5)	C(51) - C(55)	1.441(5)
C(10) - C(11)	1.425(5)	C(52) - C(53)	1.421(6)
C(11) - C(12)	1.417(6)	C(53) - C(54)	1.414(7)
C(12) - C(13)	1.425(5)	C(54) - C(55)	1.425(5)
C(14) - C(15)	1.406(8)	C(56) - C(57)	1.404(7)
C(14) - C(18)	1.413(8)	C(56) - C(60)	1.400(8)
C(15) - C(16)	1.402(8)	C(57) - C(58)	1.408(7)
C(16) - C(17)	1.41(1)	C(58) - C(59)	1.429(8)
C(17) - C(18)	1.403(8)	C(59) - C(60)	1.405(8)
C(19) - C(20)	1.496(7)	C(61) - C(62)	1.509(6)
C(20) - C(21)	1.520(6)	C(62) - C(63)	1.532(6)
Fe(2) - C(30)	2.027(3)	Fe(4) - C(72)	2.026(4)
Fe(2) - C(31)	2.033(4)	Fe(4) - C(73)	2.035(4)
Fe(2) - C(32)	2.045(4)	Fe(4) - C(74)	2.056(4)
Fe(2) - C(33)	2.056(4)	Fe(4) - C(75)	2.053(4)
Fe(2) - C(34)	2.050(4)	Fe(4) - C(76)	2.041(4)
Fe(2) - C(35)	2.036(5)	Fe(4) - C(77)	2.041(4)
Fe(2) - C(36)	2.047(5)	Fe(4) - C(78)	2.057(5)
Fe(2) - C(37)	2.040(5)	Fe(4) - C(79)	2.060(5)
Fe(2) - C(38)	2.036(5)	Fe(4) - C(80)	2.026(5)
Fe(2) - C(39)	2.032(5)	Fe(4) - C(81)	2.031(5)
O(3) - C(29)	1.221(4)	O(7) - C(71)	1.229(4)
O(4) - C(22)	1.388(4)	O(8) - C(64)	1.388(4)
O(4) - C(40)	1.443(4)	O(8) - C(82)	1.447(4)
N(2) - C(25)	1.426(4)	N(4) - C(67)	1.429(4)
N(2) - C(29)	1.362(4)	N(4) - C(71)	1.353(4)
C(22) - C(23)	1.402(4)	C(64) - C(65)	1.397(4)
C(22) - C(27)	1.391(4)	C(64) - C(69)	1.394(4)
C(23) - C(24)	1.396(4)	C(65) - C(66)	1.395(4)
C(24) - C(25)	1.393(4)	C(66) - C(67)	1.388(4)
C(25) - C(26)	1.390(4)	C(67) - C(68)	1.389(4)
C(26) - C(27)	1.392(4)	C(68) - C(69)	1.388(4)
C(27) - C(28)	1.531(4)	C(69) - C(70)	1.521(4)
C(28) - C(44)	1.515(4)	C(70) - C(2)	1.521(4)
C(29) - C(30)	1.481(5)	C(71) - C(72)	1.484(5)
C(30) - C(31)	1.426(5)	C(72) - C(73)	1.431(5)
C(30) - C(34)	1.439(5)	C(72) - C(76)	1.432(5)

C(31) - C(32)	1.420(5)	C(73) - C(74)	1.416(6)
C(32) - C(33)	1.420(7)	C(74) - C(75)	1.415(7)
C(33) - C(34)	1.427(6)	C(75) - C(76)	1.427(6)
C(35) - C(36)	1.394(8)	C(77) - C(78)	1.416(8)
C(35) - C(39)	1.354(9)	C(77) - C(81)	1.392(8)
C(36) - C(37)	1.422(8)	C(78) - C(79)	1.422(8)
C(37) - C(38)	1.398(9)	C(79) - C(80)	1.389(9)
C(38) - C(39)	1.410(9)	C(80) - C(81)	1.462(9)
C(40) - C(41)	1.491(5)	C(82) - C(83)	1.504(6)
C(41) - C(42)	1.521(7)	C(83) - C(84)	1.481(8)
O(9) - C(85)	1.429(5)	O(10) - C(86)	1.428(5)
O(11) - C(87)	1.43(1)	Cl(1) - C(88)	1.753(5)
Cl(7) - C(90)	1.790(6)	Cl(2) - C(88)	1.746(5)
Cl(7) - C(91)	1.749(8)	Cl(3) - C(88)	1.765(5)
Cl(8) - C(90)	1.759(6)	Cl(4) - C(89)	1.701(7)
Cl(9) - C(90)	1.779(6)	Cl(5) - C(89)	1.757(6)
Cl(10) - C(91)	1.774(8)	Cl(6) - C(89)	1.727(5)
Cl(11) - C(91)	1.746(8)		

Table F.2.6: Bond angles (°)
(H atoms have been excluded)

C(9) - Fe(1) - C(10)	41.18(13)	C(51) - Fe(3) - C(52)	41.33(14)
C(9) - Fe(1) - C(11)	68.60(13)	C(51) - Fe(3) - C(53)	68.85(14)
C(10) - Fe(1) - C(11)	40.51(15)	C(52) - Fe(3) - C(53)	40.58(16)
C(9) - Fe(1) - C(12)	69.18(13)	C(51) - Fe(3) - C(54)	68.99(15)
C(10) - Fe(1) - C(12)	68.61(15)	C(52) - Fe(3) - C(54)	68.48(18)
C(11) - Fe(1) - C(12)	40.28(16)	C(53) - Fe(3) - C(54)	40.34(19)
C(9) - Fe(1) - C(13)	41.56(13)	C(51) - Fe(3) - C(55)	41.57(14)
C(10) - Fe(1) - C(13)	69.35(14)	C(52) - Fe(3) - C(55)	69.55(16)
C(11) - Fe(1) - C(13)	68.46(14)	C(53) - Fe(3) - C(55)	68.80(16)
C(12) - Fe(1) - C(13)	40.96(13)	C(54) - Fe(3) - C(55)	40.92(15)
C(9) - Fe(1) - C(14)	106.00(16)	C(51) - Fe(3) - C(56)	106.46(16)
C(10) - Fe(1) - C(14)	119.85(17)	C(52) - Fe(3) - C(56)	122.04(17)
C(11) - Fe(1) - C(14)	155.65(19)	C(53) - Fe(3) - C(56)	158.3(2)
C(12) - Fe(1) - C(14)	162.06(19)	C(54) - Fe(3) - C(56)	159.6(2)
C(13) - Fe(1) - C(14)	124.16(17)	C(55) - Fe(3) - C(56)	122.59(17)
C(9) - Fe(1) - C(15)	125.56(19)	C(51) - Fe(3) - C(57)	123.70(16)
C(10) - Fe(1) - C(15)	108.8(2)	C(52) - Fe(3) - C(57)	108.45(18)
C(11) - Fe(1) - C(15)	122.2(2)	C(53) - Fe(3) - C(57)	123.6(2)
C(12) - Fe(1) - C(15)	156.01(19)	C(54) - Fe(3) - C(57)	158.5(2)
C(13) - Fe(1) - C(15)	162.39(19)	C(55) - Fe(3) - C(57)	159.81(17)
C(9) - Fe(1) - C(16)	164.0(3)	C(51) - Fe(3) - C(58)	160.77(18)
C(10) - Fe(1) - C(16)	128.0(3)	C(52) - Fe(3) - C(58)	124.77(19)
C(11) - Fe(1) - C(16)	110.82(19)	C(53) - Fe(3) - C(58)	109.23(19)
C(12) - Fe(1) - C(16)	121.43(18)	C(54) - Fe(3) - C(58)	122.77(18)

C(13) - Fe(1) - C(16)	154.2(2)	C(55) - Fe(3) - C(58)	157.10(18)
C(9) - Fe(1) - C(17)	152.4(2)	C(51) - Fe(3) - C(59)	155.9(2)
C(10) - Fe(1) - C(17)	165.2(2)	C(52) - Fe(3) - C(59)	161.7(2)
C(11) - Fe(1) - C(17)	127.8(2)	C(53) - Fe(3) - C(59)	125.3(2)
C(12) - Fe(1) - C(17)	107.83(19)	C(54) - Fe(3) - C(59)	108.00(19)
C(13) - Fe(1) - C(17)	118.0(2)	C(55) - Fe(3) - C(59)	120.40(19)
C(9) - Fe(1) - C(18)	117.57(19)	C(51) - Fe(3) - C(60)	120.11(18)
C(10) - Fe(1) - C(18)	153.52(19)	C(52) - Fe(3) - C(60)	156.8(2)
C(11) - Fe(1) - C(18)	163.3(2)	C(53) - Fe(3) - C(60)	160.6(2)
C(12) - Fe(1) - C(18)	125.0(2)	C(54) - Fe(3) - C(60)	123.5(2)
C(13) - Fe(1) - C(18)	105.1(2)	C(55) - Fe(3) - C(60)	105.63(18)
C(14) - Fe(1) - C(15)	40.5(2)	C(56) - Fe(3) - C(57)	40.3(2)
C(14) - Fe(1) - C(16)	67.58(19)	C(56) - Fe(3) - C(58)	67.9(2)
C(15) - Fe(1) - C(16)	40.2(2)	C(57) - Fe(3) - C(58)	40.3(2)
C(14) - Fe(1) - C(17)	68.0(2)	C(56) - Fe(3) - C(59)	67.6(2)
C(15) - Fe(1) - C(17)	68.3(3)	C(57) - Fe(3) - C(59)	67.8(2)
C(16) - Fe(1) - C(17)	40.6(3)	C(58) - Fe(3) - C(59)	40.8(2)
C(14) - Fe(1) - C(18)	40.7(2)	C(56) - Fe(3) - C(60)	40.3(2)
C(15) - Fe(1) - C(18)	68.4(2)	C(57) - Fe(3) - C(60)	67.9(2)
C(16) - Fe(1) - C(18)	67.8(3)	C(58) - Fe(3) - C(60)	68.3(2)
C(17) - Fe(1) - C(18)	40.3(2)	C(59) - Fe(3) - C(60)	40.3(2)
C(1) - O(2) - C(19)	115.8(3)	C(43) - O(6) - C(61)	115.0(2)
C(4) - N(1) - C(8)	123.5(3)	C(46) - N(3) - C(50)	123.8(3)
O(2) - C(1) - C(2)	120.2(3)	O(6) - C(43) - C(44)	118.6(3)
O(2) - C(1) - C(6)	118.0(3)	O(6) - C(43) - C(48)	120.2(3)
C(2) - C(1) - C(6)	121.5(3)	C(44) - C(43) - C(48)	121.1(3)
C(1) - C(2) - C(3)	118.8(3)	C(28) - C(44) - C(43)	120.9(3)
C(1) - C(2) - C(70)	121.1(3)	C(28) - C(44) - C(45)	120.3(3)
C(70) - C(2) - C(3)	119.8(3)	C(43) - C(44) - C(45)	118.6(3)
C(2) - C(3) - C(4)	120.7(3)	C(44) - C(45) - C(46)	120.9(3)
N(1) - C(4) - C(3)	121.5(3)	N(3) - C(46) - C(45)	121.0(3)
N(1) - C(4) - C(5)	118.6(3)	N(3) - C(46) - C(47)	119.3(3)
C(3) - C(4) - C(5)	119.9(3)	C(45) - C(46) - C(47)	119.7(3)
C(4) - C(5) - C(6)	120.8(3)	C(46) - C(47) - C(48)	121.2(3)
C(1) - C(6) - C(5)	118.1(3)	C(43) - C(48) - C(47)	118.1(3)
C(1) - C(6) - C(7)	120.9(3)	C(43) - C(48) - C(49)	120.9(3)
C(5) - C(6) - C(7)	120.9(3)	C(47) - C(48) - C(49)	120.8(3)
C(6) - C(7) - C(23)	111.1(2)	C(48) - C(49) - C(65)	110.4(2)
O(1) - C(8) - N(1)	122.6(3)	O(5) - C(50) - N(3)	123.0(3)
O(1) - C(8) - C(9)	121.3(3)	O(5) - C(50) - C(51)	120.3(3)
N(1) - C(8) - C(9)	116.1(3)	N(3) - C(50) - C(51)	116.7(3)
Fe(1) - C(9) - C(8)	118.6(2)	Fe(3) - C(51) - C(50)	121.7(2)
Fe(1) - C(9) - C(10)	70.4(2)	Fe(3) - C(51) - C(52)	69.77(19)
C(8) - C(9) - C(10)	123.5(3)	C(50) - C(51) - C(52)	123.4(3)
Fe(1) - C(9) - C(13)	69.19(19)	Fe(3) - C(51) - C(55)	69.37(19)
C(8) - C(9) - C(13)	128.1(3)	C(50) - C(51) - C(55)	128.7(3)
C(10) - C(9) - C(13)	107.8(3)	C(52) - C(51) - C(55)	107.7(3)
Fe(1) - C(10) - C(9)	68.42(19)	Fe(3) - C(52) - C(51)	68.90(19)
Fe(1) - C(10) - C(11)	70.3(2)	Fe(3) - C(52) - C(53)	70.3(2)
C(9) - C(10) - C(11)	107.5(3)	C(51) - C(52) - C(53)	107.9(3)

Fe(1) - C(11) - C(10)	69.2(2)	Fe(3) - C(53) - C(52)	69.1(2)
Fe(1) - C(11) - C(12)	69.3(2)	Fe(3) - C(53) - C(54)	69.4(2)
C(10) - C(11) - C(12)	108.8(3)	C(52) - C(53) - C(54)	108.3(3)
Fe(1) - C(12) - C(11)	70.4(2)	Fe(3) - C(54) - C(53)	70.3(2)
Fe(1) - C(12) - C(13)	68.50(19)	Fe(3) - C(54) - C(55)	69.1(2)
C(11) - C(12) - C(13)	108.0(3)	C(53) - C(54) - C(55)	108.9(3)
Fe(1) - C(13) - C(9)	69.26(19)	Fe(3) - C(55) - C(51)	69.06(19)
Fe(1) - C(13) - C(12)	70.5(2)	Fe(3) - C(55) - C(54)	70.0(2)
C(9) - C(13) - C(12)	107.9(3)	C(51) - C(55) - C(54)	107.2(3)
Fe(1) - C(14) - C(15)	70.0(3)	Fe(3) - C(56) - C(57)	70.0(3)
Fe(1) - C(14) - C(18)	70.0(2)	Fe(3) - C(56) - C(60)	69.7(3)
C(15) - C(14) - C(18)	108.6(4)	C(57) - C(56) - C(60)	108.4(4)
Fe(1) - C(15) - C(14)	69.5(3)	Fe(3) - C(57) - C(56)	69.7(2)
Fe(1) - C(15) - C(16)	70.1(3)	Fe(3) - C(57) - C(58)	70.2(3)
C(14) - C(15) - C(16)	107.4(5)	C(56) - C(57) - C(58)	108.4(4)
Fe(1) - C(16) - C(15)	69.7(3)	Fe(3) - C(58) - C(57)	69.5(2)
Fe(1) - C(16) - C(17)	69.5(3)	Fe(3) - C(58) - C(59)	69.5(2)
C(15) - C(16) - C(17)	108.5(5)	C(57) - C(58) - C(59)	107.1(4)
Fe(1) - C(17) - C(16)	69.9(3)	Fe(3) - C(59) - C(58)	69.7(2)
Fe(1) - C(17) - C(18)	69.9(3)	Fe(3) - C(59) - C(60)	69.3(2)
C(16) - C(17) - C(18)	107.8(5)	C(58) - C(59) - C(60)	107.9(4)
Fe(1) - C(18) - C(14)	69.3(3)	Fe(3) - C(60) - C(56)	70.0(3)
Fe(1) - C(18) - C(17)	69.8(3)	Fe(3) - C(60) - C(59)	70.4(3)
C(14) - C(18) - C(17)	107.7(5)	C(56) - C(60) - C(59)	108.2(4)
O(2) - C(19) - C(20)	114.4(3)	O(6) - C(61) - C(62)	113.1(3)
C(19) - C(20) - C(21)	111.4(4)	C(61) - C(62) - C(63)	109.8(4)
C(30) - Fe(2) - C(31)	41.13(15)	C(72) - Fe(4) - C(73)	41.26(15)
C(30) - Fe(2) - C(32)	68.63(16)	C(72) - Fe(4) - C(74)	68.72(15)
C(31) - Fe(2) - C(32)	40.76(15)	C(73) - Fe(4) - C(74)	40.50(17)
C(30) - Fe(2) - C(33)	68.94(15)	C(72) - Fe(4) - C(75)	68.84(15)
C(31) - Fe(2) - C(33)	68.85(17)	C(73) - Fe(4) - C(75)	68.34(18)
C(32) - Fe(2) - C(33)	40.5(2)	C(74) - Fe(4) - C(75)	40.3(2)
C(30) - Fe(2) - C(34)	41.34(14)	C(72) - Fe(4) - C(76)	41.24(15)
C(31) - Fe(2) - C(34)	69.26(17)	C(73) - Fe(4) - C(76)	69.10(17)
C(32) - Fe(2) - C(34)	68.39(19)	C(74) - Fe(4) - C(76)	68.45(18)
C(33) - Fe(2) - C(34)	40.66(17)	C(75) - Fe(4) - C(76)	40.79(16)
C(30) - Fe(2) - C(35)	112.19(17)	C(72) - Fe(4) - C(77)	106.76(17)
C(31) - Fe(2) - C(35)	110.1(2)	C(73) - Fe(4) - C(77)	119.85(19)
C(32) - Fe(2) - C(35)	137.0(2)	C(74) - Fe(4) - C(77)	155.0(2)
C(33) - Fe(2) - C(35)	177.1(2)	C(75) - Fe(4) - C(77)	163.1(2)
C(34) - Fe(2) - C(35)	141.88(19)	C(76) - Fe(4) - C(77)	125.32(19)
C(30) - Fe(2) - C(36)	141.05(19)	C(72) - Fe(4) - C(78)	120.63(19)
C(31) - Fe(2) - C(36)	112.2(2)	C(73) - Fe(4) - C(78)	155.5(2)
C(32) - Fe(2) - C(36)	111.3(2)	C(74) - Fe(4) - C(78)	163.1(2)
C(33) - Fe(2) - C(36)	137.6(2)	C(75) - Fe(4) - C(78)	126.6(2)
C(34) - Fe(2) - C(36)	177.52(19)	C(76) - Fe(4) - C(78)	108.4(2)
C(30) - Fe(2) - C(37)	175.9(2)	C(72) - Fe(4) - C(79)	156.3(2)
C(31) - Fe(2) - C(37)	143.0(2)	C(73) - Fe(4) - C(79)	161.7(2)
C(32) - Fe(2) - C(37)	114.9(2)	C(74) - Fe(4) - C(79)	125.9(2)
C(33) - Fe(2) - C(37)	112.08(19)	C(75) - Fe(4) - C(79)	109.1(2)

C(34) - Fe(2) - C(37)	136.9(2)	C(76) - Fe(4) - C(79)	121.6(2)
C(30) - Fe(2) - C(38)	135.7(2)	C(72) - Fe(4) - C(80)	162.0(2)
C(31) - Fe(2) - C(38)	175.2(2)	C(73) - Fe(4) - C(80)	124.7(2)
C(32) - Fe(2) - C(38)	144.0(3)	C(74) - Fe(4) - C(80)	107.78(19)
C(33) - Fe(2) - C(38)	114.4(2)	C(75) - Fe(4) - C(80)	120.70(19)
C(34) - Fe(2) - C(38)	110.6(2)	C(76) - Fe(4) - C(80)	155.6(2)
C(30) - Fe(2) - C(39)	109.31(19)	C(72) - Fe(4) - C(81)	123.0(2)
C(31) - Fe(2) - C(39)	134.8(2)	C(73) - Fe(4) - C(81)	105.9(2)
C(32) - Fe(2) - C(39)	175.0(2)	C(74) - Fe(4) - C(81)	120.4(2)
C(33) - Fe(2) - C(39)	143.7(2)	C(75) - Fe(4) - C(81)	156.1(2)
C(34) - Fe(2) - C(39)	113.4(2)	C(76) - Fe(4) - C(81)	160.9(2)
C(35) - Fe(2) - C(36)	39.9(2)	C(77) - Fe(4) - C(78)	40.4(2)
C(35) - Fe(2) - C(37)	67.0(2)	C(77) - Fe(4) - C(79)	68.0(2)
C(36) - Fe(2) - C(37)	40.7(2)	C(78) - Fe(4) - C(79)	40.4(2)
C(35) - Fe(2) - C(38)	66.8(2)	C(77) - Fe(4) - C(80)	68.5(2)
C(36) - Fe(2) - C(38)	68.0(2)	C(78) - Fe(4) - C(80)	67.8(2)
C(37) - Fe(2) - C(38)	40.1(3)	C(79) - Fe(4) - C(80)	39.7(3)
C(35) - Fe(2) - C(39)	38.9(3)	C(77) - Fe(4) - C(81)	40.0(2)
C(36) - Fe(2) - C(39)	67.1(2)	C(78) - Fe(4) - C(81)	68.1(3)
C(37) - Fe(2) - C(39)	67.4(2)	C(79) - Fe(4) - C(81)	68.7(3)
C(38) - Fe(2) - C(39)	40.6(3)	C(80) - Fe(4) - C(81)	42.3(2)
C(22) - O(4) - C(40)	111.8(2)	C(64) - O(8) - C(82)	111.9(3)
C(25) - N(2) - C(29)	123.2(3)	C(67) - N(4) - C(71)	122.4(3)
O(4) - C(22) - C(23)	119.3(3)	O(8) - C(64) - C(65)	119.5(3)
O(4) - C(22) - C(27)	119.6(3)	O(8) - C(64) - C(69)	119.2(3)
C(23) - C(22) - C(27)	121.1(3)	C(65) - C(64) - C(69)	121.3(3)
C(7) - C(23) - C(22)	122.0(3)	C(49) - C(65) - C(64)	121.7(3)
C(7) - C(23) - C(24)	119.3(3)	C(49) - C(65) - C(66)	120.1(3)
C(22) - C(23) - C(24)	118.7(3)	C(64) - C(65) - C(66)	118.1(3)
C(23) - C(24) - C(25)	120.6(3)	C(65) - C(66) - C(67)	121.1(3)
N(2) - C(25) - C(24)	122.2(3)	N(4) - C(67) - C(66)	122.3(3)
N(2) - C(25) - C(26)	118.5(3)	N(4) - C(67) - C(68)	118.2(3)
C(24) - C(25) - C(26)	119.3(3)	C(66) - C(67) - C(68)	119.4(3)
C(25) - C(26) - C(27)	121.2(3)	C(67) - C(68) - C(69)	120.7(3)
C(22) - C(27) - C(26)	118.6(3)	C(64) - C(69) - C(68)	118.9(3)
C(22) - C(27) - C(28)	121.7(3)	C(64) - C(69) - C(70)	121.6(3)
C(26) - C(27) - C(28)	119.7(3)	C(68) - C(69) - C(70)	119.4(3)
C(27) - C(28) - C(44)	109.6(2)	C(2) - C(70) - C(69)	110.4(2)
O(3) - C(29) - N(2)	123.8(3)	O(7) - C(71) - N(4)	123.6(3)
O(3) - C(29) - C(30)	120.8(3)	O(7) - C(71) - C(72)	120.3(3)
N(2) - C(29) - C(30)	115.3(3)	N(4) - C(71) - C(72)	116.1(3)
Fe(2) - C(30) - C(29)	123.5(2)	Fe(4) - C(72) - C(71)	123.4(2)
Fe(2) - C(30) - C(31)	69.7(2)	Fe(4) - C(72) - C(73)	69.7(2)
C(29) - C(30) - C(31)	129.5(3)	C(71) - C(72) - C(73)	123.9(3)
Fe(2) - C(30) - C(34)	70.2(2)	Fe(4) - C(72) - C(76)	69.9(2)
C(29) - C(30) - C(34)	122.3(3)	C(71) - C(72) - C(76)	128.4(3)
C(31) - C(30) - C(34)	108.1(3)	C(73) - C(72) - C(76)	107.7(3)
Fe(2) - C(31) - C(30)	69.2(2)	Fe(4) - C(73) - C(72)	69.0(2)
Fe(2) - C(31) - C(32)	70.1(2)	Fe(4) - C(73) - C(74)	70.5(3)
C(30) - C(31) - C(32)	107.5(4)	C(72) - C(73) - C(74)	108.0(4)

Fe(2) - C(32) - C(31)	69.2(2)	Fe(4) - C(74) - C(73)	68.9(2)
Fe(2) - C(32) - C(33)	70.2(2)	Fe(4) - C(74) - C(75)	69.8(2)
C(31) - C(32) - C(33)	109.0(4)	C(73) - C(74) - C(75)	108.4(3)
Fe(2) - C(33) - C(32)	69.3(2)	Fe(4) - C(75) - C(74)	70.0(2)
Fe(2) - C(33) - C(34)	69.4(2)	Fe(4) - C(75) - C(76)	69.1(2)
C(32) - C(33) - C(34)	107.9(3)	C(74) - C(75) - C(76)	108.4(4)
Fe(2) - C(34) - C(30)	68.5(2)	Fe(4) - C(76) - C(72)	68.8(2)
Fe(2) - C(34) - C(33)	69.9(2)	Fe(4) - C(76) - C(75)	70.1(2)
C(30) - C(34) - C(33)	107.5(4)	C(72) - C(76) - C(75)	107.5(4)
Fe(2) - C(35) - C(36)	70.5(3)	Fe(4) - C(77) - C(78)	70.4(3)
Fe(2) - C(35) - C(39)	70.4(3)	Fe(4) - C(77) - C(81)	69.6(3)
C(36) - C(35) - C(39)	110.3(5)	C(78) - C(77) - C(81)	109.2(5)
Fe(2) - C(36) - C(35)	69.6(3)	Fe(4) - C(78) - C(77)	69.2(3)
Fe(2) - C(36) - C(37)	69.4(3)	Fe(4) - C(78) - C(79)	69.9(3)
C(35) - C(36) - C(37)	106.0(5)	C(77) - C(78) - C(79)	107.8(5)
Fe(2) - C(37) - C(36)	69.9(3)	Fe(4) - C(79) - C(78)	69.7(3)
Fe(2) - C(37) - C(38)	69.8(3)	Fe(4) - C(79) - C(80)	68.8(3)
C(36) - C(37) - C(38)	108.1(5)	C(78) - C(79) - C(80)	108.2(5)
Fe(2) - C(38) - C(37)	70.1(3)	Fe(4) - C(80) - C(79)	71.5(3)
Fe(2) - C(38) - C(39)	69.6(3)	Fe(4) - C(80) - C(81)	69.1(3)
C(37) - C(38) - C(39)	107.1(5)	C(79) - C(80) - C(81)	108.2(5)
Fe(2) - C(39) - C(35)	70.7(3)	Fe(4) - C(81) - C(77)	70.4(3)
Fe(2) - C(39) - C(38)	69.9(3)	Fe(4) - C(81) - C(80)	68.7(3)
C(35) - C(39) - C(38)	108.4(5)	C(77) - C(81) - C(80)	106.6(5)
O(4) - C(40) - C(41)	109.2(3)	O(8) - C(82) - C(83)	108.5(3)
C(40) - C(41) - C(42)	111.1(4)	C(82) - C(83) - C(84)	113.5(5)
Cl(1) - C(88) - Cl(2)	108.3(3)	Cl(7) - C(90) - Cl(8)	108.4(3)
Cl(1) - C(88) - Cl(3)	109.9(3)	Cl(7) - C(90) - Cl(9)	111.7(3)
Cl(2) - C(88) - Cl(3)	109.4(3)	Cl(8) - C(90) - Cl(9)	109.6(3)
Cl(4) - C(89) - Cl(5)	111.1(3)	Cl(7) - C(91) - Cl(10)	113.5(6)
Cl(4) - C(89) - Cl(6)	115.3(4)	Cl(7) - C(91) - Cl(11)	104.3(5)
Cl(5) - C(89) - Cl(6)	110.8(3)	Cl(10) - C(91) - Cl(11)	108.1(6)

F.3 Crystal data for $23 \cdot 3\text{CH}_3\text{OH} \cdot 3\text{CHCl}_3$ [§]

X-ray quality crystals (orange-yellow blocks) of $23 \cdot 3\text{CH}_3\text{OH} \cdot 3\text{CHCl}_3$ were obtained from a chloroform solution of the compound exposed to methanol. Although a crystal structure was obtained, the crystals were not of sufficient quality to enable good refinement of the data. The non-hydrogen atom numbering system is outlined in the schematic structure shown in Figure

F.3.1.

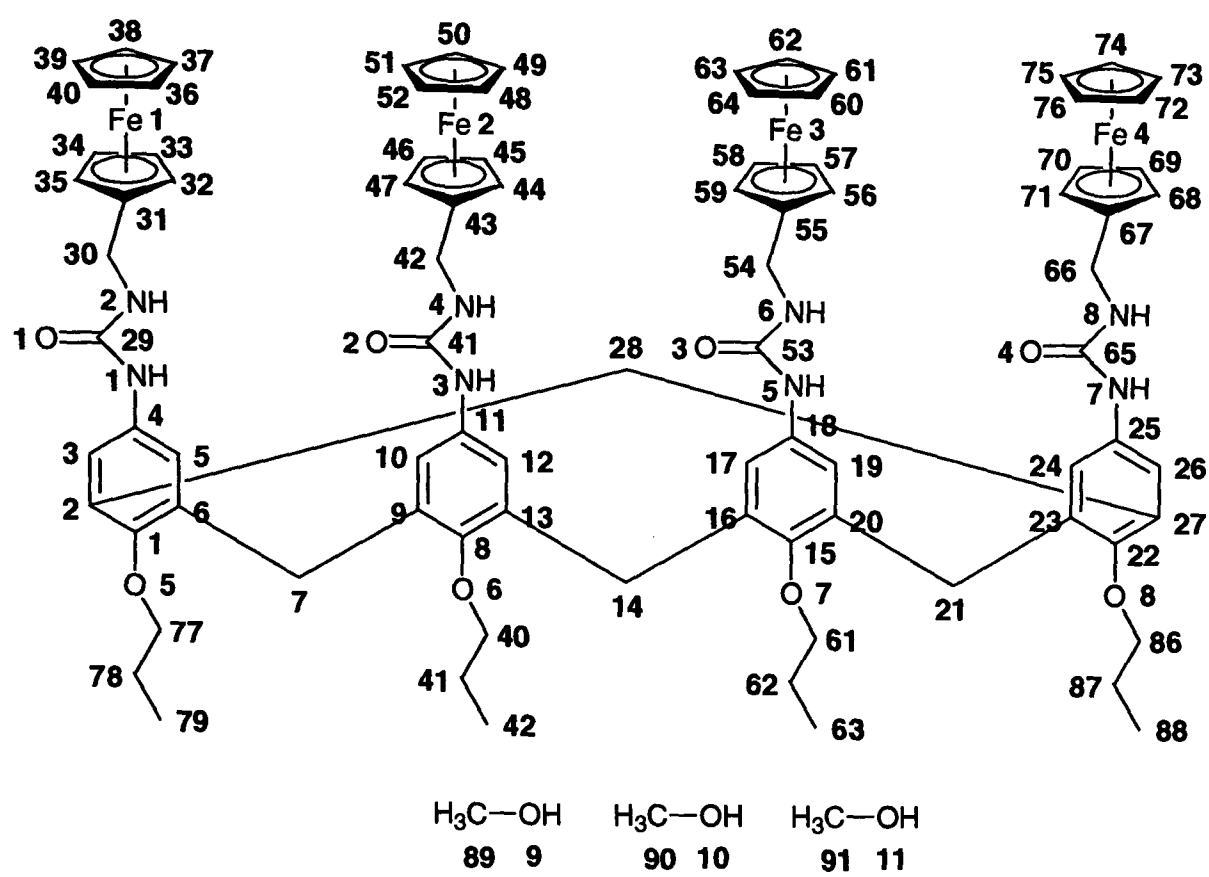


Figure F.3.1: Atom numbering system.

Table F.3.1: Crystal data and refinement details

Crystal identification	
Chemical formula	$\text{C}_{94}\text{H}_{111}\text{Cl}_9\text{Fe}_4\text{N}_8\text{O}_{11}$
Formula weight	2071.44
Temperature (K)	150
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	$P \bar{1}$
a (Å)	17.7798(2)
b (Å)	18.4727(2)
c (Å)	18.7924(2)
α (°)	69.8027(4)
β (°)	66.3924(4)
γ (°)	62.3163(4)
Cell volume (Å ³)	4910.9
Z	2
Calculated density (Mg/m ³)	1.401
Absorption coefficient (mm ⁻¹)	0.885
F_{000}	2157.095
Crystal size (mm)	0.1 x 0.2 x 0.3
Description of crystal	Orange-yellow blocks
Absorption correction	Semi-empirical from equivalent reflections
Transmission coefficients (min,max)	0.78, 0.92
θ range for data collection (°)	$5.1 \leq \theta \leq 27.5$
Index ranges	$-20 \leq h \leq 23, -22 \leq k \leq 23, 0 \leq l \leq 24$
Reflections measured	81514
Unique reflections	22298

R_{int}	0.047
Observed reflections ($I > 3\sigma(I)$)	11673
Refinement method	Full-matrix least-squares on F
Parameters refined	1105
Weighting scheme	Chebyshev 3-term polynomial
Goodness of fit	1.0225
R	0.1061
wR	0.1229
Residual electron density (min,max) ($\text{e}\text{\AA}^{-3}$)	-2.05, 2.94

Table F.3.2: Atomic coordinates, equivalent isotropic thermal parameters ($\text{\AA}^2$) and site occupancies (where not unity) of non-hydrogen atoms

Atom	x	y	z	U_{equiv}	Occupancy
C(1)	0.7653(4)	0.0871(4)	0.3433(4)	0.0339	
C(2)	0.7958(4)	0.0397(4)	0.2859(4)	0.0359	
C(3)	0.7691(5)	-0.0268(4)	0.3055(4)	0.0343	
C(4)	0.7112(5)	-0.0429(4)	0.3788(4)	0.0358	
C(5)	0.6768(4)	0.0087(4)	0.4327(3)	0.0323	
C(6)	0.7031(4)	0.0752(4)	0.4154(3)	0.0301	
C(7)	0.6559(5)	0.1384(4)	0.4675(4)	0.0346	
C(8)	0.6061(4)	0.2950(4)	0.4093(3)	0.0308	
C(9)	0.5954(4)	0.2197(4)	0.4270(3)	0.0301	
C(10)	0.5319(4)	0.2178(4)	0.4036(3)	0.0314	
C(11)	0.4789(4)	0.2903(4)	0.3627(3)	0.0303	
C(12)	0.4943(4)	0.3634(4)	0.3422(3)	0.0306	
C(13)	0.5586(4)	0.3656(4)	0.3645(3)	0.0308	
C(14)	0.5758(5)	0.4469(4)	0.3364(4)	0.0386	
C(15)	0.6595(5)	0.4272(4)	0.1967(4)	0.0343	
C(16)	0.5884(5)	0.4744(4)	0.2484(4)	0.0340	
C(17)	0.5212(5)	0.5429(4)	0.2202(4)	0.0377	
C(18)	0.5252(4)	0.5594(4)	0.1406(4)	0.0366	
C(19)	0.5958(5)	0.5068(4)	0.0908(4)	0.0381	
C(20)	0.6641(5)	0.4399(4)	0.1176(4)	0.0346	
C(21)	0.7334(5)	0.3769(4)	0.0672(4)	0.0418	
C(22)	0.7895(4)	0.2204(4)	0.1254(3)	0.0338	
C(23)	0.7222(5)	0.2933(4)	0.1012(3)	0.0335	
C(24)	0.6414(4)	0.2901(4)	0.1147(4)	0.0345	
C(25)	0.6262(4)	0.2174(4)	0.1520(3)	0.0336	
C(26)	0.6915(4)	0.1464(4)	0.1786(4)	0.0348	
C(27)	0.7744(4)	0.1470(4)	0.1663(3)	0.0324	
C(28)	0.8423(4)	0.0699(4)	0.2008(4)	0.0379	
N(1)	0.6835(4)	-0.1106(4)	0.4000(3)	0.0421	
C(29)	0.6437(5)	-0.1198(4)	0.3576(4)	0.0379	
O(1)	0.6426(4)	-0.0813(3)	0.2892(3)	0.0498	
N(2)	0.6041(5)	-0.1752(4)	0.3961(3)	0.0455	
C(30)	0.5627(5)	-0.1970(5)	0.3581(5)	0.0476	
C(31)	0.6260(5)	-0.2651(5)	0.3118(4)	0.0436	
C(32)	0.7180(6)	-0.2856(5)	0.2747(4)	0.0498	

C(33)	0.7508(6)	-0.3534(6)	0.2368(4)	0.0574
C(34)	0.6790(7)	-0.3744(6)	0.2502(5)	0.0579
C(35)	0.6023(6)	-0.3214(6)	0.2969(5)	0.0551
Fe(1)	0.69625(8)	-0.38559(7)	0.35546(6)	0.0422
C(36)	0.6701(12)	-0.3976(6)	0.4729(5)	0.0959
C(37)	0.7596(12)	-0.4169(9)	0.4353(7)	0.1004
C(38)	0.7911(7)	-0.4859(8)	0.4007(6)	0.0760
C(39)	0.7232(8)	-0.5056(6)	0.4157(6)	0.0666
C(40)	0.6470(7)	-0.4551(7)	0.4597(6)	0.0690
N(3)	0.4123(4)	0.2911(3)	0.3385(3)	0.0332
C(41)	0.3534(4)	0.2539(4)	0.3848(4)	0.0334
O(2)	0.3556(3)	0.2131(3)	0.4524(3)	0.0415
N(4)	0.2949(4)	0.2637(4)	0.3501(3)	0.0382
C(42)	0.2254(5)	0.2302(5)	0.3938(4)	0.0417
C(43)	0.1405(5)	0.2915(5)	0.4362(4)	0.0507
C(44)	0.1258(7)	0.3185(6)	0.5048(5)	0.0641
C(45)	0.0385(11)	0.3776(7)	0.5235(8)	0.1113
C(46)	0.0002(9)	0.3861(9)	0.4693(7)	0.1375
C(47)	0.0611(7)	0.334(1)	0.4152(6)	0.1145
Fe(2)	0.03702(7)	0.26716(9)	0.52620(7)	0.0531
C(48)	0.0768(8)	0.1402(8)	0.5741(8)	0.0848
C(49)	0.0404(7)	0.1827(7)	0.6338(6)	0.0777
C(50)	-0.0475(7)	0.2381(8)	0.6318(8)	0.0831
C(51)	-0.0647(8)	0.2263(11)	0.5754(11)	0.1126
C(52)	0.018(1)	0.164(1)	0.5349(9)	0.1022
N(5)	0.4579(4)	0.6279(4)	0.1094(3)	0.0433
C(53)	0.3698(5)	0.6479(4)	0.1438(4)	0.0350
O(3)	0.3376(3)	0.6205(3)	0.2143(3)	0.0460
N(6)	0.3198(4)	0.7000(4)	0.0945(3)	0.0454
C(54)	0.2233(5)	0.7263(5)	0.1192(4)	0.0451
C(55)	0.1784(5)	0.8170(4)	0.0888(4)	0.0381
C(56)	0.0868(5)	0.8672(6)	0.1198(5)	0.0521
C(57)	0.0690(6)	0.9483(6)	0.0717(6)	0.0600
C(58)	0.1481(5)	0.9502(5)	0.0114(4)	0.0494
C(59)	0.2148(5)	0.8676(5)	0.0217(4)	0.0435
Fe(3)	0.16767(8)	0.91682(7)	0.11998(6)	0.0465
C(60)	0.1404(12)	0.9225(9)	0.2345(6)	0.0955
C(61)	0.128(1)	1.0045(8)	0.1842(6)	0.0919
C(62)	0.211(1)	0.9956(8)	0.1279(7)	0.0843
C(63)	0.2753(9)	0.9142(9)	0.1380(7)	0.0872
C(64)	0.2300(12)	0.8688(8)	0.2050(8)	0.0929
N(7)	0.5441(4)	0.2118(4)	0.1668(3)	0.0398
C(65)	0.5035(4)	0.2362(4)	0.1094(4)	0.0374
O(4)	0.5257(4)	0.2799(4)	0.0451(3)	0.0505
N(8)	0.4384(5)	0.2091(5)	0.1298(4)	0.0561
C(66)	0.3857(6)	0.2324(7)	0.0757(5)	0.0641
C(67)	0.2900(5)	0.2516(5)	0.1193(5)	0.0497
C(68)	0.2367(7)	0.2112(6)	0.1234(6)	0.0614
C(69)	0.1494(6)	0.2503(7)	0.1684(6)	0.0695
C(70)	0.1484(6)	0.3138(7)	0.1946(5)	0.0655

C(71)	0.2336(6)	0.3157(6)	0.1645(5)	0.0546	
Fe(4)	0.18735(8)	0.33431(7)	0.07414(6)	0.0458	
C(72)	0.2411(7)	0.3801(8)	-0.0413(5)	0.0749	
C(73)	0.1801(8)	0.3468(7)	-0.0353(6)	0.0772	
C(74)	0.0972(7)	0.3905(7)	0.0116(6)	0.0706	
C(75)	0.1049(6)	0.4510(6)	0.0342(5)	0.0604	
C(76)	0.1943(7)	0.4440(6)	0.0018(5)	0.0637	
O(5)	0.7907(3)	0.1525(3)	0.3250(3)	0.0420	
C(77)	0.850(1)	0.1360(11)	0.3669(9)	0.070(4)	0.441(5)
C(78)	0.9481(11)	0.106(3)	0.3182(17)	0.159(11)	0.441(5)
C(79)	1.0086(16)	0.085(3)	0.369(2)	0.132(8)	0.441(5)
C(177)	0.8826(6)	0.1264(9)	0.316(1)	0.070(4)	0.559(5)
C(178)	0.8992(15)	0.145(2)	0.3809(12)	0.159(11)	0.559(5)
C(179)	0.9853(18)	0.161(2)	0.3489(18)	0.132(8)	0.559(5)
O(6)	0.6697(3)	0.2970(3)	0.4338(2)	0.0336	
C(80)	0.6335(4)	0.3184(4)	0.5109(4)	0.0351	
C(81)	0.7098(5)	0.2992(4)	0.5398(4)	0.0373	
C(82)	0.6744(6)	0.3284(6)	0.6184(5)	0.0542	
O(97)	0.7266(4)	0.3587(3)	0.2242(3)	0.0445	
C(83)	0.7801(9)	0.3761(8)	0.2493(8)	0.0919	
C(84)	0.847(1)	0.3862(8)	0.1838(6)	0.1080	
C(85)	0.9127(8)	0.411(1)	0.2109(9)	0.1041	
O(8)	0.8719(3)	0.2213(3)	0.1113(2)	0.0392	
C(86)	0.925(1)	0.2145(16)	0.0316(7)	0.045(2)	0.438(5)
C(87)	1.002(1)	0.2397(12)	0.0120(9)	0.063(3)	0.438(5)
C(88)	1.0553(12)	0.1874(12)	0.0717(12)	0.060(3)	0.438(5)
C(186)	0.9330(7)	0.2004(12)	0.0367(6)	0.045(2)	0.562(5)
C(187)	1.0248(8)	0.1951(11)	0.0279(7)	0.063(3)	0.562(5)
C(188)	1.088(1)	0.1897(12)	-0.0564(8)	0.070(3)	0.562(5)
O(9)	0.5005(5)	0.0725(4)	0.2748(4)	0.0807	
C(89)	0.4496(8)	0.0526(6)	0.3499(7)	0.0825	
O(10)	0.3234(4)	0.4146(3)	0.2205(3)	0.0489	
C(90)	0.3673(7)	0.4469(6)	0.1424(5)	0.0650	
O(11)	0.2188(4)	0.5497(3)	0.2935(3)	0.0485	
C(91)	0.2191(6)	0.5181(5)	0.3743(4)	0.0558	
C(92)	0.0566(7)	0.5963(6)	0.2366(6)	0.0657	
Cl(1)	0.1080(3)	0.5804(3)	0.13973(19)	0.1089	
Cl(2)	-0.0343(5)	0.6854(4)	0.2469(4)	0.1974	
Cl(3)	0.0406(5)	0.5085(4)	0.2984(3)	0.1967	
C(93)	0.249(1)	-0.0286(8)	0.3228(8)	0.136(7)	0.441(5)
Cl(4)	0.351(1)	-0.115(1)	0.3180(12)	0.1404(13)	0.441(5)
Cl(5)	0.2583(8)	0.0678(7)	0.2706(7)	0.1404(13)	0.441(5)
Cl(6)	0.1840(8)	-0.0227(7)	0.4205(6)	0.1404(13)	0.441(5)
C(193)	0.2290(8)	-0.0308(7)	0.3347(8)	0.136(7)	0.559(5)
Cl(104)	0.3333(8)	-0.1117(8)	0.328(1)	0.1404(13)	0.559(5)

Cl(105)	0.2327(6)	0.0607(5)	0.3373(6)	0.1404(13)	0.559(5)
Cl(106)	0.1451(6)	-0.0558(6)	0.4146(6)	0.1404(13)	0.559(5)
C(94)	0.6597(8)	-0.0935(7)	0.124(1)	0.099(6)	0.438(5)
Cl(7)	0.6233(8)	0.0130(7)	0.0787(8)	0.1319(12)	0.438(5)
Cl(8)	0.6122(8)	-0.1517(7)	0.1090(8)	0.1319(12)	0.438(5)
Cl(9)	0.7760(6)	-0.1388(6)	0.1008(7)	0.1319(12)	0.438(5)
C(194)	0.5990(6)	-0.0643(7)	0.1308(8)	0.099(6)	0.562(5)
Cl(107)	0.6429(7)	0.0139(6)	0.0911(6)	0.1319(12)	0.562(5)
Cl(108)	0.6531(6)	-0.1449(5)	0.0760(6)	0.1319(12)	0.562(5)
Cl(109)	0.4825(5)	-0.0239(5)	0.1550(5)	0.1319(12)	0.562(5)

Table F.3.3: Atomic coordinates, isotropic thermal parameters ($\text{\AA}^2$) and site occupancies (where not unity) of hydrogen atoms

Atom	x	y	z	U_{iso}	Occupancy
H(1)	0.6941	-0.1534	0.4488	0.0520	
H(2)	0.6033	-0.2021	0.4524	0.0574	
H(3)	0.4085	0.3210	0.2836	0.0426	
H(4)	0.2992	0.2941	0.2939	0.0484	
H(5)	0.4773	0.6642	0.0581	0.0443	
H(6)	0.3499	0.7215	0.0389	0.0451	
H(7)	0.5145	0.1887	0.2219	0.0441	
H(8)	0.4252	0.1723	0.1827	0.0668	
H(31)	0.7921	-0.0629	0.2663	0.0386	
H(51)	0.6327	-0.0017	0.4845	0.0389	
H(71)	0.7005	0.1496	0.4772	0.0412	
H(72)	0.6193	0.1163	0.5192	0.0412	
H(101)	0.5237	0.1643	0.4160	0.0382	
H(121)	0.4585	0.4147	0.3111	0.0380	
H(141)	0.6304	0.4368	0.3481	0.0510	
H(142)	0.5240	0.4910	0.3644	0.0510	
H(171)	0.4707	0.5797	0.2566	0.0453	
H(191)	0.5972	0.5177	0.0345	0.0441	
H(211)	0.7936	0.3690	0.0656	0.0485	
H(212)	0.7275	0.3977	0.0123	0.0485	
H(241)	0.5931	0.3413	0.0970	0.0364	
H(261)	0.6795	0.0943	0.2067	0.0383	
H(281)	0.8910	0.0838	0.1994	0.0406	
H(282)	0.8677	0.0254	0.1695	0.0406	
H(301)	0.5154	-0.2158	0.4000	0.0583	
H(302)	0.5352	-0.1461	0.3211	0.0583	
H(321)	0.7538	-0.2571	0.2750	0.0590	
H(331)	0.8137	-0.3812	0.2062	0.0636	
H(341)	0.6819	-0.4194	0.2300	0.0758	
H(351)	0.5418	-0.3229	0.3163	0.0746	
H(361)	0.6292	-0.3520	0.5035	0.1002	
H(371)	0.7956	-0.3872	0.4331	0.1493	
H(381)	0.8537	-0.5149	0.3703	0.0890	

H(391)	0.7272	-0.5521	0.3970	0.0824	
H(401)	0.5870	-0.4578	0.4788	0.0758	
H(421)	0.2474	0.1798	0.4338	0.0532	
H(422)	0.2125	0.2140	0.3556	0.0532	
H(441)	0.1698	0.2989	0.5345	0.0785	
H(451)	0.0096	0.4079	0.5684	0.1059	
H(461)	-0.0620	0.4240	0.4684	0.0970	
H(471)	0.0499	0.3281	0.3698	0.0984	
H(481)	0.1385	0.0975	0.5613	0.1050	
H(491)	0.0700	0.1762	0.6722	0.0824	
H(501)	-0.0894	0.2791	0.6672	0.0935	
H(511)	-0.1224	0.2541	0.5625	0.1338	
H(521)	0.0275	0.1440	0.4878	0.1347	
H(541)	0.2017	0.7151	0.1784	0.0514	
H(542)	0.2079	0.6934	0.0986	0.0514	
H(561)	0.0431	0.8484	0.1671	0.0605	
H(571)	0.0103	0.9961	0.0792	0.0636	
H(581)	0.1560	0.9994	-0.0304	0.0526	
H(591)	0.2772	0.8492	-0.0133	0.0479	
H(601)	0.0945	0.9065	0.2815	0.1277	
H(611)	0.0721	1.0559	0.1885	0.1185	
H(621)	0.2241	1.0424	0.0851	0.1151	
H(631)	0.3386	0.8928	0.1054	0.1205	
H(641)	0.2569	0.8083	0.2279	0.1271	
H(661)	0.3924	0.2827	0.0351	0.0792	
H(662)	0.4083	0.1850	0.0487	0.0792	
H(681)	0.2578	0.1627	0.0983	0.0737	
H(691)	0.0975	0.2359	0.1797	0.0826	
H(701)	0.0956	0.3512	0.2291	0.0752	
H(711)	0.2517	0.3551	0.1732	0.0668	
H(721)	0.3056	0.3611	-0.0710	0.0858	
H(731)	0.1943	0.3004	-0.0602	0.0940	
H(741)	0.0417	0.3804	0.0266	0.0864	
H(751)	0.0559	0.4920	0.0675	0.0713	
H(761)	0.2195	0.4788	0.0085	0.0746	
H(771)	0.8350	0.1884	0.3832	0.0842	0.4413
H(772)	0.8420	0.0919	0.4151	0.0842	0.4413
H(781)	0.9579	0.1512	0.2716	0.1904	0.4413
H(782)	0.9633	0.0553	0.2993	0.1904	0.4413
H(791)	1.0720	0.0656	0.3359	0.1580	0.4413
H(792)	0.9937	0.1356	0.3876	0.1580	0.4413
H(793)	0.9992	0.0397	0.4153	0.1580	0.4413
H(1771)	0.9099	0.1560	0.2636	0.0842	0.5587
H(1772)	0.9116	0.0649	0.3180	0.0842	0.5587
H(1781)	0.9041	0.0960	0.4261	0.1904	0.5587
H(1782)	0.8484	0.1953	0.3998	0.1904	0.5587
H(1791)	0.9949	0.1728	0.3919	0.1580	0.5587
H(1792)	1.0364	0.1106	0.3300	0.1580	0.5587
H(1793)	0.9807	0.2099	0.3038	0.1580	0.5587
H(801)	0.5952	0.3791	0.5070	0.0445	

H(802)	0.5974	0.2849	0.5485	0.0445	
H(811)	0.7488	0.3287	0.4994	0.0476	
H(812)	0.7447	0.2377	0.5480	0.0476	
H(821)	0.7254	0.3155	0.6372	0.0705	
H(822)	0.6395	0.3899	0.6103	0.0705	
H(823)	0.6354	0.2989	0.6589	0.0705	
H(831)	0.7451	0.4281	0.2715	0.0956	
H(832)	0.8044	0.3286	0.2904	0.0956	
H(841)	0.8220	0.4323	0.1421	0.0972	
H(842)	0.8827	0.3334	0.1628	0.0972	
H(851)	0.9628	0.4190	0.1637	0.1391	
H(852)	0.8764	0.4638	0.2321	0.1391	
H(853)	0.9371	0.3649	0.2527	0.1391	
H(861)	0.9482	0.1556	0.0255	0.0538	0.4377
H(862)	0.8880	0.2521	-0.0052	0.0538	0.4377
H(871)	0.9792	0.3000	0.0139	0.0756	0.4377
H(872)	1.0420	0.2307	-0.0424	0.0756	0.4377
H(881)	1.1059	0.2045	0.0582	0.0718	0.4377
H(882)	1.0159	0.1965	0.1261	0.0718	0.4377
H(883)	1.0787	0.1271	0.0698	0.0718	0.4377
H(1861)	0.9101	0.2442	-0.0071	0.0538	0.5623
H(1862)	0.9381	0.1453	0.0335	0.0538	0.5623
H(1871)	1.0173	0.2459	0.0421	0.0756	0.5623
H(1872)	1.0519	0.1444	0.0652	0.0756	0.5623
H(1881)	1.1465	0.1864	-0.0584	0.0838	0.5623
H(1882)	1.0620	0.2404	-0.0944	0.0838	0.5623
H(1883)	1.0966	0.1388	-0.0713	0.0838	0.5623
H(9)	0.5511	0.0177	0.2799	0.0832	
H(891)	0.3911	0.1002	0.3608	0.0828	
H(892)	0.4808	0.0414	0.3889	0.0828	
H(893)	0.4398	0.0018	0.3548	0.0828	
H(10)	0.2854	0.4637	0.2470	0.0568	
H(901)	0.4067	0.4006	0.1125	0.0670	
H(902)	0.4038	0.4732	0.1453	0.0670	
H(903)	0.3222	0.4897	0.1147	0.0670	
H(11)	0.2634	0.5763	0.2638	0.0563	
H(911)	0.1743	0.4917	0.4033	0.0605	
H(912)	0.2039	0.5648	0.3992	0.0605	
H(913)	0.2793	0.4755	0.3769	0.0605	
H(921)	0.0977	0.6058	0.2531	0.0824	
H(931)	0.2196	-0.0397	0.2949	0.1633	0.4413
H(1931)	0.2134	-0.0219	0.2860	0.1633	0.5587
H(941)	0.6361	-0.0961	0.1821	0.1190	0.4377
H(1941)	0.6129	-0.0928	0.1825	0.1190	0.5623

Table F.3.4: Anisotropic thermal parameters (Å²)

Atom	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂
C(1)	0.033(3)	0.031(3)	0.034(3)	0.006(3)	-0.014(3)	-0.014(3)
C(2)	0.034(3)	0.030(3)	0.031(3)	0.002(3)	-0.009(3)	-0.008(3)
C(3)	0.039(4)	0.029(3)	0.028(3)	-0.002(3)	-0.009(3)	-0.010(3)
C(4)	0.042(4)	0.032(3)	0.031(3)	0.007(3)	-0.014(3)	-0.018(3)
C(5)	0.035(3)	0.039(4)	0.022(3)	0.002(2)	-0.009(3)	-0.020(3)
C(6)	0.031(3)	0.029(3)	0.025(3)	0.003(2)	-0.013(2)	-0.009(3)
C(7)	0.041(4)	0.037(4)	0.025(3)	0.004(3)	-0.015(3)	-0.016(3)
C(8)	0.038(3)	0.039(4)	0.018(3)	-0.002(2)	-0.007(2)	-0.021(3)
C(9)	0.033(3)	0.034(3)	0.019(3)	0.000(2)	-0.008(2)	-0.013(3)
C(10)	0.037(3)	0.037(3)	0.021(3)	-0.002(2)	-0.007(2)	-0.019(3)
C(11)	0.038(3)	0.035(3)	0.018(3)	-0.001(2)	-0.008(2)	-0.018(3)
C(12)	0.038(3)	0.033(3)	0.024(3)	-0.002(2)	-0.011(3)	-0.017(3)
C(13)	0.045(4)	0.033(3)	0.019(3)	0.002(2)	-0.011(3)	-0.022(3)
C(14)	0.058(4)	0.035(4)	0.035(3)	0.005(3)	-0.024(3)	-0.026(3)
C(15)	0.039(4)	0.025(3)	0.038(3)	0.003(3)	-0.015(3)	-0.015(3)
C(16)	0.046(4)	0.031(3)	0.030(3)	0.004(3)	-0.016(3)	-0.022(3)
C(17)	0.048(4)	0.040(4)	0.024(3)	0.001(3)	-0.005(3)	-0.026(3)
C(18)	0.035(3)	0.031(3)	0.032(3)	0.004(3)	-0.006(3)	-0.013(3)
C(19)	0.044(4)	0.041(4)	0.025(3)	0.008(3)	-0.011(3)	-0.022(3)
C(20)	0.041(4)	0.033(3)	0.029(3)	0.003(3)	-0.006(3)	-0.023(3)
C(21)	0.054(4)	0.038(4)	0.029(3)	0.005(3)	-0.012(3)	-0.022(3)
C(22)	0.036(3)	0.042(4)	0.021(3)	-0.004(3)	-0.001(3)	-0.021(3)
C(23)	0.042(4)	0.028(3)	0.023(3)	-0.000(2)	-0.001(3)	-0.017(3)
C(24)	0.036(3)	0.033(3)	0.022(3)	-0.001(2)	-0.006(3)	-0.008(3)
C(25)	0.035(3)	0.040(4)	0.022(3)	-0.002(3)	-0.006(3)	-0.016(3)
C(26)	0.037(4)	0.033(3)	0.026(3)	-0.002(3)	-0.002(3)	-0.015(3)
C(27)	0.032(3)	0.034(3)	0.023(3)	-0.004(2)	-0.003(2)	-0.011(3)
C(28)	0.034(3)	0.038(4)	0.030(3)	0.001(3)	-0.005(3)	-0.013(3)
N(1)	0.065(4)	0.038(3)	0.027(3)	0.008(2)	-0.013(3)	-0.033(3)
C(29)	0.051(4)	0.036(4)	0.027(3)	-0.005(3)	-0.009(3)	-0.020(3)
O(1)	0.074(4)	0.048(3)	0.030(2)	0.003(2)	-0.015(2)	-0.032(3)
N(2)	0.070(4)	0.042(3)	0.031(3)	-0.004(2)	-0.013(3)	-0.031(3)
C(30)	0.055(5)	0.049(4)	0.042(4)	-0.003(3)	-0.009(3)	-0.030(4)
C(31)	0.058(5)	0.049(4)	0.029(3)	-0.001(3)	-0.013(3)	-0.029(4)
C(32)	0.056(5)	0.056(5)	0.035(4)	-0.007(3)	0.000(3)	-0.033(4)
C(33)	0.072(6)	0.058(5)	0.028(4)	-0.009(3)	-0.002(4)	-0.025(5)
C(34)	0.090(7)	0.064(5)	0.035(4)	-0.006(4)	-0.025(4)	-0.039(5)
C(35)	0.079(6)	0.061(5)	0.046(4)	-0.001(4)	-0.025(4)	-0.045(5)
Fe(1)	0.0568(7)	0.0495(6)	0.0273(5)	-0.0076(4)	-0.0093(4)	-0.0279(5)
C(36)	0.175(14)	0.052(6)	0.023(4)	-0.008(4)	-0.023(6)	-0.017(7)
C(37)	0.188(15)	0.128(11)	0.057(6)	0.031(7)	-0.075(9)	-0.119(12)
C(38)	0.065(6)	0.095(8)	0.063(6)	-0.018(6)	-0.023(5)	-0.020(6)
C(39)	0.092(8)	0.054(5)	0.061(5)	-0.011(4)	-0.041(5)	-0.017(5)
C(40)	0.072(6)	0.068(6)	0.050(5)	0.015(5)	-0.019(5)	-0.030(5)
N(3)	0.041(3)	0.040(3)	0.025(2)	0.002(2)	-0.015(2)	-0.022(3)
C(41)	0.040(4)	0.028(3)	0.030(3)	0.004(3)	-0.014(3)	-0.015(3)
O(2)	0.049(3)	0.051(3)	0.033(2)	0.009(2)	-0.018(2)	-0.032(2)

N(4)	0.037(3)	0.051(4)	0.033(3)	0.001(2)	-0.017(2)	-0.022(3)
C(42)	0.035(4)	0.052(4)	0.046(4)	-0.013(3)	-0.010(3)	-0.022(3)
C(43)	0.046(4)	0.050(5)	0.034(4)	0.002(3)	-0.008(3)	-0.011(4)
C(44)	0.078(6)	0.061(6)	0.057(5)	-0.024(4)	0.009(5)	-0.044(5)
C(45)	0.134(12)	0.055(6)	0.076(8)	-0.013(6)	0.042(8)	-0.041(7)
C(46)	0.091(9)	0.10(1)	0.052(6)	0.025(6)	0.004(6)	0.050(7)
C(47)	0.054(6)	0.153(12)	0.038(5)	0.007(6)	-0.016(4)	0.021(7)
Fe(2)	0.0348(6)	0.0733(8)	0.0459(6)	-0.0163(6)	-0.0098(5)	-0.0146(6)
C(48)	0.083(8)	0.087(8)	0.092(8)	-0.005(7)	-0.010(7)	-0.060(7)
C(49)	0.071(7)	0.077(7)	0.058(6)	0.008(5)	-0.013(5)	-0.026(6)
C(50)	0.060(6)	0.090(8)	0.084(8)	-0.019(6)	0.008(6)	-0.038(6)
C(51)	0.059(7)	0.146(13)	0.130(13)	-0.02(1)	-0.011(8)	-0.053(8)
C(52)	0.10(1)	0.120(11)	0.120(11)	-0.039(9)	-0.035(9)	-0.051(9)
N(5)	0.040(3)	0.043(3)	0.028(3)	0.008(2)	-0.006(2)	-0.014(3)
C(53)	0.040(4)	0.030(3)	0.033(3)	-0.005(3)	-0.008(3)	-0.014(3)
O(3)	0.045(3)	0.065(3)	0.026(2)	0.004(2)	-0.008(2)	-0.029(3)
N(6)	0.039(3)	0.039(3)	0.035(3)	0.002(2)	-0.007(3)	-0.006(3)
C(54)	0.042(4)	0.043(4)	0.043(4)	0.001(3)	-0.018(3)	-0.013(3)
C(55)	0.035(4)	0.043(4)	0.034(3)	-0.008(3)	-0.014(3)	-0.009(3)
C(56)	0.038(4)	0.061(5)	0.052(4)	-0.017(4)	-0.006(3)	-0.017(4)
C(57)	0.042(4)	0.054(5)	0.064(5)	-0.016(4)	-0.011(4)	-0.002(4)
C(58)	0.053(5)	0.044(4)	0.034(4)	-0.001(3)	-0.021(3)	-0.003(4)
C(59)	0.046(4)	0.050(4)	0.025(3)	-0.005(3)	-0.008(3)	-0.012(3)
Fe(3)	0.0565(7)	0.0501(7)	0.0304(5)	-0.0076(4)	-0.0089(5)	-0.0214(5)
C(60)	0.187(15)	0.099(9)	0.033(4)	-0.004(5)	-0.028(7)	-0.09(1)
C(61)	0.160(12)	0.085(8)	0.051(6)	-0.024(5)	-0.011(7)	-0.072(8)
C(62)	0.131(11)	0.096(9)	0.061(6)	-0.009(6)	-0.032(7)	-0.072(8)
C(63)	0.11(1)	0.11(1)	0.081(8)	-0.006(7)	-0.051(7)	-0.063(8)
C(64)	0.149(13)	0.091(9)	0.078(8)	0.003(7)	-0.075(9)	-0.055(9)
N(7)	0.038(3)	0.044(3)	0.029(3)	0.004(2)	-0.007(2)	-0.018(3)
C(65)	0.035(4)	0.036(4)	0.026(3)	0.003(3)	-0.009(3)	-0.007(3)
O(4)	0.051(3)	0.064(3)	0.026(2)	0.011(2)	-0.013(2)	-0.025(3)
N(8)	0.047(4)	0.073(5)	0.046(4)	0.016(3)	-0.024(3)	-0.032(4)
C(66)	0.056(5)	0.100(7)	0.042(4)	-0.003(4)	-0.020(4)	-0.037(5)
C(67)	0.050(4)	0.066(5)	0.041(4)	0.006(4)	-0.024(4)	-0.031(4)
C(68)	0.068(6)	0.055(5)	0.061(5)	0.008(4)	-0.033(5)	-0.025(5)
C(69)	0.052(5)	0.087(7)	0.068(6)	0.006(5)	-0.019(5)	-0.038(5)
C(70)	0.052(5)	0.099(8)	0.037(4)	-0.006(4)	-0.014(4)	-0.026(5)
C(71)	0.060(5)	0.067(5)	0.040(4)	-0.007(4)	-0.022(4)	-0.023(4)
Fe(4)	0.0486(6)	0.0596(7)	0.0352(5)	-0.0011(5)	-0.0193(5)	-0.0251(6)
C(72)	0.077(7)	0.101(8)	0.036(4)	0.011(5)	-0.023(4)	-0.037(6)
C(73)	0.103(9)	0.082(7)	0.050(5)	-0.017(5)	-0.040(6)	-0.020(6)
C(74)	0.075(7)	0.077(7)	0.064(6)	-0.001(5)	-0.042(5)	-0.023(6)
C(75)	0.061(5)	0.058(5)	0.059(5)	0.008(4)	-0.032(4)	-0.022(4)
C(76)	0.067(6)	0.068(6)	0.051(5)	0.011(4)	-0.022(4)	-0.034(5)
O(5)	0.041(3)	0.046(3)	0.042(3)	-0.002(2)	-0.008(2)	-0.027(2)
O(6)	0.042(3)	0.042(3)	0.022(2)	-0.0025(18)	-0.0105(18)	-0.022(2)
C(80)	0.036(4)	0.044(4)	0.030(3)	-0.010(3)	-0.013(3)	-0.015(3)
C(81)	0.041(4)	0.044(4)	0.034(3)	-0.007(3)	-0.014(3)	-0.020(3)
C(82)	0.060(5)	0.072(6)	0.044(4)	-0.022(4)	-0.020(4)	-0.024(4)

O(7)	0.057(3)	0.033(3)	0.048(3)	-0.002(2)	-0.033(3)	-0.010(2)
C(83)	0.083(8)	0.074(7)	0.082(8)	-0.013(6)	-0.016(6)	-0.009(6)
C(84)	0.124(11)	0.073(7)	0.046(5)	0.004(5)	-0.006(6)	0.000(7)
C(85)	0.058(6)	0.171(14)	0.12(1)	-0.09(1)	-0.014(6)	-0.039(8)
O(8)	0.038(3)	0.042(3)	0.032(2)	-0.000(2)	-0.004(2)	-0.021(2)
O(9)	0.082(5)	0.064(4)	0.061(4)	0.020(3)	-0.003(3)	-0.038(4)
C(89)	0.081(7)	0.054(6)	0.072(6)	-0.014(5)	0.015(6)	-0.024(5)
O(10)	0.063(3)	0.045(3)	0.034(3)	0.002(2)	-0.019(2)	-0.019(3)
C(90)	0.076(6)	0.053(5)	0.038(4)	0.002(4)	-0.007(4)	-0.018(5)
O(11)	0.047(3)	0.057(3)	0.037(3)	-0.000(2)	-0.008(2)	-0.026(3)
C(91)	0.061(5)	0.056(5)	0.034(4)	-0.003(3)	-0.002(4)	-0.023(4)
C(92)	0.068(6)	0.075(6)	0.063(6)	-0.005(5)	-0.017(5)	-0.041(5)
Cl(1)	0.133(3)	0.130(3)	0.0715(18)	-0.0301(18)	0.0033(19)	-0.076(2)
Cl(2)	0.187(5)	0.151(4)	0.221(6)	-0.107(5)	-0.118(5)	0.060(4)
Cl(3)	0.302(8)	0.179(5)	0.121(3)	-0.050(3)	0.068(4)	-0.194(6)

Table F.3.5: Bond lengths (Å)
(H atoms have been excluded)

C(1) - C(2)	1.40(1)	C(50) - C(51)	1.32(2)
C(1) - C(6)	1.388(9)	C(51) - C(52)	1.48(2)
C(1) - O(5)	1.371(8)	N(5) - C(53)	1.351(9)
C(2) - C(3)	1.40(1)	C(53) - O(3)	1.241(8)
C(2) - C(28)	1.518(9)	C(53) - N(6)	1.350(9)
C(3) - C(4)	1.383(9)	N(6) - C(54)	1.46(1)
C(4) - C(5)	1.39(1)	C(54) - C(55)	1.49(1)
C(4) - N(1)	1.426(9)	C(55) - C(56)	1.44(1)
C(5) - C(6)	1.402(9)	C(55) - C(59)	1.41(1)
C(6) - C(7)	1.499(9)	C(55) - Fe(3)	2.028(7)
C(7) - C(9)	1.536(9)	C(56) - C(57)	1.419(13)
C(8) - C(9)	1.400(9)	C(56) - Fe(3)	2.034(8)
C(8) - C(13)	1.382(9)	C(57) - C(58)	1.417(12)
C(8) - O(6)	1.399(8)	C(57) - Fe(3)	2.05(1)
C(9) - C(10)	1.382(9)	C(58) - C(59)	1.438(11)
C(10) - C(11)	1.404(9)	C(58) - Fe(3)	2.042(7)
C(11) - C(12)	1.395(9)	C(59) - Fe(3)	2.037(7)
C(11) - N(3)	1.420(8)	Fe(3) - C(60)	2.037(9)
C(12) - C(13)	1.389(9)	Fe(3) - C(61)	2.05(1)
C(13) - C(14)	1.542(9)	Fe(3) - C(62)	2.01(1)
C(14) - C(16)	1.507(9)	Fe(3) - C(63)	2.049(11)
C(15) - C(16)	1.37(1)	Fe(3) - C(64)	2.02(1)
C(15) - C(20)	1.397(9)	C(60) - C(61)	1.451(16)
C(15) - O(7)	1.390(8)	C(60) - C(64)	1.43(2)
C(16) - C(17)	1.40(1)	C(61) - C(62)	1.413(18)
C(17) - C(18)	1.398(9)	C(62) - C(63)	1.406(18)

C(18) - C(19)	1.40(1)	C(63) - C(64)	1.422(18)
C(18) - N(5)	1.422(9)	N(7) - C(65)	1.368(9)
C(19) - C(20)	1.39(1)	C(65) - O(4)	1.227(8)
C(20) - C(21)	1.50(1)	C(65) - N(8)	1.34(1)
C(21) - C(23)	1.529(9)	N(8) - C(66)	1.48(1)
C(22) - C(23)	1.40(1)	C(66) - C(67)	1.488(12)
C(22) - C(27)	1.398(9)	C(67) - C(68)	1.422(12)
C(22) - O(8)	1.388(8)	C(67) - C(71)	1.429(13)
C(23) - C(24)	1.38(1)	C(67) - Fe(4)	2.035(8)
C(24) - C(25)	1.378(9)	C(68) - C(69)	1.405(14)
C(25) - C(26)	1.384(9)	C(68) - Fe(4)	2.035(9)
C(25) - N(7)	1.419(9)	C(69) - C(70)	1.411(15)
C(26) - C(27)	1.404(9)	C(69) - Fe(4)	2.03(1)
C(27) - C(28)	1.515(9)	C(70) - C(71)	1.402(13)
N(1) - C(29)	1.351(9)	C(70) - Fe(4)	2.036(8)
C(29) - O(1)	1.238(8)	C(71) - Fe(4)	2.033(8)
C(29) - N(2)	1.347(9)	Fe(4) - C(72)	2.040(9)
N(2) - C(30)	1.45(1)	Fe(4) - C(73)	2.038(9)
C(30) - C(31)	1.505(11)	Fe(4) - C(74)	2.037(9)
C(31) - C(32)	1.413(11)	Fe(4) - C(75)	2.046(9)
C(31) - C(35)	1.427(11)	Fe(4) - C(76)	2.041(9)
C(31) - Fe(1)	2.040(8)	C(72) - C(73)	1.428(16)
C(32) - C(33)	1.422(12)	C(72) - C(76)	1.396(16)
C(32) - Fe(1)	2.031(8)	C(73) - C(74)	1.395(16)
C(33) - C(34)	1.408(13)	C(74) - C(75)	1.402(14)
C(33) - Fe(1)	2.038(7)	C(75) - C(76)	1.414(13)
C(34) - C(35)	1.408(14)	O(5) - C(77)	1.425(9)
C(34) - Fe(1)	2.048(7)	O(5) - C(177)	1.427(9)
C(35) - Fe(1)	2.034(9)	C(77) - C(78)	1.53(1)
Fe(1) - C(36)	2.018(8)	C(78) - C(79)	1.54(1)
Fe(1) - C(37)	2.00(1)	C(177) - C(178)	1.53(1)
Fe(1) - C(38)	2.040(11)	C(178) - C(179)	1.53(1)
Fe(1) - C(39)	2.03(1)	O(6) - C(80)	1.444(8)
Fe(1) - C(40)	2.045(9)	C(80) - C(81)	1.506(9)
C(36) - C(37)	1.38(2)	C(81) - C(82)	1.54(1)
C(36) - C(40)	1.423(18)	O(7) - C(83)	1.406(16)
C(37) - C(38)	1.407(19)	C(83) - C(84)	1.356(17)
C(38) - C(39)	1.316(15)	C(84) - C(85)	1.73(2)
C(39) - C(40)	1.360(15)	O(8) - C(86)	1.427(9)
N(3) - C(41)	1.360(8)	O(8) - C(186)	1.435(8)
C(41) - O(2)	1.239(7)	C(86) - C(87)	1.523(9)
C(41) - N(4)	1.354(8)	C(87) - C(88)	1.526(9)
N(4) - C(42)	1.459(9)	C(186) - C(187)	1.533(9)
C(42) - C(43)	1.505(11)	C(187) - C(188)	1.537(9)
C(43) - C(44)	1.426(12)	O(9) - C(89)	1.369(11)
C(43) - C(47)	1.403(13)	O(10) - C(90)	1.42(1)
C(43) - Fe(2)	2.050(8)	O(11) - C(91)	1.427(9)
C(44) - C(45)	1.406(18)	C(92) - Cl(1)	1.739(11)
C(44) - Fe(2)	2.043(9)	C(92) - Cl(2)	1.690(12)
C(45) - C(46)	1.37(2)	C(92) - Cl(3)	1.71(1)

C(45) - Fe(2)	2.035(13)	C(93) - Cl(4)	1.761(9)
C(46) - C(47)	1.399(19)	C(93) - Cl(5)	1.759(9)
C(46) - Fe(2)	2.001(12)	C(93) - Cl(6)	1.745(9)
C(47) - Fe(2)	2.01(1)	C(193) - Cl(104)	1.748(9)
Fe(2) - C(48)	2.079(12)	C(193) - Cl(105)	1.740(9)
Fe(2) - C(49)	2.09(1)	C(193) - Cl(106)	1.750(9)
Fe(2) - C(50)	2.027(11)	C(94) - Cl(7)	1.765(9)
Fe(2) - C(51)	2.035(13)	C(94) - Cl(8)	1.783(9)
Fe(2) - C(52)	2.027(14)	C(94) - Cl(9)	1.758(9)
C(48) - C(49)	1.358(17)	C(194) - Cl(107)	1.756(9)
C(48) - C(52)	1.343(18)	C(194) - Cl(108)	1.772(9)
C(49) - C(50)	1.424(16)	C(194) - Cl(109)	1.760(9)

Table F.2.6: Bond angles (°)
(H atoms have been excluded)

C(2) - C(1) - C(6)	121.9(6)	Fe(2) - C(48) - C(52)	68.8(8)
C(2) - C(1) - O(5)	119.2(6)	C(49) - C(48) - C(52)	110.0(12)
C(6) - C(1) - O(5)	118.6(6)	Fe(2) - C(49) - C(48)	70.6(7)
C(1) - C(2) - C(3)	118.5(6)	Fe(2) - C(49) - C(50)	67.5(6)
C(1) - C(2) - C(28)	119.9(6)	C(48) - C(49) - C(50)	107.7(11)
C(3) - C(2) - C(28)	120.7(6)	Fe(2) - C(50) - C(49)	72.0(6)
C(2) - C(3) - C(4)	120.4(6)	Fe(2) - C(50) - C(51)	71.4(8)
C(3) - C(4) - C(5)	120.0(6)	C(49) - C(50) - C(51)	108.8(12)
C(3) - C(4) - N(1)	121.2(6)	Fe(2) - C(51) - C(50)	70.7(7)
C(5) - C(4) - N(1)	118.7(6)	Fe(2) - C(51) - C(52)	68.4(7)
C(4) - C(5) - C(6)	121.0(6)	C(50) - C(51) - C(52)	107.0(12)
C(1) - C(6) - C(5)	117.9(6)	Fe(2) - C(52) - C(48)	73.0(7)
C(1) - C(6) - C(7)	120.8(6)	Fe(2) - C(52) - C(51)	68.9(8)
C(5) - C(6) - C(7)	120.7(6)	C(48) - C(52) - C(51)	106.4(13)
C(6) - C(7) - C(9)	109.7(5)	C(18) - N(5) - C(53)	125.1(5)
C(9) - C(8) - C(13)	121.0(6)	N(5) - C(53) - O(3)	123.0(6)
C(9) - C(8) - O(6)	119.0(6)	N(5) - C(53) - N(6)	114.1(6)
C(13) - C(8) - O(6)	119.9(5)	O(3) - C(53) - N(6)	122.9(6)
C(7) - C(9) - C(8)	121.4(6)	C(53) - N(6) - C(54)	122.7(6)
C(7) - C(9) - C(10)	119.4(6)	N(6) - C(54) - C(55)	112.1(6)
C(8) - C(9) - C(10)	119.1(6)	C(54) - C(55) - C(56)	125.7(7)
C(9) - C(10) - C(11)	120.6(6)	C(54) - C(55) - C(59)	127.1(6)
C(10) - C(11) - C(12)	119.0(6)	C(56) - C(55) - C(59)	107.0(7)
C(10) - C(11) - N(3)	122.3(6)	C(54) - C(55) - Fe(3)	128.9(5)
C(12) - C(11) - N(3)	118.7(5)	C(56) - C(55) - Fe(3)	69.5(4)
C(11) - C(12) - C(13)	120.7(6)	C(59) - C(55) - Fe(3)	70.1(4)
C(8) - C(13) - C(12)	119.3(6)	C(55) - C(56) - C(57)	108.2(7)
C(8) - C(13) - C(14)	122.4(6)	C(55) - C(56) - Fe(3)	69.1(4)
C(12) - C(13) - C(14)	118.2(5)	C(57) - C(56) - Fe(3)	70.3(5)
C(13) - C(14) - C(16)	108.5(5)	C(56) - C(57) - C(58)	108.7(7)
C(16) - C(15) - C(20)	122.6(6)	C(56) - C(57) - Fe(3)	69.1(5)
C(16) - C(15) - O(7)	119.8(6)	C(58) - C(57) - Fe(3)	69.4(5)
C(20) - C(15) - O(7)	117.2(6)	C(57) - C(58) - C(59)	106.8(7)

C(14) - C(16) - C(15)	120.8(6)	C(57) - C(58) - Fe(3)	70.0(5)
C(14) - C(16) - C(17)	119.3(6)	C(59) - C(58) - Fe(3)	69.2(4)
C(15) - C(16) - C(17)	119.4(6)	C(55) - C(59) - C(58)	109.3(7)
C(16) - C(17) - C(18)	119.4(6)	C(55) - C(59) - Fe(3)	69.4(4)
C(17) - C(18) - C(19)	119.6(6)	C(58) - C(59) - Fe(3)	69.5(4)
C(17) - C(18) - N(5)	121.4(6)	C(55) - Fe(3) - C(56)	41.4(3)
C(19) - C(18) - N(5)	119.1(6)	C(55) - Fe(3) - C(57)	69.1(3)
C(18) - C(19) - C(20)	121.6(6)	C(56) - Fe(3) - C(57)	40.7(4)
C(15) - C(20) - C(19)	117.2(6)	C(55) - Fe(3) - C(58)	69.5(3)
C(15) - C(20) - C(21)	120.9(6)	C(56) - Fe(3) - C(58)	68.8(4)
C(19) - C(20) - C(21)	121.4(6)	C(57) - Fe(3) - C(58)	40.5(3)
C(20) - C(21) - C(23)	110.6(5)	C(55) - Fe(3) - C(59)	40.5(3)
C(23) - C(22) - C(27)	121.2(6)	C(56) - Fe(3) - C(59)	68.3(3)
C(23) - C(22) - O(8)	119.9(6)	C(57) - Fe(3) - C(59)	68.2(3)
C(27) - C(22) - O(8)	118.9(6)	C(58) - Fe(3) - C(59)	41.3(3)
C(21) - C(23) - C(22)	121.6(6)	C(55) - Fe(3) - C(60)	122.8(4)
C(21) - C(23) - C(24)	119.5(6)	C(56) - Fe(3) - C(60)	106.7(5)
C(22) - C(23) - C(24)	118.6(6)	C(57) - Fe(3) - C(60)	121.7(6)
C(23) - C(24) - C(25)	121.1(6)	C(58) - Fe(3) - C(60)	157.2(6)
C(24) - C(25) - C(26)	120.3(6)	C(59) - Fe(3) - C(60)	159.7(5)
C(24) - C(25) - N(7)	122.7(6)	C(55) - Fe(3) - C(61)	160.8(4)
C(26) - C(25) - N(7)	116.9(6)	C(56) - Fe(3) - C(61)	124.0(5)
C(25) - C(26) - C(27)	120.4(6)	C(57) - Fe(3) - C(61)	107.7(5)
C(22) - C(27) - C(26)	118.3(6)	C(58) - Fe(3) - C(61)	121.1(4)
C(22) - C(27) - C(28)	122.7(6)	C(59) - Fe(3) - C(61)	157.5(4)
C(26) - C(27) - C(28)	119.0(6)	C(55) - Fe(3) - C(62)	155.9(5)
C(2) - C(28) - C(27)	108.1(5)	C(56) - Fe(3) - C(62)	162.2(5)
C(4) - N(1) - C(29)	123.3(5)	C(57) - Fe(3) - C(62)	126.4(5)
N(1) - C(29) - O(1)	124.0(6)	C(58) - Fe(3) - C(62)	109.1(4)
N(1) - C(29) - N(2)	114.2(6)	C(59) - Fe(3) - C(62)	122.6(4)
O(1) - C(29) - N(2)	121.8(7)	C(55) - Fe(3) - C(63)	119.0(5)
C(29) - N(2) - C(30)	121.9(6)	C(56) - Fe(3) - C(63)	155.6(5)
N(2) - C(30) - C(31)	113.9(7)	C(57) - Fe(3) - C(63)	161.6(5)
C(30) - C(31) - C(32)	127.7(7)	C(58) - Fe(3) - C(63)	124.0(4)
C(30) - C(31) - C(35)	125.1(7)	C(59) - Fe(3) - C(63)	106.4(4)
C(32) - C(31) - C(35)	107.1(7)	C(55) - Fe(3) - C(64)	105.5(4)
C(30) - C(31) - Fe(1)	127.0(5)	C(56) - Fe(3) - C(64)	120.5(5)
C(32) - C(31) - Fe(1)	69.3(5)	C(57) - Fe(3) - C(64)	156.8(5)
C(35) - C(31) - Fe(1)	69.3(5)	C(58) - Fe(3) - C(64)	160.6(6)
C(31) - C(32) - C(33)	108.5(7)	C(59) - Fe(3) - C(64)	123.1(5)
C(31) - C(32) - Fe(1)	70.0(4)	C(60) - Fe(3) - C(61)	41.6(5)
C(33) - C(32) - Fe(1)	69.8(4)	C(60) - Fe(3) - C(62)	68.0(5)
C(32) - C(33) - C(34)	107.7(8)	C(61) - Fe(3) - C(62)	40.8(5)
C(32) - C(33) - Fe(1)	69.3(4)	C(60) - Fe(3) - C(63)	69.5(6)
C(34) - C(33) - Fe(1)	70.2(4)	C(61) - Fe(3) - C(63)	70.1(6)
C(33) - C(34) - C(35)	108.4(7)	C(62) - Fe(3) - C(63)	40.5(5)
C(33) - C(34) - Fe(1)	69.5(4)	C(60) - Fe(3) - C(64)	41.1(6)
C(35) - C(34) - Fe(1)	69.3(5)	C(61) - Fe(3) - C(64)	69.7(6)
C(31) - C(35) - C(34)	108.3(8)	C(62) - Fe(3) - C(64)	67.5(5)
C(31) - C(35) - Fe(1)	69.7(5)	C(63) - Fe(3) - C(64)	40.9(5)

C(34) - C(35) - Fe(1)	70.4(5)	Fe(3) - C(60) - C(61)	69.5(5)
C(31) - Fe(1) - C(32)	40.6(3)	Fe(3) - C(60) - C(64)	68.9(6)
C(31) - Fe(1) - C(33)	68.7(3)	C(61) - C(60) - C(64)	107.8(11)
C(32) - Fe(1) - C(33)	40.9(3)	Fe(3) - C(61) - C(60)	68.9(6)
C(31) - Fe(1) - C(34)	68.4(3)	Fe(3) - C(61) - C(62)	68.3(6)
C(32) - Fe(1) - C(34)	68.1(3)	C(60) - C(61) - C(62)	104.5(13)
C(33) - Fe(1) - C(34)	40.3(4)	Fe(3) - C(62) - C(61)	70.9(6)
C(31) - Fe(1) - C(35)	41.0(3)	Fe(3) - C(62) - C(63)	71.3(6)
C(32) - Fe(1) - C(35)	68.4(3)	C(61) - C(62) - C(63)	113.1(11)
C(33) - Fe(1) - C(35)	68.2(4)	Fe(3) - C(63) - C(62)	68.2(7)
C(34) - Fe(1) - C(35)	40.3(4)	Fe(3) - C(63) - C(64)	68.6(6)
C(31) - Fe(1) - C(36)	107.9(4)	C(62) - C(63) - C(64)	104.8(12)
C(32) - Fe(1) - C(36)	123.0(4)	Fe(3) - C(64) - C(60)	70.0(6)
C(33) - Fe(1) - C(36)	158.9(6)	Fe(3) - C(64) - C(63)	70.6(6)
C(34) - Fe(1) - C(36)	159.7(6)	C(60) - C(64) - C(63)	109.8(11)
C(35) - Fe(1) - C(36)	123.8(5)	C(25) - N(7) - C(65)	123.3(5)
C(31) - Fe(1) - C(37)	123.1(5)	N(7) - C(65) - O(4)	121.8(7)
C(32) - Fe(1) - C(37)	107.8(4)	N(7) - C(65) - N(8)	114.4(6)
C(33) - Fe(1) - C(37)	122.9(5)	O(4) - C(65) - N(8)	123.8(6)
C(34) - Fe(1) - C(37)	158.7(6)	C(65) - N(8) - C(66)	121.3(6)
C(35) - Fe(1) - C(37)	159.6(6)	N(8) - C(66) - C(67)	111.4(7)
C(31) - Fe(1) - C(38)	160.0(4)	C(66) - C(67) - C(68)	127.2(9)
C(32) - Fe(1) - C(38)	124.2(4)	C(66) - C(67) - C(71)	126.1(8)
C(33) - Fe(1) - C(38)	108.3(4)	C(68) - C(67) - C(71)	106.7(8)
C(34) - Fe(1) - C(38)	122.9(4)	C(66) - C(67) - Fe(4)	125.3(6)
C(35) - Fe(1) - C(38)	157.9(4)	C(68) - C(67) - Fe(4)	69.6(5)
C(31) - Fe(1) - C(39)	160.2(4)	C(71) - C(67) - Fe(4)	69.4(5)
C(32) - Fe(1) - C(39)	158.6(4)	C(67) - C(68) - C(69)	109.0(9)
C(33) - Fe(1) - C(39)	123.6(4)	C(67) - C(68) - Fe(4)	69.5(5)
C(34) - Fe(1) - C(39)	109.7(4)	C(69) - C(68) - Fe(4)	69.5(6)
C(35) - Fe(1) - C(39)	124.7(4)	C(68) - C(69) - C(70)	107.4(8)
C(31) - Fe(1) - C(40)	124.3(4)	C(68) - C(69) - Fe(4)	70.0(5)
C(32) - Fe(1) - C(40)	160.2(4)	C(70) - C(69) - Fe(4)	70.0(5)
C(33) - Fe(1) - C(40)	158.0(4)	C(69) - C(70) - C(71)	108.9(8)
C(34) - Fe(1) - C(40)	123.3(4)	C(69) - C(70) - Fe(4)	69.4(5)
C(35) - Fe(1) - C(40)	108.7(4)	C(71) - C(70) - Fe(4)	69.7(5)
C(36) - Fe(1) - C(37)	40.2(6)	C(67) - C(71) - Fe(4)	69.5(4)
C(36) - Fe(1) - C(38)	67.3(5)	C(70) - C(71) - Fe(4)	70.0(5)
C(37) - Fe(1) - C(38)	40.7(6)	C(67) - Fe(4) - C(68)	40.9(3)
C(36) - Fe(1) - C(39)	66.5(4)	C(67) - Fe(4) - C(69)	69.0(3)
C(37) - Fe(1) - C(39)	66.0(4)	C(68) - Fe(4) - C(69)	40.5(4)
C(38) - Fe(1) - C(39)	37.7(4)	C(67) - Fe(4) - C(70)	68.5(4)
C(36) - Fe(1) - C(40)	41.0(5)	C(68) - Fe(4) - C(70)	67.8(4)
C(37) - Fe(1) - C(40)	67.6(5)	C(69) - Fe(4) - C(70)	40.6(4)
C(38) - Fe(1) - C(40)	65.8(4)	C(67) - Fe(4) - C(71)	41.1(4)
C(39) - Fe(1) - C(40)	38.9(4)	C(68) - Fe(4) - C(71)	68.4(4)
Fe(1) - C(36) - C(37)	69.3(5)	C(69) - Fe(4) - C(71)	68.6(4)
Fe(1) - C(36) - C(40)	70.5(5)	C(70) - Fe(4) - C(71)	40.3(4)
C(37) - C(36) - C(40)	106.8(9)	C(67) - Fe(4) - C(72)	107.1(4)
Fe(1) - C(37) - C(36)	70.5(7)	C(68) - Fe(4) - C(72)	121.9(5)

Fe(1) - C(37) - C(38)	71.1(6)	C(69) - Fe(4) - C(72)	157.0(5)
C(36) - C(37) - C(38)	107.6(10)	C(70) - Fe(4) - C(72)	160.8(5)
Fe(1) - C(38) - C(37)	68.2(7)	C(71) - Fe(4) - C(72)	124.2(4)
Fe(1) - C(38) - C(39)	70.9(6)	C(67) - Fe(4) - C(73)	126.0(4)
C(37) - C(38) - C(39)	107.6(11)	C(68) - Fe(4) - C(73)	109.6(4)
Fe(1) - C(39) - C(38)	71.4(7)	C(69) - Fe(4) - C(73)	121.9(5)
Fe(1) - C(39) - C(40)	71.0(5)	C(70) - Fe(4) - C(73)	156.4(5)
C(38) - C(39) - C(40)	112.0(10)	C(71) - Fe(4) - C(73)	162.6(5)
Fe(1) - C(40) - C(36)	68.5(5)	C(67) - Fe(4) - C(74)	163.3(4)
Fe(1) - C(40) - C(39)	70.1(6)	C(68) - Fe(4) - C(74)	126.9(4)
C(36) - C(40) - C(39)	106.0(10)	C(69) - Fe(4) - C(74)	108.8(4)
C(11) - N(3) - C(41)	124.4(5)	C(70) - Fe(4) - C(74)	121.4(4)
N(3) - C(41) - O(2)	121.9(6)	C(71) - Fe(4) - C(74)	154.8(4)
N(3) - C(41) - N(4)	114.4(5)	C(67) - Fe(4) - C(75)	154.5(4)
O(2) - C(41) - N(4)	123.6(6)	C(68) - Fe(4) - C(75)	163.1(4)
C(41) - N(4) - C(42)	120.6(5)	C(69) - Fe(4) - C(75)	125.7(4)
N(4) - C(42) - C(43)	113.1(6)	C(70) - Fe(4) - C(75)	107.8(4)
C(42) - C(43) - C(44)	126.6(8)	C(71) - Fe(4) - C(75)	119.6(4)
C(42) - C(43) - C(47)	126.7(9)	C(67) - Fe(4) - C(76)	119.4(4)
C(44) - C(43) - C(47)	106.7(9)	C(68) - Fe(4) - C(76)	155.5(4)
C(42) - C(43) - Fe(2)	127.8(6)	C(69) - Fe(4) - C(76)	161.9(5)
C(44) - C(43) - Fe(2)	69.3(5)	C(70) - Fe(4) - C(76)	124.5(5)
C(47) - C(43) - Fe(2)	68.4(6)	C(71) - Fe(4) - C(76)	106.3(4)
C(43) - C(44) - C(45)	108.0(11)	C(72) - Fe(4) - C(73)	41.0(5)
C(43) - C(44) - Fe(2)	69.9(5)	C(72) - Fe(4) - C(74)	68.1(4)
C(45) - C(44) - Fe(2)	69.5(7)	C(73) - Fe(4) - C(74)	40.0(4)
C(44) - C(45) - C(46)	107.7(10)	C(72) - Fe(4) - C(75)	67.7(4)
C(44) - C(45) - Fe(2)	70.1(6)	C(73) - Fe(4) - C(75)	67.5(4)
C(46) - C(45) - Fe(2)	68.9(9)	C(74) - Fe(4) - C(75)	40.2(4)
C(45) - C(46) - C(47)	109.8(11)	C(72) - Fe(4) - C(76)	40.0(4)
C(45) - C(46) - Fe(2)	71.5(6)	C(73) - Fe(4) - C(76)	67.9(4)
C(47) - C(46) - Fe(2)	70.1(7)	C(74) - Fe(4) - C(76)	67.9(4)
C(43) - C(47) - C(46)	107.7(13)	C(75) - Fe(4) - C(76)	40.5(4)
C(43) - C(47) - Fe(2)	71.2(5)	Fe(4) - C(72) - C(73)	69.4(5)
C(46) - C(47) - Fe(2)	69.1(6)	Fe(4) - C(72) - C(76)	70.1(5)
C(43) - Fe(2) - C(44)	40.8(4)	C(73) - C(72) - C(76)	107.6(9)
C(43) - Fe(2) - C(45)	68.2(4)	Fe(4) - C(73) - C(72)	69.5(5)
C(44) - Fe(2) - C(45)	40.3(5)	Fe(4) - C(73) - C(74)	69.9(5)
C(43) - Fe(2) - C(46)	67.9(4)	C(72) - C(73) - C(74)	107.9(10)
C(44) - Fe(2) - C(46)	67.3(7)	Fe(4) - C(74) - C(73)	70.0(6)
C(45) - Fe(2) - C(46)	39.6(7)	Fe(4) - C(74) - C(75)	70.3(5)
C(43) - Fe(2) - C(47)	40.4(4)	C(73) - C(74) - C(75)	108.4(10)
C(44) - Fe(2) - C(47)	68.1(6)	Fe(4) - C(75) - C(74)	69.5(5)
C(45) - Fe(2) - C(47)	68.0(7)	Fe(4) - C(75) - C(76)	69.6(5)
C(46) - Fe(2) - C(47)	40.8(6)	C(74) - C(75) - C(76)	108.0(9)
C(43) - Fe(2) - C(48)	109.8(4)	Fe(4) - C(76) - C(72)	69.9(6)
C(44) - Fe(2) - C(48)	115.1(4)	Fe(4) - C(76) - C(75)	69.9(5)
C(45) - Fe(2) - C(48)	145.8(7)	C(72) - C(76) - C(75)	108.1(9)
C(46) - Fe(2) - C(48)	173.7(7)	C(1) - O(5) - C(77)	111.9(7)
C(47) - Fe(2) - C(48)	133.8(6)	C(1) - O(5) - C(177)	112.9(6)

C(43) - Fe(2) - C(49)	128.4(4)	O(5) - C(77) - C(78)	113.7(9)
C(44) - Fe(2) - C(49)	105.9(5)	C(77) - C(78) - C(79)	110.7(9)
C(45) - Fe(2) - C(49)	114.7(6)	O(5) - C(177) - C(178)	113.2(8)
C(46) - Fe(2) - C(49)	148.0(6)	C(177) - C(178) - C(179)	110.7(9)
C(47) - Fe(2) - C(49)	168.0(4)	C(8) - O(6) - C(80)	112.4(5)
C(43) - Fe(2) - C(50)	166.2(5)	O(6) - C(80) - C(81)	108.1(5)
C(44) - Fe(2) - C(50)	127.4(5)	C(80) - C(81) - C(82)	109.9(6)
C(45) - Fe(2) - C(50)	107.1(5)	C(15) - O(7) - C(83)	116.3(6)
C(46) - Fe(2) - C(50)	117.3(5)	O(7) - C(83) - C(84)	105.8(12)
C(47) - Fe(2) - C(50)	151.4(5)	C(83) - C(84) - C(85)	107.6(11)
C(43) - Fe(2) - C(51)	154.5(6)	C(22) - O(8) - C(86)	111.4(6)
C(44) - Fe(2) - C(51)	164.7(6)	C(22) - O(8) - C(186)	113.4(5)
C(45) - Fe(2) - C(51)	129.7(6)	O(8) - C(86) - C(87)	109.5(8)
C(46) - Fe(2) - C(51)	112.7(7)	C(86) - C(87) - C(88)	110.1(8)
C(47) - Fe(2) - C(51)	122.7(7)	O(8) - C(186) - C(187)	110.8(6)
C(43) - Fe(2) - C(52)	118.4(5)	C(186) - C(187) - C(188)	113.2(8)
C(44) - Fe(2) - C(52)	147.2(5)	Cl(1) - C(92) - Cl(2)	114.0(6)
C(45) - Fe(2) - C(52)	172.3(6)	Cl(1) - C(92) - Cl(3)	109.9(6)
C(46) - Fe(2) - C(52)	137.1(8)	Cl(2) - C(92) - Cl(3)	114.6(7)
C(47) - Fe(2) - C(52)	114.0(7)	Cl(4) - C(93) - Cl(5)	115.2(8)
C(48) - Fe(2) - C(49)	38.1(5)	Cl(4) - C(93) - Cl(6)	111.7(8)
C(48) - Fe(2) - C(50)	66.3(5)	Cl(5) - C(93) - Cl(6)	110.6(7)
C(49) - Fe(2) - C(50)	40.5(5)	Cl(104) - C(193) - Cl(105)	110.5(7)
C(48) - Fe(2) - C(51)	66.7(6)	Cl(104) - C(193) - Cl(106)	113.0(7)
C(49) - Fe(2) - C(51)	65.5(6)	Cl(105) - C(193) - Cl(106)	111.4(7)
C(50) - Fe(2) - C(51)	37.9(6)	Cl(7) - C(94) - Cl(8)	114.4(7)
C(48) - Fe(2) - C(52)	38.2(5)	Cl(7) - C(94) - Cl(9)	111.1(7)
C(49) - Fe(2) - C(52)	65.0(6)	Cl(8) - C(94) - Cl(9)	114.1(7)
C(50) - Fe(2) - C(52)	67.5(6)	Cl(107) - C(194) - Cl(108)	114.0(7)
C(51) - Fe(2) - C(52)	42.7(6)	Cl(107) - C(194) - Cl(109)	112.8(6)
Fe(2) - C(48) - C(49)	71.3(7)	Cl(108) - C(194) - Cl(109)	114.1(6)

F.4 Crystal data for $26 \cdot 2[\text{N}(\text{C}_4\text{H}_9)_4][\text{C}_6\text{H}_5\text{CO}_2]^\S$

X-ray quality crystals (pale orange blocks) of $26 \cdot 2[\text{N}(\text{C}_4\text{H}_9)_4][\text{C}_6\text{H}_5\text{CO}_2]$ were obtained from a 1:1 CD_3CN / d_6 -DMSO solution of the compound containing a tenfold excess of tetrabutylammonium benzoate. The non-hydrogen atom numbering system is outlined in the schematic structure shown in Figure F.3.1.

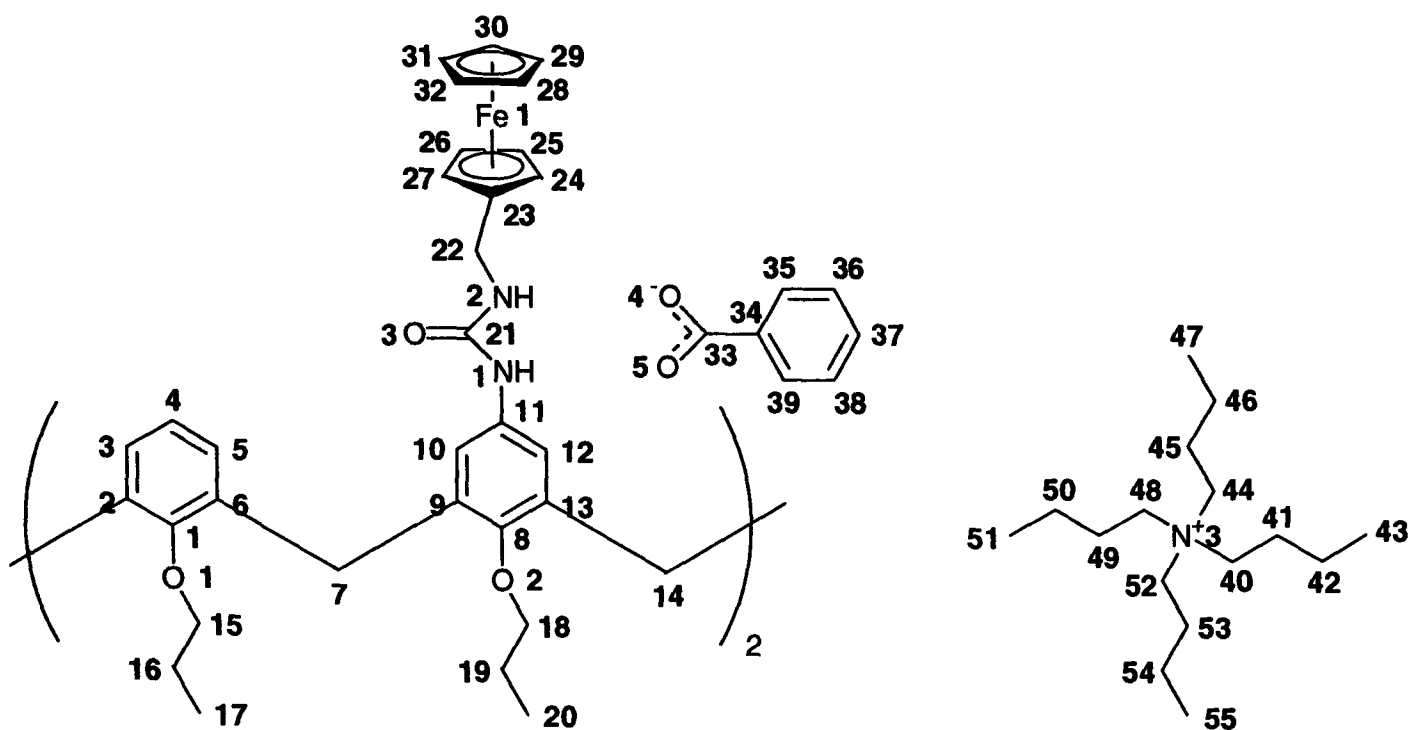


Figure F.3.1: Atom numbering system.

Table F.4.1: Crystal data and refinement details

Crystal identification	ARC233
Chemical formula	C ₁₁₀ H ₁₅₄ Fe ₂ N ₆ O ₁₀
Formula weight	1832.16
Temperature (K)	150
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	<i>C</i> 2/ <i>c</i>
<i>a</i> (Å)	20.7844(4)
<i>b</i> (Å)	9.1206(3)
<i>c</i> (Å)	53.0777(15)
α (°)	90
β (°)	95.1009(8)
γ (°)	90
Cell volume (Å ³)	10021.9
<i>Z</i>	4
Calculated density (Mg/m ³)	1.214
Absorption coefficient (mm ⁻¹)	0.351
<i>F</i> ₀₀₀	3955.099
Crystal size (mm)	0.07 x 0.16 x 0.20
Description of crystal	Pale-orange block
Absorption correction	Semi-empirical from equivalent reflections
Transmission coefficients (min,max)	0.94, 0.98
θ range for data collection (°)	5.0 ≤ θ ≤ 27.5
Index ranges	-26 ≤ <i>h</i> ≤ 26, 0 ≤ <i>k</i> ≤ 11, 0 ≤ <i>l</i> ≤ 68
Reflections measured	45147
Unique reflections	11837
<i>R</i> _{int}	0.061
Observed reflections (<i>I</i> > 3σ(<i>I</i>))	6719
Refinement method	Full-matrix least-squares on <i>F</i>

Parameters refined	585
Weighting scheme	Chebyshev 4-term polynomial
Goodness of fit	1.0915
R	0.0423
wR	0.0472
Residual electron density (min,max) (eÅ ⁻³)	-0.32, 0.32

Table F.4.2: Atomic coordinates and equivalent isotropic thermal parameters (Å²) of non-hydrogen atoms

Atom	x	y	z	U _{equiv}
C(1)	0.62533(8)	0.21873(19)	0.25471(3)	0.0179
C(2)	0.61536(8)	0.2872(2)	0.23107(3)	0.0197
C(3)	0.60547(9)	0.4384(2)	0.23055(4)	0.0245
C(4)	0.6049(1)	0.5184(2)	0.25264(4)	0.0278
C(5)	0.61330(9)	0.4481(2)	0.27582(4)	0.0244
C(6)	0.62317(8)	0.2971(2)	0.27718(3)	0.0201
C(7)	0.62757(8)	0.2216(2)	0.30279(3)	0.0211
C(8)	0.50658(8)	0.1880(2)	0.30269(3)	0.0207
C(9)	0.56429(9)	0.2405(2)	0.31501(3)	0.0199
C(10)	0.56181(8)	0.3227(2)	0.33686(3)	0.0204
C(11)	0.50271(9)	0.3575(2)	0.34633(3)	0.0214
C(12)	0.44573(8)	0.3174(2)	0.33218(3)	0.0223
C(13)	0.44748(9)	0.2342(2)	0.31030(3)	0.0213
C(14)	0.38641(8)	0.2008(2)	0.29345(3)	0.0216
O(1)	0.63653(6)	0.06860(14)	0.25593(2)	0.0204
C(15)	0.70238(9)	0.0326(2)	0.25252(4)	0.0244
C(16)	0.71138(9)	-0.1303(2)	0.25540(4)	0.0267
C(17)	0.7041(1)	-0.1840(2)	0.28202(4)	0.0321
O(2)	0.50732(6)	0.09908(15)	0.28152(2)	0.0247
C(18)	0.5249(1)	-0.0498(2)	0.28772(4)	0.0312
C(19)	0.47248(11)	-0.1377(3)	0.29900(5)	0.0359
C(20)	0.49812(13)	-0.2870(3)	0.30802(6)	0.0464
N(1)	0.50560(8)	0.4327(2)	0.36952(3)	0.0266
C(21)	0.45411(9)	0.4733(2)	0.38267(4)	0.0247
O(3)	0.39717(7)	0.46178(18)	0.37449(3)	0.0334
N(2)	0.47301(9)	0.5284(2)	0.40582(3)	0.0262
C(22)	0.4259(1)	0.5840(2)	0.42210(4)	0.0257
Fe	0.433355(14)	0.30706(4)	0.459995(6)	0.0294
C(23)	0.39349(9)	0.4712(2)	0.43732(4)	0.0263
C(24)	0.37803(11)	0.4908(3)	0.46275(4)	0.0360
C(25)	0.34438(11)	0.3633(3)	0.47009(5)	0.0418
C(26)	0.33848(11)	0.2656(3)	0.44933(5)	0.0417
C(27)	0.3686(1)	0.3316(3)	0.42918(4)	0.0346
C(28)	0.52744(12)	0.2780(3)	0.45295(6)	0.0551
C(29)	0.52454(13)	0.3404(4)	0.47688(6)	0.0575
C(30)	0.49099(14)	0.2453(4)	0.49165(6)	0.0614
C(31)	0.47207(13)	0.1237(3)	0.47701(7)	0.0567
C(32)	0.49430(14)	0.1399(3)	0.45290(7)	0.0594

O(4)	0.63509(8)	0.3923(2)	0.39611(3)	0.0426
O(5)	0.60489(8)	0.57557(18)	0.42023(3)	0.0418
C(33)	0.6415(1)	0.4721(2)	0.41545(4)	0.0316
C(34)	0.6980(1)	0.4395(2)	0.43476(4)	0.0264
C(35)	0.75442(11)	0.3762(2)	0.42790(4)	0.0311
C(36)	0.80480(11)	0.3440(3)	0.44586(4)	0.0361
C(37)	0.79823(12)	0.3707(3)	0.47122(4)	0.0387
C(38)	0.74222(12)	0.4327(3)	0.47838(4)	0.0387
C(39)	0.69257(11)	0.4698(3)	0.46027(4)	0.0337
N(3)	0.67440(8)	-0.07123(18)	0.38635(3)	0.0228
C(40)	0.6102(1)	-0.0045(2)	0.37636(4)	0.0279
C(41)	0.55061(11)	-0.0916(3)	0.38142(4)	0.0359
C(42)	0.49088(12)	0.0010(3)	0.37374(6)	0.0534
C(43)	0.42951(15)	-0.0828(5)	0.3767(1)	0.0940
C(44)	0.67744(9)	-0.0924(2)	0.41497(3)	0.0246
C(45)	0.65604(11)	0.0408(2)	0.42937(4)	0.0302
C(46)	0.67500(11)	0.0232(3)	0.45767(4)	0.0360
C(47)	0.64308(16)	-0.1064(3)	0.46925(5)	0.0514
C(48)	0.68171(9)	-0.2198(2)	0.37392(4)	0.0249
C(49)	0.7450(1)	-0.2979(2)	0.38107(4)	0.0287
C(50)	0.74913(11)	-0.4369(2)	0.36535(4)	0.0325
C(51)	0.7582(2)	-0.4072(3)	0.33800(6)	0.0780
C(52)	0.7278(1)	0.0341(2)	0.38035(4)	0.0257
C(53)	0.7431(1)	0.0404(2)	0.35293(4)	0.0274
C(54)	0.7847(1)	0.1744(2)	0.34882(4)	0.0301
C(55)	0.81131(11)	0.1759(3)	0.32311(5)	0.0390

Table F.4.3: Atomic coordinates and isotropic thermal parameters ($\text{\AA}^2$) of hydrogen atoms

Atom	x	y	z	U_{iso}
H(1)	0.5422(13)	0.435(3)	0.3778(5)	0.033(6)
H(2)	0.5107(12)	0.540(2)	0.4104(4)	0.021(6)
H(31)	0.5987	0.4898	0.2139	0.0293
H(41)	0.5983	0.6270	0.2519	0.0332
H(51)	0.6123	0.5063	0.2918	0.0293
H(71)	0.6637	0.2658	0.3140	0.0252
H(72)	0.6361	0.1147	0.3005	0.0252
H(101)	0.6030	0.3580	0.3461	0.0243
H(121)	0.4032	0.3488	0.3378	0.0268
H(141)	0.3480	0.2278	0.3026	0.0259
H(142)	0.3850	0.0937	0.2895	0.0259
H(151)	0.7318	0.0846	0.2655	0.0292
H(152)	0.7127	0.0634	0.2353	0.0292
H(161)	0.7556	-0.1563	0.2509	0.0320
H(162)	0.6784	-0.1807	0.2435	0.0320
H(171)	0.7106	-0.2926	0.2828	0.0386
H(172)	0.7371	-0.1352	0.2941	0.0386

H(173)	0.6599	-0.1597	0.2868	0.0386
H(181)	0.5638	-0.0483	0.3002	0.0378
H(182)	0.5357	-0.1001	0.2719	0.0378
H(191)	0.4574	-0.0827	0.3137	0.0433
H(192)	0.4355	-0.1520	0.2859	0.0433
H(201)	0.4630	-0.3432	0.3154	0.0556
H(202)	0.5351	-0.2733	0.3212	0.0556
H(203)	0.5132	-0.3426	0.2934	0.0556
H(221)	0.4484	0.6552	0.4342	0.0309
H(222)	0.3915	0.6361	0.4112	0.0309
H(241)	0.3889	0.5787	0.4736	0.0437
H(251)	0.3279	0.3462	0.4870	0.0512
H(261)	0.3169	0.1675	0.4489	0.0499
H(271)	0.3719	0.2875	0.4121	0.0410
H(281)	0.5487	0.3216	0.4385	0.0667
H(291)	0.5434	0.4371	0.4825	0.0678
H(301)	0.4821	0.2617	0.5096	0.0729
H(311)	0.4468	0.0385	0.4827	0.0681
H(321)	0.4882	0.0690	0.4385	0.0717
H(351)	0.7588	0.3534	0.4097	0.0371
H(361)	0.8459	0.3016	0.4406	0.0431
H(371)	0.8341	0.3450	0.4843	0.0455
H(381)	0.7373	0.4511	0.4967	0.0462
H(391)	0.6528	0.5184	0.4655	0.0404
H(401)	0.6068	0.0943	0.3843	0.0332
H(402)	0.6105	0.0070	0.3576	0.0332
H(411)	0.5520	-0.1161	0.3998	0.0428
H(412)	0.5490	-0.1843	0.3713	0.0428
H(421)	0.4917	0.0905	0.3847	0.0637
H(422)	0.4916	0.0308	0.3556	0.0637
H(431)	0.3914	-0.0192	0.3716	0.1120
H(432)	0.4282	-0.1126	0.3948	0.1120
H(433)	0.4282	-0.1723	0.3658	0.1120
H(441)	0.7231	-0.1158	0.4213	0.0293
H(442)	0.6489	-0.1767	0.4186	0.0293
H(451)	0.6772	0.1305	0.4231	0.0365
H(452)	0.6081	0.0512	0.4264	0.0365
H(461)	0.7229	0.0101	0.4603	0.0433
H(462)	0.6624	0.1143	0.4665	0.0433
H(471)	0.6574	-0.1118	0.4877	0.0621
H(472)	0.6556	-0.1986	0.4608	0.0621
H(473)	0.5951	-0.0944	0.4669	0.0621
H(481)	0.6459	-0.2844	0.3787	0.0297
H(482)	0.6776	-0.2050	0.3552	0.0297
H(491)	0.7477	-0.3244	0.3994	0.0343
H(492)	0.7817	-0.2314	0.3779	0.0343
H(501)	0.7865	-0.4966	0.3727	0.0396
H(502)	0.7083	-0.4938	0.3662	0.0396

H(511)	0.7606	-0.5023	0.3287	0.0967
H(512)	0.7992	-0.3511	0.3368	0.0967
H(513)	0.7209	-0.3484	0.3303	0.0967
H(521)	0.7681	0.0046	0.3908	0.0305
H(522)	0.7147	0.1348	0.3854	0.0305
H(531)	0.7670	-0.0503	0.3487	0.0329
H(532)	0.7019	0.0471	0.3417	0.0329
H(541)	0.8218	0.1755	0.3622	0.0361
H(542)	0.7579	0.2644	0.3504	0.0361
H(551)	0.8381	0.2660	0.3215	0.0475
H(552)	0.8386	0.0869	0.3213	0.0475
H(553)	0.7747	0.1759	0.3095	0.0475

Table F.4.4: Anisotropic thermal parameters ($\text{\AA}^2$)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C(1)	0.0134(7)	0.0175(9)	0.0227(9)	0.0018(7)	0.0011(6)	-0.0006(6)
C(2)	0.0148(8)	0.025(1)	0.0196(9)	0.0007(7)	0.0012(6)	0.0012(7)
C(3)	0.0256(9)	0.026(1)	0.0214(9)	0.0064(8)	0.0003(7)	-0.0005(7)
C(4)	0.033(1)	0.0184(9)	0.0319(11)	0.0010(8)	0.0014(8)	0.0011(8)
C(5)	0.0242(9)	0.026(1)	0.023(1)	-0.0053(8)	0.0014(7)	-0.0021(7)
C(6)	0.0156(8)	0.0225(9)	0.0221(9)	0.0025(7)	0.0017(6)	-0.0008(7)
C(7)	0.0193(8)	0.0262(11)	0.0176(9)	0.0001(7)	0.0002(6)	0.0001(7)
C(8)	0.0231(9)	0.0243(9)	0.0149(8)	0.0018(8)	0.0023(6)	-0.0000(8)
C(9)	0.0212(8)	0.0227(9)	0.0158(8)	0.0039(7)	0.0016(6)	0.0025(7)
C(10)	0.0200(8)	0.0237(9)	0.0170(8)	0.0031(7)	-0.0015(6)	-0.0008(7)
C(11)	0.0264(9)	0.0224(9)	0.0154(9)	0.0030(7)	0.0024(7)	0.0021(7)
C(12)	0.0209(8)	0.028(1)	0.0184(8)	0.0014(8)	0.0025(6)	0.0035(8)
C(13)	0.0217(9)	0.024(1)	0.0176(9)	0.0035(7)	0.0004(7)	-0.0017(7)
C(14)	0.0206(8)	0.026(1)	0.0180(8)	0.0003(8)	0.0015(6)	-0.0027(7)
O(1)	0.0176(6)	0.0199(7)	0.0240(6)	0.0002(5)	0.0035(5)	0.0028(5)
C(15)	0.0179(9)	0.026(1)	0.029(1)	0.0032(8)	0.0019(7)	0.0027(7)
C(16)	0.0230(9)	0.025(1)	0.0322(11)	-0.0012(8)	0.0020(7)	0.0041(8)
C(17)	0.0361(11)	0.025(1)	0.0351(11)	0.0043(9)	0.0032(8)	0.0067(9)
O(2)	0.0252(6)	0.0300(8)	0.0193(6)	-0.0050(6)	0.0034(5)	-0.0002(6)
C(18)	0.029(1)	0.0286(11)	0.0370(12)	-0.0088(9)	0.0070(8)	0.0014(8)
C(19)	0.0301(11)	0.0325(11)	0.0456(13)	-0.004(1)	0.0062(9)	-0.0021(9)
C(20)	0.0434(13)	0.0274(13)	0.0682(18)	-0.0009(11)	0.0039(12)	-0.003(1)
N(1)	0.0232(8)	0.037(1)	0.0190(8)	-0.0047(7)	0.0005(6)	0.0031(7)
C(21)	0.029(1)	0.026(1)	0.0190(9)	0.0003(8)	0.0022(7)	0.0045(8)
O(3)	0.0249(7)	0.052(1)	0.0226(7)	-0.0075(7)	-0.0021(5)	0.0080(6)
N(2)	0.0249(9)	0.036(1)	0.0181(8)	-0.0048(7)	0.0014(6)	0.0009(7)
C(22)	0.034(1)	0.023(1)	0.0204(9)	-0.0028(8)	0.0044(7)	0.0056(8)
Fe	0.02555(15)	0.03083(17)	0.03215(17)	0.00713(13)	0.00371(11)	0.00675(12)
C(23)	0.0254(9)	0.0288(11)	0.025(1)	0.0010(8)	0.0020(7)	0.0088(8)
C(24)	0.0412(12)	0.0378(12)	0.0303(11)	0.0066(9)	0.0098(9)	0.017(1)
C(25)	0.0343(12)	0.0508(14)	0.0429(13)	0.0217(11)	0.018(1)	0.016(1)
C(26)	0.024(1)	0.0447(14)	0.0560(16)	0.0159(12)	0.0015(9)	0.0014(9)
C(27)	0.0305(11)	0.0379(13)	0.0341(11)	0.002(1)	-0.0043(8)	0.0012(9)

C(28)	0.0278(11)	0.0649(19)	0.0740(19)	0.0347(15)	0.0126(11)	0.0181(12)
C(29)	0.0326(13)	0.0649(19)	0.072(2)	0.0053(15)	-0.0115(12)	0.0005(12)
C(30)	0.0405(14)	0.089(2)	0.0525(17)	0.0271(17)	-0.0080(12)	0.0098(15)
C(31)	0.0382(13)	0.0488(16)	0.083(2)	0.0345(16)	0.0063(13)	0.0111(12)
C(32)	0.0466(15)	0.0531(17)	0.080(2)	0.0013(15)	0.0118(14)	0.0261(13)
O(4)	0.0373(9)	0.0615(11)	0.0273(8)	0.0002(8)	-0.0060(6)	-0.0103(8)
O(5)	0.0315(8)	0.0352(9)	0.0563(11)	0.0079(8)	-0.0097(7)	-0.0032(7)
C(33)	0.0302(11)	0.0325(12)	0.0309(11)	0.0093(9)	-0.0028(8)	-0.0108(9)
C(34)	0.030(1)	0.020(1)	0.0282(11)	0.0029(8)	-0.0021(8)	-0.0061(8)
C(35)	0.0385(11)	0.0285(11)	0.0258(11)	-0.0025(9)	0.0010(8)	-0.0014(9)
C(36)	0.0394(12)	0.0330(12)	0.0353(12)	-0.0039(9)	0.0007(9)	0.0103(9)
C(37)	0.0425(13)	0.0389(13)	0.0323(12)	0.001(1)	-0.0101(9)	0.008(1)
C(38)	0.0452(13)	0.0467(14)	0.0234(11)	-0.004(1)	-0.0006(9)	0.0021(11)
C(39)	0.0335(11)	0.0370(12)	0.0305(11)	-0.0024(9)	0.0032(8)	0.0013(9)
N(3)	0.0269(8)	0.0209(8)	0.0201(8)	0.0012(6)	-0.0010(6)	0.0017(6)
C(40)	0.029(1)	0.027(1)	0.026(1)	0.0039(8)	-0.0023(7)	0.0049(8)
C(41)	0.027(1)	0.0386(13)	0.0413(13)	0.009(1)	-0.0008(9)	0.0014(9)
C(42)	0.0289(12)	0.0615(18)	0.0689(19)	0.0291(15)	-0.0003(11)	0.0050(12)
C(43)	0.0286(15)	0.094(3)	0.157(4)	0.058(3)	-0.0024(18)	0.0001(16)
C(44)	0.030(1)	0.023(1)	0.0205(9)	0.0033(7)	-0.0012(7)	-0.0006(8)
C(45)	0.0424(12)	0.023(1)	0.026(1)	0.0006(8)	0.0070(8)	0.0010(8)
C(46)	0.0418(13)	0.0402(13)	0.0263(11)	-0.0042(9)	0.0050(9)	0.003(1)
C(47)	0.0798(19)	0.0454(16)	0.0299(12)	0.0060(11)	0.0103(12)	-0.0001(14)
C(48)	0.029(1)	0.021(1)	0.025(1)	-0.0009(7)	-0.0008(7)	-0.0036(7)
C(49)	0.033(1)	0.022(1)	0.031(1)	-0.0015(8)	0.0008(8)	0.0005(8)
C(50)	0.0422(12)	0.0246(11)	0.0321(11)	0.0034(9)	0.0105(9)	0.0040(9)
C(51)	0.160(4)	0.0368(16)	0.0450(16)	0.0050(13)	0.052(2)	0.0189(19)
C(52)	0.031(1)	0.023(1)	0.023(1)	0.0022(8)	-0.0013(7)	-0.0043(8)
C(53)	0.031(1)	0.0267(11)	0.024(1)	0.0003(8)	0.0018(8)	0.0005(8)
C(54)	0.031(1)	0.0289(11)	0.0307(11)	0.0045(9)	0.0017(8)	-0.0002(8)
C(55)	0.0354(11)	0.0427(14)	0.0405(12)	0.0043(11)	0.0119(9)	-0.001(1)

Table F.4.5: Bond lengths (Å)
(geometrically-positioned H atoms have been excluded)
*related by crystallographic twofold axis

C(1) - C(2)	1.400(2)	Fe(1) - C(30)	2.054(3)
C(1) - C(6)	1.395(3)	Fe(1) - C(31)	2.033(3)
C(1) - O(1)	1.389(2)	Fe(1) - C(32)	2.039(3)
C(2) - C(3)	1.394(3)	C(23) - C(24)	1.426(3)
C(2) - C(14)*	1.519(2)	C(23) - C(27)	1.427(3)
C(3) - C(4)	1.383(3)	C(24) - C(25)	1.429(4)
C(4) - C(5)	1.385(3)	C(25) - C(26)	1.414(4)
C(5) - C(6)	1.393(3)	C(26) - C(27)	1.420(3)
C(6) - C(7)	1.519(3)	C(28) - C(29)	1.398(5)
C(7) - C(9)	1.527(2)	C(28) - C(32)	1.436(5)
C(8) - C(9)	1.398(3)	C(29) - C(30)	1.396(5)

C(8) - C(13)	1.392(3)	C(30) - C(31)	1.390(5)
C(8) - O(2)	1.387(2)	C(31) - C(32)	1.407(5)
C(9) - C(10)	1.386(3)	O(4) - C(33)	1.256(3)
C(10) - C(11)	1.405(3)	O(5) - C(33)	1.253(3)
C(11) - C(12)	1.394(3)	C(33) - C(34)	1.518(3)
C(11) - N(1)	1.406(3)	C(34) - C(35)	1.384(3)
C(12) - C(13)	1.391(3)	C(34) - C(39)	1.396(3)
C(13) - C(14)	1.517(2)	C(35) - C(36)	1.383(3)
O(1) - C(15)	1.434(2)	C(36) - C(37)	1.387(3)
C(15) - C(16)	1.504(3)	C(37) - C(38)	1.378(3)
C(16) - C(17)	1.516(3)	C(38) - C(39)	1.388(3)
O(2) - C(18)	1.437(3)	N(3) - C(40)	1.518(2)
C(18) - C(19)	1.517(3)	N(3) - C(44)	1.527(2)
C(19) - C(20)	1.524(3)	N(3) - C(48)	1.521(2)
N(1) - C(21)	1.379(3)	N(3) - C(52)	1.522(2)
N(1) - H(1)	0.84(3)	C(40) - C(41)	1.516(3)
C(21) - O(3)	1.228(2)	C(41) - C(42)	1.527(3)
C(21) - N(2)	1.353(3)	C(42) - C(43)	1.508(4)
N(2) - C(22)	1.454(2)	C(44) - C(45)	1.523(3)
N(2) - H(2)	0.81(2)	C(45) - C(46)	1.527(3)
C(22) - C(23)	1.503(3)	C(46) - C(47)	1.512(4)
Fe(1) - C(23)	2.049(2)	C(48) - C(49)	1.514(3)
Fe(1) - C(24)	2.045(2)	C(49) - C(50)	1.525(3)
Fe(1) - C(25)	2.036(2)	C(50) - C(51)	1.505(3)
Fe(1) - C(26)	2.038(2)	C(52) - C(53)	1.519(3)
Fe(1) - C(27)	2.036(2)	C(53) - C(54)	1.524(3)
Fe(1) - C(28)	2.041(2)	C(54) - C(55)	1.517(3)
Fe(1) - C(29)	2.046(3)		

Table F.4.6: Bond angles (°)
 (geometrically-positioned H atoms have been excluded)
 *related by crystallographic twofold axis

C(2) - C(1) - C(6)	121.62(17)	C(25) - Fe(1) - C(32)	146.19(12)
C(2) - C(1) - O(1)	119.48(16)	C(26) - Fe(1) - C(32)	114.32(12)
C(6) - C(1) - O(1)	118.90(15)	C(27) - Fe(1) - C(32)	108.12(12)
C(1) - C(2) - C(3)	117.96(17)	C(28) - Fe(1) - C(29)	40.00(13)
C(1) - C(2) - C(14)*	121.80(17)	C(28) - Fe(1) - C(30)	67.38(12)
C(3) - C(2) - C(14)*	120.23(16)	C(29) - Fe(1) - C(30)	39.83(13)
C(2) - C(3) - C(4)	121.20(17)	C(28) - Fe(1) - C(31)	68.08(11)
C(3) - C(4) - C(5)	119.93(18)	C(29) - Fe(1) - C(31)	67.22(13)
C(4) - C(5) - C(6)	120.68(18)	C(30) - Fe(1) - C(31)	39.78(14)
C(1) - C(6) - C(5)	118.57(17)	C(28) - Fe(1) - C(32)	41.22(13)
C(1) - C(6) - C(7)	121.91(17)	C(29) - Fe(1) - C(32)	68.00(14)
C(5) - C(6) - C(7)	119.43(17)	C(30) - Fe(1) - C(32)	67.61(14)
C(6) - C(7) - C(9)	110.06(14)	C(31) - Fe(1) - C(32)	40.42(13)
C(9) - C(8) - C(13)	120.24(17)	C(22) - C(23) - Fe	129.67(14)
C(9) - C(8) - O(2)	120.53(16)	C(22) - C(23) - C(24)	124.90(19)
C(13) - C(8) - O(2)	119.04(16)	Fe(1) - C(23) - C(24)	69.47(12)

C(7) - C(9) - C(8)	119.89(16)	C(22) - C(23) - C(27)	127.97(18)
C(7) - C(9) - C(10)	120.93(16)	Fe(1) - C(23) - C(27)	69.04(12)
C(8) - C(9) - C(10)	118.82(16)	C(24) - C(23) - C(27)	107.00(19)
C(9) - C(10) - C(11)	121.38(16)	Fe(1) - C(24) - C(23)	69.77(12)
C(10) - C(11) - C(12)	118.43(17)	Fe(1) - C(24) - C(25)	69.17(13)
C(10) - C(11) - N(1)	116.94(17)	C(23) - C(24) - C(25)	108.2(2)
C(12) - C(11) - N(1)	124.62(17)	Fe(1) - C(25) - C(24)	69.85(12)
C(11) - C(12) - C(13)	120.62(16)	Fe(1) - C(25) - C(26)	69.76(13)
C(8) - C(13) - C(12)	119.78(17)	C(24) - C(25) - C(26)	108.1(2)
C(8) - C(13) - C(14)	118.83(16)	Fe(1) - C(26) - C(25)	69.63(14)
C(12) - C(13) - C(14)	121.26(16)	Fe(1) - C(26) - C(27)	69.51(12)
C(2)* - C(14) - C(13)	110.87(15)	C(25) - C(26) - C(27)	107.8(2)
C(1) - O(1) - C(15)	112.16(13)	Fe(1) - C(27) - C(23)	70.08(11)
O(1) - C(15) - C(16)	108.95(15)	Fe(1) - C(27) - C(26)	69.68(13)
C(15) - C(16) - C(17)	113.08(17)	C(23) - C(27) - C(26)	108.8(2)
C(8) - O(2) - C(18)	112.85(15)	Fe(1) - C(28) - C(29)	70.20(15)
O(2) - C(18) - C(19)	114.41(17)	Fe(1) - C(28) - C(32)	69.32(14)
C(18) - C(19) - C(20)	110.67(18)	C(29) - C(28) - C(32)	107.4(3)
C(11) - N(1) - C(21)	126.82(17)	Fe(1) - C(29) - C(28)	69.79(15)
C(11) - N(1) - H(1)	116.0(17)	Fe(1) - C(29) - C(30)	70.38(16)
C(21) - N(1) - H(1)	115.5(17)	C(28) - C(29) - C(30)	108.7(3)
N(1) - C(21) - O(3)	124.39(18)	Fe(1) - C(30) - C(29)	69.79(16)
N(1) - C(21) - N(2)	112.55(17)	Fe(1) - C(30) - C(31)	69.29(16)
O(3) - C(21) - N(2)	123.06(18)	C(29) - C(30) - C(31)	108.2(3)
C(21) - N(2) - C(22)	120.83(17)	Fe(1) - C(31) - C(30)	70.92(16)
C(21) - N(2) - H(2)	121.2(16)	Fe(1) - C(31) - C(32)	70.02(15)
C(22) - N(2) - H(2)	117.6(16)	C(30) - C(31) - C(32)	109.0(3)
N(2) - C(22) - C(23)	116.00(17)	Fe(1) - C(32) - C(28)	69.46(15)
C(23) - Fe(1) - C(24)	40.76(8)	Fe(1) - C(32) - C(31)	69.55(15)
C(23) - Fe(1) - C(25)	68.97(8)	C(28) - C(32) - C(31)	106.7(3)
C(24) - Fe(1) - C(25)	41.0(1)	O(4) - C(33) - O(5)	125.4(2)
C(23) - Fe(1) - C(26)	68.99(9)	O(4) - C(33) - C(34)	117.3(2)
C(24) - Fe(1) - C(26)	68.62(11)	O(5) - C(33) - C(34)	117.28(19)
C(25) - Fe(1) - C(26)	40.61(11)	C(33) - C(34) - C(35)	121.76(19)
C(23) - Fe(1) - C(27)	40.88(9)	C(33) - C(34) - C(39)	119.45(19)
C(24) - Fe(1) - C(27)	68.4(1)	C(35) - C(34) - C(39)	118.76(19)
C(25) - Fe(1) - C(27)	68.5(1)	C(34) - C(35) - C(36)	120.95(19)
C(26) - Fe(1) - C(27)	40.8(1)	C(35) - C(36) - C(37)	119.9(2)
C(23) - Fe(1) - C(28)	109.35(9)	C(36) - C(37) - C(38)	119.9(2)
C(24) - Fe(1) - C(28)	132.34(11)	C(37) - C(38) - C(39)	120.2(2)
C(25) - Fe(1) - C(28)	171.27(13)	C(34) - C(39) - C(38)	120.3(2)
C(26) - Fe(1) - C(28)	147.62(13)	C(40) - N(3) - C(44)	110.83(14)
C(27) - Fe(1) - C(28)	116.29(11)	C(40) - N(3) - C(48)	108.94(15)
C(23) - Fe(1) - C(29)	117.34(11)	C(44) - N(3) - C(48)	108.79(14)
C(24) - Fe(1) - C(29)	110.60(12)	C(40) - N(3) - C(52)	107.91(14)
C(25) - Fe(1) - C(29)	132.44(13)	C(44) - N(3) - C(52)	108.74(14)
C(26) - Fe(1) - C(29)	170.07(12)	C(48) - N(3) - C(52)	111.65(14)
C(27) - Fe(1) - C(29)	148.87(12)	N(3) - C(40) - C(41)	115.73(17)
C(23) - Fe(1) - C(30)	148.98(13)	C(40) - C(41) - C(42)	108.69(19)
C(24) - Fe(1) - C(30)	117.22(13)	C(41) - C(42) - C(43)	111.5(2)

C(25) - Fe(1) - C(30)	109.35(11)	N(3) - C(44) - C(45)	114.23(16)
C(26) - Fe(1) - C(30)	131.00(11)	C(44) - C(45) - C(46)	110.39(17)
C(27) - Fe(1) - C(30)	169.50(12)	C(45) - C(46) - C(47)	113.4(2)
C(23) - Fe(1) - C(31)	170.26(12)	N(3) - C(48) - C(49)	115.38(16)
C(24) - Fe(1) - C(31)	147.73(12)	C(48) - C(49) - C(50)	110.13(17)
C(25) - Fe(1) - C(31)	115.1(1)	C(49) - C(50) - C(51)	113.3(2)
C(26) - Fe(1) - C(31)	107.82(11)	N(3) - C(52) - C(53)	116.32(15)
C(27) - Fe(1) - C(31)	130.91(12)	C(52) - C(53) - C(54)	109.74(16)
C(23) - Fe(1) - C(32)	131.56(11)	C(53) - C(54) - C(55)	113.11(18)
C(24) - Fe(1) - C(32)	171.36(12)		

F.5 Crystal data for 66·CH₃OH[#]

X-ray quality crystals (green platelets) of 66·CH₃OH were obtained by slow evaporation of a chloroform / methanol solution of the receptor. The non-hydrogen atom numbering system is outlined in the schematic structure shown in Figure F.3.1.

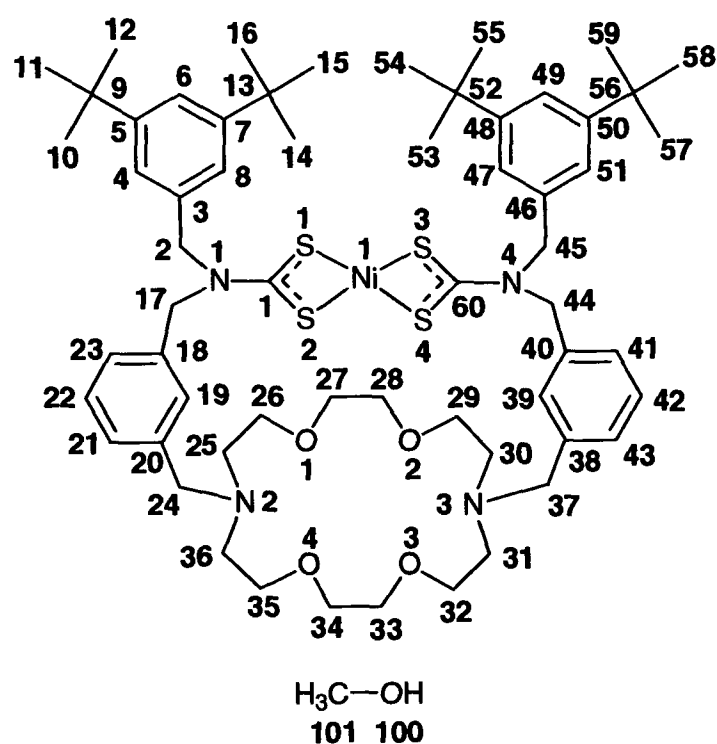


Figure F.3.1: Atom numbering system.

Table F.5.1: Crystal data and refinement details

Crystal identification	aeni
Chemical formula	C ₆₁ H ₉₀ NiN ₄ O ₅ S ₄
Formula weight	1146.38
Temperature (K)	150
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	P 21/c

<i>a</i> (Å)	14.4778(1)
<i>b</i> (Å)	27.8112(2)
<i>c</i> (Å)	16.8734(1)
β (°)	111.8454(6)
Cell volume (Å ³)	6306.12(9)
<i>Z</i>	4
Calculated density (Mg/m ³)	1.21
Absorption coefficient (mm ⁻¹)	0.488
<i>F</i> ₀₀₀	2467.894
Crystal size (mm)	0.04 x 0.15 x 0.20
Description of crystal	Green plate
Absorption correction	Semi-empirical from equivalent reflections
Transmission coefficients (min,max)	0.93, 0.98
θ range for data collection (°)	5.0 ≤ θ ≤ 27.0
Index ranges	-18 ≤ <i>h</i> ≤ 18, -31 ≤ <i>k</i> ≤ 36, -21 ≤ <i>l</i> ≤ 21
Reflections measured	24696
Unique reflections	14319
<i>R</i> _{int}	0.071
Observed reflections (<i>I</i> > 3σ(<i>I</i>))	7466
Refinement method	Full-matrix least-squares on <i>F</i>
Parameters refined	676
Weighting scheme	Chebychev 3-term polynomial
Goodness of fit	1.045
<i>R</i>	0.043
<i>wR</i>	0.047
Residual electron density (min,max) (eÅ ⁻³)	-0.44, 0.30

Table F.5.2: Atomic coordinates and equivalent isotropic thermal parameters (Å²) of non-hydrogen atoms

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> _{iso}
Ni(1)	-0.00506(3)	0.442078(14)	0.33809(2)	0.0335
S(1)	-0.02225(6)	0.36345(3)	0.34142(5)	0.0409
S(2)	-0.00803(6)	0.43336(3)	0.46685(5)	0.0362
S(3)	0.00613(6)	0.52085(3)	0.33306(5)	0.0349
S(4)	-0.00851(6)	0.45131(3)	0.20763(5)	0.0403
C(1)	-0.0321(2)	0.3738(1)	0.43873(18)	0.0326
N(1)	-0.05657(18)	0.34090(8)	0.48406(15)	0.0335
C(2)	-0.0739(2)	0.2904(1)	0.45659(19)	0.0365
C(3)	-0.1771(2)	0.2738(1)	0.44776(18)	0.0341
C(4)	-0.1878(2)	0.23815(11)	0.50087(19)	0.0379
C(5)	-0.2818(2)	0.22156(12)	0.4938(2)	0.0445
C(6)	-0.3638(2)	0.24240(12)	0.4313(2)	0.0449
C(7)	-0.3558(2)	0.27862(11)	0.3770(2)	0.0429
C(8)	-0.2613(2)	0.29400(11)	0.38571(19)	0.0387
C(9)	-0.2900(3)	0.18205(15)	0.5538(2)	0.0624
C(10)	-0.2388(4)	0.1982(2)	0.6463(3)	0.0866
C(11)	-0.2363(5)	0.13735(18)	0.5396(4)	0.1045
C(12)	-0.3970(4)	0.1680(2)	0.5369(3)	0.1076

C(13)	-0.4506(3)	0.29760(13)	0.3070(2)	0.0530
C(14)	-0.4320(3)	0.34259(15)	0.2641(3)	0.0730
C(15)	-0.5291(3)	0.3089(2)	0.3444(3)	0.0871
C(16)	-0.4889(3)	0.25832(15)	0.2388(3)	0.0730
C(17)	-0.0668(2)	0.3524(1)	0.56556(19)	0.0359
C(18)	0.0124(2)	0.3282(1)	0.64115(18)	0.0351
C(19)	0.1124(2)	0.3389(1)	0.65996(19)	0.0379
C(20)	0.1868(2)	0.31815(11)	0.7302(2)	0.0431
C(21)	0.1582(3)	0.28726(12)	0.7819(2)	0.0492
C(22)	0.0590(3)	0.27675(11)	0.7637(2)	0.0474
C(23)	-0.0140(3)	0.29702(11)	0.6932(2)	0.0423
C(24)	0.2944(3)	0.32990(12)	0.7487(2)	0.0494
N(2)	0.3129(2)	0.3819(1)	0.75461(17)	0.0425
C(25)	0.4081(3)	0.39429(13)	0.7475(2)	0.0512
C(26)	0.3954(3)	0.41450(15)	0.6613(3)	0.0659
O(1)	0.3521(2)	0.37960(11)	0.59606(17)	0.0739
C(27)	0.2616(4)	0.39275(19)	0.5292(3)	0.0819
C(28)	0.2763(3)	0.40939(17)	0.4508(3)	0.0721
O(2)	0.32665(19)	0.4540(1)	0.46580(15)	0.0580
C(29)	0.3163(3)	0.47827(15)	0.3890(2)	0.0588
C(30)	0.3733(3)	0.52421(15)	0.4066(2)	0.0532
N(3)	0.33771(19)	0.5590(1)	0.45357(16)	0.0439
C(31)	0.3771(2)	0.55019(13)	0.54642(19)	0.0454
C(32)	0.2947(2)	0.55404(13)	0.57999(19)	0.0445
O(3)	0.33576(15)	0.54367(8)	0.66897(13)	0.0427
C(33)	0.2628(3)	0.54555(13)	0.7066(2)	0.0482
C(34)	0.3104(3)	0.53414(13)	0.8000(2)	0.0464
O(4)	0.34213(16)	0.48520(8)	0.81728(14)	0.0434
C(35)	0.2646(3)	0.45367(13)	0.8167(2)	0.0487
C(36)	0.3004(3)	0.40273(13)	0.8294(2)	0.0482
C(37)	0.3535(2)	0.60855(13)	0.4322(2)	0.0488
C(38)	0.2835(2)	0.62206(12)	0.3435(2)	0.0423
C(39)	0.1881(2)	0.60277(11)	0.31058(19)	0.0369
C(40)	0.1196(2)	0.6171(1)	0.23158(18)	0.0350
C(41)	0.1478(3)	0.65060(11)	0.1837(2)	0.0425
C(42)	0.2435(3)	0.66934(13)	0.2154(2)	0.0520
C(43)	0.3108(3)	0.65573(13)	0.2947(2)	0.0493
C(44)	0.0150(2)	0.5972(1)	0.20158(18)	0.0339
N(4)	0.00891(17)	0.54593(8)	0.17880(14)	0.0302
C(45)	0.0148(2)	0.5343(1)	0.09555(17)	0.0317
C(46)	-0.0773(2)	0.5501(1)	0.02167(17)	0.0315
C(47)	-0.1638(2)	0.52263(11)	-0.00549(18)	0.0353
C(48)	-0.2478(2)	0.53680(12)	-0.07542(19)	0.0391
C(49)	-0.2425(2)	0.58022(12)	-0.1145(2)	0.0426
C(50)	-0.1573(2)	0.60863(11)	-0.08917(19)	0.0411
C(51)	-0.0744(2)	0.59241(11)	-0.02141(18)	0.0361
C(52)	-0.3393(2)	0.50407(13)	-0.1095(2)	0.0465
C(53)	-0.3763(3)	0.49081(16)	-0.0389(2)	0.0614
C(54)	-0.3089(3)	0.45749(15)	-0.1442(3)	0.0608
C(55)	-0.4237(3)	0.52588(15)	-0.1844(3)	0.0615

C(56)	-0.1580(3)	0.65640(12)	-0.1352(2)	0.0528
C(57)	-0.0548(4)	0.67826(16)	-0.1070(3)	0.0844
C(58)	-0.2287(4)	0.69063(16)	-0.1156(3)	0.0841
C(59)	-0.1936(3)	0.64801(14)	-0.2320(2)	0.0564
C(60)	0.0030(2)	0.5118(1)	0.23105(17)	0.0298
O(100)	0.4440(3)	0.30323(18)	0.5493(3)	0.1303
C(101)	0.3610(6)	0.2746(3)	0.5071(5)	0.1375

Table F.5.3: Atomic coordinates and isotropic thermal parameters ($\text{\AA}^2$) of hydrogen atoms

Atom	x/a	y/b	z/c	U_{iso}
H(21)	-0.0223	0.2689	0.5041	0.0383
H(22)	-0.0642	0.2854	0.4041	0.0383
H(41)	-0.1277	0.2228	0.5470	0.0387
H(61)	-0.4321	0.2304	0.4261	0.0484
H(81)	-0.2518	0.3195	0.3511	0.0407
H(101)	-0.2456	0.1706	0.6856	0.0914
H(102)	-0.2720	0.2263	0.6576	0.0914
H(103)	-0.1676	0.2030	0.6589	0.0914
H(111)	-0.2446	0.1103	0.5763	0.1168
H(112)	-0.1678	0.1441	0.5505	0.1168
H(113)	-0.2727	0.1268	0.4773	0.1168
H(121)	-0.4013	0.1422	0.5779	0.1173
H(122)	-0.4351	0.1970	0.5473	0.1173
H(123)	-0.4324	0.1570	0.4777	0.1173
H(141)	-0.4937	0.3538	0.2222	0.0663
H(142)	-0.4043	0.3682	0.3118	0.0663
H(143)	-0.3797	0.3361	0.2411	0.0663
H(151)	-0.5907	0.3211	0.2998	0.0900
H(152)	-0.5034	0.3331	0.3920	0.0900
H(153)	-0.5463	0.2787	0.3702	0.0900
H(161)	-0.5495	0.2702	0.1930	0.0665
H(162)	-0.5035	0.2290	0.2657	0.0665
H(163)	-0.4354	0.2513	0.2160	0.0665
H(171)	-0.0608	0.3864	0.5768	0.0395
H(172)	-0.1323	0.3396	0.5658	0.0395
H(191)	0.1331	0.3601	0.6235	0.0418
H(211)	0.2149	0.2725	0.8354	0.0491
H(221)	0.0444	0.2540	0.8055	0.0525
H(231)	-0.0830	0.2884	0.6838	0.0448
H(241)	0.3399	0.3152	0.8057	0.0499
H(242)	0.3162	0.3169	0.7032	0.0499
H(251)	0.4454	0.4182	0.7942	0.0549
H(252)	0.4526	0.3647	0.7581	0.0549
H(261)	0.3550	0.4438	0.6530	0.0796
H(262)	0.4663	0.4247	0.6647	0.0796
H(271)	0.2338	0.4202	0.5544	0.0945

H(272)	0.2194	0.3655	0.5184	0.0945
H(281)	0.2097	0.4141	0.4066	0.0769
H(282)	0.3168	0.3865	0.4352	0.0769
H(291)	0.2438	0.4859	0.3572	0.0609
H(292)	0.3416	0.4577	0.3543	0.0609
H(301)	0.4448	0.5175	0.4415	0.0558
H(302)	0.3681	0.5392	0.3512	0.0558
H(311)	0.4283	0.5756	0.5755	0.0461
H(312)	0.4074	0.5184	0.5585	0.0461
H(321)	0.2639	0.5869	0.5699	0.0448
H(322)	0.2402	0.5302	0.5494	0.0448
H(331)	0.2308	0.5772	0.6993	0.0526
H(332)	0.2086	0.5205	0.6779	0.0526
H(341)	0.3684	0.5546	0.8256	0.0495
H(342)	0.2599	0.5393	0.8272	0.0495
H(351)	0.2419	0.4626	0.8635	0.0528
H(352)	0.2082	0.4556	0.7605	0.0528
H(361)	0.3676	0.4021	0.8792	0.0505
H(362)	0.2526	0.3829	0.8445	0.0505
H(371)	0.3417	0.6308	0.4737	0.0491
H(372)	0.4239	0.6120	0.4355	0.0491
H(391)	0.1677	0.5789	0.3436	0.0390
H(411)	0.1010	0.6612	0.1259	0.0427
H(421)	0.2661	0.6931	0.1801	0.0541
H(431)	0.3805	0.6696	0.3172	0.0523
H(441)	-0.0276	0.6164	0.1487	0.0340
H(442)	-0.0118	0.6022	0.2468	0.0340
H(451)	0.0740	0.5529	0.0898	0.0339
H(452)	0.0236	0.5006	0.0899	0.0339
H(471)	-0.1660	0.4937	0.0255	0.0368
H(491)	-0.3034	0.5915	-0.1652	0.0415
H(511)	-0.0119	0.6126	-0.0049	0.0359
H(531)	-0.4363	0.4706	-0.0629	0.0724
H(532)	-0.3959	0.5218	-0.0164	0.0724
H(533)	-0.3228	0.4751	0.0074	0.0724
H(541)	-0.3671	0.4367	-0.1655	0.0674
H(542)	-0.2851	0.4670	-0.1906	0.0674
H(543)	-0.2535	0.4428	-0.0961	0.0674
H(551)	-0.4819	0.5034	-0.2046	0.0619
H(552)	-0.4461	0.5571	-0.1683	0.0619
H(553)	-0.4006	0.5319	-0.2334	0.0619
H(571)	-0.0588	0.7086	-0.1431	0.0850
H(572)	-0.0303	0.6850	-0.0484	0.0850
H(573)	-0.0089	0.6554	-0.1233	0.0850
H(581)	-0.2309	0.7215	-0.1499	0.0900
H(582)	-0.2059	0.6963	-0.0569	0.0900
H(583)	-0.2978	0.6763	-0.1403	0.0900
H(591)	-0.1932	0.6781	-0.2646	0.0589
H(592)	-0.2623	0.6337	-0.2558	0.0589
H(593)	-0.1471	0.6241	-0.2465	0.0589

H(1001)	0.4160	0.3275	0.5649	0.1541
H(1011)	0.3812	0.2441	0.4879	0.1592
H(1012)	0.3255	0.2653	0.5489	0.1592
H(1013)	0.3103	0.2914	0.4584	0.1592

Table F.5.4: Anisotropic thermal parameters (Å²)

Atom	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂
Ni(1)	0.0395(2)	0.0320(2)	0.02847(19)	0.00012(15)	0.01192(16)	-0.00192(16)
S(1)	0.0568(5)	0.0350(4)	0.0331(4)	-0.0030(3)	0.0193(4)	-0.0034(4)
S(2)	0.0456(4)	0.0320(4)	0.0311(4)	-0.0023(3)	0.0146(3)	-0.0049(3)
S(3)	0.0442(4)	0.0342(4)	0.0267(3)	-0.0020(3)	0.0138(3)	-0.0019(3)
S(4)	0.0555(5)	0.0327(4)	0.0334(4)	-0.0025(3)	0.0174(4)	-0.0011(3)
C(1)	0.0300(15)	0.0353(15)	0.0307(15)	-0.0026(12)	0.0090(12)	-0.0027(12)
N(1)	0.0390(14)	0.0311(12)	0.0325(13)	-0.004(1)	0.0157(11)	-0.004(1)
C(2)	0.0411(17)	0.0316(15)	0.0397(16)	-0.0041(12)	0.0183(14)	-0.0010(13)
C(3)	0.0396(17)	0.0261(14)	0.0369(15)	-0.0038(12)	0.0145(13)	-0.0023(12)
C(4)	0.0405(17)	0.0338(16)	0.0347(16)	0.0005(12)	0.0086(13)	-0.0006(13)
C(5)	0.0457(19)	0.0430(18)	0.0416(18)	-0.0007(14)	0.0127(15)	-0.0097(15)
C(6)	0.0370(17)	0.0515(19)	0.0463(19)	-0.0043(15)	0.0154(15)	-0.0095(15)
C(7)	0.0397(18)	0.0411(17)	0.0413(17)	-0.0034(14)	0.0073(14)	0.0031(14)
C(8)	0.0417(18)	0.0329(15)	0.0392(17)	0.0012(13)	0.0122(14)	-0.0020(13)
C(9)	0.067(3)	0.059(2)	0.056(2)	0.0148(18)	0.0171(19)	-0.020(2)
C(10)	0.092(3)	0.111(4)	0.056(3)	0.018(3)	0.026(2)	-0.030(3)
C(11)	0.137(5)	0.055(3)	0.127(5)	0.026(3)	0.055(4)	-0.015(3)
C(12)	0.078(3)	0.147(5)	0.083(3)	0.047(3)	0.013(3)	-0.053(3)
C(13)	0.0409(19)	0.049(2)	0.056(2)	-0.0003(17)	0.0034(16)	0.0024(15)
C(14)	0.061(3)	0.061(2)	0.073(3)	0.016(2)	-0.003(2)	0.014(2)
C(15)	0.057(3)	0.110(4)	0.085(3)	0.006(3)	0.015(2)	0.031(3)
C(16)	0.062(3)	0.058(2)	0.070(3)	-0.004(2)	-0.009(2)	0.007(2)
C(17)	0.0402(17)	0.0305(15)	0.0396(16)	-0.0056(12)	0.0180(14)	-0.0039(12)
C(18)	0.0434(18)	0.0280(14)	0.0344(16)	-0.0040(12)	0.0152(13)	-0.0023(12)
C(19)	0.0486(19)	0.0298(15)	0.0379(16)	-0.0030(12)	0.0193(14)	-0.0038(13)
C(20)	0.0499(19)	0.0311(16)	0.0438(18)	-0.0041(13)	0.0123(15)	0.0006(14)
C(21)	0.064(2)	0.0362(17)	0.0405(18)	0.0025(14)	0.0118(16)	0.0049(16)
C(22)	0.068(2)	0.0354(17)	0.0401(18)	0.0037(14)	0.0210(17)	-0.0050(16)
C(23)	0.055(2)	0.0351(16)	0.0411(17)	-0.0066(14)	0.0224(15)	-0.0067(15)
C(24)	0.049(2)	0.0415(18)	0.052(2)	-0.0012(15)	0.0113(16)	0.0034(15)
N(2)	0.0426(15)	0.0429(14)	0.0412(15)	-0.0034(12)	0.0147(12)	-0.0003(12)
C(25)	0.0386(19)	0.058(2)	0.056(2)	-0.0090(17)	0.0169(16)	-0.0051(16)
C(26)	0.079(3)	0.060(2)	0.073(3)	-0.009(2)	0.046(2)	-0.009(2)
O(1)	0.102(2)	0.0719(19)	0.0521(16)	-0.0022(14)	0.0332(16)	0.0083(17)
C(27)	0.073(3)	0.092(4)	0.090(3)	-0.001(3)	0.040(3)	-0.014(3)
C(28)	0.071(3)	0.081(3)	0.059(3)	-0.008(2)	0.018(2)	-0.010(2)
O(2)	0.0591(16)	0.0713(18)	0.0410(13)	-0.0001(12)	0.0155(12)	-0.0033(13)
C(29)	0.068(2)	0.071(3)	0.0344(18)	0.0005(17)	0.0151(17)	0.022(2)
C(30)	0.048(2)	0.073(3)	0.0391(18)	0.0095(17)	0.0176(16)	0.0174(19)
N(3)	0.0392(14)	0.0601(17)	0.0297(13)	0.0036(12)	0.0098(11)	0.0082(13)

C(31)	0.0357(17)	0.066(2)	0.0307(16)	0.0047(15)	0.0080(13)	0.0058(16)
C(32)	0.0410(18)	0.059(2)	0.0325(16)	0.0040(15)	0.0126(13)	0.0062(16)
O(3)	0.0366(12)	0.0579(14)	0.0322(11)	0.002(1)	0.0112(9)	0.006(1)
C(33)	0.0430(19)	0.064(2)	0.0432(18)	0.0066(16)	0.0220(15)	0.0136(16)
C(34)	0.051(2)	0.0491(19)	0.0416(18)	-0.0005(15)	0.0206(16)	0.0043(16)
O(4)	0.0410(12)	0.0462(12)	0.0420(12)	-0.001(1)	0.014(1)	-0.001(1)
C(35)	0.0436(19)	0.056(2)	0.048(2)	-0.0094(16)	0.0197(16)	-0.0048(16)
C(36)	0.050(2)	0.0511(19)	0.0420(18)	-0.0046(15)	0.0152(15)	-0.0101(16)
C(37)	0.0367(18)	0.066(2)	0.0390(18)	0.0047(16)	0.0083(14)	-0.0076(16)
C(38)	0.0407(18)	0.0475(18)	0.0375(17)	0.0001(14)	0.0131(14)	-0.0027(14)
C(39)	0.0382(17)	0.0389(16)	0.0345(16)	-0.0005(13)	0.0147(13)	-0.0026(13)
C(40)	0.0400(17)	0.0338(15)	0.0318(15)	-0.0035(12)	0.0141(13)	-0.0003(13)
C(41)	0.054(2)	0.0368(16)	0.0349(16)	0.0018(13)	0.0141(15)	-0.0046(14)
C(42)	0.056(2)	0.050(2)	0.047(2)	0.0104(16)	0.0165(17)	-0.0106(17)
C(43)	0.0439(19)	0.053(2)	0.050(2)	-0.0019(16)	0.0154(16)	-0.0151(16)
C(44)	0.0379(16)	0.0323(14)	0.0287(14)	-0.0010(12)	0.0090(12)	0.0048(12)
N(4)	0.0315(12)	0.0325(13)	0.0255(12)	-0.0019(9)	0.010(1)	0.003(1)
C(45)	0.0338(15)	0.0351(15)	0.0263(14)	-0.0007(11)	0.0112(12)	0.0021(12)
C(46)	0.0342(15)	0.0338(15)	0.0273(14)	-0.0040(11)	0.0124(12)	0.0006(12)
C(47)	0.0389(16)	0.0368(16)	0.0322(15)	0.0019(12)	0.0156(13)	-0.0024(13)
C(48)	0.0348(17)	0.0488(18)	0.0325(16)	-0.0014(13)	0.0111(13)	-0.0027(14)
C(49)	0.0352(17)	0.0491(18)	0.0361(17)	0.0015(14)	0.0048(13)	-0.0000(14)
C(50)	0.0433(18)	0.0399(17)	0.0349(16)	0.0028(13)	0.0084(14)	-0.0019(14)
C(51)	0.0353(16)	0.0366(16)	0.0343(16)	-0.0012(12)	0.0105(13)	-0.0018(13)
C(52)	0.0368(18)	0.055(2)	0.0442(19)	-0.0012(15)	0.0105(15)	-0.0091(15)
C(53)	0.053(2)	0.080(3)	0.056(2)	-0.006(2)	0.0251(18)	-0.023(2)
C(54)	0.049(2)	0.068(2)	0.062(2)	-0.0164(19)	0.0177(18)	-0.0146(19)
C(55)	0.042(2)	0.072(3)	0.057(2)	0.0035(19)	0.0024(17)	-0.0140(18)
C(56)	0.056(2)	0.0423(18)	0.048(2)	0.0103(15)	0.0047(17)	-0.0033(16)
C(57)	0.082(3)	0.064(3)	0.075(3)	0.031(2)	-0.008(2)	-0.030(2)
C(58)	0.125(4)	0.051(2)	0.070(3)	0.008(2)	0.028(3)	0.021(3)
C(59)	0.060(2)	0.054(2)	0.048(2)	0.0133(17)	0.0116(17)	-0.0002(18)
C(60)	0.0279(14)	0.0327(15)	0.0281(14)	-0.0031(11)	0.0097(11)	-0.0011(11)
O(100)	0.111(3)	0.122(4)	0.149(4)	-0.021(3)	0.038(3)	-0.001(3)
C(101)	0.133(6)	0.108(5)	0.158(7)	-0.017(5)	0.039(5)	-0.047(4)

Table F.5.5: Bond lengths (Å)
(geometrically-positioned H atoms have been excluded)

Ni(1) - S(1)	2.2040(9)	C(28) - O(2)	1.412(5)
Ni(1) - S(2)	2.2024(8)	O(2) - C(29)	1.418(4)
Ni(1) - S(3)	2.2007(8)	C(29) - C(30)	1.490(6)
Ni(1) - S(4)	2.1982(9)	C(30) - N(3)	1.461(4)
S(1) - C(1)	1.724(3)	N(3) - C(31)	1.475(4)
S(2) - C(1)	1.722(3)	N(3) - C(37)	1.464(4)
S(3) - C(60)	1.723(3)	C(31) - C(32)	1.503(4)
S(4) - C(60)	1.723(3)	C(32) - O(3)	1.424(4)
C(1) - N(1)	1.323(4)	O(3) - C(33)	1.421(4)

N(1) - C(2)	1.471(4)	C(33) - C(34)	1.501(5)
N(1) - C(17)	1.472(4)	C(34) - O(4)	1.432(4)
C(2) - C(3)	1.517(4)	O(4) - C(35)	1.422(4)
C(3) - C(4)	1.383(4)	C(35) - C(36)	1.496(5)
C(3) - C(8)	1.396(4)	C(37) - C(38)	1.509(4)
C(4) - C(5)	1.399(4)	C(38) - C(39)	1.391(4)
C(5) - C(6)	1.388(5)	C(38) - C(43)	1.398(5)
C(5) - C(9)	1.528(5)	C(39) - C(40)	1.391(4)
C(6) - C(7)	1.395(5)	C(40) - C(41)	1.390(4)
C(7) - C(8)	1.387(4)	C(40) - C(44)	1.513(4)
C(7) - C(13)	1.533(5)	C(41) - C(42)	1.388(5)
C(9) - C(10)	1.526(6)	C(42) - C(43)	1.383(5)
C(9) - C(11)	1.531(7)	C(44) - N(4)	1.470(4)
C(9) - C(12)	1.518(6)	N(4) - C(45)	1.475(3)
C(13) - C(14)	1.520(6)	N(4) - C(60)	1.319(4)
C(13) - C(15)	1.523(6)	C(45) - C(46)	1.513(4)
C(13) - C(16)	1.533(5)	C(46) - C(47)	1.391(4)
C(17) - C(18)	1.518(4)	C(46) - C(51)	1.393(4)
C(18) - C(19)	1.394(4)	C(47) - C(48)	1.399(4)
C(18) - C(23)	1.387(4)	C(48) - C(49)	1.392(5)
C(19) - C(20)	1.395(4)	C(48) - C(52)	1.532(4)
C(20) - C(21)	1.393(5)	C(49) - C(50)	1.391(4)
C(20) - C(24)	1.507(5)	C(50) - C(51)	1.389(4)
C(21) - C(22)	1.383(5)	C(50) - C(56)	1.537(4)
C(22) - C(23)	1.383(5)	C(52) - C(53)	1.521(5)
C(24) - N(2)	1.467(4)	C(52) - C(54)	1.551(5)
N(2) - C(25)	1.468(4)	C(52) - C(55)	1.520(5)
N(2) - C(36)	1.460(4)	C(56) - C(57)	1.516(6)
C(25) - C(26)	1.505(6)	C(56) - C(58)	1.521(6)
C(26) - O(1)	1.426(5)	C(56) - C(59)	1.538(5)
O(1) - C(27)	1.422(6)	O(100) - C(101)	1.396(7)
C(27) - C(28)	1.489(6)		

Table F.5.6: Bond angles (°)
(geometrically-positioned H atoms have been excluded)

S(1) - Ni(1) - S(2)	79.73(3)	O(1) - C(27) - C(28)	113.0(4)
S(1) - Ni(1) - S(3)	177.90(4)	C(27) - C(28) - O(2)	110.4(4)
S(2) - Ni(1) - S(3)	100.16(3)	C(28) - O(2) - C(29)	112.5(3)
S(1) - Ni(1) - S(4)	100.41(3)	O(2) - C(29) - C(30)	111.4(3)
S(2) - Ni(1) - S(4)	177.72(4)	C(29) - C(30) - N(3)	113.2(3)
S(3) - Ni(1) - S(4)	79.61(3)	C(30) - N(3) - C(31)	113.1(3)
Ni(1) - S(1) - C(1)	84.7(1)	C(30) - N(3) - C(37)	111.7(3)
Ni(1) - S(2) - C(1)	84.9(1)	C(31) - N(3) - C(37)	112.6(3)
Ni(1) - S(3) - C(60)	85.3(1)	N(3) - C(31) - C(32)	109.9(3)
Ni(1) - S(4) - C(60)	85.4(1)	C(31) - C(32) - O(3)	107.7(2)
S(1) - C(1) - S(2)	110.08(16)	C(32) - O(3) - C(33)	112.0(2)
S(1) - C(1) - N(1)	124.7(2)	O(3) - C(33) - C(34)	109.5(3)
S(2) - C(1) - N(1)	125.2(2)	C(33) - C(34) - O(4)	113.7(3)

C(1) - N(1) - C(2)	122.0(2)	C(34) - O(4) - C(35)	113.1(2)
C(1) - N(1) - C(17)	122.1(2)	O(4) - C(35) - C(36)	110.6(3)
C(2) - N(1) - C(17)	115.9(2)	N(2) - C(36) - C(35)	113.6(3)
N(1) - C(2) - C(3)	111.6(2)	N(3) - C(37) - C(38)	111.7(3)
C(2) - C(3) - C(4)	119.9(3)	C(37) - C(38) - C(39)	120.1(3)
C(2) - C(3) - C(8)	120.3(3)	C(37) - C(38) - C(43)	121.2(3)
C(4) - C(3) - C(8)	119.8(3)	C(39) - C(38) - C(43)	118.6(3)
C(3) - C(4) - C(5)	121.4(3)	C(38) - C(39) - C(40)	121.4(3)
C(4) - C(5) - C(6)	117.2(3)	C(39) - C(40) - C(41)	119.4(3)
C(4) - C(5) - C(9)	119.5(3)	C(39) - C(40) - C(44)	118.9(3)
C(6) - C(5) - C(9)	123.3(3)	C(41) - C(40) - C(44)	121.7(3)
C(5) - C(6) - C(7)	123.0(3)	C(40) - C(41) - C(42)	119.6(3)
C(6) - C(7) - C(8)	118.2(3)	C(41) - C(42) - C(43)	120.8(3)
C(6) - C(7) - C(13)	119.0(3)	C(38) - C(43) - C(42)	120.2(3)
C(8) - C(7) - C(13)	122.7(3)	C(40) - C(44) - N(4)	113.4(2)
C(3) - C(8) - C(7)	120.5(3)	C(44) - N(4) - C(45)	116.3(2)
C(5) - C(9) - C(10)	109.8(3)	C(44) - N(4) - C(60)	122.3(2)
C(5) - C(9) - C(11)	108.2(3)	C(45) - N(4) - C(60)	121.3(2)
C(10) - C(9) - C(11)	108.5(4)	N(4) - C(45) - C(46)	112.0(2)
C(5) - C(9) - C(12)	112.7(3)	C(45) - C(46) - C(47)	121.5(3)
C(10) - C(9) - C(12)	109.9(4)	C(45) - C(46) - C(51)	119.1(3)
C(11) - C(9) - C(12)	107.7(4)	C(47) - C(46) - C(51)	119.4(3)
C(7) - C(13) - C(14)	112.6(3)	C(46) - C(47) - C(48)	121.1(3)
C(7) - C(13) - C(15)	110.1(3)	C(47) - C(48) - C(49)	117.4(3)
C(14) - C(13) - C(15)	108.7(4)	C(47) - C(48) - C(52)	120.5(3)
C(7) - C(13) - C(16)	107.6(3)	C(49) - C(48) - C(52)	122.0(3)
C(14) - C(13) - C(16)	107.9(3)	C(48) - C(49) - C(50)	123.1(3)
C(15) - C(13) - C(16)	109.9(4)	C(49) - C(50) - C(51)	117.7(3)
N(1) - C(17) - C(18)	112.4(2)	C(49) - C(50) - C(56)	119.8(3)
C(17) - C(18) - C(19)	119.5(3)	C(51) - C(50) - C(56)	122.5(3)
C(17) - C(18) - C(23)	120.6(3)	C(46) - C(51) - C(50)	121.3(3)
C(19) - C(18) - C(23)	119.8(3)	C(48) - C(52) - C(53)	111.0(3)
C(18) - C(19) - C(20)	120.9(3)	C(48) - C(52) - C(54)	108.1(3)
C(19) - C(20) - C(21)	118.1(3)	C(53) - C(52) - C(54)	109.0(3)
C(19) - C(20) - C(24)	119.9(3)	C(48) - C(52) - C(55)	112.9(3)
C(21) - C(20) - C(24)	122.0(3)	C(53) - C(52) - C(55)	109.9(3)
C(20) - C(21) - C(22)	121.1(3)	C(54) - C(52) - C(55)	105.8(3)
C(21) - C(22) - C(23)	120.2(3)	C(50) - C(56) - C(57)	111.6(3)
C(18) - C(23) - C(22)	119.8(3)	C(50) - C(56) - C(58)	108.0(3)
C(20) - C(24) - N(2)	112.1(3)	C(57) - C(56) - C(58)	110.2(4)
C(24) - N(2) - C(25)	112.3(3)	C(50) - C(56) - C(59)	110.0(3)
C(24) - N(2) - C(36)	111.9(3)	C(57) - C(56) - C(59)	107.2(3)
C(25) - N(2) - C(36)	113.6(3)	C(58) - C(56) - C(59)	109.8(3)
N(2) - C(25) - C(26)	112.7(3)	S(3) - C(60) - S(4)	109.62(15)
C(25) - C(26) - O(1)	110.6(3)	S(3) - C(60) - N(4)	125.4(2)
C(26) - O(1) - C(27)	116.6(3)	S(4) - C(60) - N(4)	125.0(2)

F.6 Crystal data for 67·CH₃OH[#]

X-ray quality crystals (brown blocks) of 67·CH₃OH were obtained by slow evaporation of a chloroform / methanol solution of the receptor. The non-hydrogen atom numbering system is outlined in the schematic structure shown in Figure F.3.1.

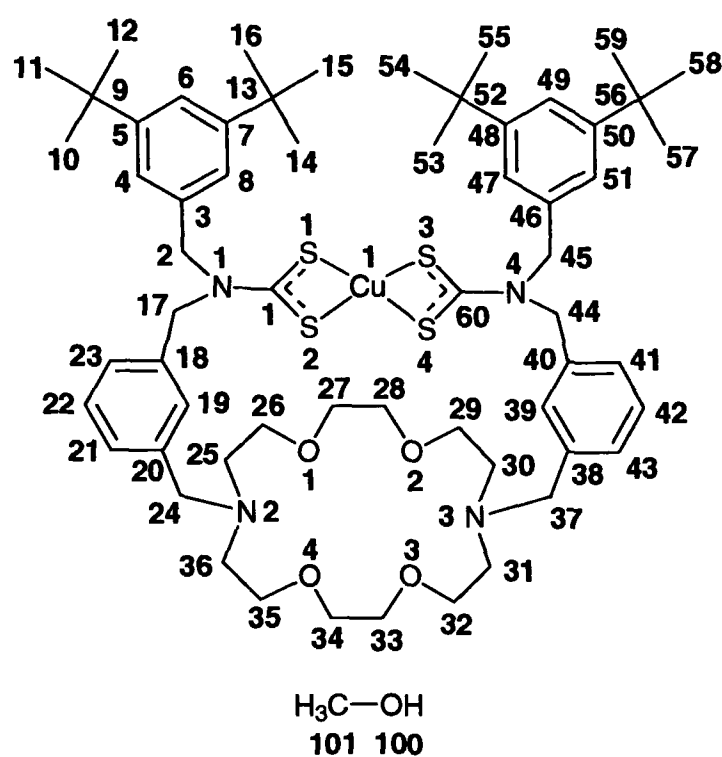


Figure F.3.1: Atom numbering system.

Table F.6.1: Crystal data and refinement details

Crystal identification	ae
Chemical formula	C ₆₁ H ₉₀ CuN ₄ O ₅ S ₄
Formula weight	1151.22
Temperature (K)	150
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	P 21/c
<i>a</i> (Å)	14.4284(1)
<i>b</i> (Å)	27.9793(2)
<i>c</i> (Å)	16.8651(1)
<i>β</i> (°)	111.7005(4)
Cell volume (Å ³)	6325.87(8)
<i>Z</i>	4
Calculated density (Mg/m ³)	1.21
Absorption coefficient (mm ⁻¹)	0.525
<i>F</i> ₀₀₀	2471.801
Crystal size (mm)	0.20 x 0.20 x 0.20
Description of crystal	Brown block
Absorption correction	Semi-empirical from equivalent reflections
Transmission coefficients (min,max)	0.90, 0.90

θ range for data collection ($^{\circ}$)	$5.0 \leq \theta \leq 27.0$
Index ranges	$-18 \leq h \leq 18, -36 \leq k \leq 35, -21 \leq l \leq 21$
Reflections measured	27694
Unique reflections	14299
R_{int}	0.059
Observed reflections ($I > 3\sigma(I)$)	7775
Refinement method	Full-matrix least-squares on F
Parameters refined	676
Weighting scheme	Chebyshev 3-term polynomial
Goodness of fit	1.043
R	0.049
wR	0.0396
Residual electron density (min,max) ($\text{e}\text{\AA}^{-3}$)	-0.48, 0.64

Table F.6.2: Atomic coordinates and equivalent isotropic thermal parameters ($\text{\AA}^2$) of non-hydrogen atoms

Atom	x/a	y/b	z/c	U_{iso}
Cu(1)	-0.00524(3)	0.441891(12)	0.33804(2)	0.0317
S(1)	-0.02212(6)	0.36024(3)	0.34363(5)	0.0386
S(2)	-0.00676(6)	0.43122(2)	0.47208(4)	0.0337
S(3)	0.00469(5)	0.52355(2)	0.33091(4)	0.0319
S(4)	-0.00995(6)	0.45298(3)	0.20234(5)	0.0389
C(1)	-0.0307(2)	0.3723(1)	0.44124(17)	0.0299
N(1)	-0.05516(16)	0.33958(8)	0.48675(14)	0.0293
C(2)	-0.0724(2)	0.2892(1)	0.46012(18)	0.0319
C(3)	-0.1760(2)	0.27291(9)	0.45049(17)	0.0304
C(4)	-0.1880(2)	0.2372(1)	0.50268(17)	0.0343
C(5)	-0.2823(2)	0.22096(11)	0.49511(19)	0.0396
C(6)	-0.3641(2)	0.24196(11)	0.4328(2)	0.0409
C(7)	-0.3552(2)	0.2782(1)	0.37896(19)	0.0363
C(8)	-0.2601(2)	0.2935(1)	0.38853(18)	0.0346
C(9)	-0.2916(3)	0.18123(14)	0.5543(2)	0.0558
C(10)	-0.2398(3)	0.19672(18)	0.6472(3)	0.0750
C(11)	-0.2395(5)	0.13651(16)	0.5378(4)	0.0933
C(12)	-0.3998(4)	0.1687(2)	0.5382(3)	0.1007
C(13)	-0.4497(2)	0.29744(12)	0.3085(2)	0.0465
C(14)	-0.4302(3)	0.34271(14)	0.2675(3)	0.0614
C(15)	-0.5293(3)	0.30844(19)	0.3459(3)	0.0770
C(16)	-0.4876(3)	0.25879(14)	0.2397(3)	0.0640
C(17)	-0.0656(2)	0.3509(1)	0.56820(18)	0.0323
C(18)	0.0143(2)	0.32745(9)	0.64377(18)	0.0310
C(19)	0.1146(2)	0.3380(1)	0.66183(18)	0.0343
C(20)	0.1895(2)	0.3180(1)	0.73250(19)	0.0367
C(21)	0.1622(3)	0.28703(11)	0.78448(19)	0.0429
C(22)	0.0628(3)	0.27627(11)	0.7672(2)	0.0431
C(23)	-0.0113(2)	0.2963(1)	0.69657(19)	0.0365
C(24)	0.2975(2)	0.33010(11)	0.7502(2)	0.0437
N(2)	0.31540(18)	0.38169(9)	0.75549(15)	0.0371

C(25)	0.4108(2)	0.39435(12)	0.7490(2)	0.0459
C(26)	0.3995(3)	0.41512(14)	0.6640(3)	0.0606
O(1)	0.3560(2)	0.3810(1)	0.59737(16)	0.0656
C(27)	0.2646(3)	0.39398(17)	0.5324(3)	0.0743
C(28)	0.2765(3)	0.41070(16)	0.4531(3)	0.0659
O(2)	0.32691(18)	0.45510(9)	0.46706(14)	0.0508
C(29)	0.3162(3)	0.47892(14)	0.3893(2)	0.0518
C(30)	0.3734(2)	0.52479(13)	0.40692(19)	0.0462
N(3)	0.33752(18)	0.55957(9)	0.45345(14)	0.0371
C(31)	0.3767(2)	0.55106(12)	0.54654(18)	0.0397
C(32)	0.2932(2)	0.55407(11)	0.57943(18)	0.0379
O(3)	0.33451(14)	0.54371(8)	0.66855(12)	0.0375
C(33)	0.2615(2)	0.54469(12)	0.7062(2)	0.0422
C(34)	0.3094(2)	0.53307(11)	0.79993(19)	0.0404
O(4)	0.34235(14)	0.48499(7)	0.81677(13)	0.0374
C(35)	0.2651(2)	0.45324(12)	0.8166(2)	0.0435
C(36)	0.3020(2)	0.40279(12)	0.83024(19)	0.0422
C(37)	0.3534(2)	0.60871(12)	0.43173(19)	0.0426
C(38)	0.2840(2)	0.62219(11)	0.34260(18)	0.0364
C(39)	0.1881(2)	0.6032(1)	0.30960(17)	0.0328
C(40)	0.1198(2)	0.6175(1)	0.23044(17)	0.0308
C(41)	0.1489(2)	0.65083(11)	0.18285(18)	0.0374
C(42)	0.2451(3)	0.66960(12)	0.2149(2)	0.0460
C(43)	0.3120(2)	0.65567(12)	0.2943(2)	0.0442
C(44)	0.0145(2)	0.59792(9)	0.20005(16)	0.0295
N(4)	0.00852(15)	0.54682(8)	0.17730(13)	0.0263
C(45)	0.01484(19)	0.5360(1)	0.09383(17)	0.0285
C(46)	-0.07757(19)	0.55152(9)	0.02018(15)	0.0272
C(47)	-0.1639(2)	0.5238(1)	-0.00597(17)	0.0306
C(48)	-0.2477(2)	0.53778(11)	-0.07605(18)	0.0346
C(49)	-0.2430(2)	0.58073(11)	-0.11645(18)	0.0373
C(50)	-0.1579(2)	0.6093(1)	-0.09164(18)	0.0359
C(51)	-0.0747(2)	0.5934(1)	-0.02329(17)	0.0311
C(52)	-0.3397(2)	0.50481(12)	-0.1097(2)	0.0413
C(53)	-0.3765(3)	0.49192(15)	-0.0392(2)	0.0574
C(54)	-0.3084(3)	0.45873(14)	-0.1435(2)	0.0556
C(55)	-0.4243(2)	0.52619(14)	-0.1855(2)	0.0554
C(56)	-0.1582(3)	0.65615(11)	-0.1385(2)	0.0466
C(57)	-0.0553(3)	0.67812(16)	-0.1111(3)	0.0805
C(58)	-0.2297(4)	0.69045(14)	-0.1198(3)	0.0765
C(59)	-0.1934(3)	0.64705(13)	-0.2351(2)	0.0511
C(60)	0.00219(19)	0.5128(1)	0.22932(16)	0.0278
O(100)	0.4430(3)	0.30338(17)	0.5503(3)	0.1238
C(101)	0.3594(6)	0.2746(3)	0.5086(5)	0.1248

Table F.6.3: Atomic coordinates and isotropic thermal parameters ($\text{\AA}^2$) of hydrogen atoms

Atom	x/a	y/b	z/c	U_{iso}
H(21)	-0.0223	0.2689	0.5041	0.0383
H(22)	-0.0642	0.2854	0.4041	0.0383
H(41)	-0.1277	0.2228	0.5470	0.0387
H(61)	-0.4321	0.2304	0.4261	0.0484
H(81)	-0.2518	0.3195	0.3511	0.0407
H(101)	-0.2456	0.1706	0.6856	0.0914
H(102)	-0.2720	0.2263	0.6576	0.0914
H(103)	-0.1676	0.2030	0.6589	0.0914
H(111)	-0.2446	0.1103	0.5763	0.1168
H(112)	-0.1678	0.1441	0.5505	0.1168
H(113)	-0.2727	0.1268	0.4773	0.1168
H(121)	-0.4013	0.1422	0.5779	0.1173
H(122)	-0.4351	0.1970	0.5473	0.1173
H(123)	-0.4324	0.1570	0.4777	0.1173
H(141)	-0.4937	0.3538	0.2222	0.0663
H(142)	-0.4043	0.3682	0.3118	0.0663
H(143)	-0.3797	0.3361	0.2411	0.0663
H(151)	-0.5907	0.3211	0.2998	0.0900
H(152)	-0.5034	0.3331	0.3920	0.0900
H(153)	-0.5463	0.2787	0.3702	0.0900
H(161)	-0.5495	0.2702	0.1930	0.0665
H(162)	-0.5035	0.2290	0.2657	0.0665
H(163)	-0.4354	0.2513	0.2160	0.0665
H(171)	-0.0608	0.3863	0.5768	0.0395
H(172)	-0.1323	0.3396	0.5658	0.0395
H(191)	0.1331	0.3601	0.6235	0.0418
H(211)	0.2149	0.2725	0.8354	0.0491
H(221)	0.0444	0.2540	0.8055	0.0525
H(231)	-0.0830	0.2884	0.6838	0.0448
H(241)	0.3399	0.3152	0.8057	0.0499
H(242)	0.3162	0.3169	0.7032	0.0499
H(251)	0.4454	0.4182	0.7942	0.0549
H(252)	0.4526	0.3647	0.7581	0.0549
H(261)	0.3550	0.4438	0.6530	0.0796
H(262)	0.4663	0.4247	0.6647	0.0796
H(271)	0.2338	0.4202	0.5544	0.0945
H(272)	0.2194	0.3655	0.5184	0.0945
H(281)	0.2097	0.4141	0.4066	0.0769
H(282)	0.3168	0.3865	0.4352	0.0769
H(291)	0.2438	0.4859	0.3572	0.0609
H(292)	0.3416	0.4577	0.3543	0.0609
H(301)	0.4448	0.5175	0.4415	0.0558
H(302)	0.3681	0.5392	0.3512	0.0558
H(311)	0.4283	0.5756	0.5755	0.0461
H(312)	0.4074	0.5184	0.5585	0.0461
H(321)	0.2639	0.5869	0.5699	0.0448

H(322)	0.2402	0.5302	0.5494	0.0448
H(331)	0.2308	0.5772	0.6993	0.0526
H(332)	0.2086	0.5205	0.6779	0.0526
H(341)	0.3684	0.5546	0.8256	0.0495
H(342)	0.2599	0.5393	0.8272	0.0495
H(351)	0.2419	0.4626	0.8635	0.0528
H(352)	0.2082	0.4556	0.7605	0.0528
H(361)	0.3676	0.4021	0.8792	0.0505
H(362)	0.2526	0.3829	0.8445	0.0505
H(371)	0.3417	0.6308	0.4737	0.0491
H(372)	0.4239	0.6120	0.4355	0.0491
H(391)	0.1677	0.5789	0.3436	0.0390
H(411)	0.1010	0.6612	0.1259	0.0427
H(421)	0.2661	0.6931	0.1801	0.0541
H(431)	0.3805	0.6696	0.3172	0.0523
H(441)	-0.0276	0.6164	0.1487	0.0340
H(442)	-0.0118	0.6022	0.2468	0.0340
H(451)	0.0740	0.5529	0.0898	0.0339
H(452)	0.0236	0.5006	0.0899	0.0339
H(471)	-0.1660	0.4937	0.0255	0.0368
H(491)	-0.3034	0.5915	-0.1652	0.0415
H(511)	-0.0119	0.6126	-0.0049	0.0359
H(531)	-0.4363	0.4706	-0.0629	0.0724
H(532)	-0.3959	0.5218	-0.0164	0.0724
H(533)	-0.3228	0.4751	0.0074	0.0724
H(541)	-0.3671	0.4367	-0.1655	0.0674
H(542)	-0.2851	0.4670	-0.1906	0.0674
H(543)	-0.2535	0.4428	-0.0961	0.0674
H(551)	-0.4819	0.5034	-0.2046	0.0619
H(552)	-0.4461	0.5571	-0.1683	0.0619
H(553)	-0.4006	0.5319	-0.2334	0.0619
H(571)	-0.0588	0.7086	-0.1431	0.0850
H(572)	-0.0303	0.6850	-0.0484	0.0850
H(573)	-0.0089	0.6553	-0.1233	0.0850
H(581)	-0.2309	0.7215	-0.1499	0.0900
H(582)	-0.2059	0.6963	-0.0569	0.0900
H(583)	-0.2978	0.6763	-0.1403	0.0900
H(591)	-0.1932	0.6781	-0.2646	0.0589
H(592)	-0.2623	0.6337	-0.2558	0.0589
H(593)	-0.1471	0.6241	-0.2465	0.0589
H(1001)	0.4160	0.3275	0.5649	0.1541
H(1011)	0.3812	0.2441	0.4879	0.1592
H(1012)	0.3255	0.2653	0.5489	0.1592
H(1013)	0.3103	0.2914	0.4584	0.1592

Table F.6.4: Anisotropic thermal parameters ($\text{\AA}^2$)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cu(1)	0.03755(19)	0.02876(18)	0.02760(18)	0.00146(13)	0.01073(14)	-0.00185(14)
S(1)	0.0573(5)	0.0308(4)	0.0302(4)	-0.0026(3)	0.0192(3)	-0.0031(3)
S(2)	0.0440(4)	0.0278(3)	0.0294(3)	-0.0011(3)	0.0137(3)	-0.0045(3)
S(3)	0.0409(4)	0.0303(4)	0.0251(3)	-0.0017(3)	0.0129(3)	-0.0031(3)
S(4)	0.0585(5)	0.0278(4)	0.0314(4)	-0.0021(3)	0.0179(3)	-0.0008(3)
C(1)	0.0283(13)	0.0301(14)	0.0294(14)	-0.0004(11)	0.0085(11)	-0.0008(11)
N(1)	0.0318(12)	0.0255(11)	0.0302(12)	-0.0024(9)	0.011(1)	-0.0011(9)
C(2)	0.0352(15)	0.0244(13)	0.0370(15)	-0.0034(11)	0.0144(12)	-0.0008(11)
C(3)	0.0350(14)	0.0240(13)	0.0318(14)	-0.0037(11)	0.0121(12)	-0.0027(11)
C(4)	0.0370(15)	0.0310(15)	0.0295(14)	-0.0001(11)	0.0061(12)	-0.0022(12)
C(5)	0.0433(17)	0.0386(16)	0.0339(15)	0.0015(12)	0.0108(13)	-0.0105(13)
C(6)	0.0366(16)	0.0419(17)	0.0443(17)	-0.0055(14)	0.0151(14)	-0.0084(13)
C(7)	0.0351(15)	0.0318(15)	0.0374(15)	-0.0049(12)	0.0080(12)	0.0005(12)
C(8)	0.0408(16)	0.0275(14)	0.0338(15)	0.0003(11)	0.0120(13)	0.0011(12)
C(9)	0.060(2)	0.054(2)	0.049(2)	0.0123(16)	0.0153(17)	-0.0214(17)
C(10)	0.082(3)	0.090(3)	0.049(2)	0.020(2)	0.020(2)	-0.026(2)
C(11)	0.133(5)	0.044(2)	0.107(4)	0.023(2)	0.048(3)	-0.014(3)
C(12)	0.069(3)	0.141(5)	0.079(3)	0.042(3)	0.012(2)	-0.052(3)
C(13)	0.0365(17)	0.0437(18)	0.0494(19)	-0.0038(14)	0.0045(14)	0.0032(13)
C(14)	0.053(2)	0.048(2)	0.062(2)	0.0096(18)	-0.0036(18)	0.0095(17)
C(15)	0.049(2)	0.093(3)	0.082(3)	0.001(2)	0.014(2)	0.024(2)
C(16)	0.055(2)	0.050(2)	0.060(2)	-0.0044(18)	-0.0092(18)	0.0037(17)
C(17)	0.0364(15)	0.0290(14)	0.0342(14)	-0.0023(11)	0.0161(12)	-0.0032(11)
C(18)	0.0374(15)	0.0223(13)	0.0344(15)	-0.0062(11)	0.0145(12)	-0.0024(11)
C(19)	0.0423(16)	0.0283(14)	0.0339(15)	-0.0027(11)	0.0159(13)	-0.0012(12)
C(20)	0.0450(17)	0.0265(14)	0.0369(15)	-0.0062(11)	0.0133(13)	-0.0002(12)
C(21)	0.057(2)	0.0331(16)	0.0328(15)	0.0001(12)	0.0096(14)	0.0035(14)
C(22)	0.061(2)	0.0316(16)	0.0383(17)	0.0045(13)	0.0201(15)	-0.0035(14)
C(23)	0.0481(17)	0.0267(14)	0.0388(16)	-0.0046(12)	0.0209(14)	-0.0083(12)
C(24)	0.0395(17)	0.0374(17)	0.0482(18)	-0.0023(14)	0.0090(14)	0.0025(13)
N(2)	0.0368(13)	0.0380(14)	0.0358(13)	-0.0034(11)	0.0128(11)	-0.0023(11)
C(25)	0.0399(17)	0.051(2)	0.0467(18)	-0.0093(15)	0.0160(15)	-0.0054(14)
C(26)	0.076(3)	0.051(2)	0.072(3)	-0.0075(18)	0.047(2)	-0.0092(19)
O(1)	0.093(2)	0.0642(17)	0.0450(14)	-0.0014(12)	0.0316(14)	0.0074(15)
C(27)	0.067(3)	0.082(3)	0.079(3)	0.001(2)	0.033(2)	-0.016(2)
C(28)	0.065(3)	0.074(3)	0.051(2)	-0.002(2)	0.0127(19)	-0.009(2)
O(2)	0.0556(14)	0.0590(15)	0.0352(12)	-0.001(1)	0.014(1)	-0.0031(11)
C(29)	0.064(2)	0.059(2)	0.0283(16)	-0.0007(15)	0.0127(15)	0.0140(18)
C(30)	0.0469(18)	0.064(2)	0.0308(15)	0.0081(14)	0.0177(14)	0.0157(16)
N(3)	0.0337(12)	0.0507(15)	0.0231(11)	-0.0004(11)	0.006(1)	0.0030(11)
C(31)	0.0325(15)	0.0548(19)	0.0281(14)	0.0041(13)	0.0068(12)	0.0034(13)
C(32)	0.0347(15)	0.0487(18)	0.0271(14)	0.0032(13)	0.0077(12)	0.0063(13)
O(3)	0.034(1)	0.0495(12)	0.029(1)	0.0038(9)	0.0112(8)	0.0056(9)
C(33)	0.0390(16)	0.0534(19)	0.0378(16)	0.0037(14)	0.0184(13)	0.0109(14)
C(34)	0.0468(17)	0.0422(17)	0.0364(16)	-0.0017(13)	0.0202(14)	0.0031(14)
O(4)	0.0356(11)	0.0395(11)	0.0359(11)	0.0006(9)	0.0119(9)	-0.0014(9)
C(35)	0.0372(16)	0.0517(19)	0.0432(17)	-0.0088(14)	0.0166(14)	-0.0038(14)

C(36)	0.0449(18)	0.0457(18)	0.0358(16)	-0.0030(13)	0.0147(14)	-0.0074(14)
C(37)	0.0334(16)	0.055(2)	0.0342(16)	0.0028(14)	0.0061(13)	-0.0077(14)
C(38)	0.0359(15)	0.0404(16)	0.0309(14)	0.0012(12)	0.0101(12)	-0.0027(12)
C(39)	0.0361(15)	0.0327(15)	0.0295(14)	-0.0009(11)	0.0121(12)	-0.0017(11)
C(40)	0.0369(15)	0.0257(13)	0.0302(14)	-0.0032(11)	0.0128(12)	-0.0002(11)
C(41)	0.0454(17)	0.0343(15)	0.0277(14)	0.0015(12)	0.0079(12)	-0.0041(13)
C(42)	0.0526(19)	0.0417(18)	0.0415(17)	0.0077(14)	0.0146(15)	-0.0108(15)
C(43)	0.0420(17)	0.0453(18)	0.0446(18)	-0.0000(14)	0.0154(14)	-0.0117(14)
C(44)	0.0359(15)	0.0263(13)	0.0239(13)	-0.0021(11)	0.0082(11)	0.0042(11)
N(4)	0.0272(11)	0.0271(11)	0.0227(11)	-0.0006(8)	0.0071(9)	0.0018(9)
C(45)	0.0296(13)	0.0297(14)	0.0257(13)	-0.004(1)	0.0094(11)	-0.0000(11)
C(46)	0.0317(13)	0.0298(14)	0.0200(12)	-0.004(1)	0.009(1)	0.0009(11)
C(47)	0.0326(14)	0.0331(15)	0.0274(13)	-0.0001(11)	0.0125(11)	-0.0027(11)
C(48)	0.0296(14)	0.0414(16)	0.0309(14)	-0.0021(12)	0.0091(12)	-0.0051(12)
C(49)	0.0321(15)	0.0410(16)	0.0316(15)	0.0061(12)	0.0035(12)	-0.0003(12)
C(50)	0.0392(16)	0.0338(15)	0.0294(14)	0.0025(11)	0.0065(12)	-0.0021(12)
C(51)	0.0309(14)	0.0307(14)	0.0289(14)	-0.0043(11)	0.0078(11)	-0.0044(11)
C(52)	0.0310(15)	0.0502(19)	0.0379(16)	0.0034(14)	0.0071(13)	-0.0060(13)
C(53)	0.047(2)	0.078(3)	0.050(2)	-0.0086(18)	0.0216(17)	-0.0218(18)
C(54)	0.0475(19)	0.061(2)	0.055(2)	-0.0158(17)	0.0147(17)	-0.0120(17)
C(55)	0.0374(18)	0.065(2)	0.051(2)	0.0050(17)	0.0016(15)	-0.0121(16)
C(56)	0.0521(19)	0.0361(17)	0.0389(17)	0.0100(13)	0.0021(14)	-0.0047(14)
C(57)	0.078(3)	0.062(3)	0.068(3)	0.033(2)	-0.012(2)	-0.032(2)
C(58)	0.117(4)	0.039(2)	0.067(3)	0.0078(18)	0.026(3)	0.016(2)
C(59)	0.055(2)	0.047(2)	0.0431(18)	0.0128(15)	0.0090(16)	-0.0017(16)
C(60)	0.0256(13)	0.0299(14)	0.0257(13)	-0.0025(11)	0.007(1)	0.001(1)
O(100)	0.106(3)	0.113(3)	0.140(4)	-0.016(3)	0.031(3)	0.001(3)
C(101)	0.126(5)	0.107(5)	0.123(5)	-0.008(4)	0.025(4)	-0.042(4)

Table F.6.5: Bond lengths (Å)
(geometrically-positioned H atoms have been excluded)

Cu(1) - S(1)	2.3032(8)	C(28) - O(2)	1.414(5)
Cu(1) - S(2)	2.2883(8)	O(2) - C(29)	1.428(4)
Cu(1) - S(3)	2.2952(8)	C(29) - C(30)	1.495(5)
Cu(1) - S(4)	2.2855(8)	C(30) - N(3)	1.460(4)
S(1) - C(1)	1.729(3)	N(3) - C(31)	1.478(4)
S(2) - C(1)	1.726(3)	N(3) - C(37)	1.462(4)
S(3) - C(60)	1.727(3)	C(31) - C(32)	1.503(4)
S(4) - C(60)	1.726(3)	C(32) - O(3)	1.427(3)
C(1) - N(1)	1.323(3)	O(3) - C(33)	1.418(3)
N(1) - C(2)	1.473(3)	C(33) - C(34)	1.508(4)
N(1) - C(17)	1.470(3)	C(34) - O(4)	1.420(4)
C(2) - C(3)	1.514(4)	O(4) - C(35)	1.425(4)
C(3) - C(4)	1.383(4)	C(35) - C(36)	1.496(5)
C(3) - C(8)	1.399(4)	C(37) - C(38)	1.514(4)
C(4) - C(5)	1.396(4)	C(38) - C(39)	1.392(4)
C(5) - C(6)	1.387(4)	C(38) - C(43)	1.396(4)
C(5) - C(9)	1.532(4)	C(39) - C(40)	1.393(4)

C(6) - C(7)	1.399(4)	C(40) - C(41)	1.393(4)
C(7) - C(8)	1.388(4)	C(40) - C(44)	1.514(4)
C(7) - C(13)	1.537(4)	C(41) - C(42)	1.393(4)
C(9) - C(10)	1.528(6)	C(42) - C(43)	1.385(5)
C(9) - C(11)	1.537(7)	C(44) - N(4)	1.475(3)
C(9) - C(12)	1.524(6)	N(4) - C(45)	1.475(3)
C(13) - C(14)	1.519(5)	N(4) - C(60)	1.320(3)
C(13) - C(15)	1.533(6)	C(45) - C(46)	1.511(4)
C(13) - C(16)	1.531(5)	C(46) - C(47)	1.393(4)
C(17) - C(18)	1.515(4)	C(46) - C(51)	1.391(4)
C(18) - C(19)	1.397(4)	C(47) - C(48)	1.398(4)
C(18) - C(23)	1.389(4)	C(48) - C(49)	1.395(4)
C(19) - C(20)	1.395(4)	C(48) - C(52)	1.542(4)
C(20) - C(21)	1.389(4)	C(49) - C(50)	1.393(4)
C(20) - C(24)	1.513(4)	C(50) - C(51)	1.394(4)
C(21) - C(22)	1.387(5)	C(50) - C(56)	1.530(4)
C(22) - C(23)	1.391(4)	C(52) - C(53)	1.514(5)
C(24) - N(2)	1.463(4)	C(52) - C(54)	1.543(5)
N(2) - C(25)	1.464(4)	C(52) - C(55)	1.526(5)
N(2) - C(36)	1.468(4)	C(56) - C(57)	1.513(5)
C(25) - C(26)	1.498(5)	C(56) - C(58)	1.524(6)
C(26) - O(1)	1.431(5)	C(56) - C(59)	1.538(5)
O(1) - C(27)	1.416(5)	O(100) - C(101)	1.403(7)
C(27) - C(28)	1.487(6)	O(1) - O(100)	2.767(5)

Table F.6.6: Bond angles (°)
(geometrically-positioned H atoms have been excluded)

S(1) - Cu(1) - S(2)	77.90(3)	O(1) - C(27) - C(28)	113.1(3)
S(1) - Cu(1) - S(3)	177.67(3)	C(27) - C(28) - O(2)	110.5(3)
S(2) - Cu(1) - S(3)	101.84(3)	C(28) - O(2) - C(29)	112.5(3)
S(1) - Cu(1) - S(4)	102.19(3)	O(2) - C(29) - C(30)	110.7(3)
S(2) - Cu(1) - S(4)	177.88(3)	C(29) - C(30) - N(3)	113.6(3)
S(3) - Cu(1) - S(4)	77.98(3)	C(30) - N(3) - C(31)	113.0(2)
Cu(1) - S(1) - C(1)	83.80(9)	C(30) - N(3) - C(37)	111.9(2)
Cu(1) - S(2) - C(1)	84.32(9)	C(31) - N(3) - C(37)	112.6(2)
Cu(1) - S(3) - C(60)	84.25(9)	N(3) - C(31) - C(32)	109.8(2)
Cu(1) - S(4) - C(60)	84.55(9)	C(31) - C(32) - O(3)	107.3(2)
S(1) - C(1) - S(2)	113.31(15)	C(32) - O(3) - C(33)	112.2(2)
S(1) - C(1) - N(1)	123.1(2)	O(3) - C(33) - C(34)	109.7(2)
S(2) - C(1) - N(1)	123.5(2)	C(33) - C(34) - O(4)	113.8(2)
C(1) - N(1) - C(2)	122.4(2)	C(34) - O(4) - C(35)	112.8(2)
C(1) - N(1) - C(17)	122.3(2)	O(4) - C(35) - C(36)	110.7(2)
C(2) - N(1) - C(17)	115.3(2)	N(2) - C(36) - C(35)	113.6(3)
N(1) - C(2) - C(3)	111.6(2)	N(3) - C(37) - C(38)	112.1(2)
C(2) - C(3) - C(4)	120.0(2)	C(37) - C(38) - C(39)	119.8(3)
C(2) - C(3) - C(8)	120.4(2)	C(37) - C(38) - C(43)	121.3(3)
C(4) - C(3) - C(8)	119.6(3)	C(39) - C(38) - C(43)	118.8(3)
C(3) - C(4) - C(5)	121.6(3)	C(38) - C(39) - C(40)	121.4(3)

C(4) - C(5) - C(6)	117.3(3)	C(39) - C(40) - C(41)	119.1(3)
C(4) - C(5) - C(9)	119.6(3)	C(39) - C(40) - C(44)	119.1(2)
C(6) - C(5) - C(9)	123.1(3)	C(41) - C(40) - C(44)	121.7(2)
C(5) - C(6) - C(7)	122.8(3)	C(40) - C(41) - C(42)	119.9(3)
C(6) - C(7) - C(8)	118.2(3)	C(41) - C(42) - C(43)	120.5(3)
C(6) - C(7) - C(13)	119.2(3)	C(38) - C(43) - C(42)	120.3(3)
C(8) - C(7) - C(13)	122.6(3)	C(40) - C(44) - N(4)	113.2(2)
C(3) - C(8) - C(7)	120.4(3)	C(44) - N(4) - C(45)	115.4(2)
C(5) - C(9) - C(10)	109.5(3)	C(44) - N(4) - C(60)	122.5(2)
C(5) - C(9) - C(11)	107.8(3)	C(45) - N(4) - C(60)	122.0(2)
C(10) - C(9) - C(11)	109.3(4)	N(4) - C(45) - C(46)	112.3(2)
C(5) - C(9) - C(12)	112.5(3)	C(45) - C(46) - C(47)	121.0(2)
C(10) - C(9) - C(12)	109.1(4)	C(45) - C(46) - C(51)	119.1(2)
C(11) - C(9) - C(12)	108.5(4)	C(47) - C(46) - C(51)	120.0(2)
C(7) - C(13) - C(14)	112.5(3)	C(46) - C(47) - C(48)	120.3(2)
C(7) - C(13) - C(15)	109.7(3)	C(47) - C(48) - C(49)	118.1(3)
C(14) - C(13) - C(15)	108.3(3)	C(47) - C(48) - C(52)	120.1(3)
C(7) - C(13) - C(16)	107.7(3)	C(49) - C(48) - C(52)	121.8(2)
C(14) - C(13) - C(16)	108.6(3)	C(48) - C(49) - C(50)	122.9(3)
C(15) - C(13) - C(16)	110.0(3)	C(49) - C(50) - C(51)	117.4(3)
N(1) - C(17) - C(18)	112.6(2)	C(49) - C(50) - C(56)	120.2(3)
C(17) - C(18) - C(19)	119.8(2)	C(51) - C(50) - C(56)	122.4(3)
C(17) - C(18) - C(23)	120.7(3)	C(46) - C(51) - C(50)	121.3(2)
C(19) - C(18) - C(23)	119.5(3)	C(48) - C(52) - C(53)	111.0(3)
C(18) - C(19) - C(20)	121.0(3)	C(48) - C(52) - C(54)	107.9(3)
C(19) - C(20) - C(21)	118.6(3)	C(53) - C(52) - C(54)	109.0(3)
C(19) - C(20) - C(24)	119.6(3)	C(48) - C(52) - C(55)	112.7(3)
C(21) - C(20) - C(24)	121.8(3)	C(53) - C(52) - C(55)	110.3(3)
C(20) - C(21) - C(22)	121.0(3)	C(54) - C(52) - C(55)	105.7(3)
C(21) - C(22) - C(23)	120.0(3)	C(50) - C(56) - C(57)	112.1(3)
C(18) - C(23) - C(22)	120.0(3)	C(50) - C(56) - C(58)	107.8(3)
C(20) - C(24) - N(2)	112.3(2)	C(57) - C(56) - C(58)	110.1(4)
C(24) - N(2) - C(25)	112.6(2)	C(50) - C(56) - C(59)	110.0(3)
C(24) - N(2) - C(36)	111.9(2)	C(57) - C(56) - C(59)	107.0(3)
C(25) - N(2) - C(36)	113.1(2)	C(58) - C(56) - C(59)	109.8(3)
N(2) - C(25) - C(26)	113.1(3)	S(3) - C(60) - S(4)	113.16(15)
C(25) - C(26) - O(1)	110.7(3)	S(3) - C(60) - N(4)	123.5(2)
C(26) - O(1) - C(27)	116.7(3)	S(4) - C(60) - N(4)	123.29(19)

¹ Z. Otwinowski, W. Minor, in *Processing of X-ray Diffraction Data Collected in Oscillation Mode, Methods Enzymol.*, ed. C. W. Carter, R. M. Sweet, Academic Press, 1997, 276.

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Appendix G: Glossary

~	approximately
°	degrees
°C	degrees Celcius
1D-EXSY	one-dimensional excitation spectroscopy
¹ H	proton
A	ampere
Å	angstrom
A ⁻	anion
AcOH	acetic acid
AIBN	1,1'-azobis(cyclohexanecarbonitrile)
AMP	adenosine monophosphate
aq	aqueous
Ar	aromatic
atm	atmosphere
ATP	adenosine triphosphate
BOC	<i>t</i> -butoxycarbonyl
BOC-anhydride	di- <i>t</i> -butyl-dicarbonate
bpy	2,2'-bipyridine
br	broad
C	coulomb
C ₃	symmetry element
cm	centimetre
conc.	concentrated
COSY	correlation spectroscopy

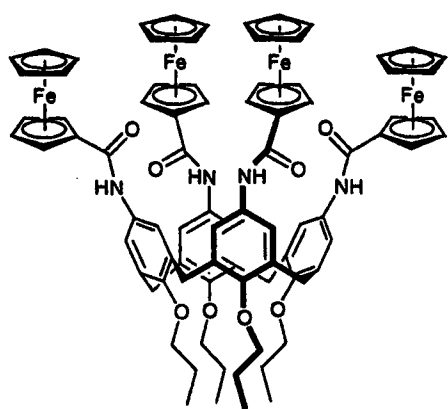
Cu(dtcEt ₂) ₂	copper(II) bis(<i>N,N</i> -diethyl-dithiocarbamate)
CV	cyclic voltammetry / voltammogram
d	doublet
DMAP	4-dimethylaminopyridine
dmf	<i>N,N</i> -dimethylformamide
DMSO	dimethylsulphoxide
E	potential
E _½	half-wave potential
EC	electrochemical – chemical
EDC	1-(3-(dimethylamino)propyl)-3-ethyl-carbodiimide
en	ethylenediamine
E _{pa}	anodic peak potential
E _{pc}	cathodic peak potential
eq	equivalent
ESMS	electrospray mass spectrometry
Et(ⁱ Pr) ₂ N	ethyldiisopropylamine
Et ₂ O	diethylether
Et ₃ N	triethylamine
EtOH	ethanol
FAB-MS	fast atom bombardment mass spectrometry
FTIR	fourier transform infrared spectroscopy
g	gram or gaseous
HPLC	high performance liquid chromatography
Hz	hertz
I	current

I_{pa}	anodic peak current
I_{pc}	cathodic peak current
J	coupling constant
K	stability constant or Kelvin
kJ	kilojoules
KO ^t Bu	potassium <i>t</i> -butoxide
L	litre
LC	ligand centred
LMCT	ligand to metal charge transfer
M	molar, mega or molecular ion
m	multiplet or milli
m/z	mass to charge ratio
MC	metal centred
MLCT	metal to ligand charge transfer
mol	mole
n	number of electrons or normal
NBS	<i>N</i> -bromosuccinimide
ⁿ BuLi	<i>n</i> -butyl lithium
Ni(dtcEt ₂) ₂	nickel(II) bis(<i>N,N</i> -diethyl-dithiocarbamate)
nm	nanometre
NMR	nuclear magnetic resonance
ⁿ PrI	<i>n</i> -propyl iodide
OAc	acetate
obs	observation
Ph ₂ O	diphenylether

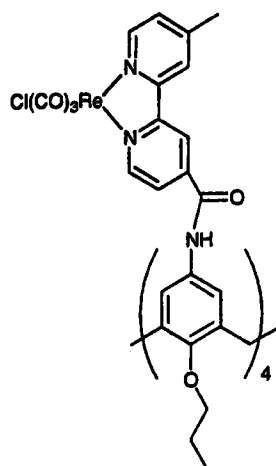
ppm	parts per million
q	quartet
quint	quintet
R^2	measure of linearity
RNA	ribonucleic acid
s	singlet or second
SAM	self-assembled monolayer
sext	sextet
sh	shoulder
SPR	surface plasmon resonance
sqrt	square root
SWV	square wave voltammetry / voltammogram
t	triplet or tertiary
t_1	relaxation rate
TBA	tetrabutylammonium
TEM	tunnelling electron microscopy
TFA	trifluoroacetic acid
thf	tetrahydrofuran
t_m	delay time
TMEDA	<i>N,N,N',N'</i> -tetramethylethylenediamine
tren	triethylenediamine
UV-VIS	ultraviolet – visible
V	volt
v/v	volume for volume
w/v	weight for volume

wrt	with respect to
XPS	X-ray photoelectron spectroscopy
x_R	mole fraction
Δ	change
β	overall stability constant
δ	chemical shift
ε	molar extinction coefficient
λ	wavelength
μ	micro

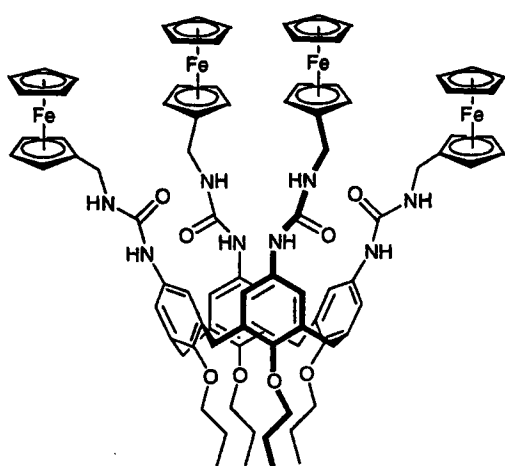
Appendix H: Summary of Receptors for Chapter Two



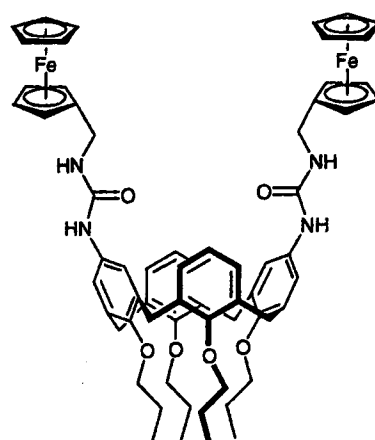
tetra(Fcamide)calix 19



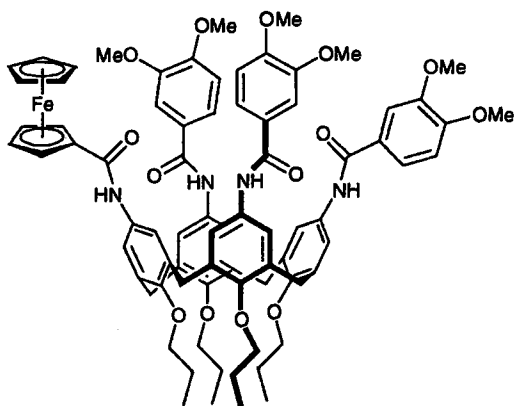
tetra(Rebpy)calix 21



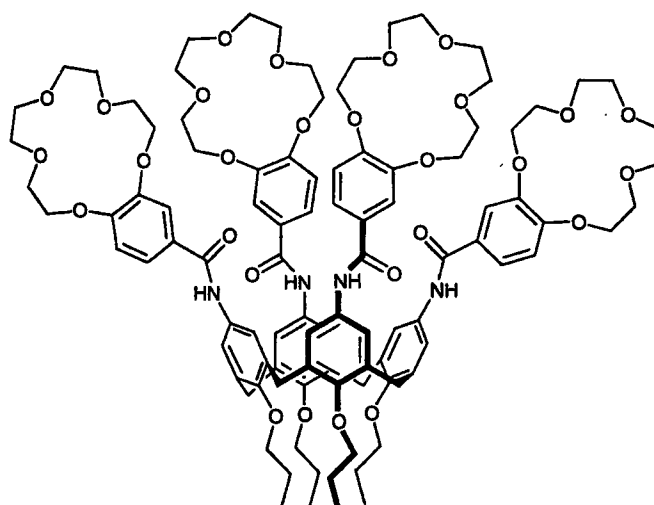
tetra(Fcurea)calix 23



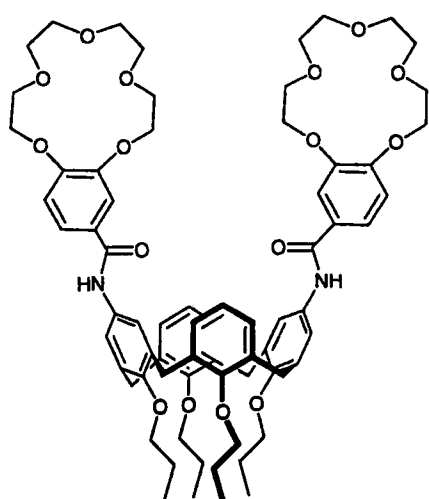
bis(Fcurea)calix 26



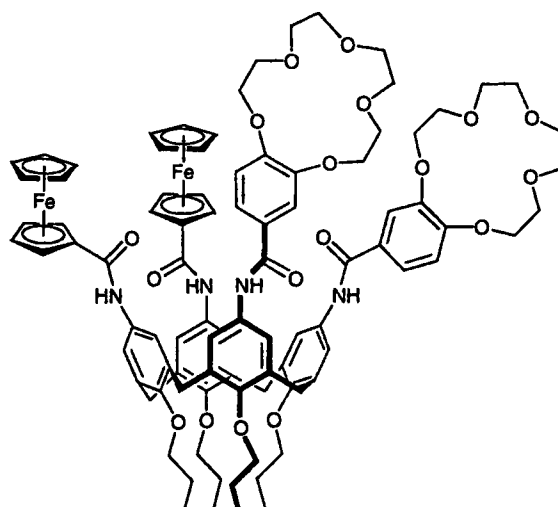
Fctri(benzo)calix 31



tetra(crown)calix 22

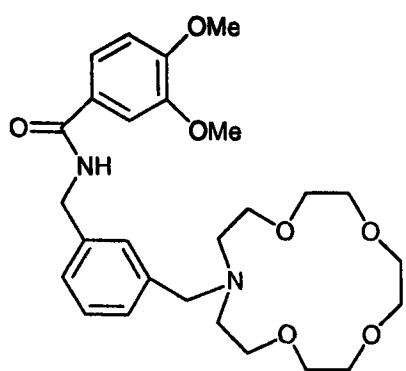


bis(crown)calix 25

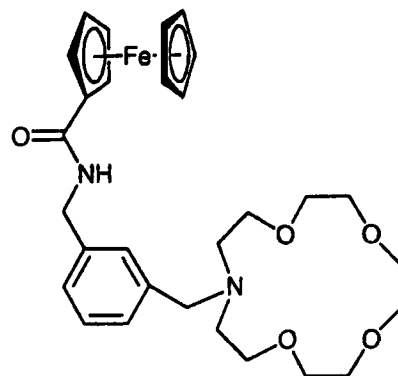


bisFc bis(crown)calix 36

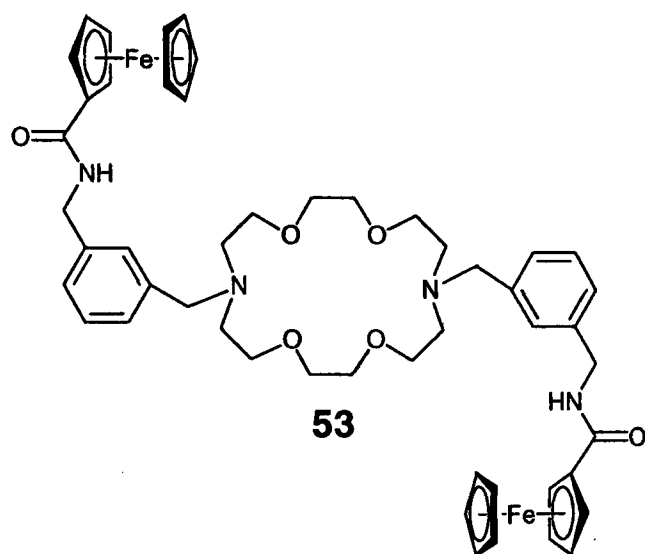
Appendix I: Summary of Receptors for Chapter Three



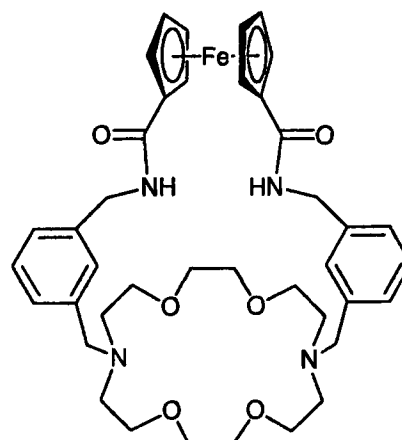
49



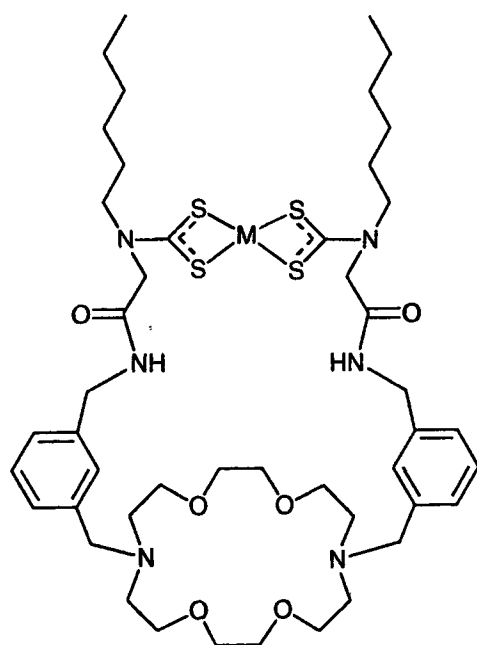
50



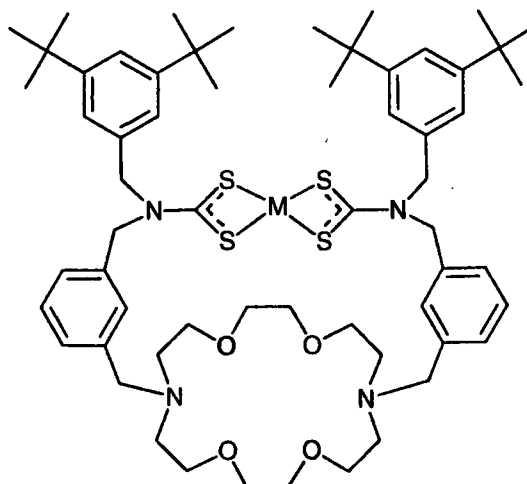
53



58



61 (M = Ni) 62 (M = Cu)



66 (M = Ni) 67 (M = Cu)

Appendix J: Summary of Receptors for Chapter Four

