

Supramolecular Chemistry Using the Dithiocarbamate Ligand *(Volume II)*

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Glossary of Terms

A	Ampere, Adenine or hyperfine coupling constant (EPR)
Å	Angstrom
AIBN	2,2'-Azobib(2-methyl-propionitrile)
Aliquat	Methyltrioctylammonium chloride
aq	Aqueous
Ar	Aryl
Boc	<i>tert</i> -Butoxycarbonyl
br	Broad
bipy	2,2'-Bipyridine
Bu	<i>n</i> -Butyl
C	Cytosine
chex	Cyclohexyl
CPK	Corey-Pauling-Koltun
CTV	Cyclotrimeratrylene
d	Doublet
dd	Doublet of doublets
DMA	<i>N,N'</i> -Dimethyl acetamide
DMF	<i>N,N'</i> -Dimethyl formamide
DMSO	Dimethyl sulphoxide
DNA	Deoxyribonucleic acid
dt	Doublet of triplets
dtc	<i>N,N'</i> -Diethyldithiocarbamate

$E_{1/2}$	Half wave potential
E_{pa}	Anodic peak potential
E_{pc}	Cathodic peak potential
ϵ	Molar extinction coefficient
en	1,2-ethylenediamine
EDC1	3-Ethyl-1-[3(dimethylamino)propyl]carbodiimide
EIMS	Electron Impact Mass Spectrometry
ESMS	Electrospray Ionisation Mass Spectrometry
FAB	Fast Atom Bombardment
G	Guanine
g	Spectroscopic splitting factor
hex	<i>n</i> -Hexyl
HSAB	Hard and soft acids and bases theory
HS/LS	High spin/ low spin
HSQC	Heteronuclear single-quantum correlated spectroscopy
Hz	Hertz
J	Coupling constant (NMR)
K	Stability Constant
k	Boltzmann's constant ($1.38 \times 10^{-23} \text{ JK}^{-1}$)
L	Ligand
LC	Ligand centred
LFSE	Ligand field stabilisation energy
LMCT	Ligand to metal charge transfer
M	Molar (moles litre^{-1})
$[M]^+$	Molecular ion

m	Multiplet
MALDI-TOF	Matrix-assisted laser desorption ionisation-time of flight
MLCT	Metal to ligand charge transfer
mol	Moles
m/z	Mass-to-charge ratio
MRI	Magnetic Resonance Imaging
NBS	<i>N</i> -Bromosuccinimide
NMR	Nuclear Magnetic Resonance
q	Quartet
s	Singlet
sh	Shoulder
T	Thymine/ Tetrahedron/ Temperature (K)
TBA	Tetra- <i>n</i> -butylammonium
TEM	Transmission electron microscopy
TFA	Trifluoroacetic acid
TLC	Thin Layer Chromatography
TTF	Tetrathiafulvalene
UV-vis	Ultraviolet-visible

Chapter Six

Gold and Silver Nanoparticle

Chemistry

Chapter Six: Gold and Silver Nanoparticle Chemistry

1 Introduction

The investigation into nanoparticles (colloids) of both transition metals¹ and inorganic semiconductors^{2,3} has undergone rapid expansion in recent years. This development is primarily the result of the unique properties resulting from the size of such particles, intermediate between the molecular level and that of bulk matter. In addition, the development in the 1980s of transmission electron microscopy (TEM) has allowed the visualisation of the size, shape, dispersity, structure and morphology of these particles⁴. Interest in the properties of such materials has attracted the attention of a variety of scientific disciplines, such as physics, chemistry, engineering and biology⁵. Such wide ranging research aims to systematically organise and manipulate matter on the nanometre length scale, thus opening the way for their use in the development of functional nanotechnological devices. In addition, there is significant industrial interest in the use of nanoparticles for both decorative and catalytic purposes. The work within this Chapter describes the investigation into gold and silver nanoparticles, which will now be explored further.

1.1 Transition Metal Nanoparticles

The synthesis of colloidal metals is by no means new. As far back as ancient times, colloidal gold was being used to make ruby glass and for the colouring of ceramics. Often alcoholic solutions were prescribed for tonics and elixirs, as well as for the treatment of arthritis⁶. The more scientific exploration of these clusters can be traced back to work performed by Faraday in the mid-nineteenth century⁷. He demonstrated the formation of deep red colloidal solutions through the reduction of tetrachloroaurate salts with elemental phosphorous. Despite continued research over the course of the following century⁸, it is only now with the advent of

new technologies, that a renaissance in its chemistry is occurring.

Transition metal nanoparticles are typically less than 10nm (100Å) in diameter and occur as a central core of metal atoms (typically between 55 and 3000 atoms) surrounded by a coating of protective ligands. Nanoparticles are only kinetically stable in solution since they are unstable with respect to agglomeration into larger materials, and eventually into the thermodynamic product, the bulk material. Agglomeration is prevented through the use of protective ligands which shield the metal core through steric and/or electrostatic barriers (Figure 1). There are several methods in which this protection may be achieved. The use of bulky ligands such as polymers and long-chained phosphines or thiols has been a successful method for the prevention of aggregation. Although such particles are attracted together by favourable van der Waals' forces, at short intramolecular distances agglomeration is prevented by the interpenetration of the long chains of the stabilising ligands being unfavourable. This is both a result of the decrease in entropy and the increase in osmotic pressure that this generates. Similarly, the formation of nanoparticles stabilised by charged ligands also prevents agglomeration. This is a result of electrostatic repulsions between the resultant electrostatic double layers of the nanoparticles. The combination of both electrostatic repulsions and steric bulk has also been employed via the use of surfactants to stabilise colloidal growth.

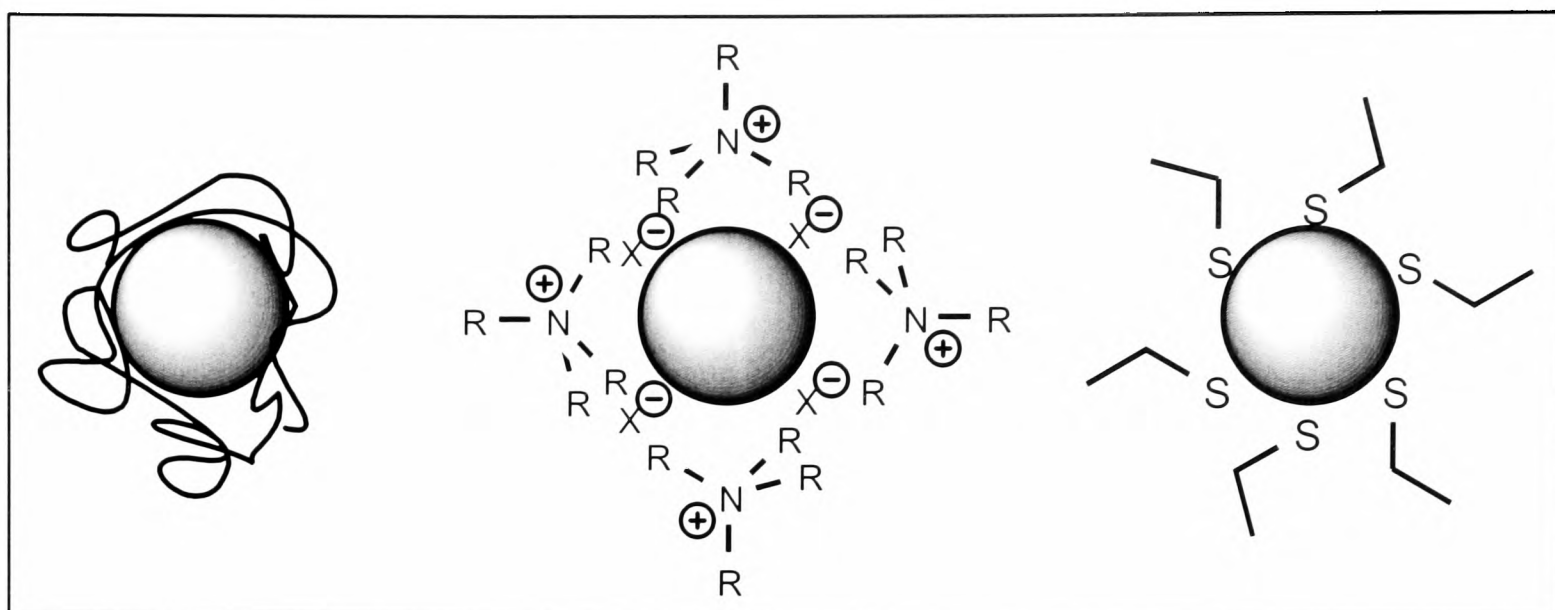


Figure 1 Nanoparticle protection: (left) polymers, (centre) surfactants, (right) donor ligands

The resultant protected nanoparticles are both stable in air and in solution, and furthermore are able to be isolated as powders and subsequently redissolved. In addition, it is possible to perform chemical reactions on the subsequent particle, for example, ligand-exchange reactions and the treatment of free functional groups of the ligand are both facile.

1.2 Uses of Nanoparticles

Much of the interest in nanoparticles is a result of their size and properties lying somewhere between those of bulk and single-particle species⁹. One of the most attractive features about nanoparticles is that the electrons within the structure are confined to a small area of space, possibly as low as just a few atoms across¹⁰. This electronic restriction has resulted in the observation of quantum size effects within nanoparticles in the range of 1 to 2nm in diameter, with the metallic clusters acting like individual atoms with their own sets of electrons and corresponding wavefunctions^{11,12}. These effects have huge potential to be utilised in the field of microelectronic quantum devices¹³.

Gold nanoparticles, for example, have been demonstrated to act as quantum dots² – a zero-dimensional quantum device whose response is based upon single-electron processes¹⁰. In theory, quantum dots may be used to create tiny computing architectures through switching of electrons between binary states in manipulated regularly spaced nanoparticle arrays. These

devices offer computing speed and power far beyond that of conventional binary devices¹⁴. Due to the quantum nature of electrons, it is possible that 1000 quantum dots may be able to hold 2^{1000} bits of data simultaneously¹⁵. The immense power of this is highlighted by the fact that it would not be possible to store such a vast amount of data upon conventional binary computers, since the 2^{1000} bits that would be required is greater than the number of atoms in the known universe. This dramatic increase is a result of quantum states being able to be superimposed until the data is read out at the end of a computation.

Much of the work undertaken upon metal nanoparticles has been a result of their unique optical properties. For example, noble metal nanoparticles exhibit very intense colours, which are both absent in the bulk material as well as individual atoms. The origin of this plasmon band is the confinement of the electrons within the particles¹⁶, and this may be modelled using Mie theory¹⁷. These electronic and optical properties of metal nanoparticles have proved particularly attractive in the development of sensors, as changes in the surface composition may lead to a perturbation in the plasmon resonance¹⁸. As illustrated in Chapter One, Mirkin and co-workers have utilised this feature to generate a reversible, colourimetric polynucleotide sensor¹⁹. The aggregation of mercaptoalkyloligonucleotide-functionalised gold nanoparticles leads to a red to blue shift in its absorption spectra, enabling sequence-specific recognition.

The non-toxic nature of gold nanoparticles makes them particularly attractive for medical applications, as does their size similarity with biomolecules²⁰. Nanoparticles may be used as a diagnostic probe (e.g. the imaging of specific organs/cells) with their novel optical, electronic, and magnetic properties enabling this monitoring process^{21,22}. In addition, it is possible to functionalise nanoparticles so they may be used as novel probes for both diagnostic and therapeutic (e.g. drug delivery) purposes^{23,24}.

It is also widely believed that nanoparticles could provide a more effective method of

catalysing a range of chemical reactions. The possibility of nano-dimensional particles being effective catalysts has long been contemplated. In 1907 Otwald considered the surface areas of cubes of iron atoms²⁵. He calculated that for a 1x1x1cm cube, only $10^{-5}\%$ of its atoms reside on the surface. However, where the sides of the theoretical cube are only 2.5nm across, 60% of the total atoms now lie on the surface, a figure that becomes all of the atoms where the cube is merely 1nm across. The use of nano-dimensional catalysts not only offers greater catalytic efficiency, with more available catalytic sites than conventional catalysts, but also may display novel and interesting properties as a result of the lowering of the average coordination numbers throughout the sample.

Metallic gold is the noblest of all metals, and does not react with elements such as hydrogen and oxygen. This is due to unfavourable repulsions between the adsorbate and the filled *d*-orbitals of the metal²⁶. However, the reduction in size of gold clusters to nanodimensions leads to a significant upturn in their catalytic ability²⁷. Gold nanoparticles, when supported on activated carbon or metal oxides²⁸ (to prevent their agglomeration) have lead to the generation of particularly effective catalysts. For example, titanium dioxide supported gold nanoparticles have displayed a high-selectivity catalytic activity for carbon monoxide oxidation at -70°C ²⁹. Careful manipulation of nanoparticles has lead to the development of numerous catalysts for a range of chemical transformations at more ambient temperatures³⁰. Indeed, these catalysts are becoming integrated into everyday living, with the development of nanoparticulate catalytic converters for cars³¹, paints containing nanoparticles to reduce the levels of carbon monoxide in internal environments³² and bizarrely the use of gold nanoparticles in Japan as a toilet deodoriser^{28,33}.

1.3 Templatation

One problem with all the chemical methods used to produce nanoparticles is that they do not produce clusters of a single homogenous size. Clusters that are nominally 10Å in size are in reality a distribution of sizes between, for example, 8 and 12Å, and this dispersity gets larger as the cluster size increases. Yet if researchers are to be able to engineer the properties, they must be able to specify the cluster size. It is therefore a priority to develop metallic nanoparticles of uniform size and shape so they may be further exploited. It is also important to be able to grow nanoparticles in the range of 1 to 2nm as particles of this size have shown significant promise in both the development of quantum dots and active catalysts. One method to achieve this has been through the use of templates to control the growth of nanoparticles.

The use of confined environments has been employed in order to generate monodispersed nanoparticles. Here, the nature of the stabilising ligands provides limited space, thus inhibiting the growth of nanoparticles. A range of stabilisers, for instance dendrimers³⁴, resorcinarenes³⁵, cyclodextrins³⁶ and biomaterials such as alfalfa plant tissues³⁷, have all been used for this purpose.

The aim of the work described in this Chapter is to explore the synthesis of gold and silver nanoparticle assemblies, using a variety of stabilising ligands. The possibility of utilising the nano-dimensional resorcinarene dithiocarbamate complexes, as described in Chapter Three, to template the formation of nanoparticles will also be investigated. Furthermore, attempts to link gold nanoparticles through coordination chemistry will be described.

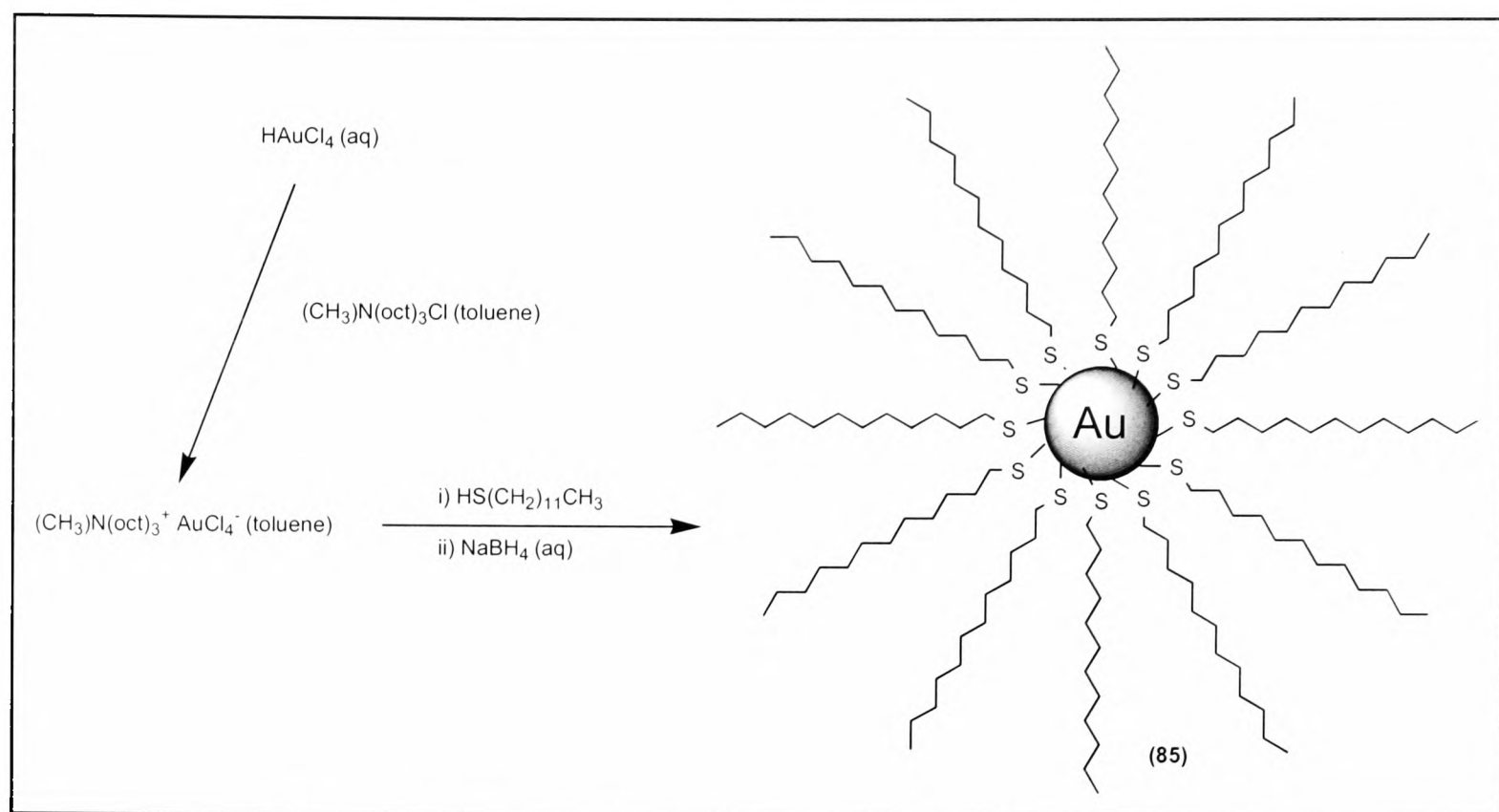
2 Gold Nanoparticles

The synthesis of gold nanoparticles was revolutionised in 1994 by the one-pot preparation devised by Brust *et. al.*³⁸. The gold nanoparticles generated via this method were particularly interesting due to the relatively small dispersity in their sizes. The strategy employed to

synthesise the nanoparticles involved the room temperature, two-phase reduction of a tetrachloroaurate salt in the presence of 1-dodecylthiol. The thiol acts as protective coating for the growing metal particle, preventing its agglomeration. Although the precise nature of the interaction between the sulphur donor ligand and the nanoparticle surface has been the cause of much speculation, it is believed that this is a gold-thiolate interaction³⁹. In addition, the ratio of thiol:gold has been shown to control the size of the resultant cluster. Purification was achieved through selective precipitation, yielding particles whose sizes are predominantly in the range 1 – 3nm.

2.1 Thiol-Stabilised Gold Nanoparticles

Initially, 1-dodecylthiol-stabilised gold nanoparticles (**85**) were prepared using a modification of the original Brust preparation. This was achieved via the phase transfer of the tetrachloroaurate anion from aqueous solution into toluene, using Aliquat®336 (methyltrioctylammonium chloride) as a phase transfer agent. The use of this phase transfer catalyst is favoured over the conventional use of tetra-*n*-octylammonium bromide, due to its lower propensity to associate with the synthesised particles. The thiol (1.8 equivalents) was then added to the vigorously stirred solution. Excess sodium borohydride (aqueous) was then added dropwise to the solution, with the organic layer turning purple instantaneously. The temperature was maintained at 10°C for this stage of the reaction, as lower temperatures encourage small particle growth. Purification was achieved by precipitation of the toluene layer via the addition of methanol, to yield a black powder (Scheme 1).



Scheme 1 Synthesis of 1-dodecylthiol stabilised gold nanoparticles (85)

The black, waxy solid was characterised by a variety of techniques, the most powerful of those being transmission electron microscopy (TEM). This was carried out by Dr. G. Goodlet, Johnson Matthey Technology Centre, Sonning Common. Transmission electron micrographs for the 1-dodecylthiol-stabilised nanoparticles **(85)** at both low- and high-resolution are displayed in Figures 2 and 3 (refer to Appendices Four and Five).

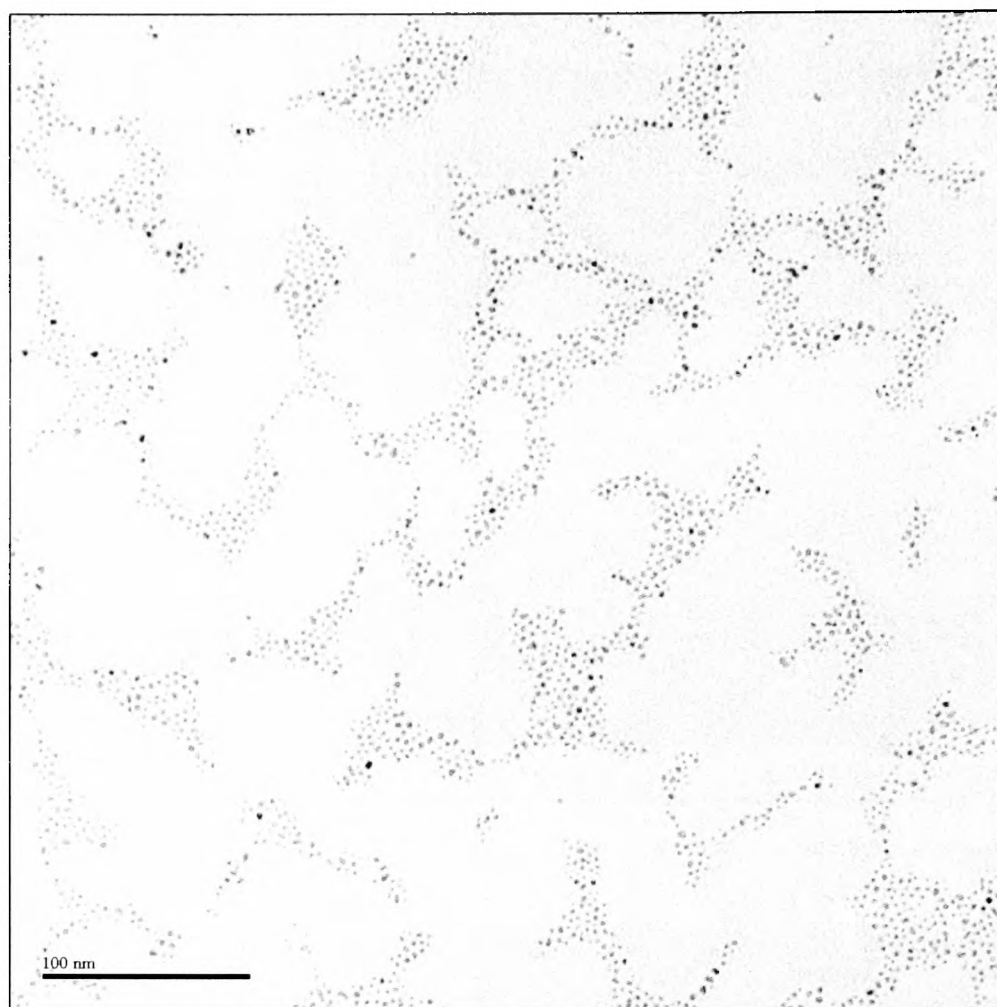


Figure 2 TEM of 1-dodecylthiol-stabilised gold nanoparticles (85) (Scale bar 100nm)

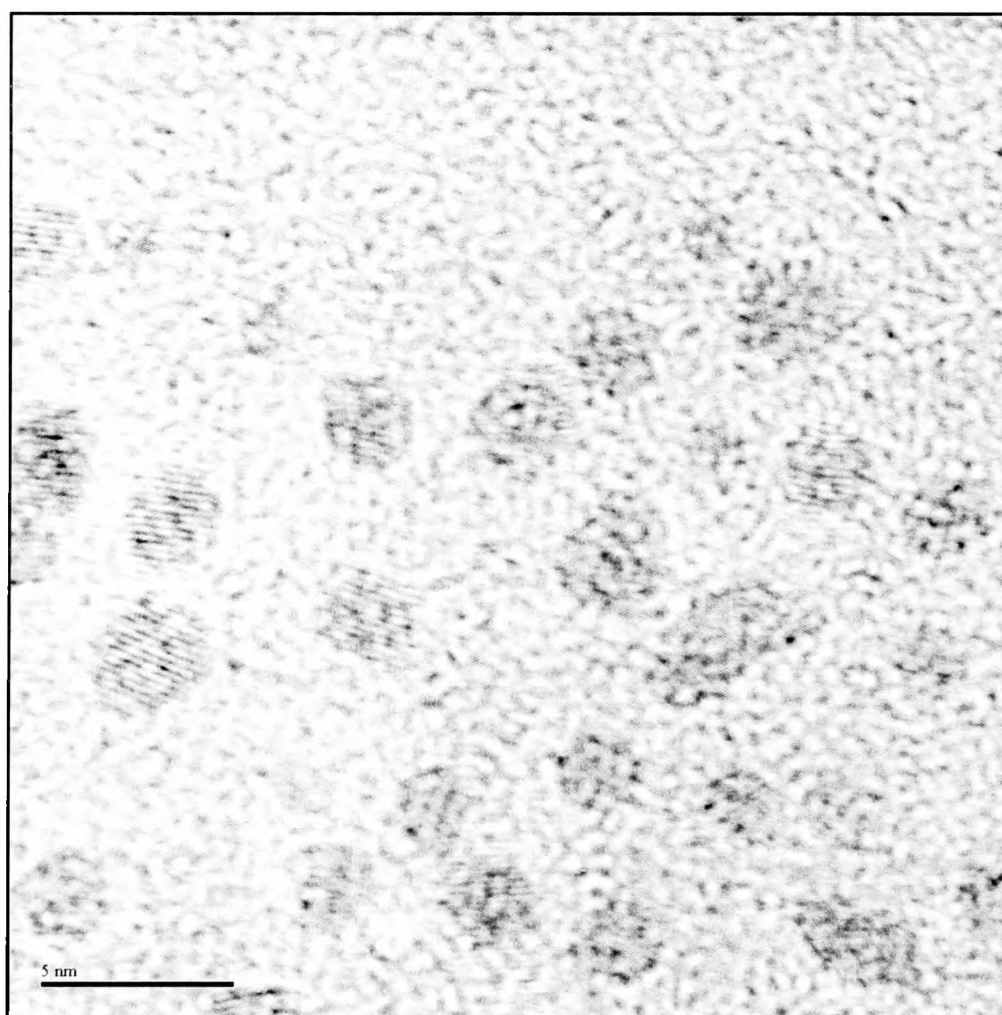


Figure 3 TEM of 1-dodecylthiol-stabilised gold nanoparticle (85) (Scale bar 5nm)

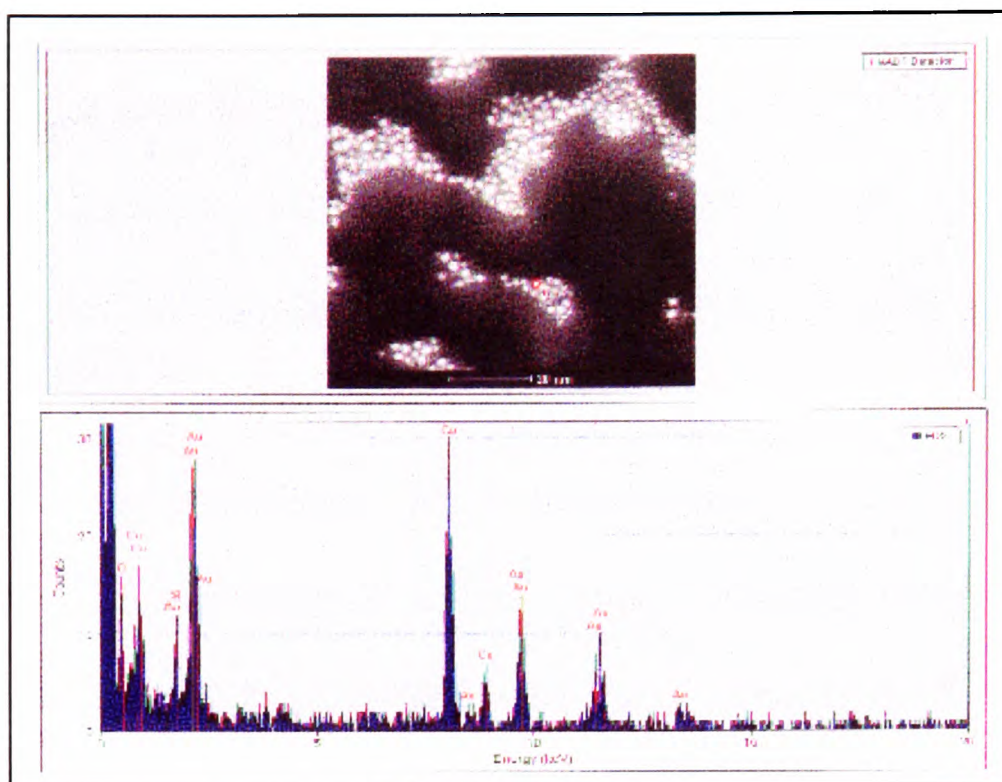


Figure 4 EDX spectrum of (85) (upper) selected gold nanoparticle for analysis

The micrographs show the formation of rounded gold nanoparticles in the range of 1 – 7nm; although having an average diameter of approximately 2nm. At low resolution, the nanoparticles are seen to pack in an approximately hexagonal pattern. Examination of the high-resolution micrograph highlights the high crystallinity of the particles, with the lattice planes of the particles clearly visible.

Visual analysis of the micrographs allows the calculation of the mean and standard deviation of the particles. This not only allows the average size of the nanoparticles to be determined, but also gives an indication of their dispersity. In the case of **(85)**, analysis of a random sample of 53 gold nanoparticles, the mean particle size was found to be 1.9nm with a standard deviation of 0.7nm. This is in agreement with Brust's original findings that this method produces small nanoparticles with a high monodispersity.

Proof that these particles are gold nanoparticles is obtained by energy dispersive X-ray spectroscopy (EDX). Here, selective electron bombardment of a single, chosen particle in the electron microscope, results in the emission of characteristic X-rays from the elements present. Not only does this characterise the particle's composition, but the relative intensities of the peaks are also proportional to their concentration within the colloid (Figure 4).

The nanoparticles are shown to consist of gold with a smaller concentration of sulphur also being present (the presence of copper peaks are a result of the copper grid the experiment is performed upon). Elemental analysis upon the nanoparticle **(85)** revealed proportions of carbon, hydrogen and gold consistent with the formation of a particle with approximately three thiol ligands for every eleven gold atoms. The absence of any nitrogen and the ratio of C:H also indicated the nanoparticles were stabilised by the thiol ligands, and not the Aliquat phase transfer catalyst. Assuming the particles have an average diameter of 2.0nm, then a typical particle is formed from approximately 150 gold atoms^{40,41}. This core is then surrounded by 40 thiol ligands, resulting in an approximate molecular mass of 37000Da.

This is further confirmed by the observation of the UV-vis spectrum of the gold nanoparticles. This revealed a weak plasmon band at 506nm, which is consistent with the formation of particles of this size. In general, for spherical gold nanoparticles, the more prominent and the larger the wavelength of the plasmon band, the larger the diameter of the particles^{42,43}. The sample was also analysed by both ¹H and ¹³C NMR spectroscopy, although the typically broad spectra were not terribly informative.

2.2 Other Thiol-Stabilised Gold Nanoparticles

In addition to the synthesis of 1-dodecylthiol-stabilised gold nanoparticles, preparation of gold nanoparticles stabilised by shorter chained ester-derivatised thiols were also attempted. Such structures are of industrial interest as they have been shown to generate high quality gold films on ceramics. The presence of an ester group upon the ligand surrounding the gold nanoparticle also allows the potential functionalisation of these particles. The preparation of ethyl-2-mercaptopropionate- and 2-mercaptoethyl acetate-stabilised gold nanoparticles **(86)** and **(87)** was therefore undertaken.

An analogous method was used for the generation of **(86)** and **(87)** as for the synthesis of the

1-dodecylthiol-stabilised gold nanoparticles (**85**). Dropwise addition of aqueous sodium borohydride to a toluene solution of the stabilising ligand and the tetrachloroaurate salt generated a purple solution which was subsequently precipitated with methanol to yield a black solid.

It was discovered that the rate of addition of the borohydride greatly affected the growth of the nanoparticle. Where addition occurred slowly (over a one hour period) a very low yield was achieved for the overall reaction with significant amounts of insoluble (extremely large) nanoparticles occurring. More rapid addition of the borohydride (over ten minutes), however, resulted in a much greater yield. This is believed to be due to the greater nucleation from the relatively rapid addition of reductant leading to the formation of many small particles. Slower addition generates fewer nucleation sites, and hence, a smaller number of larger nanoparticles are formed.

Both (**86**) and (**87**) were characterised by transmission electron microscopy, revealing the formation of gold nanoparticles in the range of 1 – 10nm, typically 4nm. However, in the case of (**87**) where a short, unbranched thiol is used, a degree of agglomeration between the nanoparticles is observed. This is likely to be a result of the lack of steric bulk of this ligand.

The particles were also analysed by elemental analysis, which showed the C:H ratio was consistent with the presence of the protecting ligand. Due to the poor solubility of these particles, it was not, however, possible to analyse the proportion of gold within these compounds and hence obtain a ratio of the stabilising ligand:gold present.

The UV-vis spectra of both (**86**) and (**87**) were recorded in toluene solution. The spectrum of (**87**) is characteristic of a spherical gold nanoparticle that is less than 5nm in diameter and is displayed in Figure 5. The baseline is broad (typical of colloidal species) and the shoulder at 510nm is the plasmon band. The relatively small intensity and wavelength of this peak is characteristic of the formation of small particles.

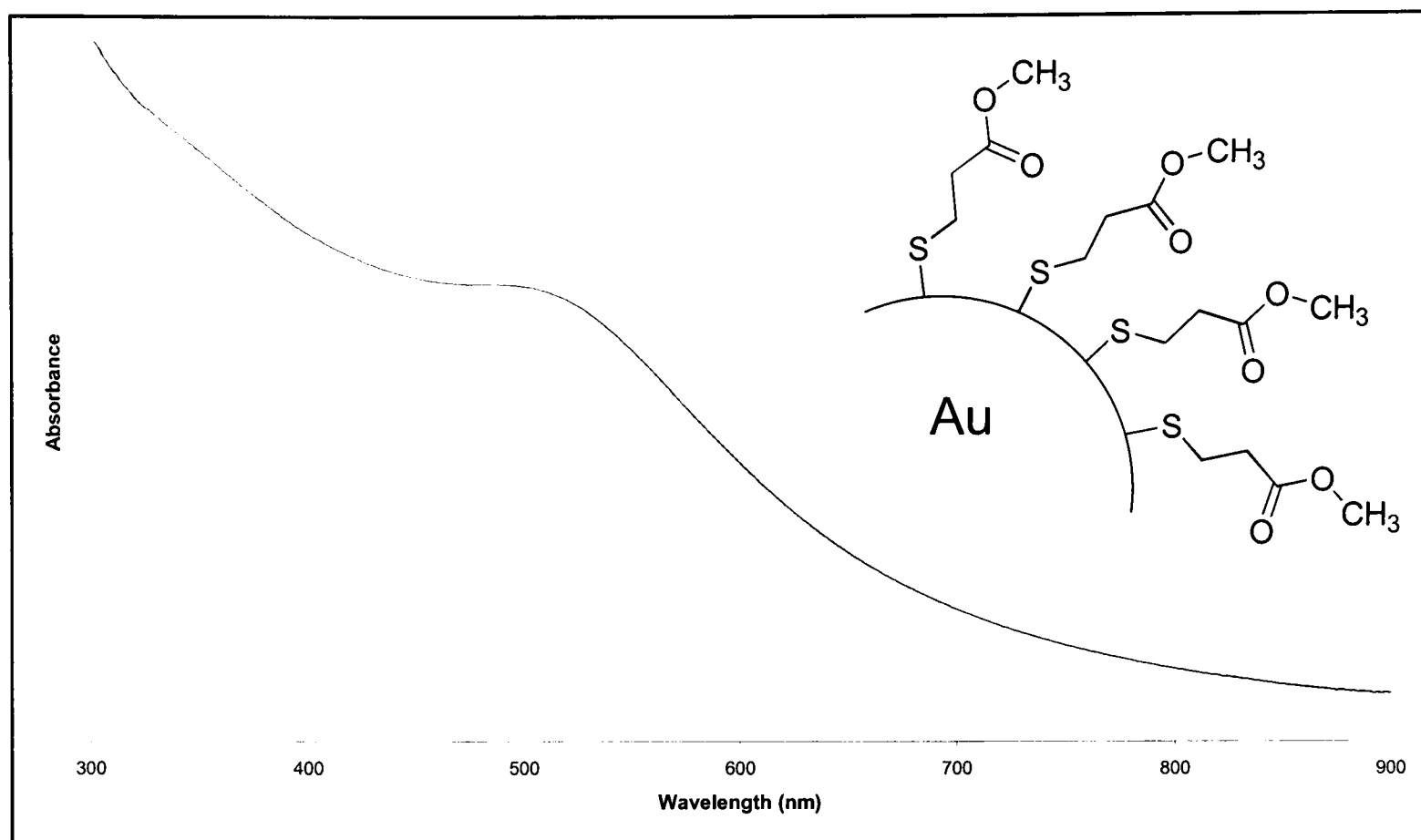


Figure 5 UV-vis spectrum of thiol-stabilised gold nanoparticle (87) recorded in toluene at 293K

The nanoparticles were further characterised by ^1H and ^{13}C NMR spectroscopy. Both (86) and (87) gave typically broad spectra. The ^1H NMR spectrum of (86) is displayed in Figure 6.

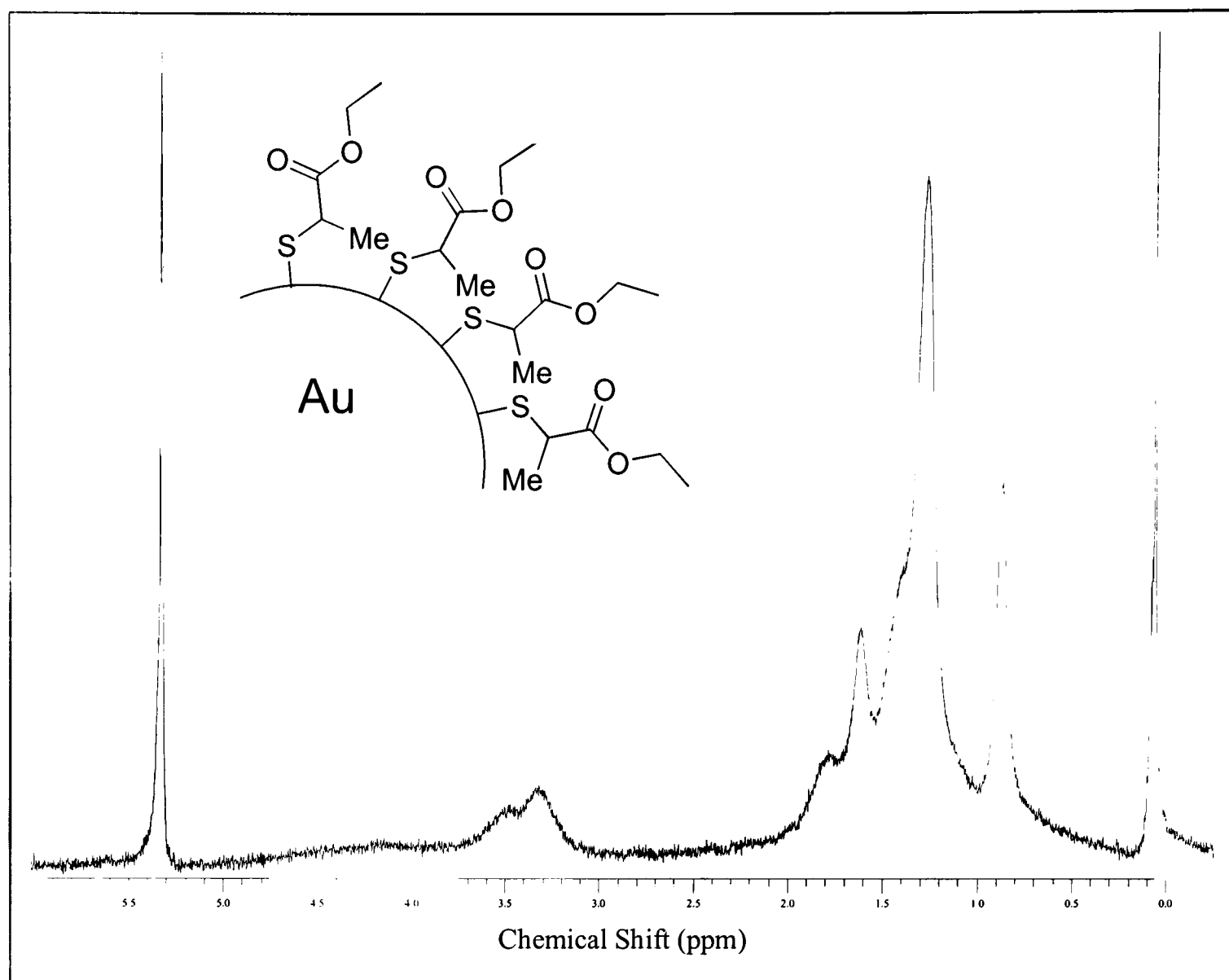


Figure 6 ^1H NMR of ethyl-2-mercaptopropionate-stabilised gold nanoparticles (86) (300MHz, CD_2Cl_2 , 293K)

The resulting spectra show broad resonances corresponding to the thiol ligands. The resonance at $\sim 3.4\text{ppm}$ is probably the result of the *CH* proton adjacent to the thiol group. The appearance of this peak as two broad peaks is possibly due to the chiral nature of the proton. The remainder of the signals appear as a collection of broad resonances at $2.0 - 0.7\text{ppm}$. The resonances are observed to be shifted to lower chemical shifts in both the carbon and proton spectra, in comparison to the free ligand, due to their adsorption onto the electron-rich gold surface. The broadness of the resulting peaks is a consequence of both the restricted rotation in solution and the variety of environments the ligands may encounter on the gold surface (e.g. surface edges, vertexes and terraces). Variable temperature experiments upon these nanoparticles failed to result in either the perturbation or the sharpening of the resultant spectra.

2.3 Interactions with Dithiocarbamate-based Complexes

One of the aims of this Chapter is to investigate whether large nano-dimensional complexes, such as those synthesised in Chapter Three (47) – (49), would be able to either template or undergo ligand-exchange reactions to form nanoparticles with well-defined sizes. Before this was attempted, an investigation was undertaken as to whether gold nanoparticles interacted with simple mononuclear transition metal dithiocarbamate complexes.

To this end, dichloromethane solutions of the bis-(*N,N'*-diethyldithiocarbamate) complexes of copper(II) (20), nickel(II) (21), palladium(II) (22), platinum(II) (23), zinc(II)⁴⁴ and gold(III) tetraphenylborate (60) were added to samples of (85) and (86). These solutions were analysed over time by UV-vis spectroscopy. Addition of the neutral complexes did not result in any significant perturbation in the spectra of the gold nanoparticles. However, addition of the positively-charged gold(III) dithiocarbamate salt did result in a significant change in the spectrum, which is highlighted in Figure 7.

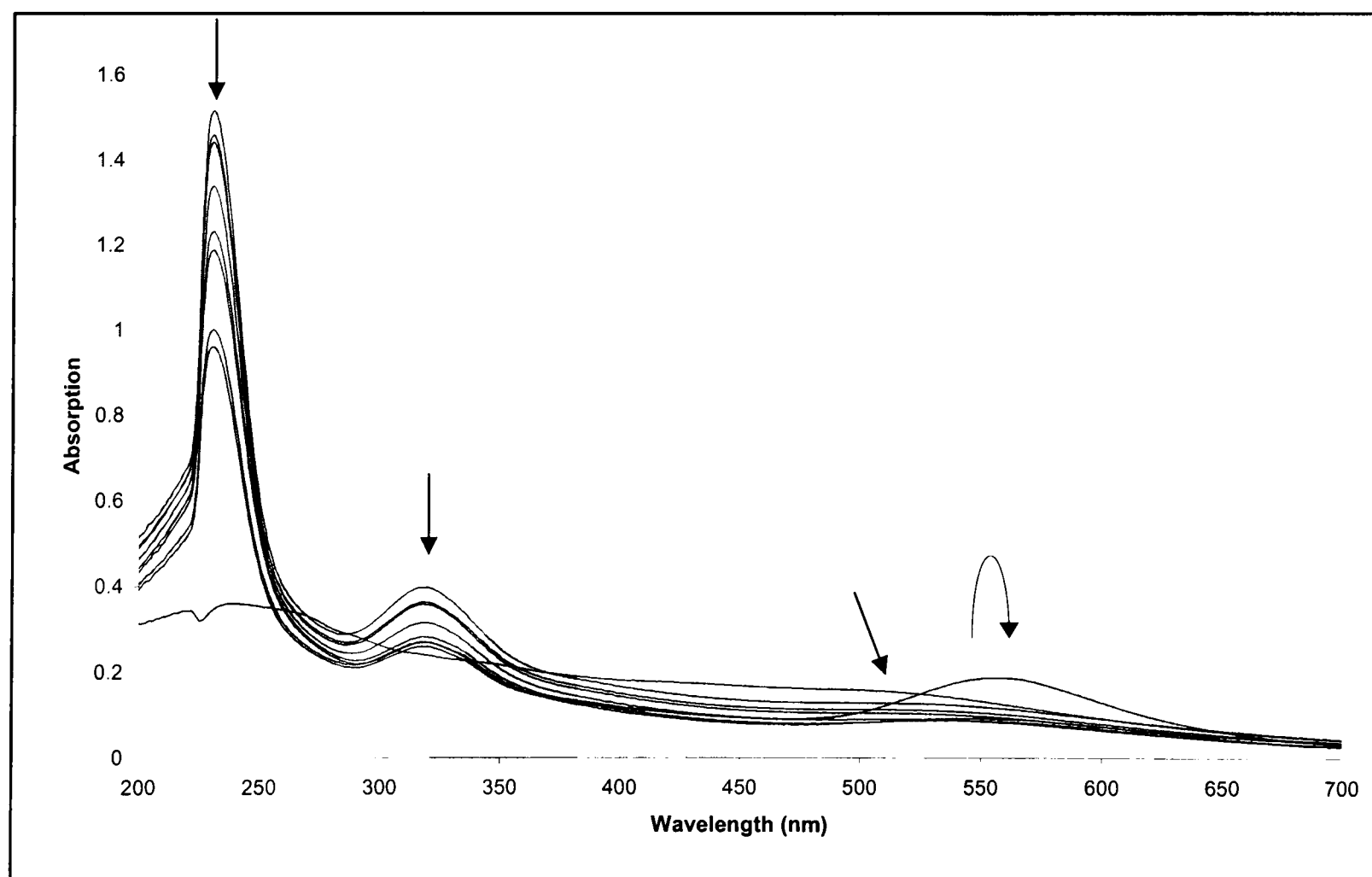


Figure 7 UV-vis spectra recorded every 15 minutes of (85) after the addition of a large excess of $\text{Au(dtc)}_2\text{BPh}_4$ in CH_2Cl_2 (293K)

The addition of gold(III) bis-(*N,N'*-diethyldithiocarbamate) tetraphenylborate (**60**) to both (**85**) and (**86**) resulted in the gradual decrease, over time, in the intensity of both the surface plasmon band of the nanoparticle (~510nm) and the peaks attributable to the added gold(III) complex (232 and 320nm). Interestingly, the reduction in the intensity of the surface plasmon band was matched by its slight shifting to higher wavelengths, indicative of the nanoparticles either growing or agglomerating⁴⁵. This is further demonstrated in the UV-vis spectra of (**85**) (Figure 7), where after two hours a new peak appears in the spectrum ($\lambda = 558\text{nm}$). This peak remains in the spectrum for thirty minutes, before it also disappears. This observation, which is not observed in the analogous experiment with (**86**) is again consistent with the growth/agglomeration of the nanoparticles upon the addition of the gold(III) dithiocarbamate complex. Interestingly, addition of tetra-*n*-butylammonium tetraphenylborate to a solution of (**85**) did not result in any discernable change in its UV-vis spectrum. This suggests that the observed spectral change upon the addition of gold(III) bis-(*N,N'*-diethyldithiocarbamate) tetraphenylborate (**60**) is a result of the cationic gold(III) dithiocarbamate complex.

Examination of the mixtures of (**85**) and (**86**) and gold(III) bis-(*N,N'*-diethyldithiocarbamate) tetraphenylborate (**60**) after 18 hours reveals the formation of a black precipitate. This solid was analysed by transmission electron microscopy, and the resulting micrograph is displayed in Figure 8.

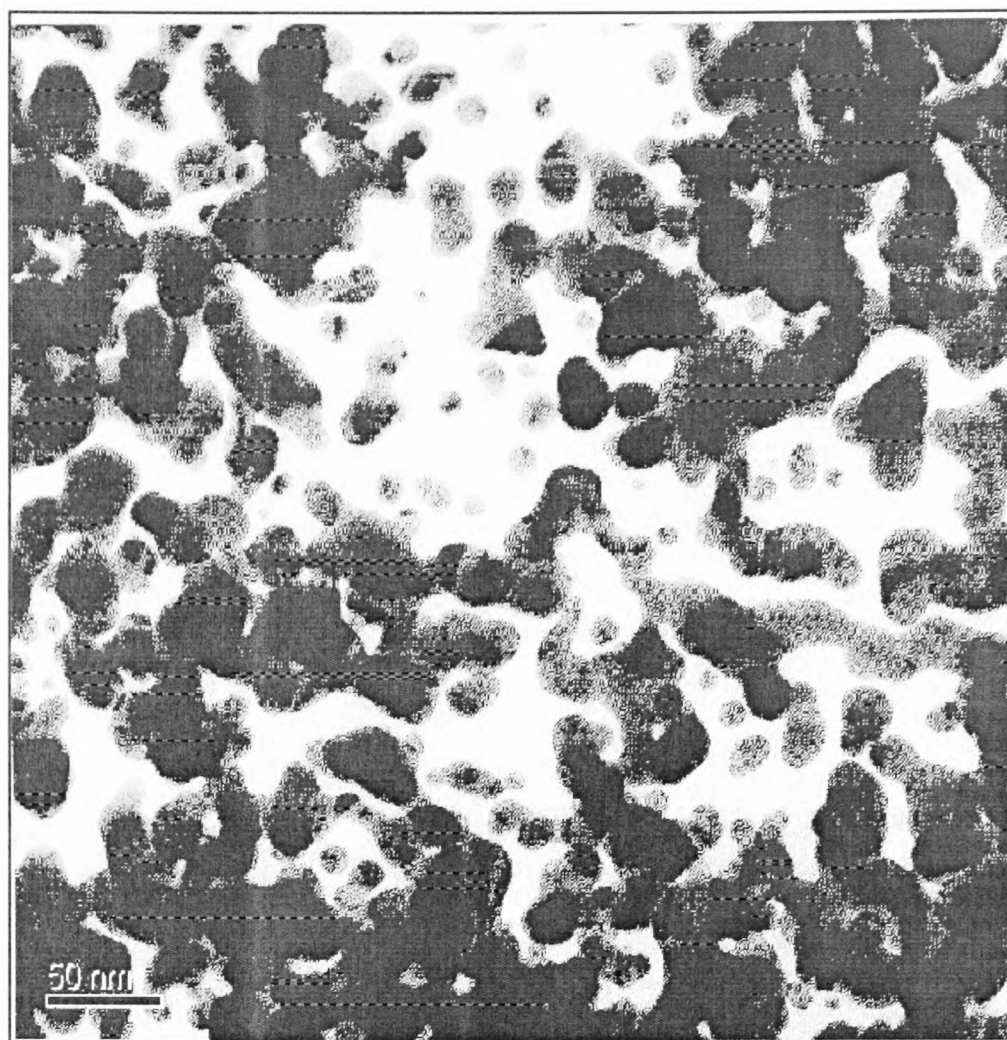


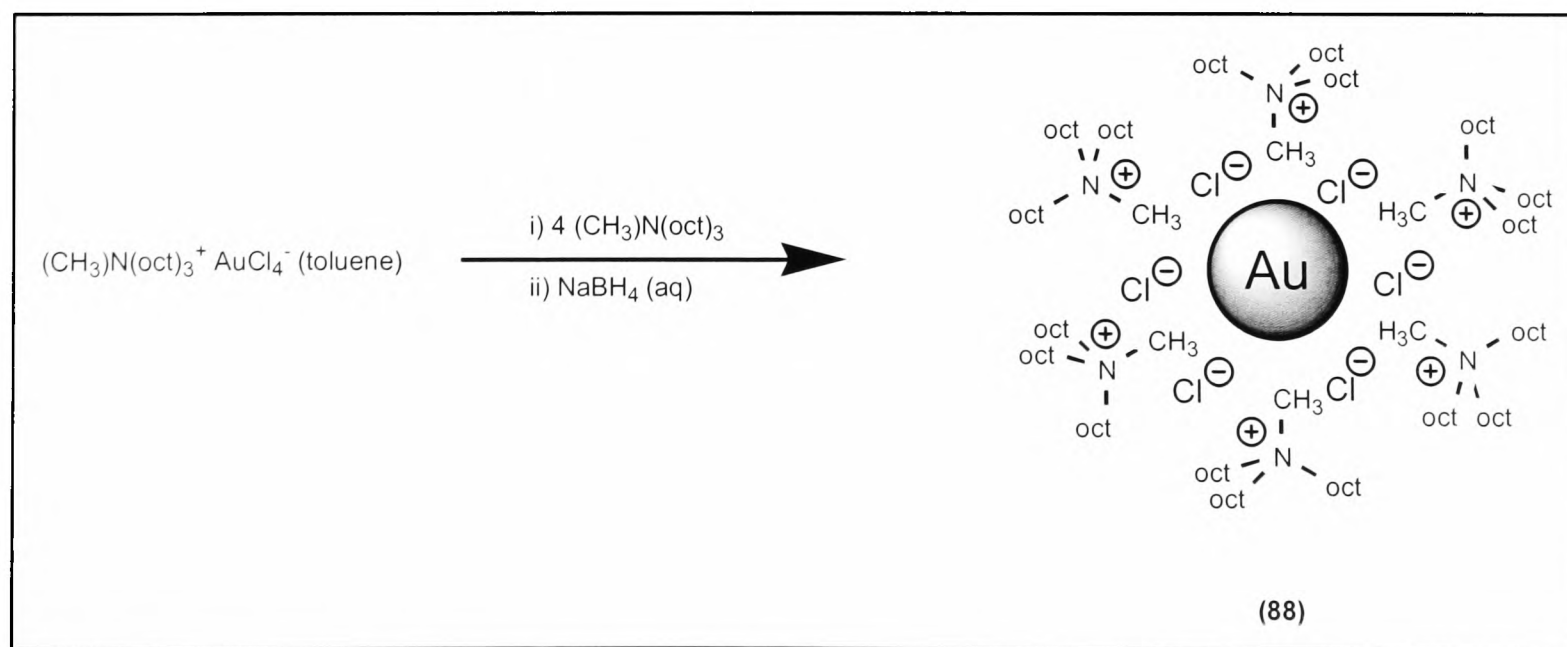
Figure 8 TEM of ethyl-2-mercaptopropionate-stabilised gold nanoparticles (86) after the addition of $\text{Au}(\text{dtc})_2\text{BPh}_4$ (60) (Scale bar 50nm)

Examination of the micrograph reveals the presence of extremely large (typically $\sim 50\text{nm}$) gold nanoparticles which are poorly soluble in organic solvents. Agglomeration of gold nanoparticles has recently been used to analyse a variety of substances such as DNA⁴⁶, lectin⁴⁷, heavy metal ions⁴⁸, C_{60} ⁴⁹ and potassium⁵⁰. A much studied agglomeration reaction occurs after the addition of pyridine to citrate-stabilised gold nanoparticles^{51,52}. In this case, the neutral ligand slowly displaces the stabilising citrate molecules, and the resulting nanoparticle loses its electrostatic stabilisation, and hence coalesces with other nanoparticles. This exchange is highlighted in the UV-vis spectra, by the reduction in intensity and shift to higher wavelength of the plasmon band of the nanoparticle, over time. It is possible that a similar process is occurring, with the gold(III) dithiocarbamate-based complex exchanging for the thiol-based ligands, over time. However, these complexes do not offer the same stabilisation as the long chained thiols and hence the nanoparticles begin to agglomerate, and gradually precipitate out of solution.

2.4 Surfactant-Stabilised Gold Nanoparticles

It has previously been observed that surfactants can also stabilise gold nanoparticles via a combination of electrostatic and steric effects⁵³. However, the use of these hydrophobic, cationic complexes tends to generate both larger particle sizes and wider dispersities than comparative thiol-stabilised nanoparticles. It is believed that these surfactant-stabilised gold nanoparticles strongly adsorb a layer of anions to the surface of the metal, which in turn are surrounded by a layer of countercations, in order to retain electroneutrality⁵⁴. However, gold nanoparticles formed using this method have a tendency to be less stable in solution, as is seen with the observation of agglomeration and their ability to readily exchange its stabilising surfactant shell.

A sample of Aliquat®336 (methyltrioctylammonium chloride)-stabilised gold nanoparticles was synthesised. This was achieved by the addition of aqueous sodium borohydride to a toluene solution of tetrachloroaurate in the presence of five equivalents of Aliquat®336 (Scheme 2). Precipitation of the purple solution afforded a black solid, which proved difficult to re-dissolve once isolated as a solid.



Scheme 2 Synthesis of aliquat-stabilised gold nanoparticles (88)

Analysis by UV-vis spectroscopy revealed a typical spectrum of a gold nanoparticle. However, unlike previously seen thiol-stabilised particles, the resulting plasmon band was

significantly more intense and at a higher wavelength (524nm), indicating that larger particle sizes are being formed. This observation is also confirmed by transmission electron microscopy data (Figure 9) which show the presence of significantly larger particle sizes (mean = 4.2nm, standard deviation = 1.0nm).

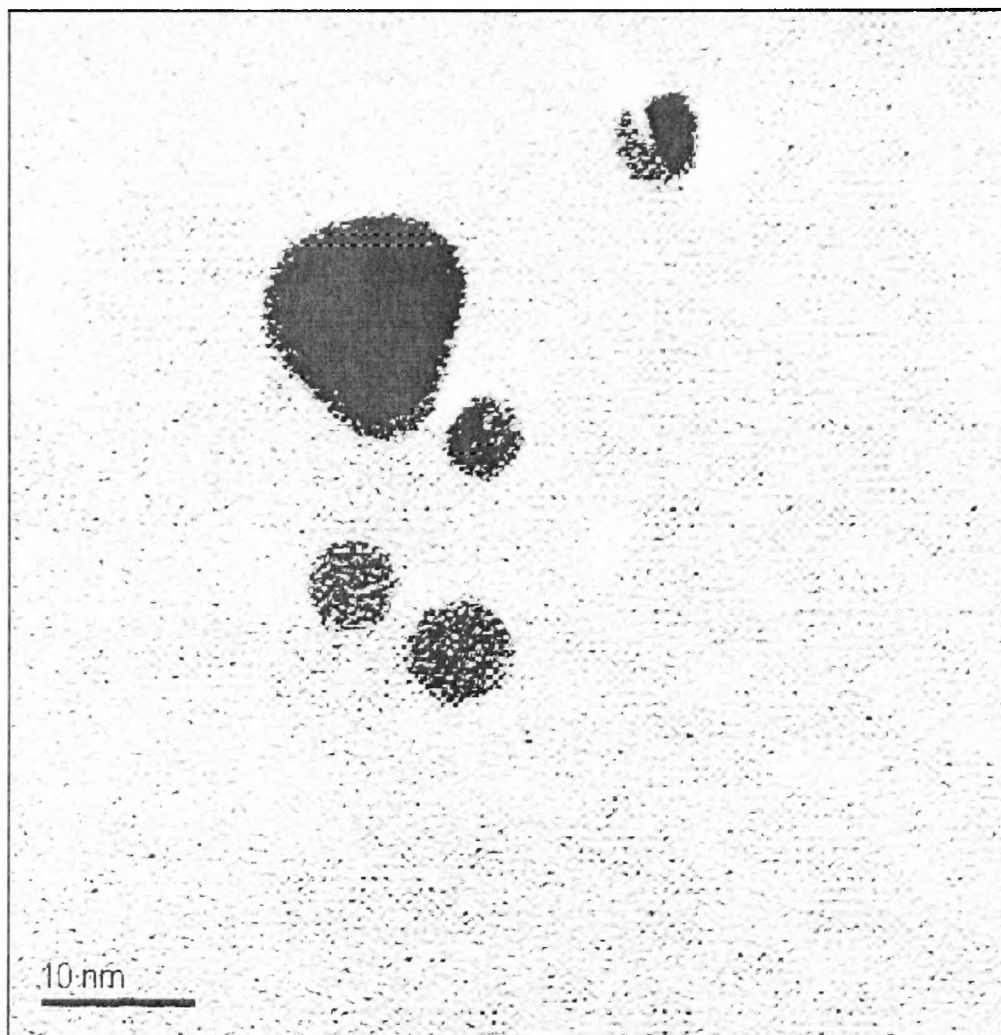
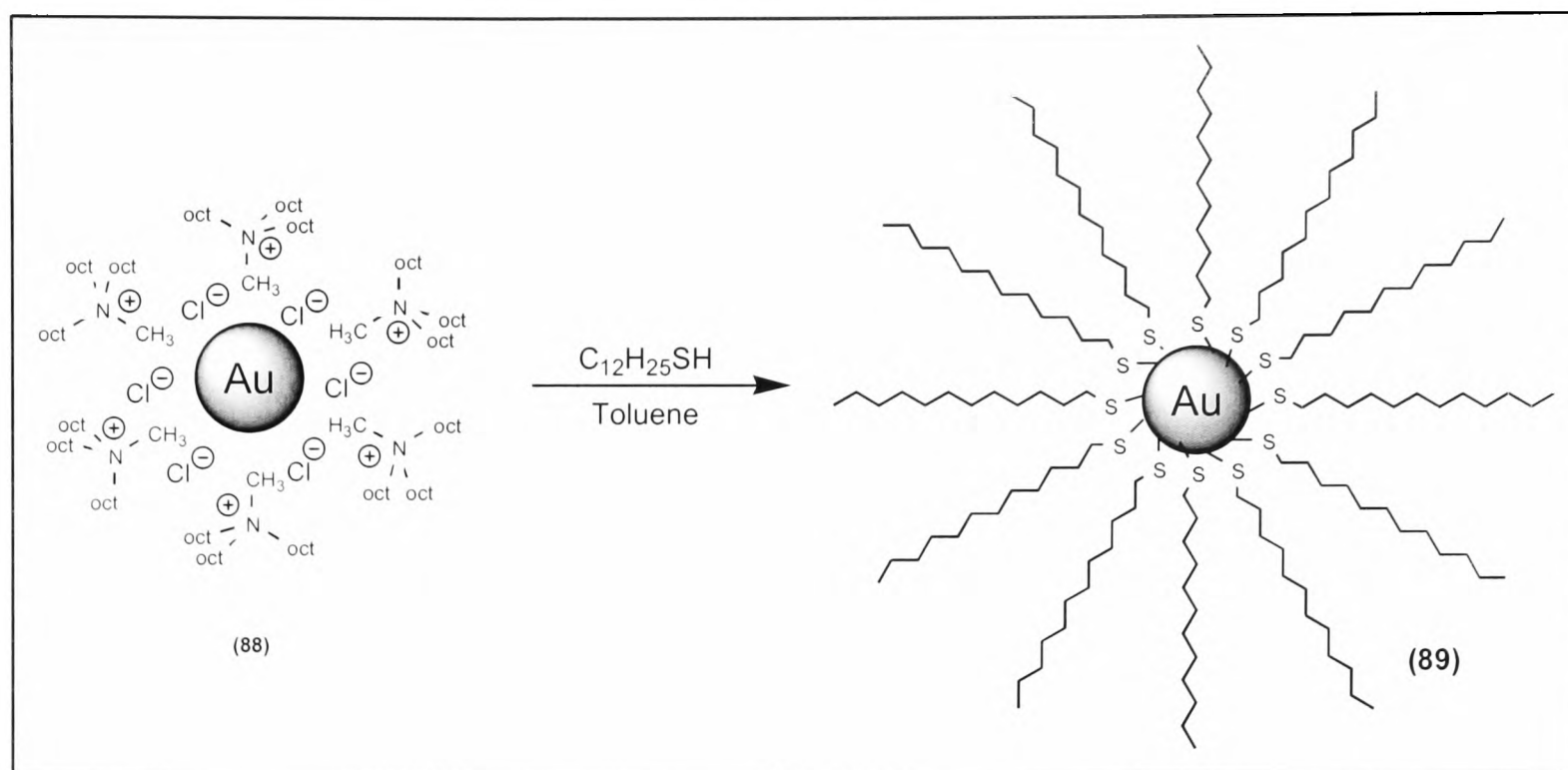


Figure 9 TEM of aliquat-stabilised gold nanoparticles (88) (Scale bar 10nm)

It has previously been demonstrated that addition of strongly adsorbing ligands, such as thiols, to pre-formed yet weakly bound gold nanoparticles (e.g. phosphine donors), results in the exchange of the stabilising ligands without significantly disrupting the central metal core⁵⁵. However, the addition of more weakly bound ligands such as amines, can lead to further growth of the nanoparticles⁵⁶.

An examination of the greater lability of the Aliquat-stabilised gold nanoparticles was undertaken. This was achieved via the addition of 1-dodecylthiol two minutes after the formation of a freshly prepared solution of **(88)** (Scheme 3). This replaces the Aliquat ligands for 1-dodecylthiol donors whilst maintaining the size of the central metallic core.



Scheme 3 Indirect synthesis of 1-dodecylthiol stabilised gold nanoparticles (89)

Examination of TEM data revealed that the addition of 1-dodecylthiol had helped to restrict the growth of the nanoparticles (mean = 3.4nm, standard deviation = 1.4nm), although the particles are significantly larger than those synthesised directly from 1-dodecylthiol. In addition elemental analysis of (89) shows the absence of nitrogen, and a carbon and hydrogen proportion consistent with the presence of 1-dodecylthiol. This suggests that the thiol ligand completely exchanges for the Aliquat, due to the superior chemisorption affinity of the former. This experiment does demonstrate that this indirect method may be utilised to generate stabilised nanoparticles via a ligand exchange reaction.

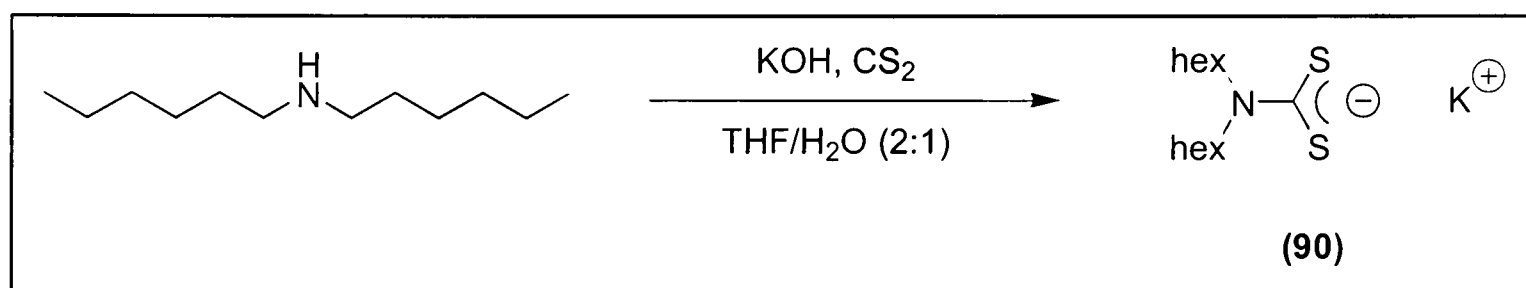
3 Dithiocarbamate Stabilised Gold Nanoparticles

The ability of the dithiocarbamate ligand to undergo metal-directed self-assembly reactions and form complexes with transition metals has been illustrated in the previous Chapters. The success of the dithiocarbamate ligand is a result of its electron-rich bidentate sulphur donors in coordinating to electron-deficient metal centres. However, it is somewhat surprising, especially considering the affinity of thiols and related ligands such as carbon disulphide⁵⁷ in stabilising gold nanoparticles, that there are no reports in the literature of the structurally

similar dithiocarbamate donors being used for this purpose.

3.1 *N,N'*-Dialkyldithiocarbamate-Stabilised Gold Nanoparticles

The synthesis of dithiocarbamate-stabilised gold nanoparticles was undertaken using the commercially available sodium *N,N'*-diethyldithiocarbamate and potassium *N,N'*-di-*n*-hexyldithiocarbamate (**90**). The synthesis of (**90**) was achieved via the addition of potassium hydroxide and carbon disulphide to di-*n*-hexylamine (Scheme 4). The crude product was recrystallised from hot hexane to afford a white waxy solid (**90**) in 68% yield.



Scheme 4 Synthesis of potassium *N,N'*-di-*n*-hexyldithiocarbamate (**90**)

Sodium *N,N'*-diethyldithiocarbamate- and potassium *N,N'*-di-*n*-hexyldithiocarbamate-stabilised gold nanoparticles were synthesised using an analogous method to the thiol-stabilised particles. Aliquat tetrachloroaurate was added to a toluene solution of 1.8 equivalents of the dithiocarbamate salt, which resulted in the formation of a yellow solid (presumably gold(III) bis-*N,N'*-di-*n*-alkyldithiocarbamate). Unfortunately, addition of an aqueous sodium borohydride solution⁵⁸ to the sodium *N,N'*-diethyldithiocarbamate complex resulted in the formation of a black insoluble solid. This is presumably a result of the stabilising ligand not being sufficiently bulky to prevent agglomeration of the formed particles. However, similar addition of the reducing agent to the hexyl-chained analogue (**90**) did lead to the formation of a purple solution, which was stirred for four hours, collected and precipitated by the addition of methanol.

The resulting black powder (**91**) was characterised by transmission electron microscopy, which revealed the formation of rounded gold nanoparticles (**91**) (mean diameter 2.0nm,

standard deviation 0.8nm). The size and dispersity of these dithiocarbamate-stabilised gold nanoparticles are comparable to the 1-dodecylthiol-stabilised gold nanoparticles generated via the Brust method (**85**) (mean diameter 1.9nm, standard deviation 0.7nm). The ^1H and ^{13}C NMR spectra of (**91**) were also studied and these are displayed in Figures 10 and 11.

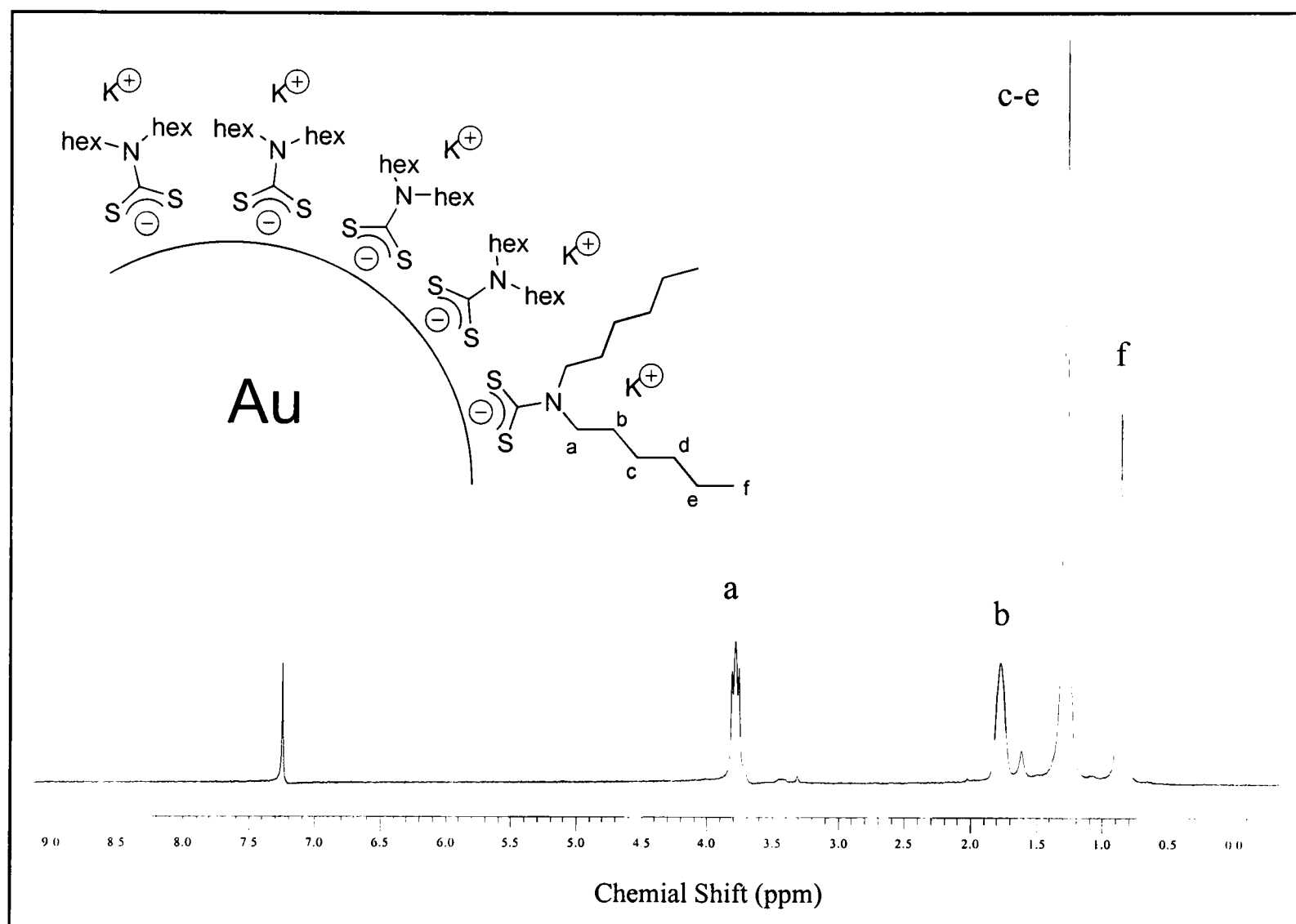


Figure 10 ^1H NMR of potassium *N,N'*-di-*n*-hexyldithiocarbamate-stabilised gold nanoparticles (**91**) (300MHz, CDCl_3 , 293K)

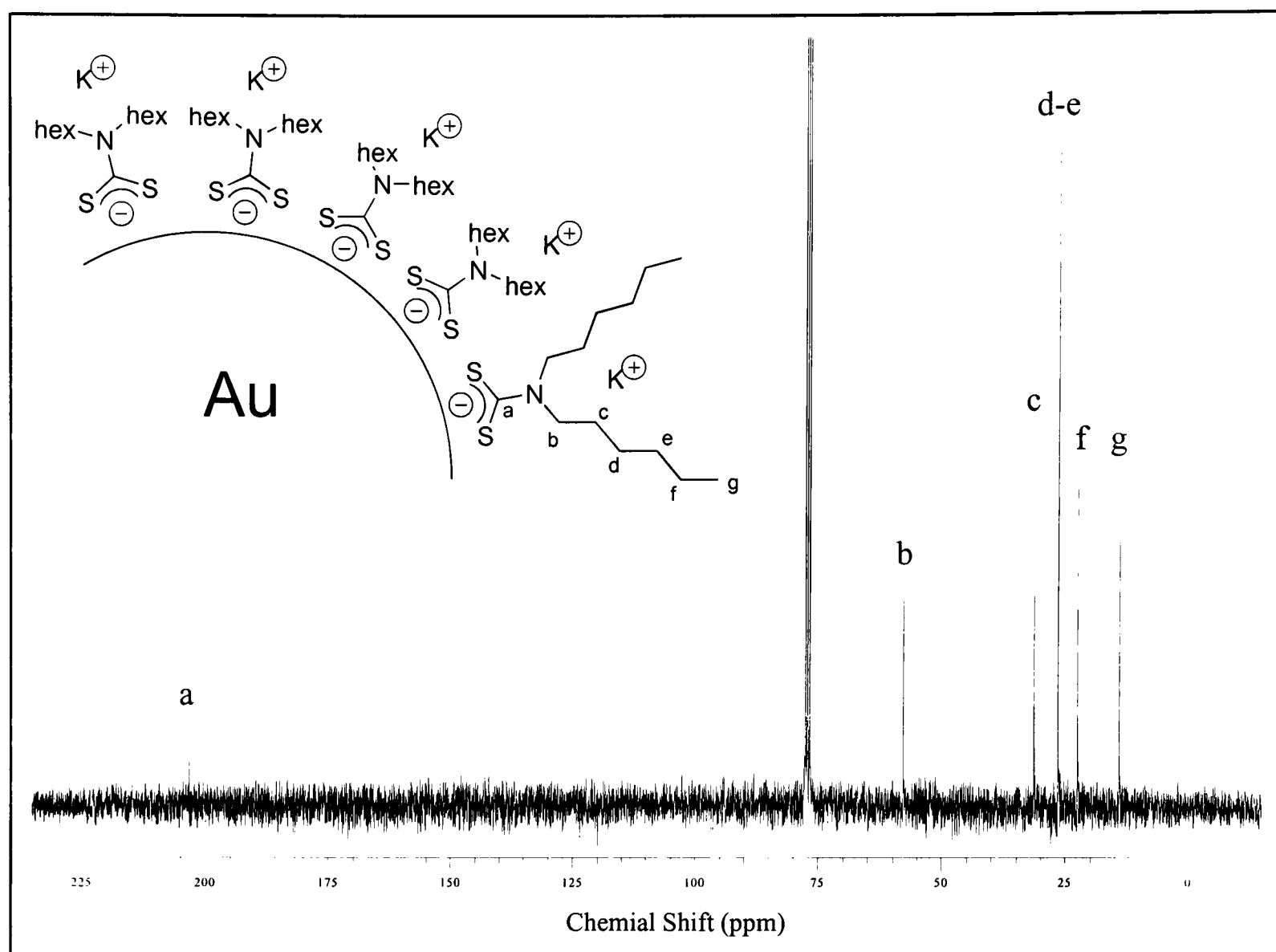


Figure 11 ¹³C NMR of potassium *N,N'*-di-*n*-hexyldithiocarbamate-stabilised gold nanoparticles (**91**) (75.4MHz, CDCl₃, 293K)

In contrast to previously observed NMR spectra for gold nanoparticles, the spectra of (**91**) are well resolved, with clear signals. This may suggest that a small proportion of the dithiocarbamate ligand precipitated out with the nanoparticles. However, the sharpness of the signals may be a result of the majority of the carbon atoms and protons being further from the surface by the planar dithiocarbamate group in comparison to the more flexible alkyl-chained thiol stabilisers. Interestingly, a peak for the dithiocarbamate carbon is clearly visible at 202.96ppm in the ¹³C NMR spectrum (Figure 11) and this value is similar to those seen in gold(I) dithiocarbamate complexes⁵⁹ (e.g. [Au(*n*-Budtc)]₂ δ_C = 203.7ppm in chloroform-*d*). This observation is in agreement with thiol stabilised gold nanoparticles, which also reveal chemical shifts similar to the analogous gold(I) thiolate complex³⁸.

Examination of the elemental analysis of (**91**) revealed the ratio of elements present was

consistent with the stabilisation of the nanoparticles with the dithiocarbamate ligand. This also shows that the counterion to the dithiocarbamate ligand must be potassium and not the cationic phase-transfer agent Aliquat (as there is not sufficient nitrogen present). Furthermore, analysing the proportion of gold present reveals that the particles are stabilised by one molecule of the potassium *N,N'*-di-*n*-hexyldithiocarbamate salt (**90**) for every gold atom present. It is therefore likely that the electron-rich dithiocarbamate group is adjacent to the metal surface, as has been seen in previous cases, with the potassium cations maintaining electroneutrality in a surrounding shell. Upon further investigation, however, the number of stabilising ligands appears abnormally high. While a particle of 2nm may be expected to have a core of 150 gold atoms, it is only sterically possible to accommodate approximately 40 dithiocarbamate ligands around this centre (not the 150 that elemental analysis suggests). It is therefore likely that there is excess ligand not directly adsorbed on the gold surface. It is possible that this excess ligand is trapped within the outer shell of the nanoparticles maybe via hydrophobic interactions between the *n*-hexyl chains of the “adsorbed” and “free” ligands. Despite this, the dithiocarbamate ligand has been shown stabilise gold nanoparticles of a similar size and dispersity to Brust’s original method, using 1-dodecylthiol.

Interestingly, addition of trifluoroacetic acid to a chloroform solution of (**91**) leads to the precipitation of a black insoluble solid. This is a result of the acid dissociating the dithiocarbamate ligand and hence no longer being able to stabilise the gold nanoparticles. In the absence of this stabilising ligand the particles agglomerate. This feature is potentially interesting since it offers a facile method of removal of the stabilising ligands, an important feature if supported nanoparticles are to be used as potential catalysts.

3.2 Tetrakis-dithiocarbamate-functionalised Resorcinarene-Stabilised Gold Nanoparticles

Since it has been shown that the dithiocarbamate ligand (**90**) can effectively stabilise gold nanoparticles, it was further investigated whether a more preorganised dithiocarbamate salt could also achieve this. To this end, a potassium tetrakis-dithiocarbamate-functionalised resorcinarene was synthesised. Unfunctionalised resorcinarenes have previously been demonstrated to be effective at stabilising gold nanoparticles^{60,61}. Recently, a tetra-thiolated resorcinarene cavitand has also been shown to stabilise the formation of a range of gold nanoparticles (Figure 12)⁶². This ligand not only has the advantage of cooperative multidentate interactions with the surface of the nanoparticle, but also the appended alkyl chains retain a significant degree of conformational freedom, regardless of how densely packed the resorcinarene headgroups are on the surface of the nanoparticle.

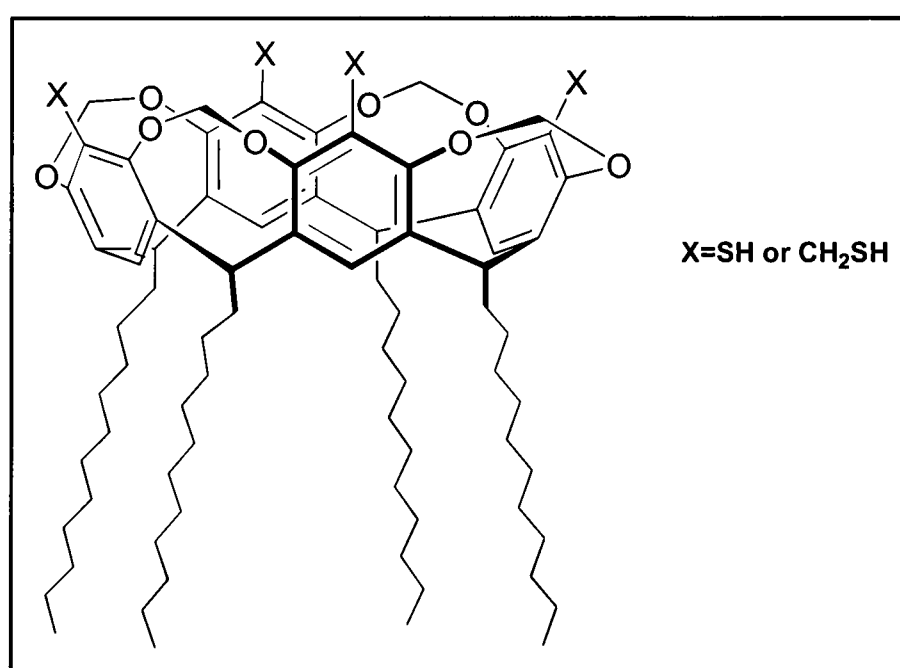
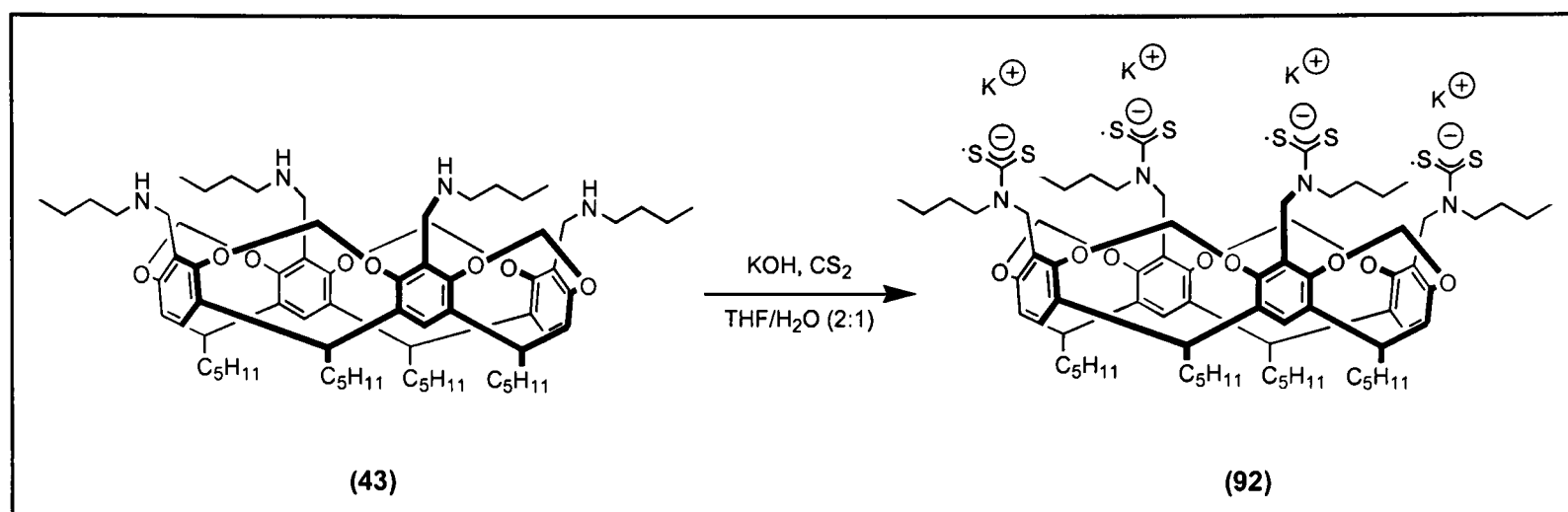


Figure 12 Tetra-thiolated resorcinarene cavitand stabilisers

The synthesis of potassium {tetrakis[(butylaminodithiocarbamate)methyl]resorcinarene} cavitand (**92**) was achieved via the addition of five equivalents of potassium hydroxide and carbon disulphide to a solution of tetra-amine (**43**) (Scheme 5). Precipitation of a methanolic solution of the crude product by the addition of diethyl ether afforded an off-white solid (**92**).



Scheme 5 Synthesis of potassium {tetrakis[(butylaminodithiocarbamate)methyl] resorcinarene} cavitand (92)

The tetra-substituted dithiocarbamate functionalised resorcinarene **(92)** was used to synthesise gold nanoparticles. This was achieved in an analogous reaction to the synthesis of the potassium *N,N'*-di-*n*-hexyldithiocarbamate-stabilised gold nanoparticles **(91)**, with the exception that 0.45 equivalents of the ligand were used, so that an equivalent number of coordinating dithiocarbamate units are present. Initially the use of the milder reducing agent dimethylaminoborane was attempted, although this did not prove powerful enough to reduce the gold(III) salt. Reduction of the toluene layer was achieved by the addition of sodium borohydride leading to the formation of a purple solution. This solution was analysed by UV-vis spectroscopy (revealing a small plasmon band at 520nm) and transmission electron microscopy (Figure 12).

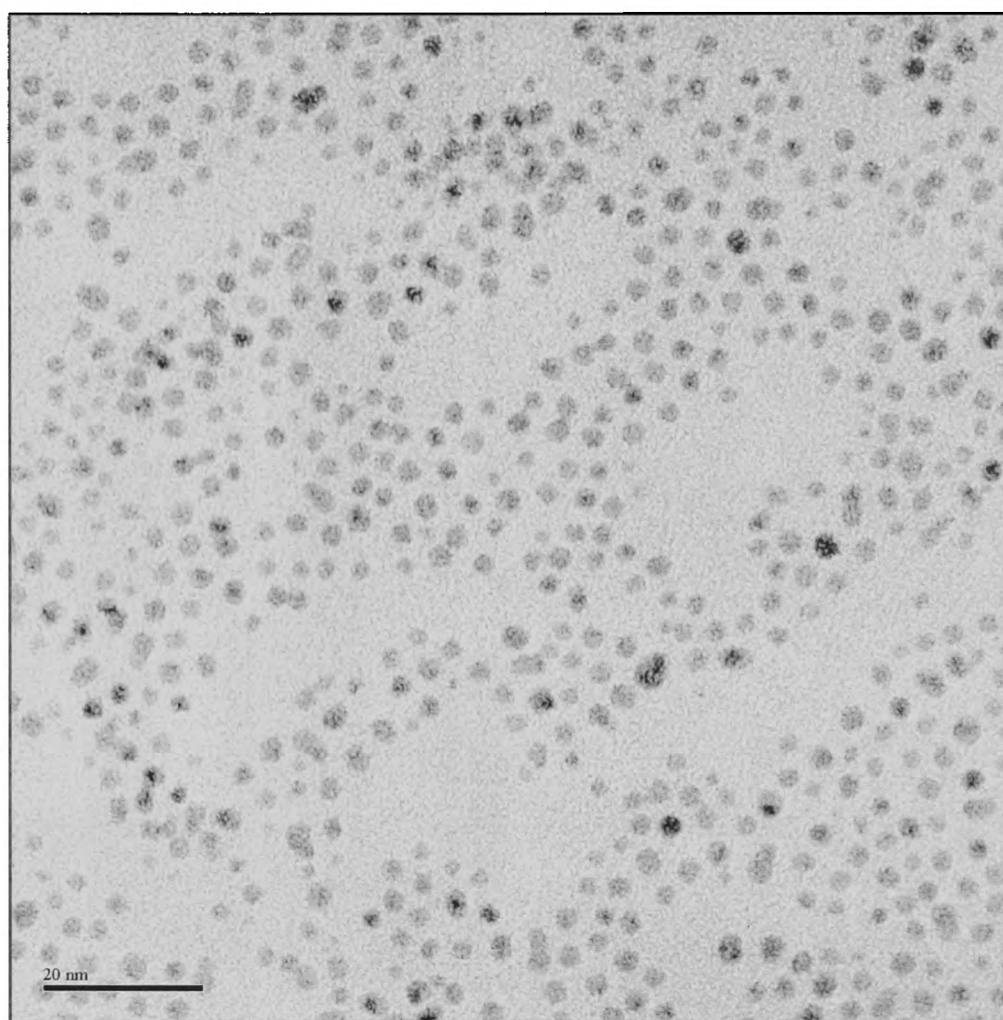


Figure 13 TEM of potassium {tetrakis[(butylaminodithiocarbamate)methyl]resorcinarene} cavitand stabilised gold nanoparticles (93) (Scale bar 20nm)

Analysis of the micrograph shows the formation of spherical gold nanoparticles (average diameter 2.8nm). Interestingly, the particles exhibit a high degree of monodispersity (standard deviation 0.6nm) which is highlighted in Figure 14.

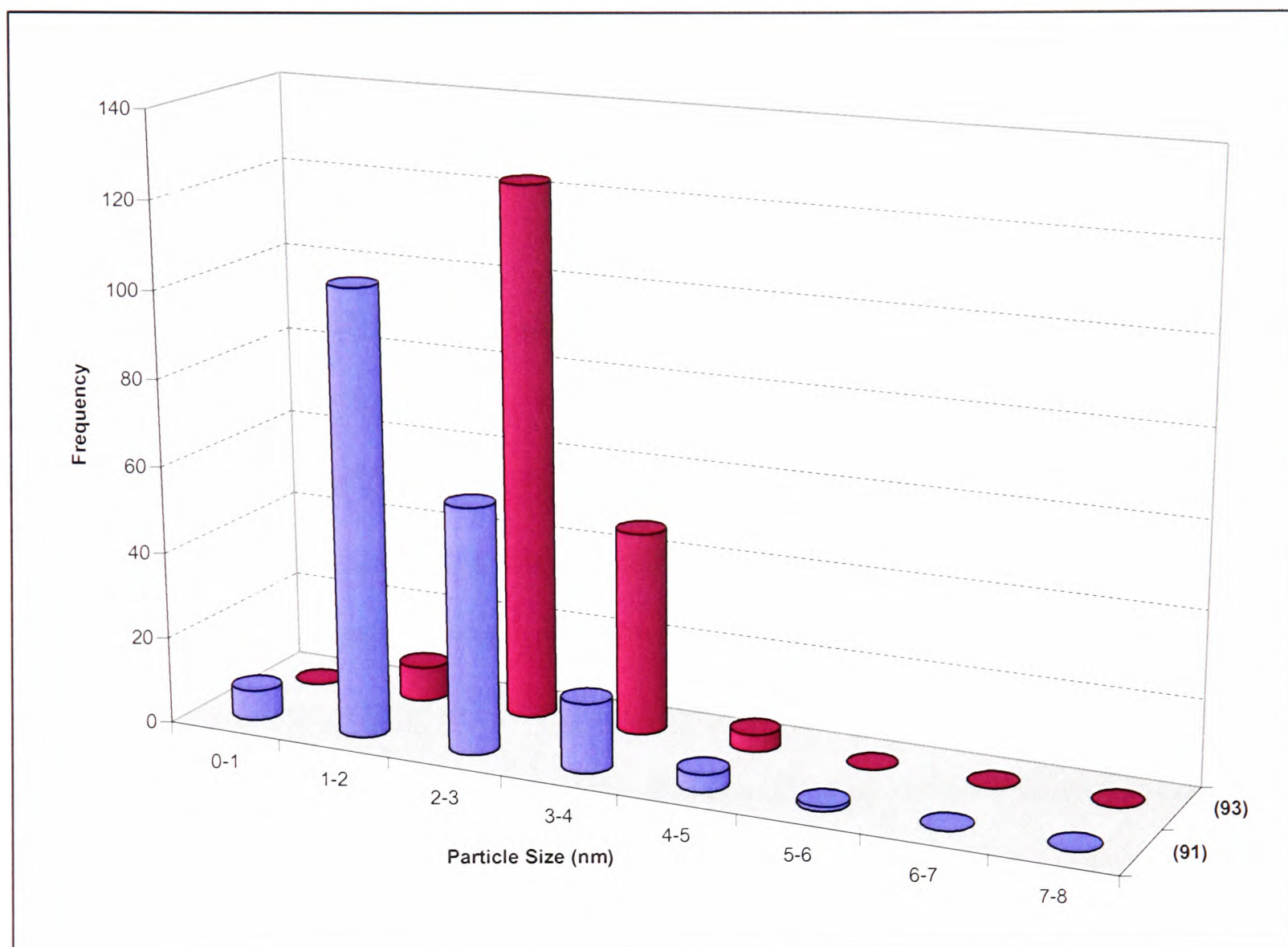


Figure 14 Histogram illustrating the size distribution of dithiocarbamate-stabilised gold nanoparticles (91) and (93)

The histogram (Figure 14) shows the effect of the dithiocarbamate based ligands (90) and (92) in stabilising small gold nanoparticles. The monodithiocarbamate ligand (90) forms gold nanoparticles (91) with a smaller average diameter than the corresponding tetrafunctionalised ligand (92). However, the larger particles (93) exhibit a higher degree of monodispersity in comparison to (91). This is possibly a result of the more preorganised nature of the stabilising ligand being more favourable in stabilising nanoparticles of a particular size.

3.2 Indirect Preparation of Dithiocarbamate Stabilised Nanoparticles

Potassium {tetrakis[(butylaminodithiocarbamate)methyl]resorcinarene} cavitand-stabilised gold nanoparticles were also formed via an indirect method. Aliquat-stabilised gold nanoparticles (88) were freshly prepared as previously discussed. After two minutes

potassium {tetrakis[(butylaminodithiocarbamate)methyl]resorcinarene} cavitand (**92**) was added to the solution and this was stirred for a further four hours. This should replace the Aliquat-stabilising ligands for resorcinarene-based donors whilst maintaining the size of the central metallic core.

The purple solution (**94**) was analysed with ^1H NMR spectroscopy, UV-vis spectroscopy and transmission electron microscopy. The ^1H NMR spectrum of (**94**) showed broad peaks representative of the added ligand suggesting that the resorcinarene has exchanged with the Aliquat ligand and is stabilising the nanoparticle. In addition the micrographs indicate the displacement by the resorcinarene ligands result in the stabilisation of significantly smaller particle sizes (average diameter 2.3nm, standard deviation 1.4nm). This suggests that the ligand exchange process was rapid, with the preorganised dithiocarbamate-functionalised structure again proving to stabilise gold nanoparticles of sizes between 2 and 3nm.

3.3 Attempted Templatation Using Nano-dimensional Dithiocarbamate-based Complexes

It has been shown, in the solid state, that zinc(II) and cadmium(II) dithiocarbamate-functionalised resorcurene complexes (described in Chapter Three) adopt a hexanuclear, trimeric loop structure with a central cavity of nanodimensions (1.65nm). It was hoped that this cavity might be able to either template the formation of nanoparticles of fixed dimensions or “sieve” a mixture of nanoparticles to generate monodispersed nanoparticles.

Initially the preparation of gold nanoparticles was attempted in the presence of (**48**) and (**49**) as potential templates. Unfortunately, the addition of tetrachloroaurate anions to the multinuclear dithiocarbamate-based complexes, and subsequent reduction with sodium borohydride, led to the formation of insoluble black solids.

Since direct reduction would probably interfere with the weak coordinate bonds an exchange

reaction was undertaken, whereby a water soluble, glycine-functionalised thiol-stabilised nanoparticle was partitioned with a dichloromethane solution of the zinc(II) and cadmium(II) complexes (48) and (49) and stirred vigorously. Unfortunately, even after prolonged heating, no reaction was observed.

4 Amide Functionalised Gold Nanoparticles

It has recently been demonstrated that gold nanoparticles may be decorated with well-known binding motifs for the molecular recognition⁶³ of cationic⁶⁴ and anionic⁶⁵ guests. For example, it was recently claimed that a gold nanoparticle that is surface-modified with amide ligands is able to act as an optical anion sensor⁶⁶ (Figure 15). Addition of anions to a dichloromethane solution of these 4nm gold nanoparticles resulted in a dramatic change within the plasmon band of the nanoparticle. The addition of a substoichiometric amount of dihydrogen phosphate leads to anion-induced aggregation between gold nanoparticles resulting in a decrease in optical intensity and notable red shift in the wavelength. However, continued addition of the anion restores the original optical response, as increased anion coordination results in mutual electrostatic repulsions between gold nanoparticles.

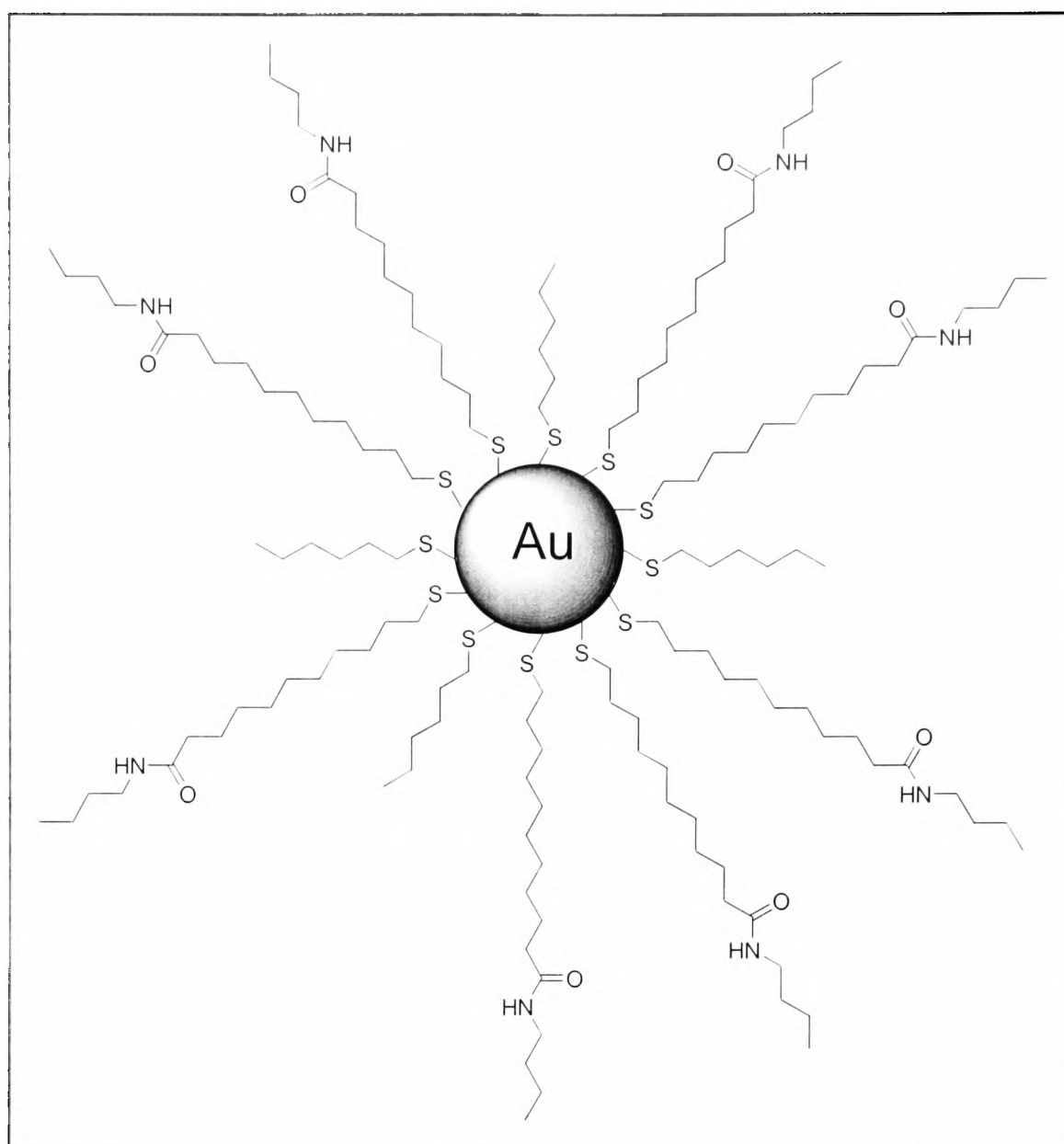
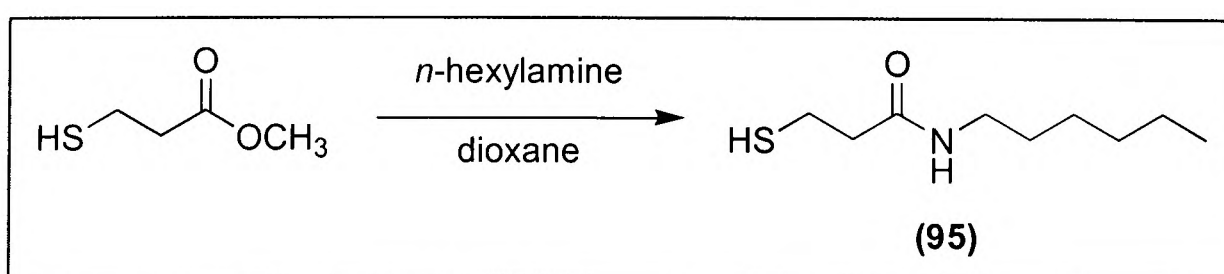


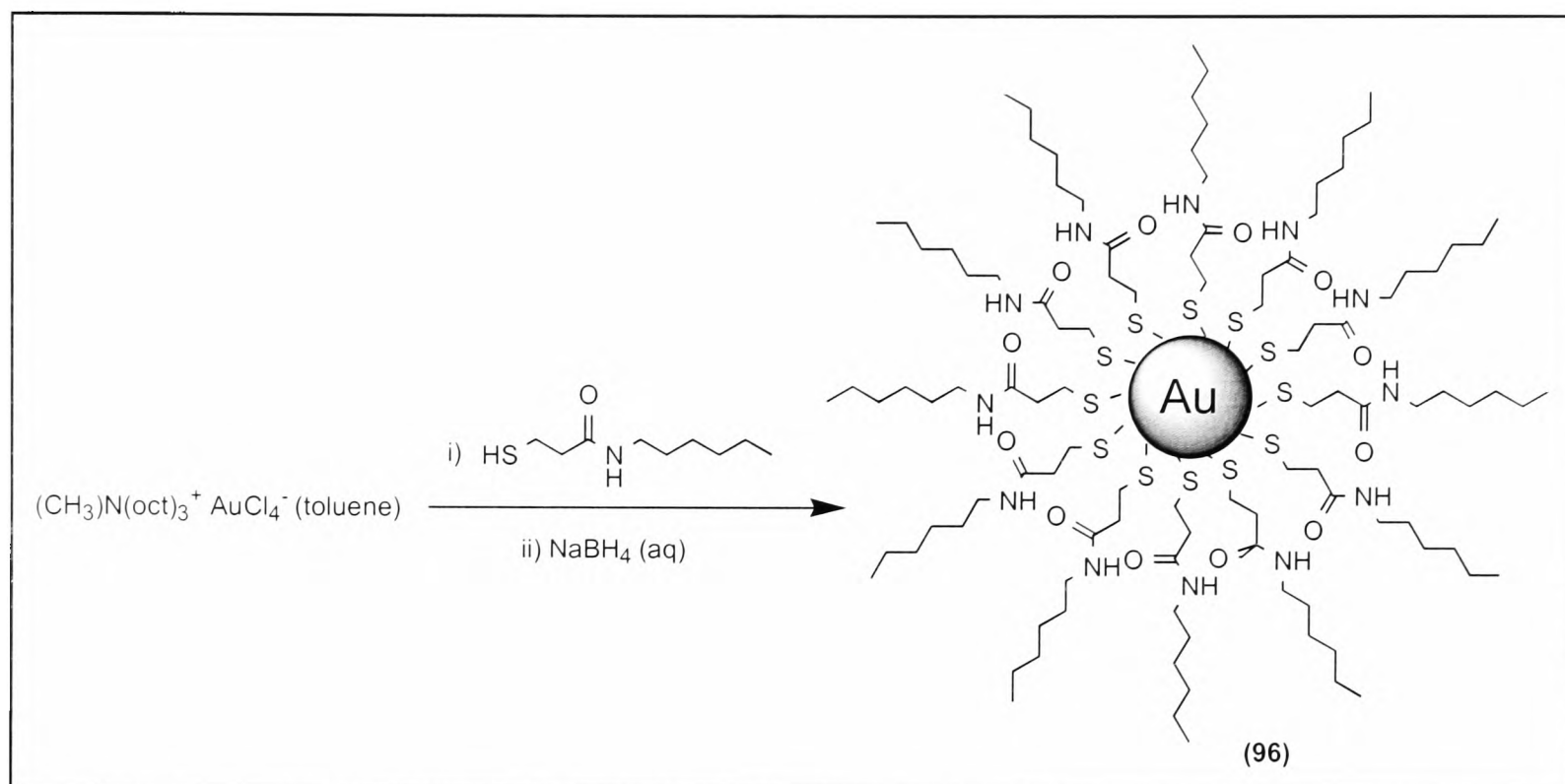
Figure 15 Amide-functionalised gold nanoparticle that acts as an optical anion sensor

An investigation was undertaken into whether other functionalised gold nanoparticles could be synthesised and act as anion sensors. To this end, an amide-functionalised thiol (**95**) was prepared. This was achieved by the combination of methyl 3-mercaptopropionate and *n*-hexylamine (Scheme 6). The resulting crude product was recrystallised from hot dichloromethane affording a white crystalline solid in 81% yield.



Scheme 6 Synthesis of thio-amide (95)

The use of the ligand **(95)** was designed so the amide moiety is close to the surface of the entire gold nanoparticle, such that the effect of binding upon the plasmon resonance is maximised. The preparation of the thio-amide-stabilised gold nanoparticles **(96)** was undertaken using standard procedures, with a black powder being collected after precipitation of a toluene solution by the addition of methanol (Scheme 7).



Scheme 7 Synthesis of amide-functionalised gold nanoparticles (96)

The nanoparticles were analysed by transmission electron microscopy, which revealed the formation of rounded gold particles with a high monodispersity (Figure 16). In addition, the micrograph shows the hexagonal close packing of gold nanoparticles. A size distribution histogram of **(96)** is highlighted in Figure 17.

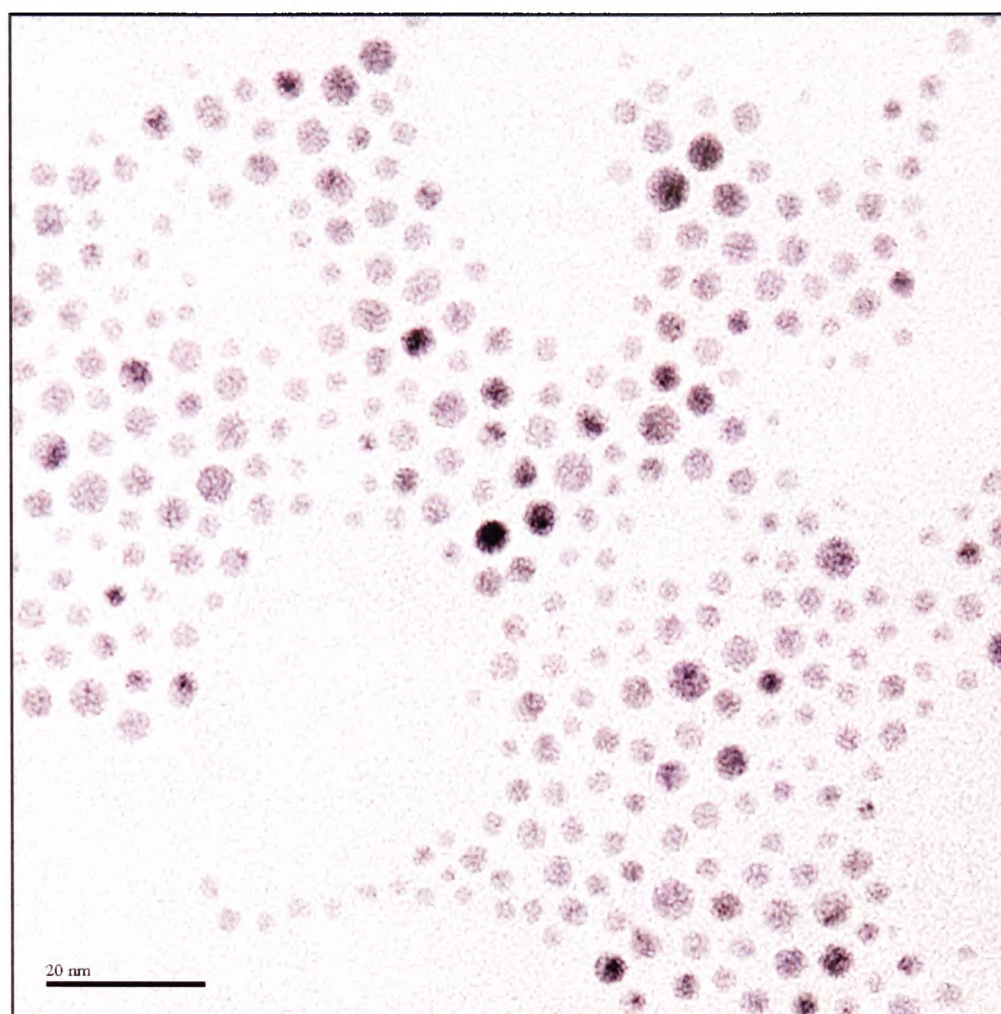


Figure 16 TEM of amide-functionalised gold nanoparticles (96) (Scale bar 20nm)

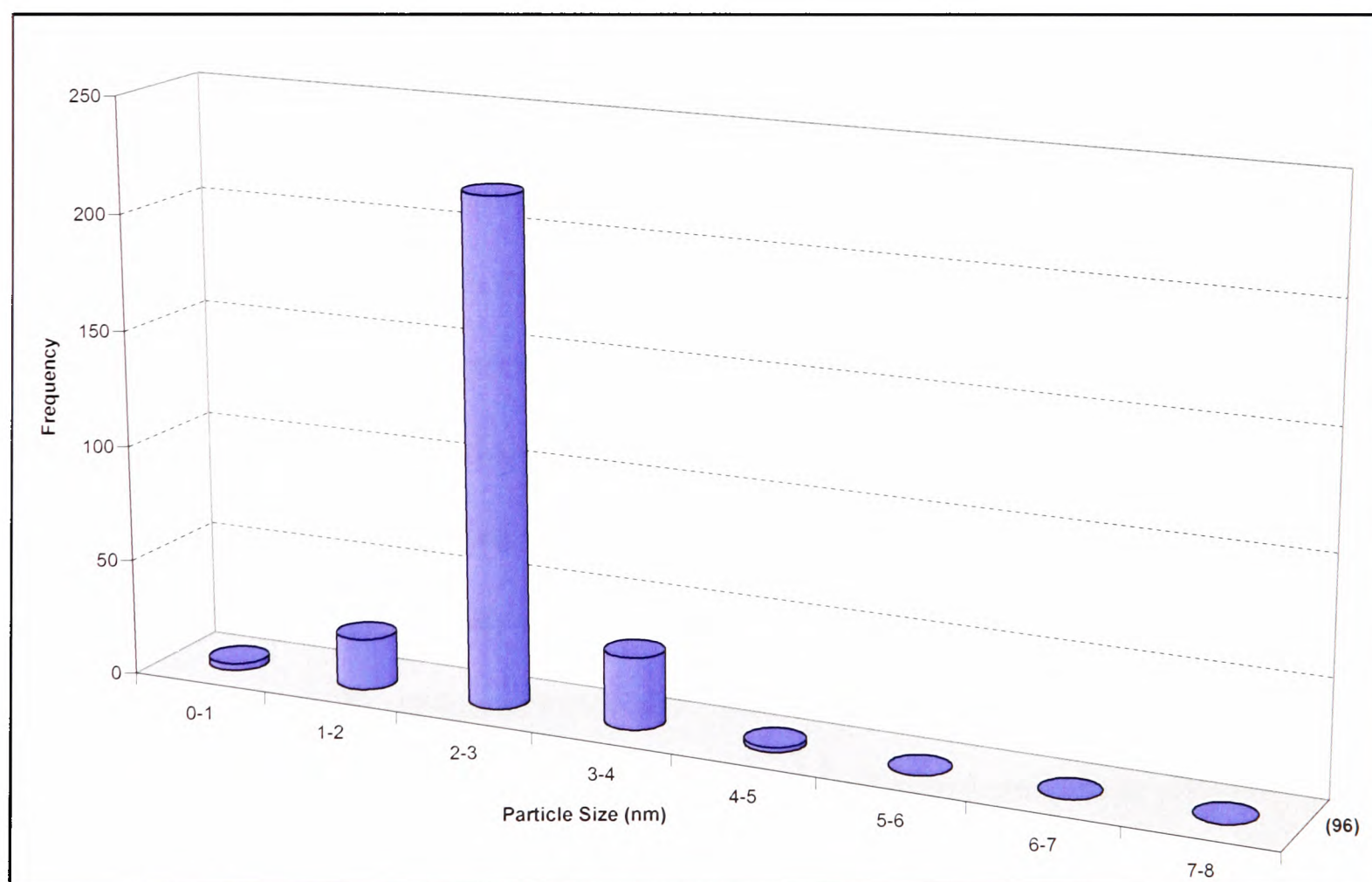


Figure 17 Histogram illustrating the size distribution of amide-functionalised gold nanoparticles (96)

Analysis of the micrograph revealed the particles had a high monodispersity with a mean diameter of 2.5nm and a standard deviation of 0.5nm. This narrow distribution of sizes may be a result of the hydrogen bond donor/acceptor groups of the amide being in close proximity to the thiol group. This structural feature may assist in the formation of small particles by favourable hydrogen bond formation, hence preorganising the stabilising ligands.

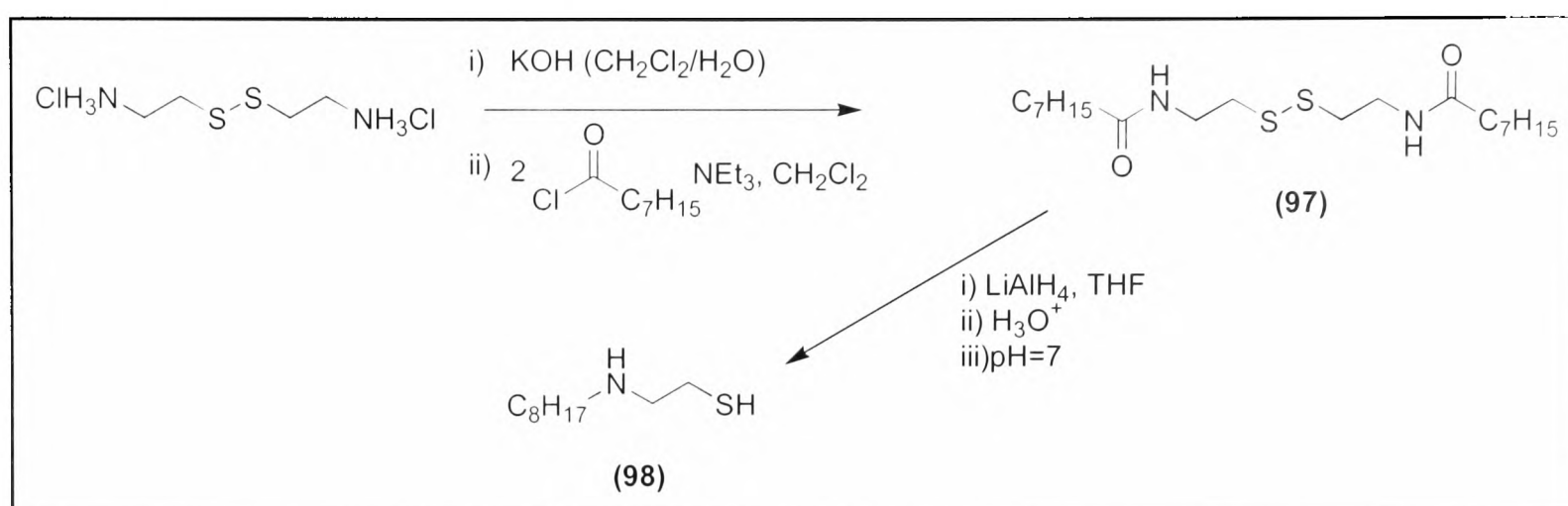
The gold nanoparticles were also analysed by ^1H NMR spectroscopy, which revealed a broad spectrum, with the amide peak unable to be resolved. In addition, UV-vis spectroscopy of **(96)** in dichloromethane exhibited a plasmon band at 518nm. The effect upon this plasmon band was investigated after the addition of a range of anions (in the form of their tetra-*n*-butylammonium salt). Unfortunately, the addition of any of the anions to the solution did not result in any discernable change in the spectrum. This is possibly a result of the amide groups being inaccessible to the incoming anion, hence no binding is observed.

5 Attempted Synthesis of Dithiocarbamate Linked Gold Nanoparticles

It has previously been demonstrated by Mirkin and co-workers, that gold nanoparticles may be linked to form assemblies by favourable hydrogen bonding interactions. An analogous attempt to link gold nanoparticles with coordinate bonds was undertaken. The combination of nanoparticles via dithiocarbamate-based linkages may lead to novel optical and electrochemical properties being exhibited.

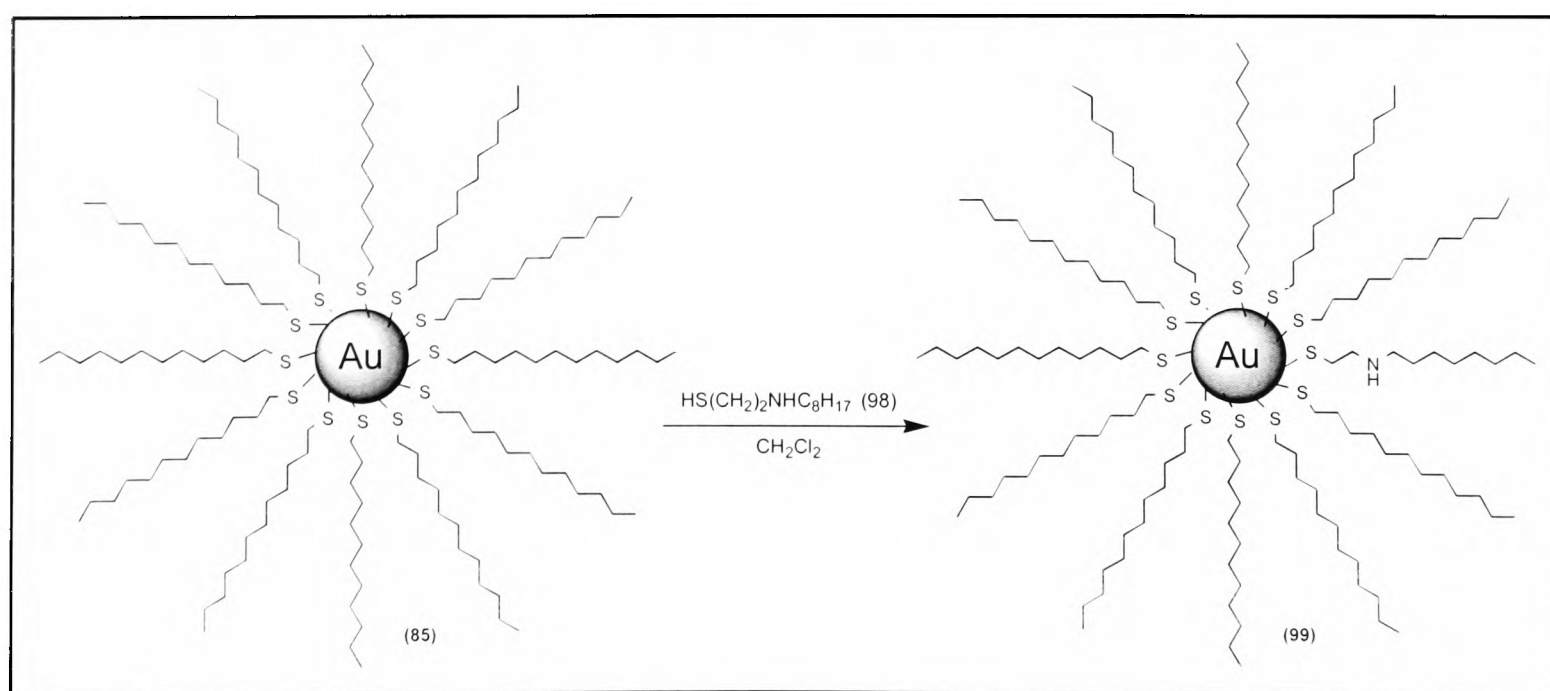
To this end, amine functionalised thiols were prepared via a two step process (Scheme 8). Initially, cystamine dihydrogenchloride was basified and combined with two equivalents of octanoyl chloride and triethylamine in dry dichloromethane. Recrystallisation from dimethylsulphoxide/water yielded a white powder **(97)**, which was characterised by ^1H and ^{13}C NMR, electrospray mass spectrometry and elemental analysis. Subsequent reduction of the bis-amide using lithium aluminium hydride in tetrahydrofuran afforded the desired thio-

amine (**98**) as a brown oil in 87% yield.



Scheme 8 Synthesis of thio-amine (**98**)

An amine-functionalised gold nanoparticle (**99**) was synthesised by the ligand exchange reaction⁶⁷ with the alkanethiolate-protected nanoparticle (**85**). A dichloromethane solution of (**98**) was stirred at room temperature for 24 hours with (**85**). The resulting solution was repeatedly precipitated by the addition of methanol, in order to ensure the complete removal of excess thiol. Examination of the subsequent elemental analysis of (**99**) revealed the presence of nitrogen, whose only source is the amine. The ratio of this suggested that there was one molecule of (**98**) for every 11 molecules of 1-dodecylthiol on the surface of the nanoparticle; hence there are approximately three molecules of (**98**) per nanoparticle.



Scheme 9 Ligand exchange to form amino-functionalised gold nanoparticle (**99**)

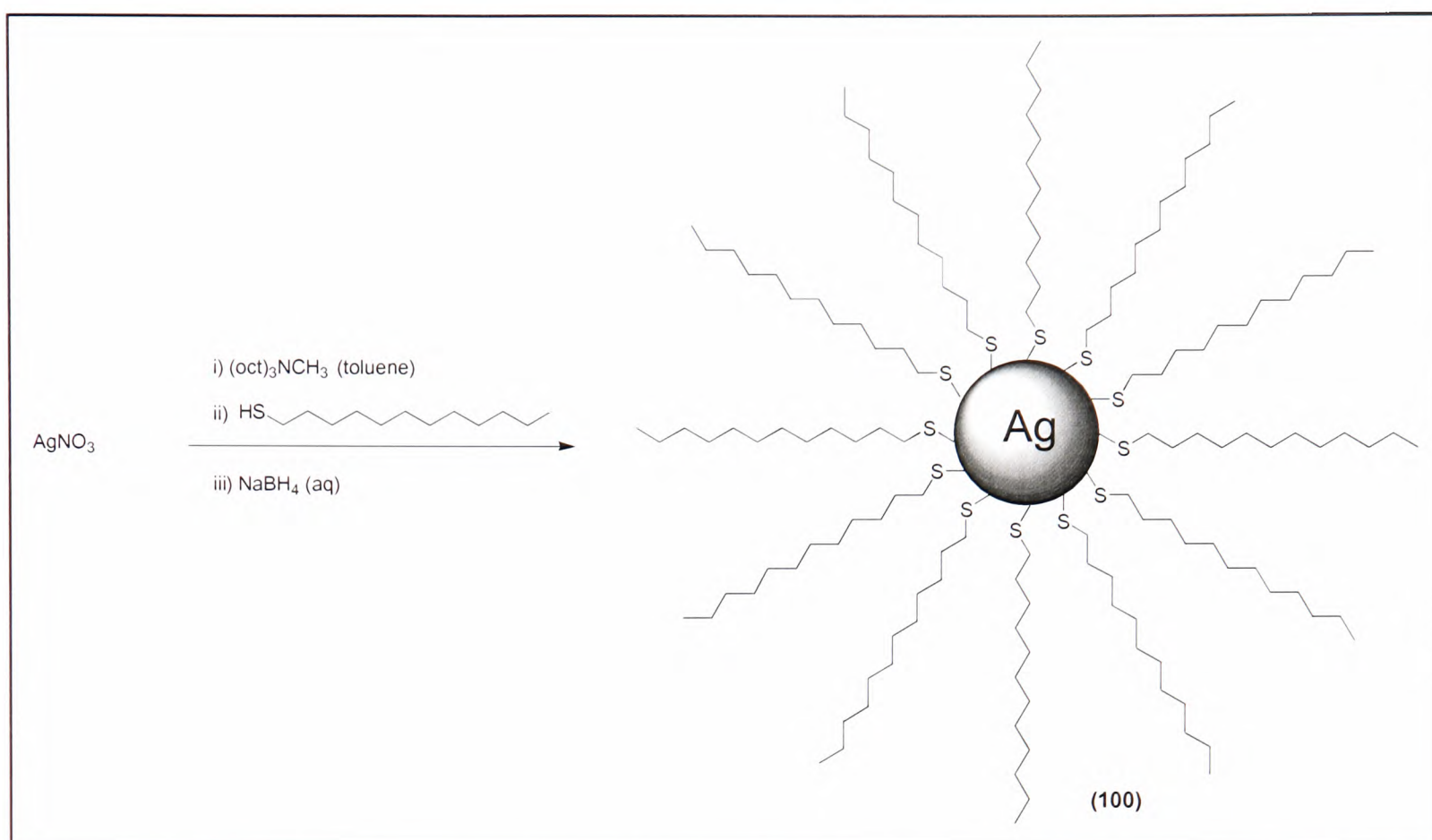
It was subsequently attempted to use the amine-functionalised gold nanoparticle (**99**) to form copper(II) dithiocarbamate linkages. This was achieved by treating (**99**) with five equivalents of potassium hydroxide carbon disulphide and copper(II) acetate in a tetrahydrofuran/water (2:1) solution. Unfortunately, this led to the formation of a highly insoluble black solid. The variation of the solvent system employed failed to result in a complex with improved solubility.

6 Silver Nanoparticles

In addition to the formation of gold nanoparticles it has been demonstrated that the reduction of silver can also form nanoparticles⁶⁸. The study of such structures has provided significant interest due to their potential as catalysts^{69,70}, quantum dots⁷¹ and to be used in photographic processes^{72,73}, biocompatible intracellular monitors⁷⁴ and sensors^{75,76}. For example, colloidal silver in aqueous solution exhibits a surface plasmon absorption in its UV-vis spectrum at 390nm, which is seen to be significantly dampened upon adsorption of anions such as I^- , SH^- or $C_6H_5S^-$ ⁷⁷.

6.1 Thiol Stabilised Silver Nanoparticles

1-Dodecylthiol-stabilised silver nanoparticles (**100**) were formed according to a literature preparation via an analogous method to the preparation of gold nanoparticles⁷⁸ (Scheme 10). An aqueous solution of silver(I) ions was treated with the phase transfer agent Aliquat®336 (methyltrioctylammonium chloride). 1-Dodecylthiol was then added to the stirred solution which was subsequently treated with an aqueous sodium borohydride solution. The brown organic layer was collected, washed with ethanol and precipitated from a dichloromethane/ethanol system, yielding a brown solid.



Scheme 10 Synthesis of 1-dodecylthiol stabilised silver nanoparticles (100)

Energy dispersive X-ray spectroscopy (EDX) upon the resultant nanoparticles reveal that the particles consist of silver, as shown by the characteristic spectral peaks (Figure 18).

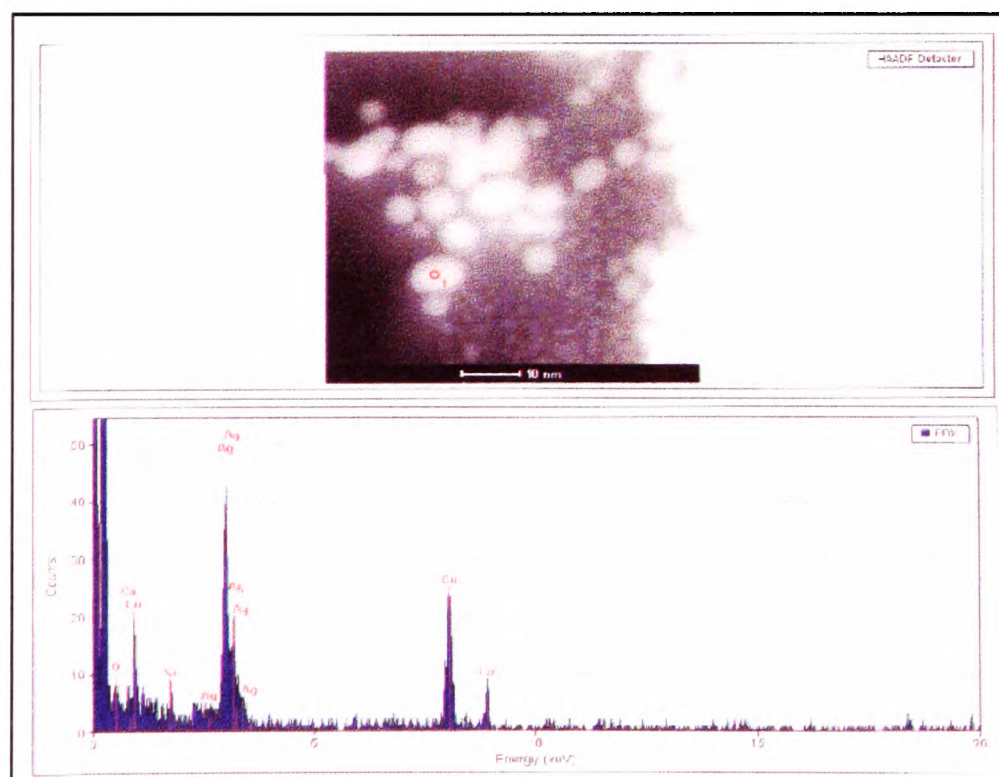


Figure 18 EDX spectrum of (100) (upper) selected silver nanoparticle for analysis

Examination of the transmission electron micrographs revealed the formation of a wider range of particle sizes in comparison with the analogous gold-stabilised nanoparticle **(85)** (Figure 19). Indeed, calculation of a size distribution for these particles (Figure 22) shows a bimodal

distribution of sizes. This highlights that a much wider range of sizes are observed (ranging from 1nm to 40nm) with particles of 2nm and 8nm being particularly prevalent. Further examination of high resolution transmission electron micrographs highlights the high crystallinity of the particles, with the lattice plans clearly visible.

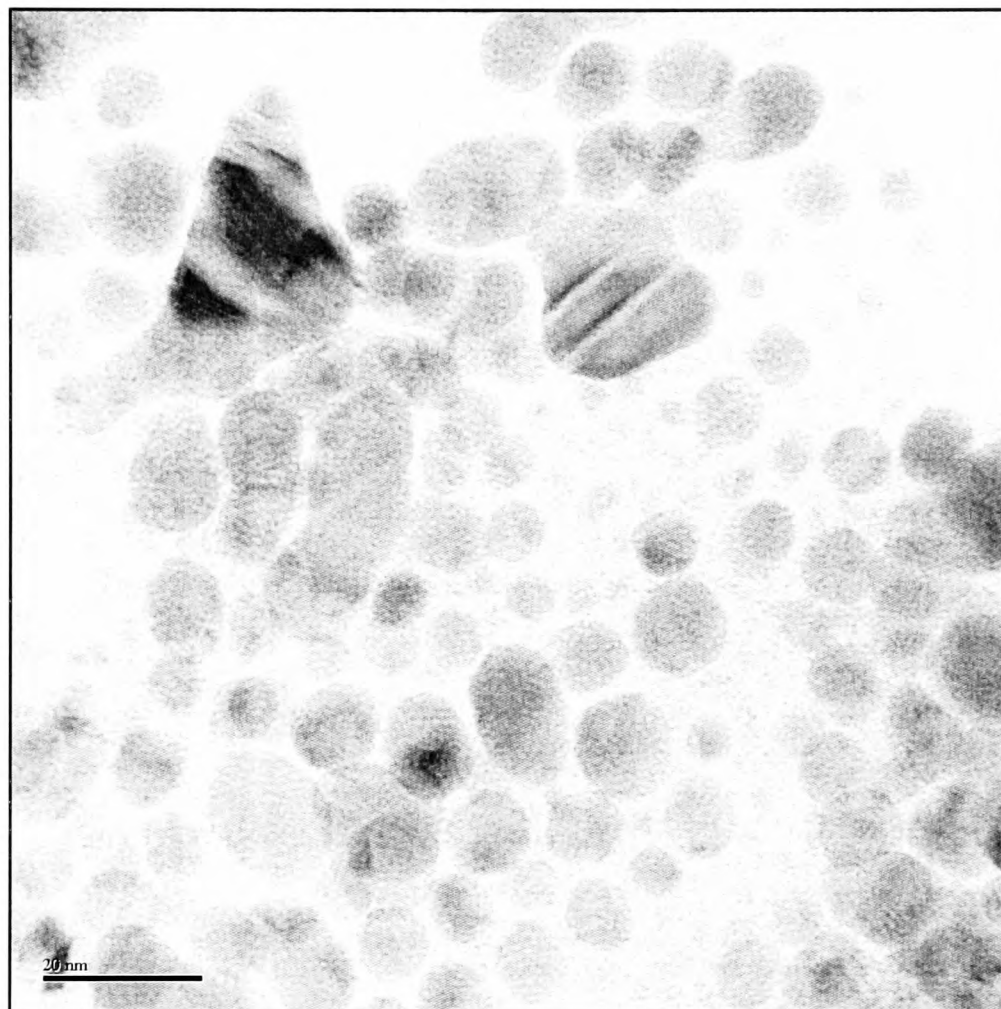


Figure 19 TEM of 1-Dodecylthiol-Stabilised Silver Nanoparticle (100) (Scale bar 20nm)

Unfortunately, ^1H NMR spectroscopy of **(100)** resulted in an extremely broad spectrum that was not possible to assign. However, the UV-vis spectroscopy proved more informative with the spectrum of **(100)** in dichloromethane revealing a surface plasmon band at 459nm (Figure 20).

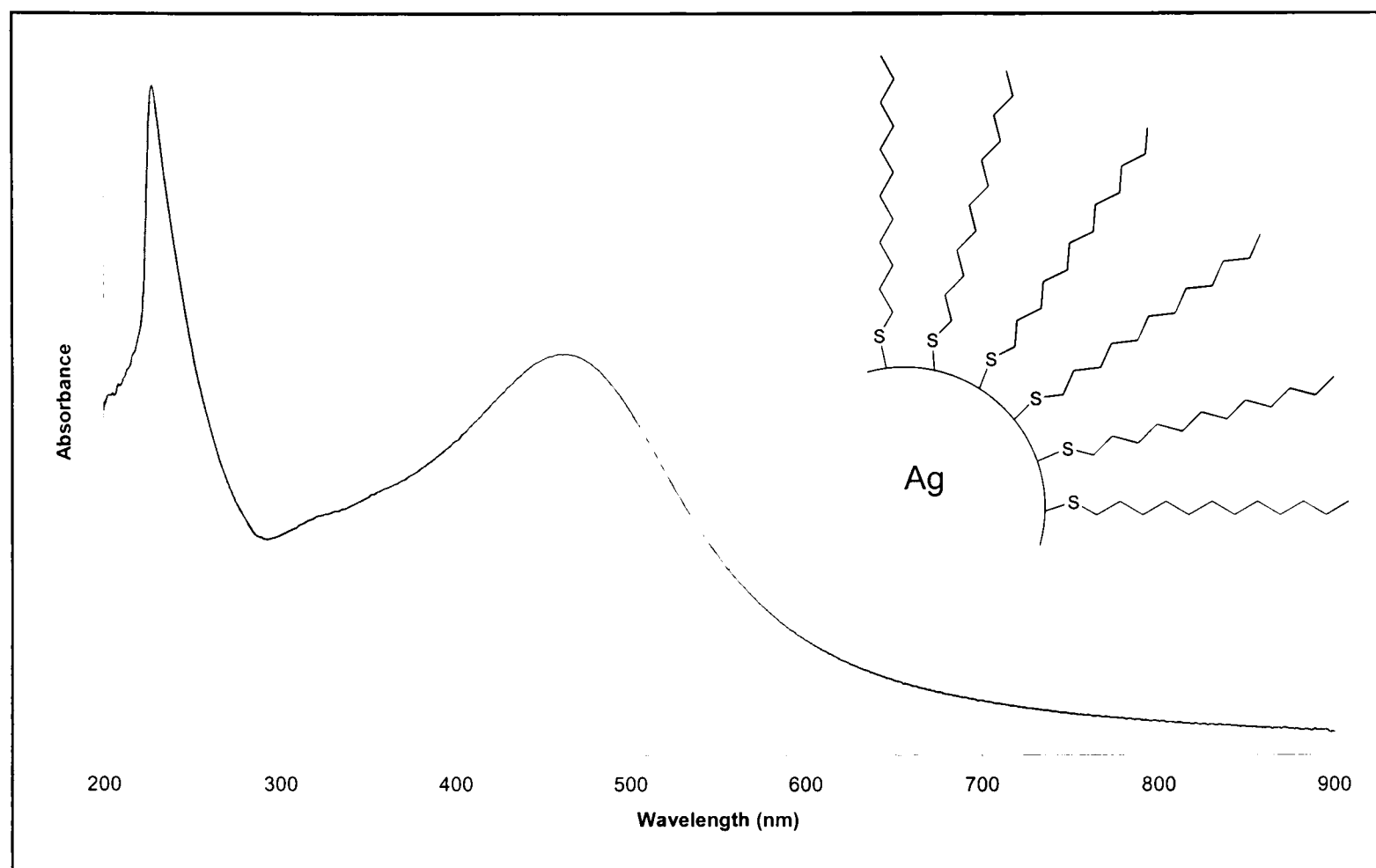


Figure 20 UV-vis spectrum of 1-dodecylthiol stabilised silver nanoparticles in CH_2Cl_2 (100)

Since it has been shown that the addition of anions to aqueous solutions of silver nanoparticles result in a significant perturbation in its optical properties, it was attempted to synthesise a silver nanoparticle stabilised with the amide appended thiol (**95**). This may have allowed the binding of anionic guests in organic solvents in close proximity to the nanoparticle's surface, and may consequently have resulted in changes within the UV-vis spectrum of the particle. Unfortunately, the attempted preparation of silver nanoparticles stabilised with (**95**) was unsuccessful, with the borohydride reduction of silver(I) in the presence of the thio-amide resulting in the formation of an insoluble brown solid.

6.2 Dithiocarbamate Stabilised Silver Nanoparticles

Recently, it has been shown that cyclodextrins may be derivatised with dithiocarbamate groups, which can be chemisorbed onto silver electrode surfaces⁷⁹. The resulting self-assembled monolayers can electrochemically distinguish between different isomers of the nitrobenzoate anion. However, this work demonstrated that the dithiocarbamate ligand

exhibits a high affinity for silver surfaces. An investigation into the potential stabilisation of silver nanoparticles by the dithiocarbamate ligand was therefore undertaken.

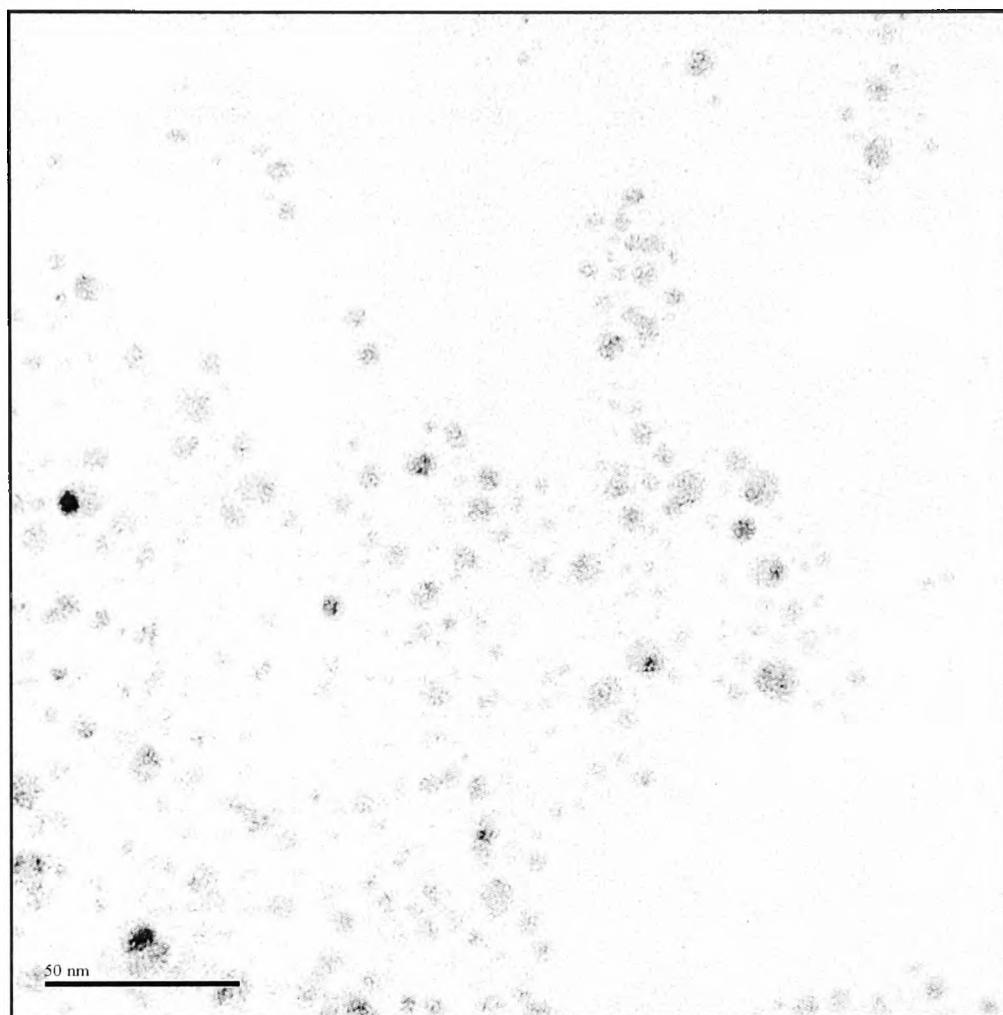


Figure 21 TEM of potassium {tetrakis[(butylaminodithiocarbamate)methyl]resorcinarene} cavitand-stabilised silver nanoparticles (102**) (Scale bar 50nm)**

Initially the preparation of silver nanoparticles stabilised by sodium *N,N'*-diethyldithiocarbamate was attempted. Sodium borohydride reduction of a toluene solution of phase transferred silver(I) nitrate in the presence of the dithiocarbamate salt resulted in the formation of a brown solution. This was precipitated via the addition of methanol, yielding a brown solid (**101**) whose composition was shown by elemental analysis to be 19 silver atoms: 8 dithiocarbamate ligands. ^1H NMR spectroscopy revealed a sharp spectrum similar to that previously seen in the case of (**91**). However, the precipitation of a dark solid occurred if (**101**) was allowed to stand for any prolonged period of time. This is likely to be a result of the relatively short alkyl chains upon the dithiocarbamate ligand, which help prevent the agglomeration of the silver nanoparticles in solution.

It has already been demonstrated that potassium {tetrakis[(butylaminodithiocarbamate) methyl] resorcinarene} cavitand resorcinarene (**92**) is able to stabilise the formation of gold nanoparticles with a high monodispersity (**93**). An investigation was undertaken as to whether (**92**) could similarly stabilise the formation of silver nanoparticles.

The sodium borohydride reduction of a toluene solution of phase-transferred silver(I) nitrate in the presence of the tetra-substituted dithiocarbamate salt (**93**) resulted in the formation of a brown solution. This was precipitated via the addition of methanol, yielding a brown solid (**102**). UV-vis spectroscopy of a dichloromethane solution of (**102**) revealed a broad plasmon band centred at 490nm, implying the formation of the desired silver nanoparticles. Examination of this solution by transmission electron microscopy (Figure 21) showed the formation of rounded crystalline particles in the size range of 2 to 15nm.

The transmission electron micrograph of (**102**) was analysed for the size distribution of the resultant silver nanoparticles. A histogram of the results and for the analogous 1-dodecylthiol-stabilised particles (**100**) is displayed in Figure 22.

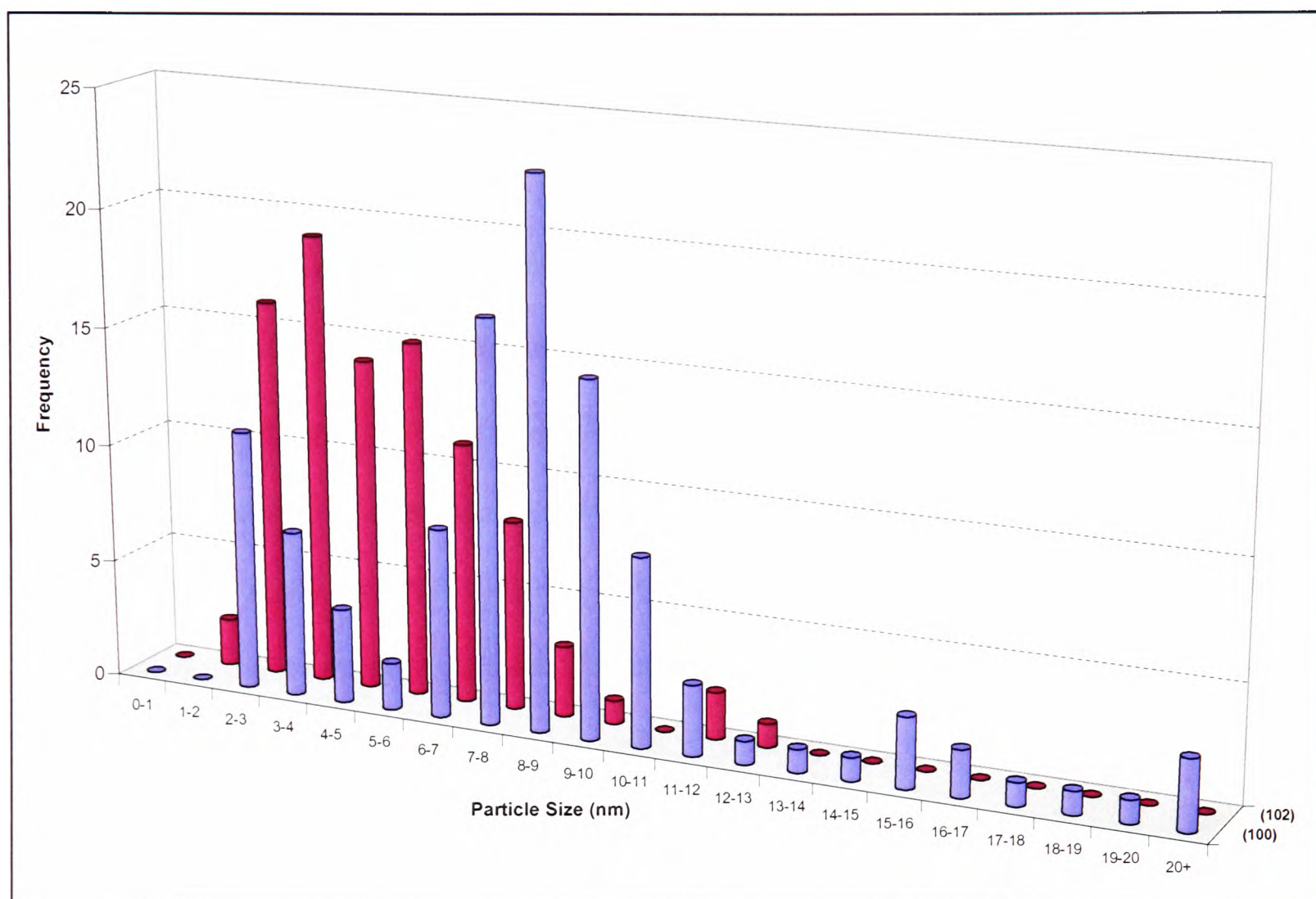


Figure 22 Histogram illustrating the size distribution of silver nanoparticles (100) and (102)

The histogram shows that in comparison to the variable sizes shown in the 1-dodecylthiol-stabilised silver nanoparticles (100) a smaller range of particle sizes is shown for the dithiocarbamate-stabilised particles (102). In particular the use of the tetra-substituted dithiocarbamate salt (92) significantly reduced the number of large particles being formed, stabilising smaller nanoparticles (average diameter 5.3nm, standard deviation 2.3nm). This observation is in agreement with the stabilisation of gold nanoparticles with tetradithiocarbamate-functionalised resorcinarene cavitands (93). This demonstrated that the dithiocarbamate ligand is an effective stabiliser of both silver and gold nanoparticles. The more preorganised (93) assists in the formation of smaller nanoparticles with a greater monodispersity than analogous methods.

7 Conclusion

It has been demonstrated within this Chapter that a range of gold and silver nanoparticles can be synthesised via chemical methods. The creation of such arrays is currently an active and exciting area of research, due to their unique properties that have lead to their incorporation in a variety of nanotechnological devices and catalytic systems.

The synthesis of gold nanoparticles has been undertaken using a variety of thiol-based stabilising ligands. The resulting crystalline particles have been characterised by transmission electron microscopy, energy dispersive X-ray spectroscopy, UV-vis spectroscopy, ^1H NMR spectroscopy and elemental analysis. The use of an amide-functionalised thiol as a stabilising ligand has been shown to form gold nanoparticles with a high monodispersity, possibly due to favourable hydrogen bonding interactions between the amide moieties. Unfortunately, the addition of anions to the amide-functionalised gold nanoparticle did not result in any significant perturbation in its plasmon band.

The dithiocarbamate ligand has also been shown to stabilise the formation of small gold nanoparticles with a high monodispersity. In particular, the tetra-dithiocarbamate-functionalised cavitand complex (**92**) stabilises gold nanoparticles with a small size distribution. The generation of nanoparticles with a narrow size distribution is important for the future development of nanotechnological devices and effective catalysts, as both of these show significant size effects.

It has also been demonstrated that silver nanoparticles can be stabilised both via thiol and dithiocarbamate-based stabilisers. The range of sizes for silver nanoparticles is significantly greater than those of comparable gold nanoparticles. However, the stabilisation of these particles by the tetra-dithiocarbamate functionalised cavitand complex (**92**) considerably reduced the dispersity of silver nanoparticles.

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Chapter Seven

Ruthenium(II) bis(2,2'- Bipyridine) Dithiocarbamate Chemistry

Chapter Seven: Ruthenium(II) bis(2,2'-Bipyridine)

Dithiocarbamate Chemistry

1 Introduction

Over the last 30 years there has been a large amount of research into transition metal bipyridine complexes, and in particular those of ruthenium. The interest in ruthenium bipyridine systems stems from their chemical stability, redox properties, excited state reactivity and luminescence emission^{1,2}. Luminescent sensors and probes have been developed for a wide range of guests^{3,4} and work has been undertaken into the possibility of using these complexes as solar energy convertors,⁵ photocatalysts,⁶ and self-assembled nano-dimensional structures⁷. Despite the highly studied ruthenium(II) tris(2,2'-bipyridine) systems (Figure 1), there is relatively little work on the analogous dithiocarbamate-substituted complexes.

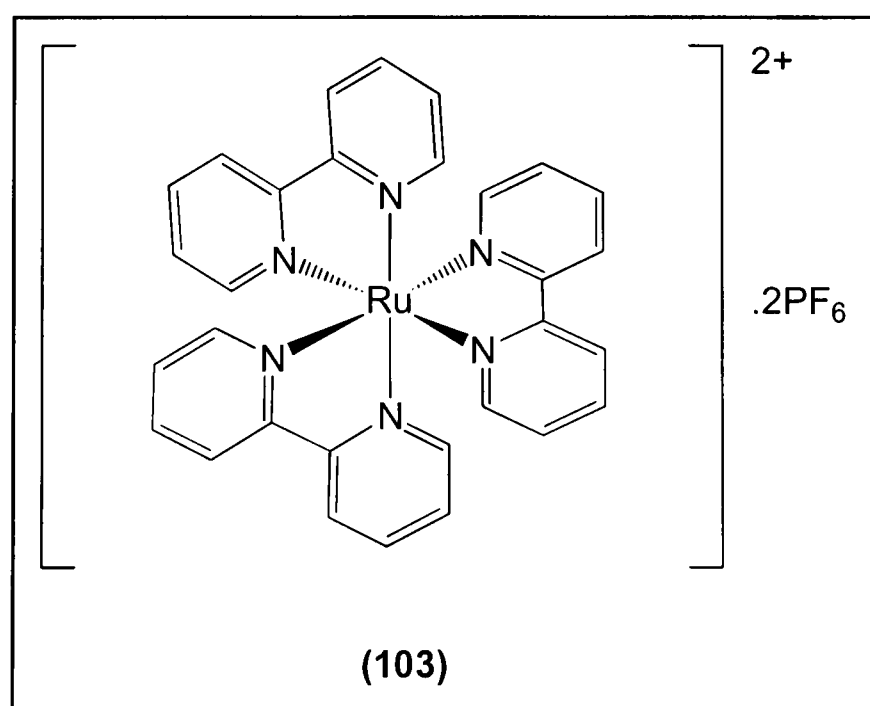


Figure 1 Ruthenium(II) tris(2,2'-bipyridine) dihexafluorophosphate (103)

2 Ruthenium(II) bis(2,2'-bipyridine) Dithiocarbamate Complexes

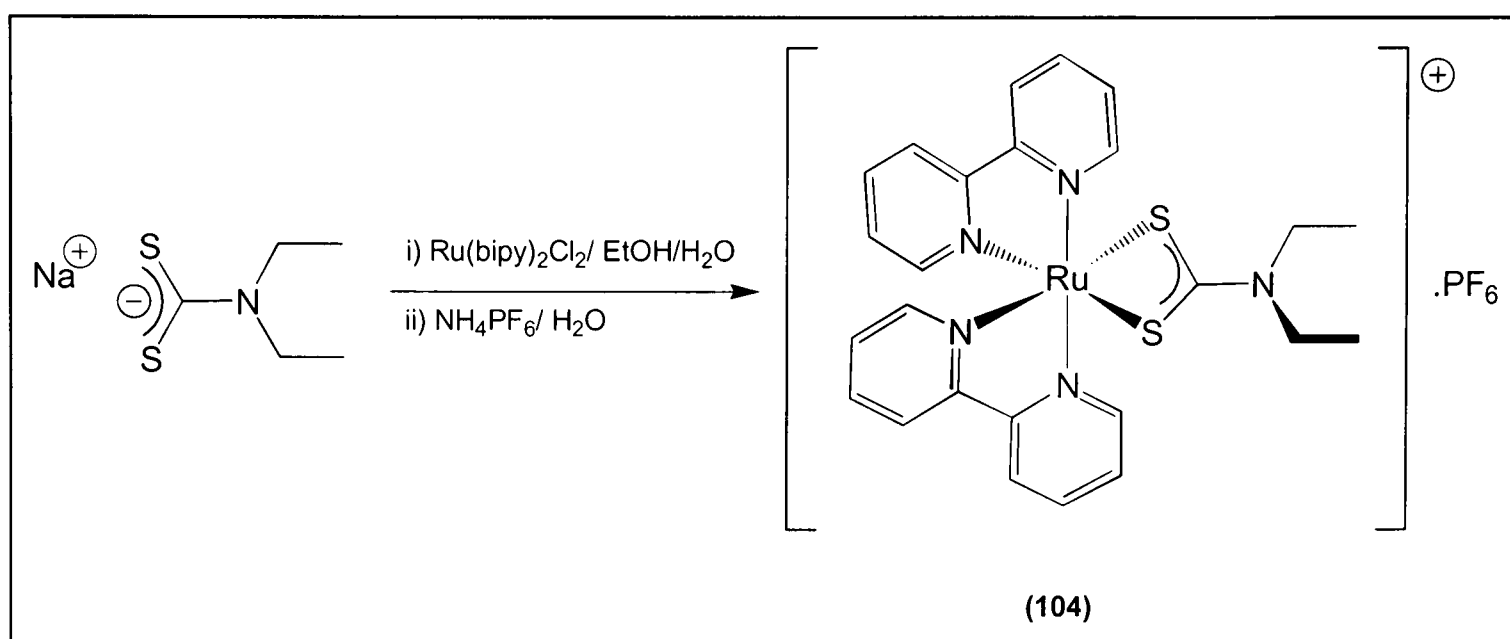
There has only been a handful of examples of the synthesis of ruthenium(II) bis(2,2'-bipyridine) dithiocarbamate complexes^{8,9}. Much of the interest in these complexes has been due to their ability to be appended with carboxylate-functionalised bipyridine units and subsequently luminesce at room temperature¹⁰. The anchoring of these fluorophores to titanium dioxide electrodes has led to the development of photovoltaic devices^{11,12}, where visible light is converted into electricity in photoelectrochemical cells^{13,14,15}.

An investigation was undertaken into the preparation and subsequent properties of new ruthenium(II) bis(2,2'-bipyridine) dithiocarbamate-based complexes. A variety of multinuclear architectures and structures appended with recognition sites were synthesised and their properties in the presence and absence of suitable guests explored.

2.1 Synthesis of Ruthenium(II) bis(2,2'-bipyridine) *N,N'*-diethyldithiocarbamate Complex (104)

Although the synthesis of ruthenium(II) bis(2,2'-bipyridine) alkyl-substituted dithiocarbamate-based complexes have previously been reported^{8,16}, their characterisation has not been extensive. To this end, the *N,N'*-diethyl-functionalised, mononuclear mixed-ligand ruthenium(II) dithiocarbamate complex (**104**) was prepared. This was achieved via modification of a literature procedure, by refluxing sodium *N,N'*-diethyldithiocarbamate with *cis*-dichlorobis(2,2'-bipyridine) ruthenium(II), for 18 hours, in ethanol/water (2:1). This was carried out under nitrogen to prevent oxidation to the corresponding ruthenium(III) species. The reaction was performed using an excess of the dithiocarbamate salt and was subsequently purified by precipitation via the addition of ammonium hexafluorophosphate (Scheme 1). The hexafluorophosphate anion was chosen as a counteranion due to its non-coordinating

properties, enabling the binding properties of these systems to be investigated as well as conferring the complex with solubility in a wide range of organic solvents.



Scheme 1 Synthesis of Ru(II) bis(2,2'-bipyridine) (*N,N'*-diethyldithiocarbamate) hexafluorophosphate (**104**)

The purple solid **(104)** was isolated in 92% yield, and characterised by ^1H , ^{13}C , ^{19}F , ^{31}P , NMR, electrospray mass spectrometry and elemental analysis. In addition, ^1H - ^1H COSY and ^1H - ^{13}C HSQC NMR experiments were performed for the aid of characterising the aromatic protons. The ^1H NMR spectrum of **(104)** and its assignments are displayed in Figure 2.

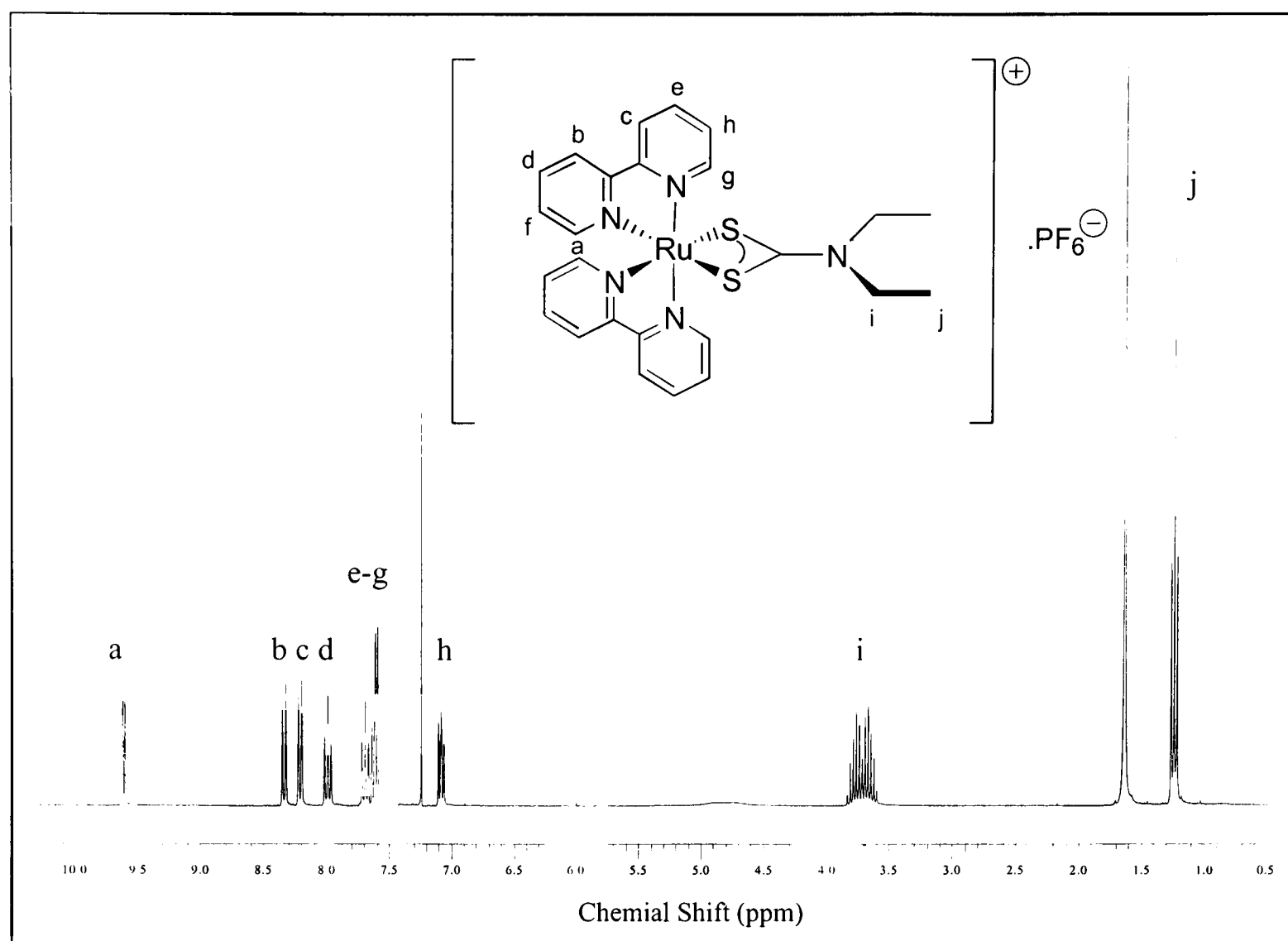


Figure 2 ^1H NMR spectrum of Ru(II) bis(2,2'-bipyridine)(*N,N'*-diethyldithiocarbamate) hexafluorophosphate (**104**) (300MHz, CDCl_3)

The spectrum reveals a well-resolved aromatic region, corresponding to the protons of the bipyridine units (a - h). The high field region of the spectrum consists of the peaks of the ethyl chain of the dithiocarbamate ligands (i and j). Interestingly, the methylene protons (i) are diastereotopic, consisting of two closely spaced quartets (3.6 – 3.8 ppm) as a result of the adjacent chiral ruthenium centre.

2.1.1 X-Ray Crystallography

A single crystal of the complex (**104**) suitable for X-ray structural analysis was grown via vapour diffusion of isopropyl ether into a solution of 1,2-dichloroethane. The structure of this was solved by Dr R. Paul and Dr. A Cowley, University of Oxford, and is displayed in Figure 3. Important crystallographic parameters are highlighted in Table 1.

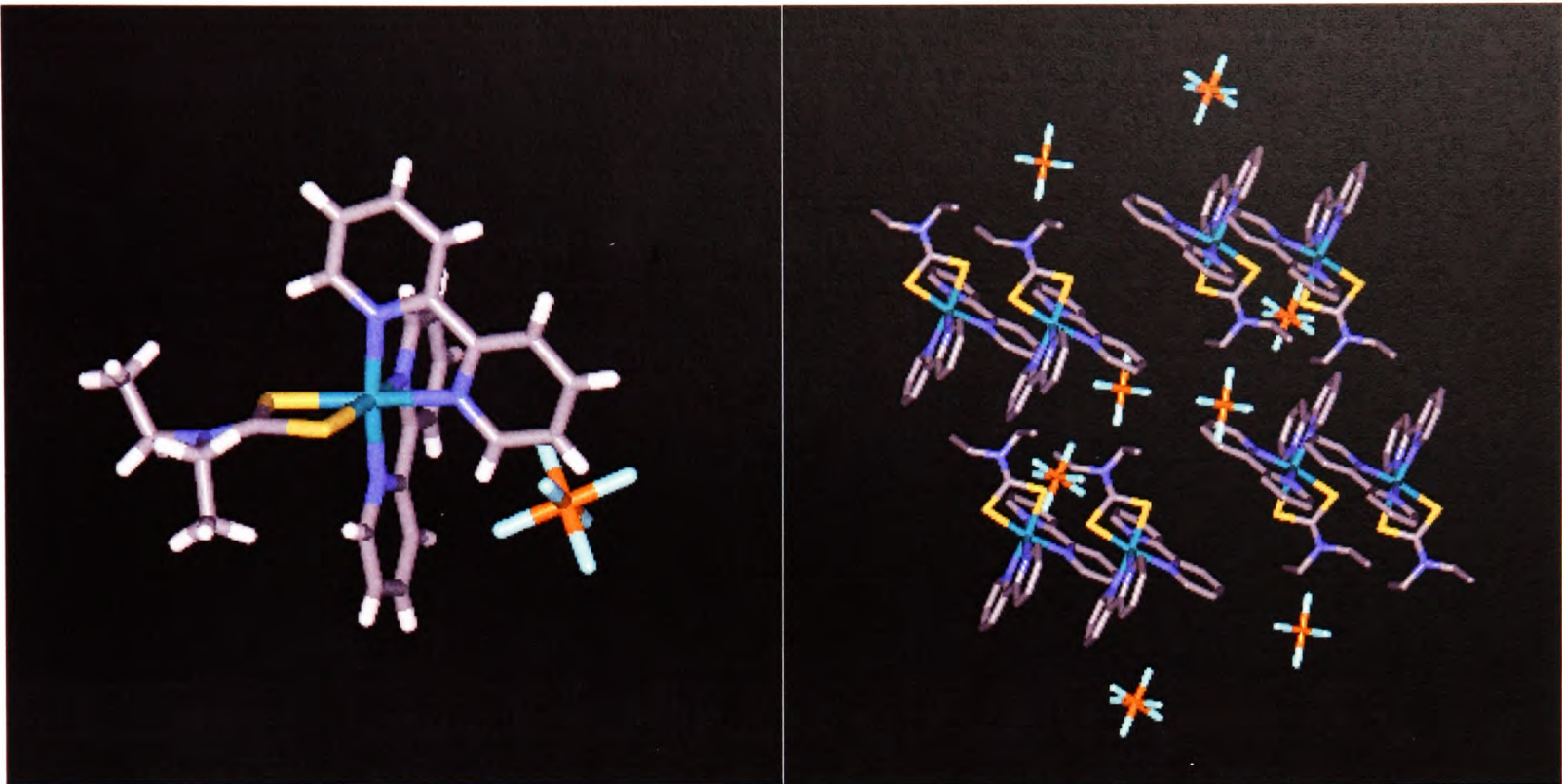


Figure 3 X-Ray crystal structure of Ru(II) bis(2,2'-bipyridine)(N,N'-diethyldithiocarbamate) hexafluorophosphate (104) Right: Crystal packing structure illustrating π - π stacking along the crystallographic a -axis (Key: C – grey, H – white, N – blue, S – yellow, P – orange, F – light blue, Ru – green)

	(104)
d(Ru-S) Å	2.40
d(Ru-N) Å	2.05, 2.06 2.07, 2.07
d(N-C(S ₂)) Å	1.32
θ (S-Ru-S) ^o	72.6
θ (N-Ru-N) ^o	78.4, 78.5

Table 1 Selected crystallographic parameters for (104)

The ruthenium centre adopts a pseudo-octahedral geometry, due to the restricted bite-angles of the surrounding bidentate ligands (sulphur-ruthenium-sulphur angle 72.63°, nitrogen-ruthenium-nitrogen angles 78.52° and 78.38°). Ruthenium-nitrogen distances are analogous to those in ruthenium tris(2,2'-bipyridine) systems¹⁷. The coordination three bidentate ligands about the metal centre results in the formation of a chiral centre.

As was also seen in the gold(III) dithiocarbamate complexes described in Chapter Four, the length of the nitrogen-carbon bond of the dithiocarbamate linkage is considerably less than would be expected for a typical single carbon-nitrogen bond ($1.47\text{\AA}$) and closer to that of a carbon-nitrogen double bond ($1.28\text{\AA}$)¹⁸. This demonstrates the high covalent character of the metal-sulphur bonds typical of a third row transition metal complex. The hexafluorophosphate anion is reasonably close to the cation (phosphorous-ruthenium distance $7.23\text{\AA}$), with the charge of the ruthenium centre possibly transferred through to the anion via hydrogen bonding of the fluorine atoms with the bipyridine protons (hydrogen bonding distance $2.56\text{\AA}$).

2.1.2 Optical Properties

The electronic absorption spectrum of the purple ruthenium(II) bis(2,2'-bipyridine) dithiocarbamate complex (**104**) was recorded at 293K in acetonitrile. The resulting spectrum displayed two metal to ligand charge transfer bands (MLCT) at 520 ($\epsilon = 7600\text{ M}^{-1}\text{cm}^{-1}$ ($\pm 10\%$)) and 351nm ($\epsilon = 10000\text{ M}^{-1}\text{cm}^{-1}$ ($\pm 10\%$)). There are also a number of ligand centred transitions at lower wavelengths.

The solution was also examined in order to determine whether it exhibited luminescent emission at room temperature. Unfortunately, in contrast to the tris(2,2'-bipyridine) complex (**103**), excitation at either metal to ligand charge transfer band failed to result in electronic emission.

2.1.3 Electrochemistry

Ruthenium(II) bis(2,2'-bipyridine) dithiocarbamate complexes have been shown to display electrochemical properties similar to those of the ruthenium tris(2,2'-bipyridine) systems⁸. At negative potential there are two reversible, one electron reductions of each of the bipyridine ligands (Figure 4). At positive potential there is a reversible one electron oxidation

corresponding to the ruthenium(II/III) couple and at higher potential ($E_{1/2} = 1.30\text{V}$), an irreversible process, possibly the result of the oxidation of the dithiocarbamate ligand.

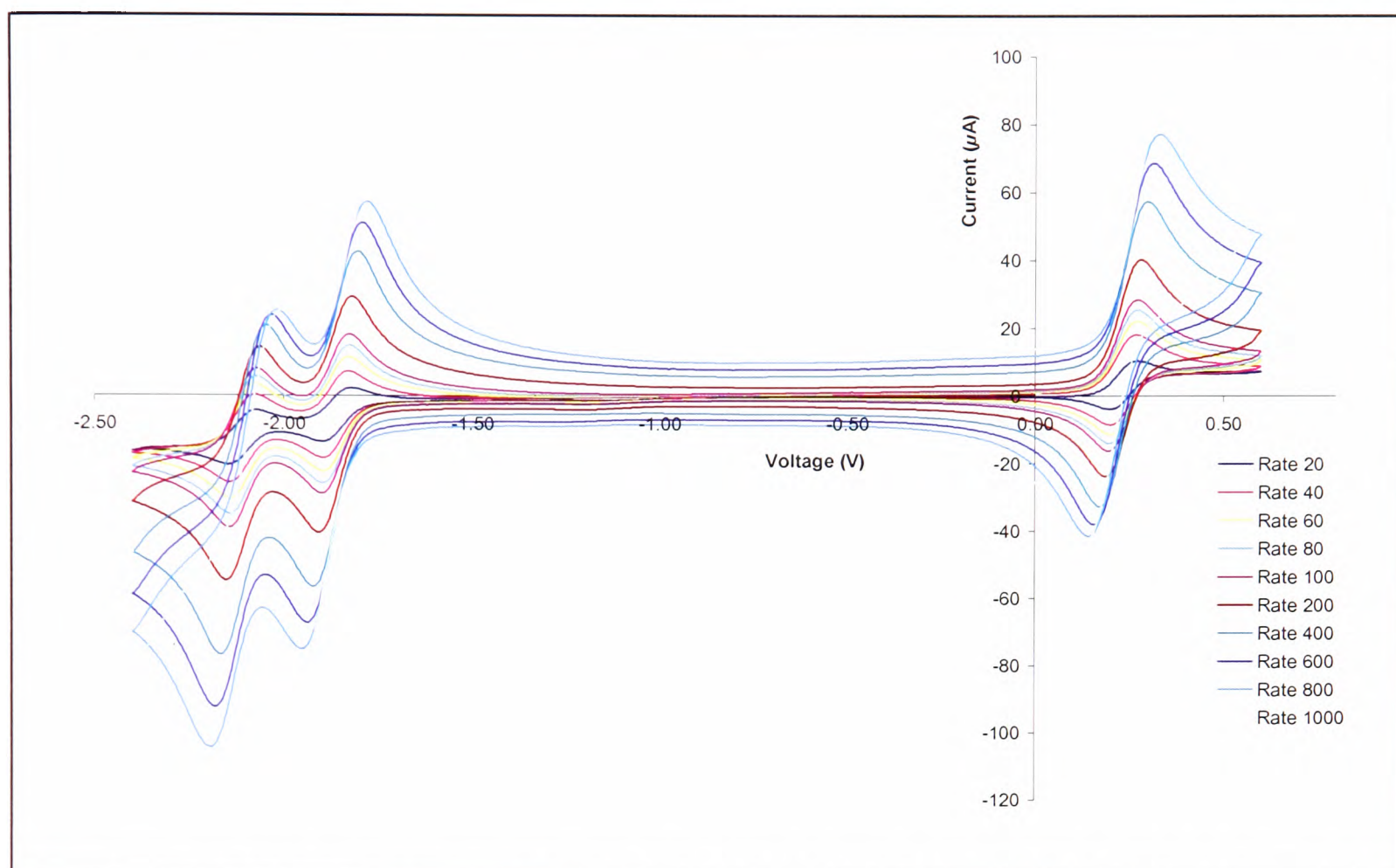


Figure 4 Cyclic voltammograms of the Ru(II) bis(2,2'-bipyridine) *N,N'*-diethylthiocarbamate hexafluorophosphate complex (104) at varying scan rates (mVs^{-1}), performed in MeCN containing 0.1M TBABF₄, sample $\sim 1 \times 10^{-3}\text{M}$ with reference to Ag/AgNO₃ at 293K, working electrode glassy carbon

It is noteworthy that the potential of the ruthenium(II/III) couple is significantly lowered when one of the bipyridine groups are replaced by a dithiocarbamate ligand (Table 2). This further illustrates the dithiocarbamate ligand's ability to stabilise metals in higher oxidation states (also refer to Section 7.1).

		Ru(II/III)	bipyH1	bipyH2	bipyH3
(103)	$E_{1/2}$	0.96V	-1.64V	-1.83V	-2.08V
	E_{pa}	1.00V	-1.61V	-1.80V	-2.04V
	E_{pc}	0.92V	-1.68V	-1.87V	-2.12V
(104)	$E_{1/2}$	0.24V	-1.86V	-2.11V	-
	E_{pa}	0.27V	-1.82V	-2.07V	-
	E_{pc}	0.20V	-1.90V	-2.15V	-

Table 2 Electrochemical data for Ru(II) bis(2,2'-bipyridine) *N,N'*-diethyldithiocarbamate hexafluorophosphate complex (104) and Ru(II) tris(2,2'-bipyridine) hexafluorophosphate (103) in MeCN with TBABF₄ as the supporting electrolyte, Ag/AgNO₃ as the reference electrode and glassy carbon as the working electrode. Sample 1x10⁻³M, scan rate 100mVs⁻¹, frequency 5Hz, T = 293K, errors ±5mV

3 Multinuclear Ruthenium Bis(2,2'-bipyridine) Dithiocarbamate

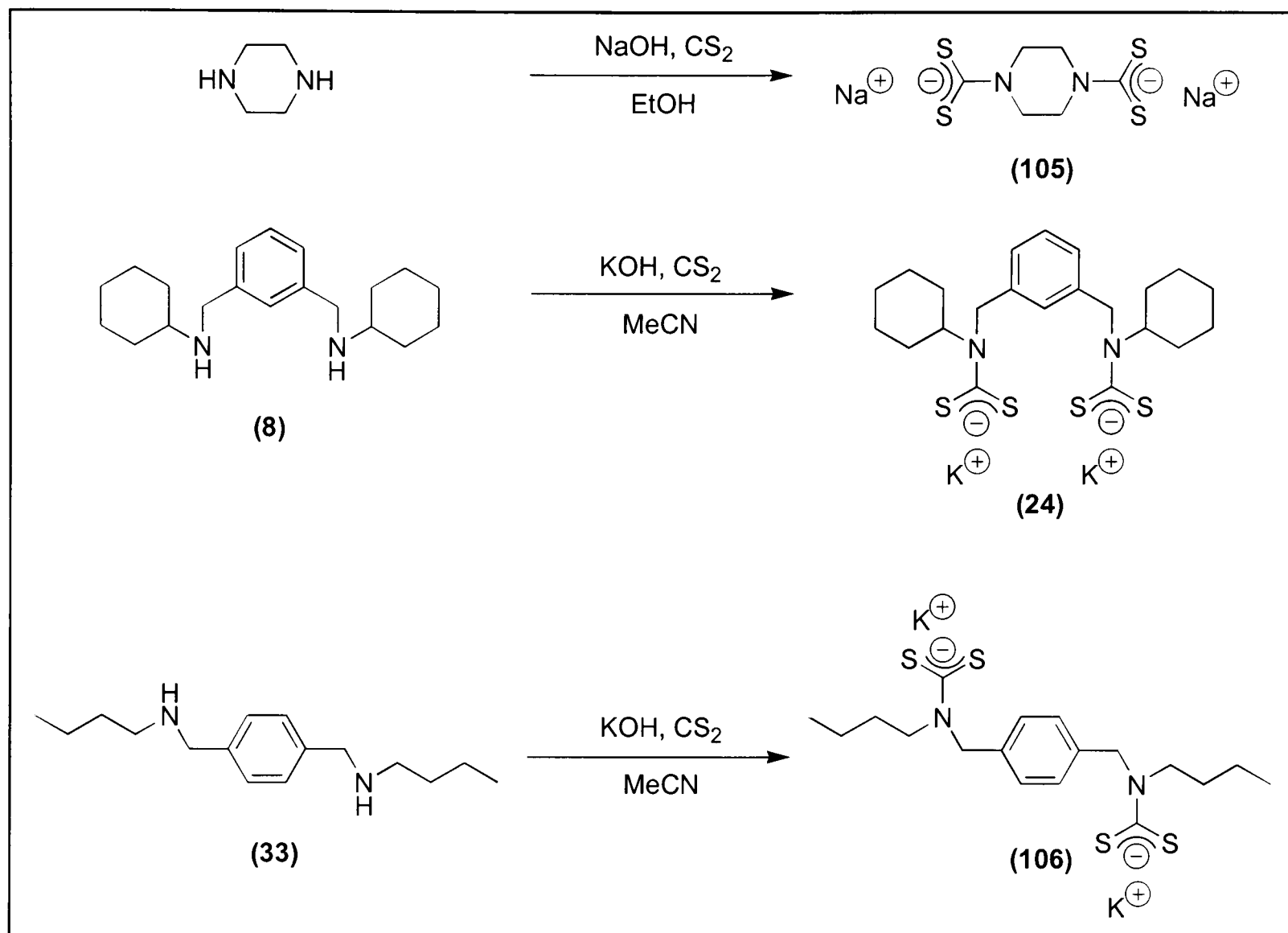
Complexes

It has been shown in Chapter Two that dinuclear copper(II) dithiocarbamate complexes may be synthesised in which the metal centres are able to electrochemically communicate with each other. The development of such species is potentially interesting for the development of information transfer- and molecular electronic devices^{19,20,21,22}. To this end, a number of multinuclear ruthenium bis(2,2'-bipyridine) dithiocarbamate based systems were designed and their properties investigated.

3.1 Synthesis and Characterisation of Dinuclear Complexes

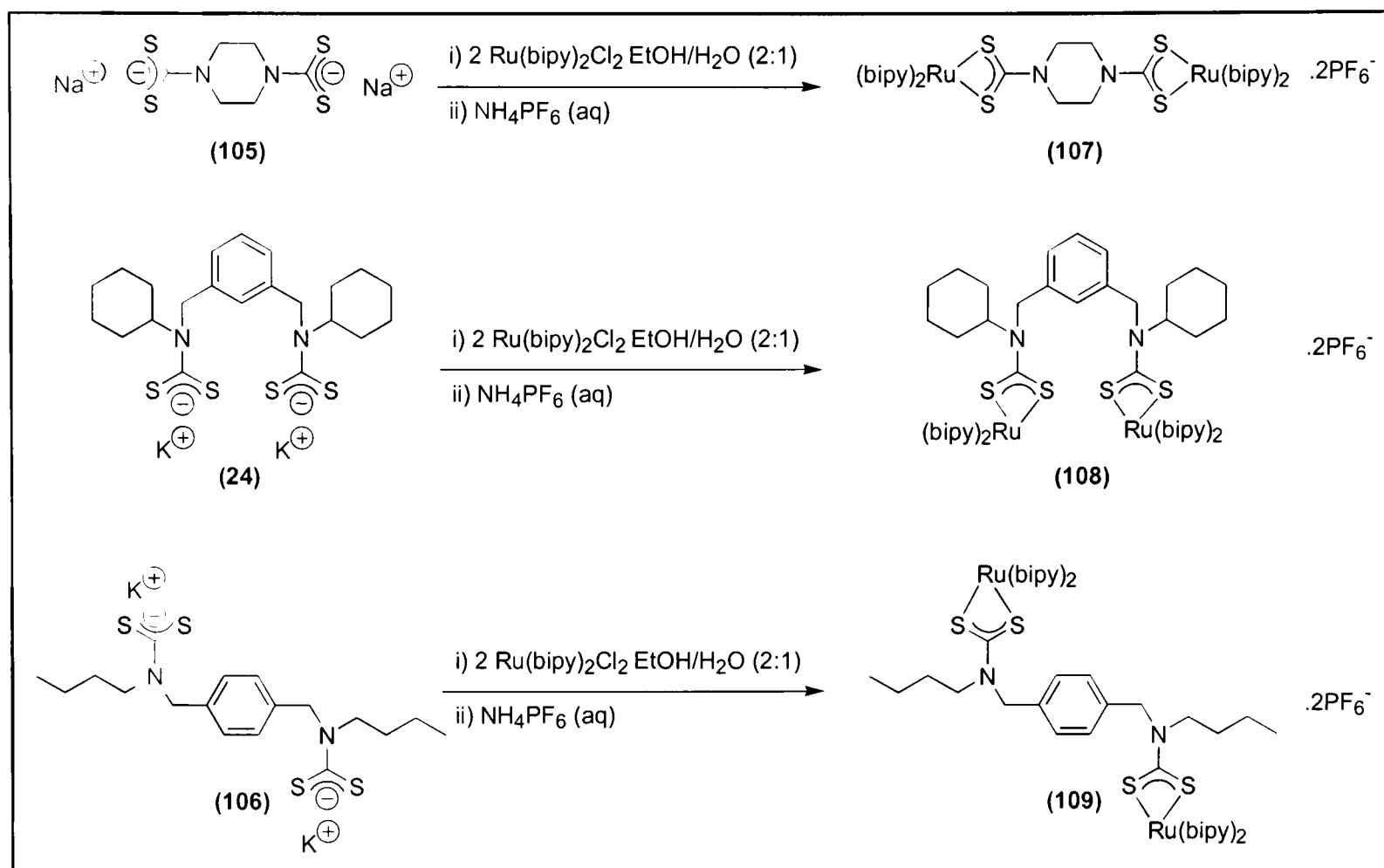
Initially, a series of dinuclear ruthenium-based complexes were prepared. This was achieved via the initial preparation of an alkali metal bis-dithiocarbamate salt incorporating a short spacing moiety. In general, the synthesis of these salts was achieved by the addition of carbon disulphide to a secondary bis-amine in basic acetonitrile solution (Scheme 2). The bis-

dithiocarbamate salts were isolated as white solids (**105**) and (**106**) via filtration and precipitation upon addition of diethyl ether in 86% and 95% yields, respectively. The resulting salts were characterised via ^1H and ^{13}C NMR spectroscopy and elemental analysis.



Scheme 2 Synthesis of bis-dithiocarbamate salts

The alkali metal bis-dithiocarbamate salts (**105**), (**106**) and (**24**) were treated with two equivalents of *cis*-dichlorobis(2,2'-bipyridine) ruthenium(II) and refluxed for 18 hours in an ethanol/water (2:1) solvent mixture under nitrogen. The crude product was purified by column chromatography over Sephadex LH-20 eluted with acetonitrile/methanol (95:5) and collecting the second fraction. The addition of ammonium hexafluorophosphate to an aqueous solution of the dinuclear complex precipitated the desired hexafluorophosphate products (**107**) - (**109**) in high yields (Scheme 3).



Scheme 3 Synthesis of dinuclear Ru(II) bis(2,2'-bipyridine) dithiocarbamate-based complexes

The synthesis of the dinuclear ruthenium complexes was also attempted via a one-pot reaction from the bis-amines (8) and (33). Two equivalents of potassium hydroxide, carbon disulphide and *cis*-dichlorobis(2,2'-bipyridine) ruthenium(II) were reacted in both 2:1 tetrahydrofuran/water and acetonitrile/water solvent systems. It was necessary to use a non-alcoholic solvent for this reaction in order to prevent the formation of competing xanthate complexes. Unfortunately, examination by electrospray mass spectrometry of the crude products after 18 hours of refluxing did not reveal the formation of the desired dinuclear products. It is therefore apparent that the use of an alcoholic solvent is necessary in order for the reaction to proceed.

This feature is further apparent after the examination of the electrospray mass spectrum of the crude product of (107) when performed in an ethanol/water (2:1) solvent system. In addition to the predominant dicationic peak in the spectrum (m/z 639.35) a smaller peak could also be observed corresponding to the formation of a singly-charged adducts with anionic species (Figure 5). In addition to the expected peak with chloride, a significant peak was also

observable with an ethoxide anion. This suggests that the solvent ethanol plays a crucial part in the synthesis of the dithiocarbamate-functionalised complexes, possibly acting as a nucleophilic catalyst.

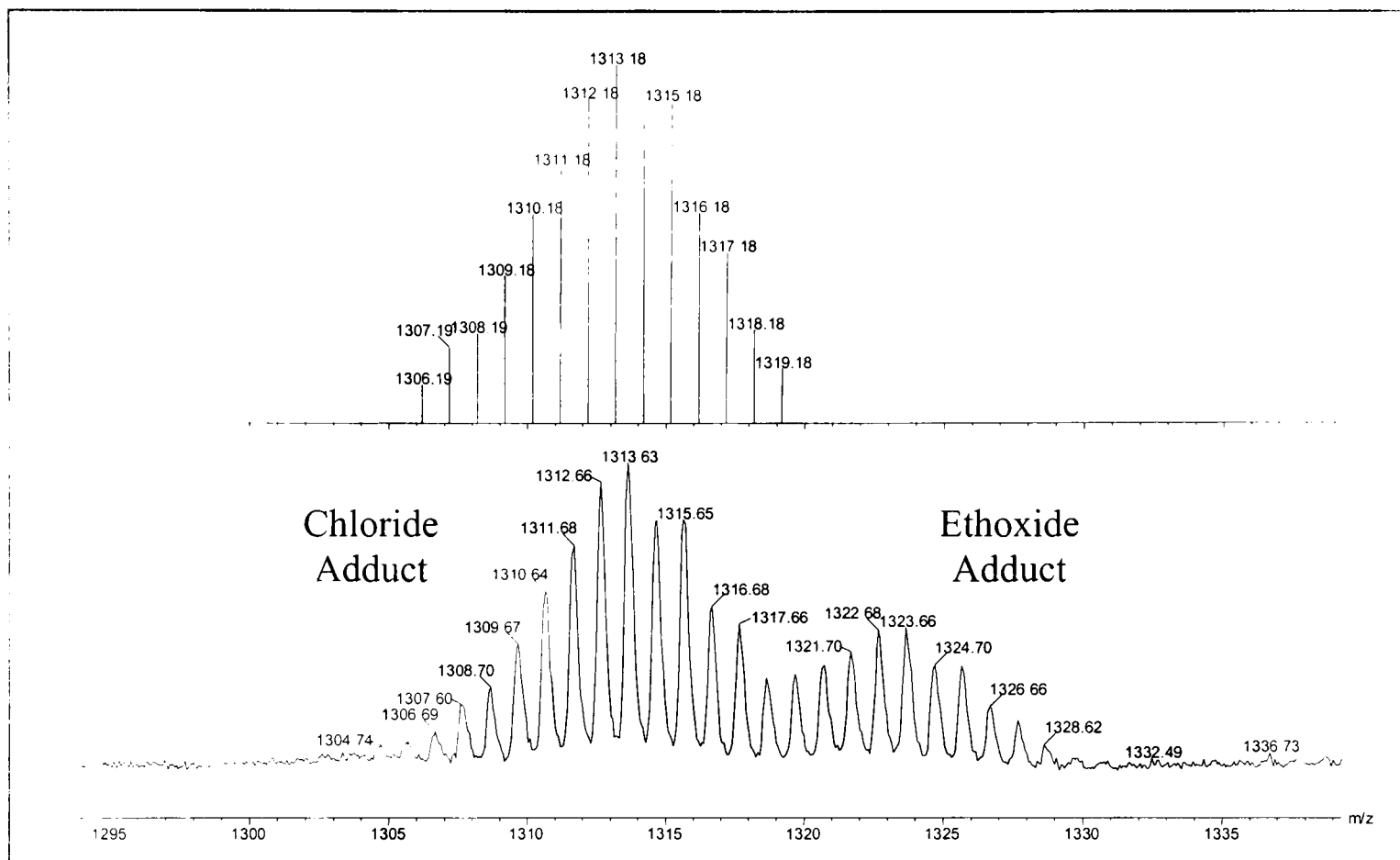


Figure 5 Electrospray mass spectrum of crude product of (107) showing both a chloride (left) and ethoxide (right) adduct (above) predicted isotope pattern for chloride adduct

The dinuclear ruthenium complexes were characterised by ^1H , ^{13}C , ^{19}F , ^{31}P and ^1H - ^1H COSY NMR spectroscopy. The spectra of the xylyl-spaced dinuclear complexes (108) and (109) are difficult to interpret as a number of peaks are visible for each bipyridyl proton, due to the conformations these flexible molecules may adopt in solution. In comparison, the smaller piperazine spacing group restricts the solution state conformers in (107), resulting in the observation of a sharp spectrum. The ^1H - ^1H COSY NMR spectrum of (107) is displayed in Figure 6, and this clearly shows the coupling between the bipyridine protons.

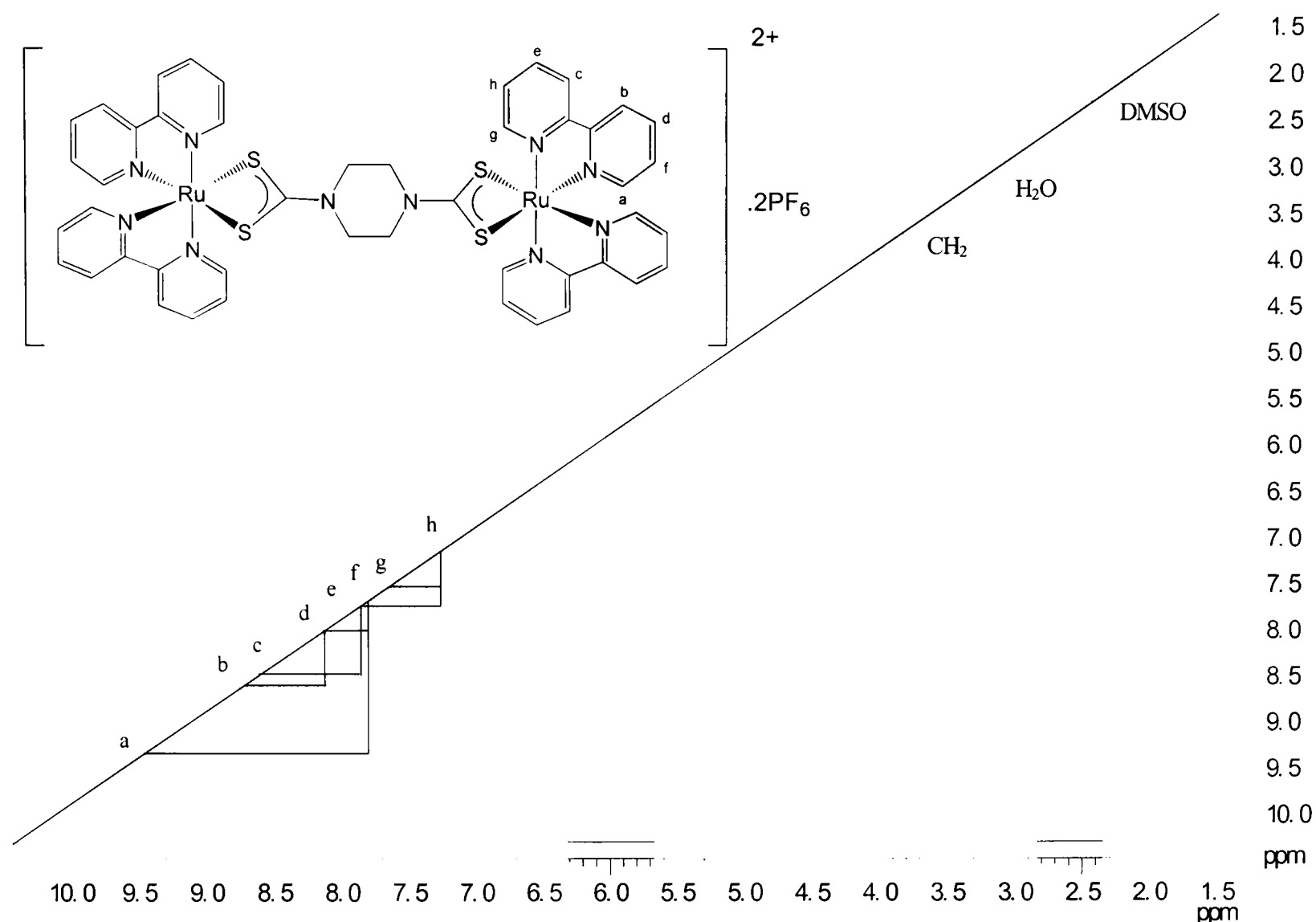


Figure 6 ^1H - ^1H COSY NMR spectrum of dinuclear piperazine spaced Ru(II) bis(2,2'-bipyridine) dithiocarbamate complex

The dinuclear complexes were also characterised via electrospray mass spectrometry, elemental analysis and UV-vis spectroscopy. In addition, the electrochemical properties of the complexes were analysed via cyclic and square wave voltammetry. This was performed in an acetonitrile solution of the dinuclear complex containing 0.1M tetra-*n*-butylammonium tetrafluoroborate as a background electrolyte. The resulting voltammograms displayed redox waves analogous to the mononuclear complex (**104**), with one ruthenium(II/III) oxidation and two bipyridine reduction couples being observed. The electrochemical data of the dinuclear complexes (**107**) - (**109**) is displayed in Table 3.

		Ru(II/III)	bipyH1	bipyH2
(107)	$E_{1/2}$	0.30V	-1.84V	-2.10V
	E_{pa}	0.34V	-1.80V	-2.05V
	E_{pc}	0.25V	-1.88V	-2.13V
(108)	$E_{1/2}$	0.27V	-1.85V	-2.11V
	E_{pa}	0.31V	-1.81V	-2.07V
	E_{pc}	0.23V	-1.89V	-2.15V
(109)	$E_{1/2}$	0.27V	-1.86V	-2.11V
	E_{pa}	0.31V	-1.80V	-2.07V
	E_{pc}	0.23V	-1.89V	-2.15V

Table 3 Electrochemical data for dinuclear Ru(II) bis(2,2'-bipyridine) dithiocarbamate complexes (107) - (109) recorded in MeCN with TBABF₄ as the supporting electrolyte, Ag/AgNO₃ as the reference electrode and glassy carbon as the working electrode. Sample 1x10⁻³M, scan rate 100mVs⁻¹, frequency 5Hz, T = 293K, errors ±5mV

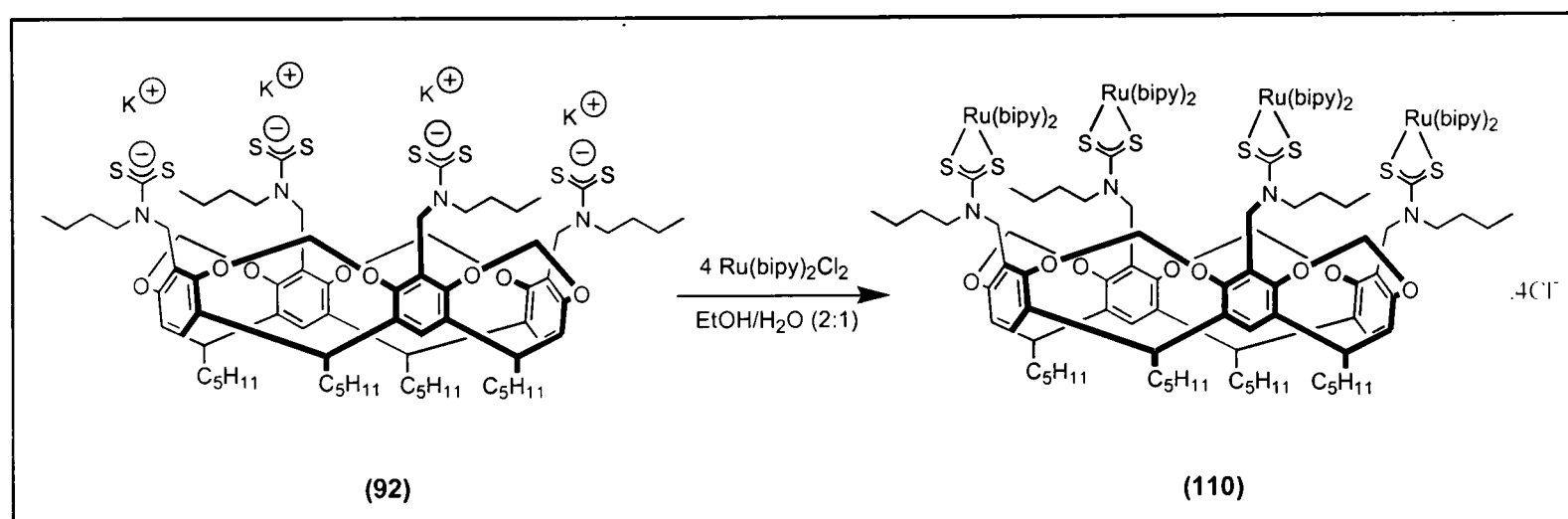
The observation of only one wave for the three redox waves for the dinuclear complexes suggests that the metal centres are behaving independent of one another, i.e. the oxidation/reduction of one of the centres does not electrochemically perturb the other through space. It is noticeable, however, that all of the complexes show peaks that are anodically shifted with respect to that of the mononuclear complex (104). This feature is maximised in the more rigid piperazine-spaced complex (107), where the two positively-charged ruthenium centres are closest together through space.

3.2 Tetranuclear Resorcinarene Complex

It has been shown that dinuclear ruthenium bis(2,2'-bipyridine) dithiocarbamate complexes may be formed from the reaction of bis-dithiocarbamate salts with *cis*-dichlorobis(2,2'-

bipyridine) ruthenium(II). An investigation was undertaken to examine whether analogous multinuclear complexes could also be synthesised. This was attempted by coordination upon a tetrakis-dithiocarbamate resorcinarene framework. Such compounds may prove to have interesting optical and electrochemical properties. In addition, the incorporation of the positively-charged redox-active group in close proximity to the hydrophobic cavity may act as a novel receptor for the binding of electron-rich guests.

The potassium tetrakis-dithiocarbamate-functionalised resorcinarene salt (**92**) was reacted with five equivalents of *cis*-dichlorobis(2,2'-bipyridine) ruthenium(II) and refluxed under nitrogen for 18 hours, in an ethanol/water (2:1) solvent mixture (Scheme 4).



Scheme 4 Synthesis of tetranuclear Ru(II) (bis-bipyridine) dithiocarbamate-functionalised resorcinarene complex (**110**)

The resulting mixture was purified by column chromatography over Sephadex LH-20 eluted with acetonitrile/methanol (95:5) collecting the second fraction. This crude product (**110**) was analysed by both 1H NMR spectroscopy and electrospray mass spectrometry. The 1H NMR spectrum displayed peaks characteristic of molecular framework, although these were rather broad, an effect due to the numerous stereoisomers and conformers the complex is able to adopt. Analysis of the electrospray mass spectrum did reveal the formation of the desired tetranuclear product (Figure 7). This is shown by the formation of the tetracationic complex (m/z 777.90) and the tricationic complex with chloride (m/z 1048.91).

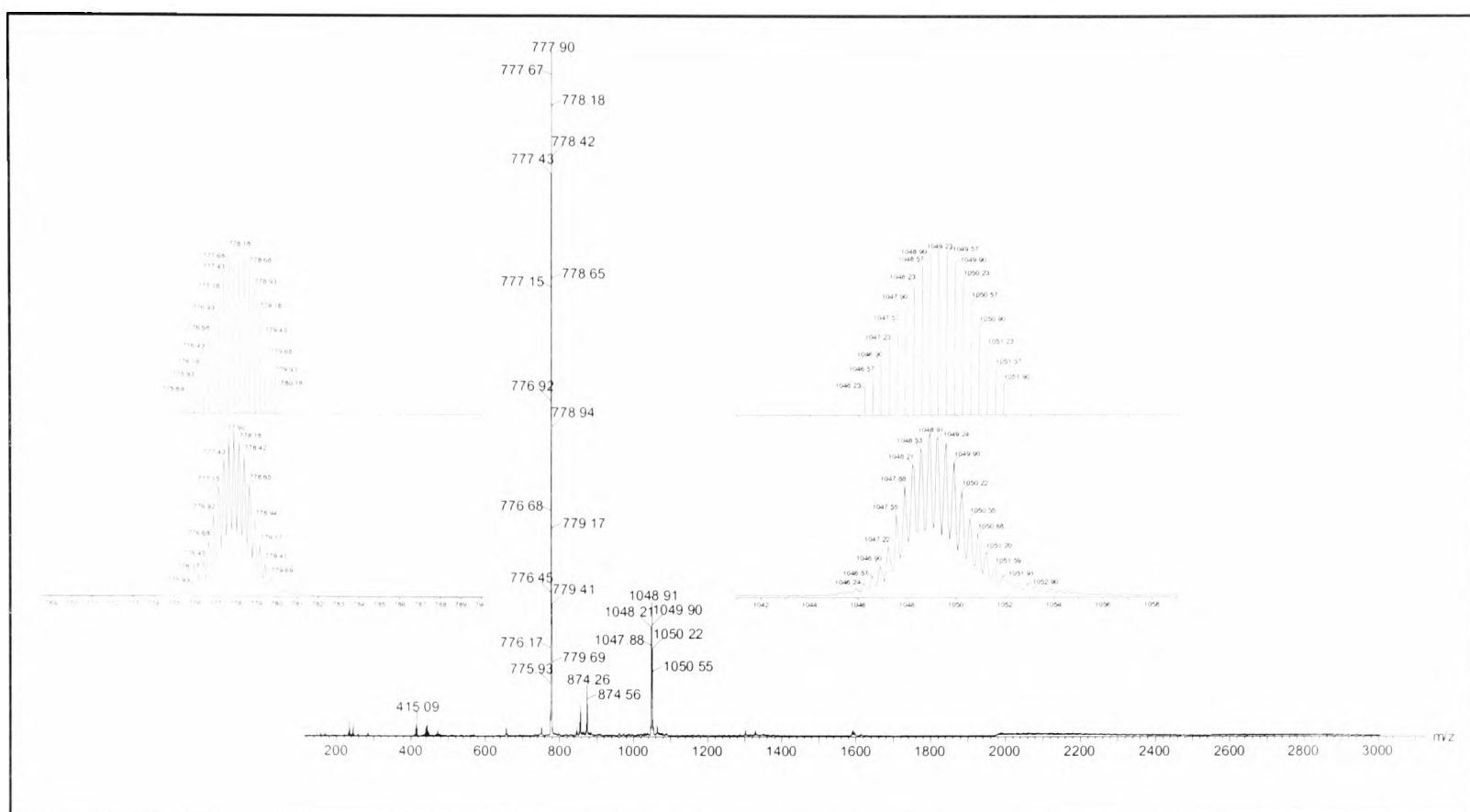


Figure 7 Electrospray mass spectrum of tetranuclear Ru(II) (bis-bipyridine) dithiocarbamate-functionalised resorcinarene complex (110) Inset(left) predicted (upper) and actual (lower) isotope pattern for $[M]^{4+}$ peak (m/z 777.9), Inset(right) predicted (upper) and actual (lower) isotope pattern for $[M.Cl]^{3+}$ peak (m/z 1048.9)

Ammonium hexafluorophosphate was added to an aqueous solution of the crude product in order to isolate the salt of the non-coordinating anion. The resulting precipitate was collected and analysed by electrospray mass spectrometry, ^1H NMR spectroscopy and elemental analysis. Unfortunately, none of these techniques were consistent with the formation of the desired salt, and suggested that the tetranuclear product had dissociated. It is possible that the chloride anion acts as a template for the formation of the tetracationic complex, and indeed acts to stabilise this architecture, as is indicated by the presence of a large peak within the electrospray mass spectrum of the crude product (Figure 7). Exchange of the chloride with the bulkier, non-coordinating counteranion may not provide the same electrostatic stabilisation and results in the decomposition of the tetranuclear complex.

4 Cation Binding

It has been illustrated in Chapter One that receptors containing crown ether derivatives exhibit a high affinity for s-block cationic metal species. Despite this, there have been few examples of cation-binding receptors based upon transition metal dithiocarbamate complexes appended with crown ethers. One example of this is the copper(II) dithiocarbamate-linked aza-15-crown-5²³ (Figure 8). This complex exhibited a 10mV anodic shift in its copper(II/III) oxidation couple upon addition of an excess of sodium cations in acetonitrile solution.

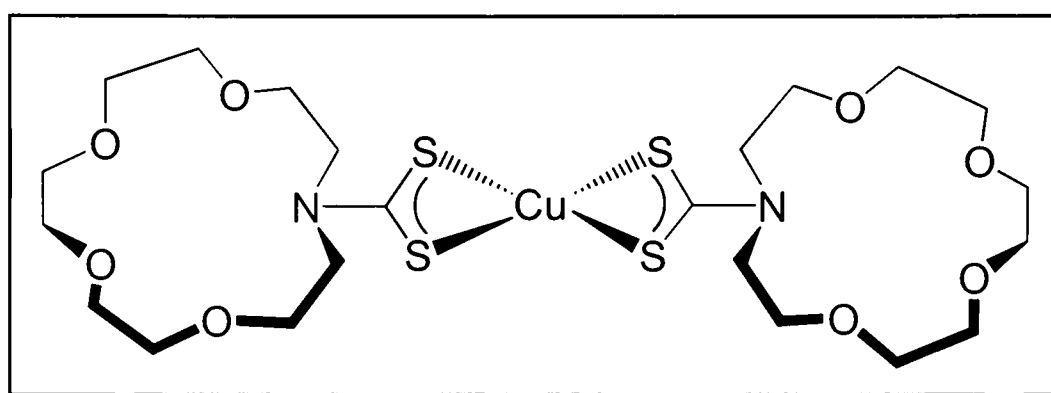


Figure 8 Crown ether appended Cu(II) dithiocarbamate-based complex

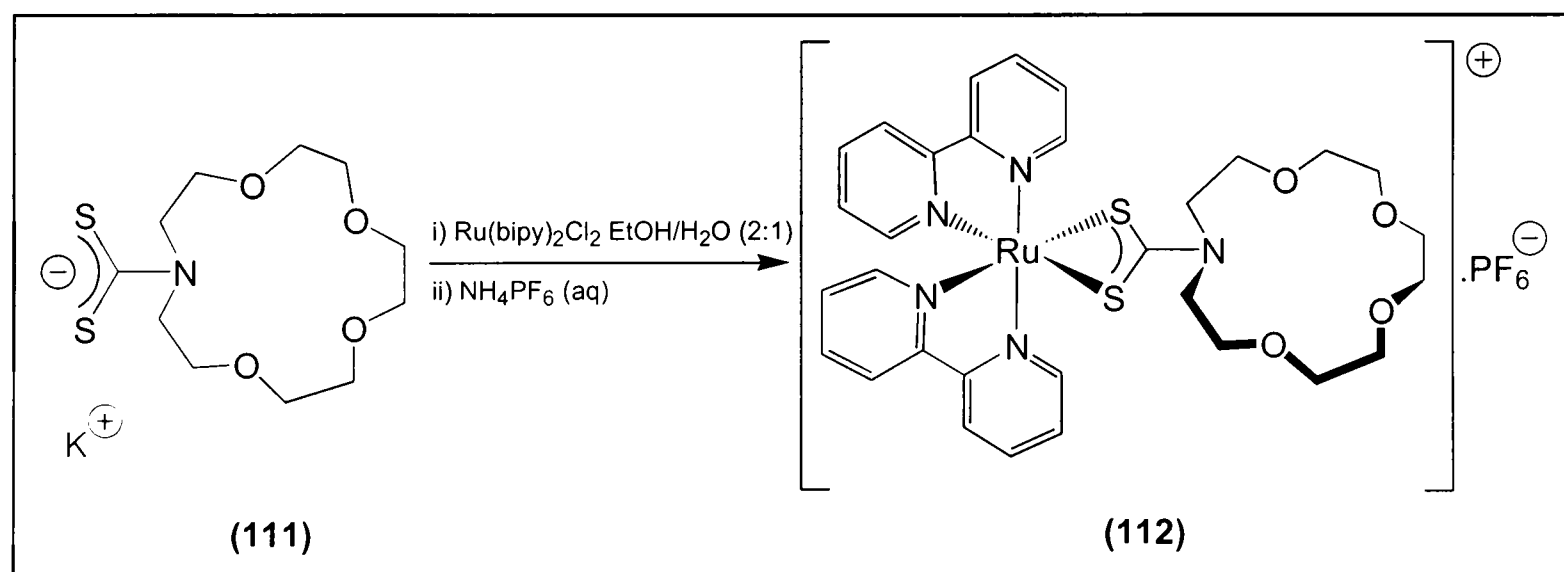
In contrast, there have been numerous examples of ruthenium tris(2,2'-bipyridine) complexes being functionalised with crown ether derivatives. Such complexes have been used for the electro-chemiluminescent detection of cationic guests, the modulation of energy transfer between metal centres and the development of electro-optical devices and energy conversion applications.^{24,25,26}

The synthesis of a receptor was undertaken where the dithiocarbamate-functionalised crown ether moiety was coordinated to a ruthenium bis(2,2'-bipyridine) unit. The close proximity of the redox- and photo-active group to the binding site may allow the sensing of alkali metal ions in the established crown ether cation binding site.

4.1 Aza-Crown Appended Ruthenium(II) bis(2,2'-Bipyridine)

Dithiocarbamate Complex (112)

Aza-15-crown-5 was converted to the corresponding potassium dithiocarbamate salt by the addition of potassium hydroxide and carbon disulphide in an acetonitrile solution. The product was isolated as a white solid (**111**) in 62% yield, after the addition of diethyl ether. The dithiocarbamate salt was treated with ruthenium(II) bis(2,2'-bipyridine) dichloride in an ethanol/water (2:1) solvent system. The residue was purified by column chromatography over Sephadex LH-20 eluted with acetonitrile/methanol (95:5) collecting the second band. The addition of ammonium hexafluorophosphate precipitated (**112**) in an overall yield of 90% (Scheme 5). The resulting red solid was characterised via ^1H , ^{13}C and ^1H - ^1H COSY NMR spectroscopy, electrospray mass spectrometry and elemental analysis.



Scheme 5 Synthesis of aza-15-crown-5 appended Ru(II) bis(2,2'-bipyridine) dithiocarbamate complex (**112**)

The cation binding properties of (**112**) was investigated by a variety of techniques. Initially, an electrospray mass spectrometry competition experiment was performed. Ten equivalents of lithium, sodium, potassium, rubidium and caesium cations (added as either their hexafluorophosphate or perchlorate salts) were coinjected with an acetonitrile solution of (**112**). Surprisingly, there was no observable adducts with the added metal cations, with the only peak in the spectrum being that of the molecular ion (m/z 708.09).

The UV-vis spectrum of **(112)** was recorded in an acetonitrile solution. This showed characteristic peaks for ruthenium bis(2,2'-bipyridine) dithiocarbamate complex, with two metal to ligand charge transfer bands being displayed at 464nm ($\epsilon = 12000 \text{ M}^{-1}\text{cm}^{-1}$ ($\pm 10\%$)) and 517nm ($\epsilon = 9000 \text{ M}^{-1}\text{cm}^{-1}$ ($\pm 10\%$)). Unfortunately, the addition of cationic guests to an acetonitrile solution of **(112)** did not result in any observable perturbation within its electronic spectrum.

The electrochemical properties of **(112)** were investigated using cyclic and square wave voltammetry in acetonitrile. The electrochemical characteristics of **(112)** are displayed in Table.4

(112)	Ru(II/III)	bipyH1	bipyH2
$E_{1/2}$	0.26V	-1.86V	-2.10V
E_{pa}	0.29V	-1.82V	-2.07V
E_{pc}	0.22V	-1.90V	-2.14V

Table 4 Electrochemical data for aza-15-crown-5-functionalised Ru(II) bis(2,2'-bipyridine) dithiocarbamate complex (**112**) recorded in MeCN with TBABF₄ as the supporting electrolyte, Ag/AgNO₃ as the reference electrode and glassy carbon as the working electrode.
Sample $1 \times 10^{-3} \text{ M}$, scan rate 100 mVs^{-1} , frequency 5Hz, T = 293K, errors $\pm 5 \text{ mV}$

The electrochemical cation sensing properties of receptor **(112)** was investigated by the addition of ten equivalents of lithium, sodium and potassium hexafluorophosphate to the host and re-recording their cyclic and square wave voltammograms. Surprisingly, the addition of these guests did not reveal any perturbation in either the ruthenium(II/III) oxidation or the bipyridyl reduction couples.

Despite the well known and strong binding capabilities of crown ether complexes, there is no evidence either by electrospray mass spectrometry, UV-vis spectroscopy or electrochemistry of cationic binding within **(112)**. This is possibly a result of the positive charge of the ruthenium metal centre being effectively delocalised across the dithiocarbamate group. In

particular, an important resonance structure places this charge on the nitrogen atom of the aza-crown. It is therefore likely that the binding of cationic guests within the macrocyclic host is disfavoured due to mutual electrostatic repulsions (Figure 9).

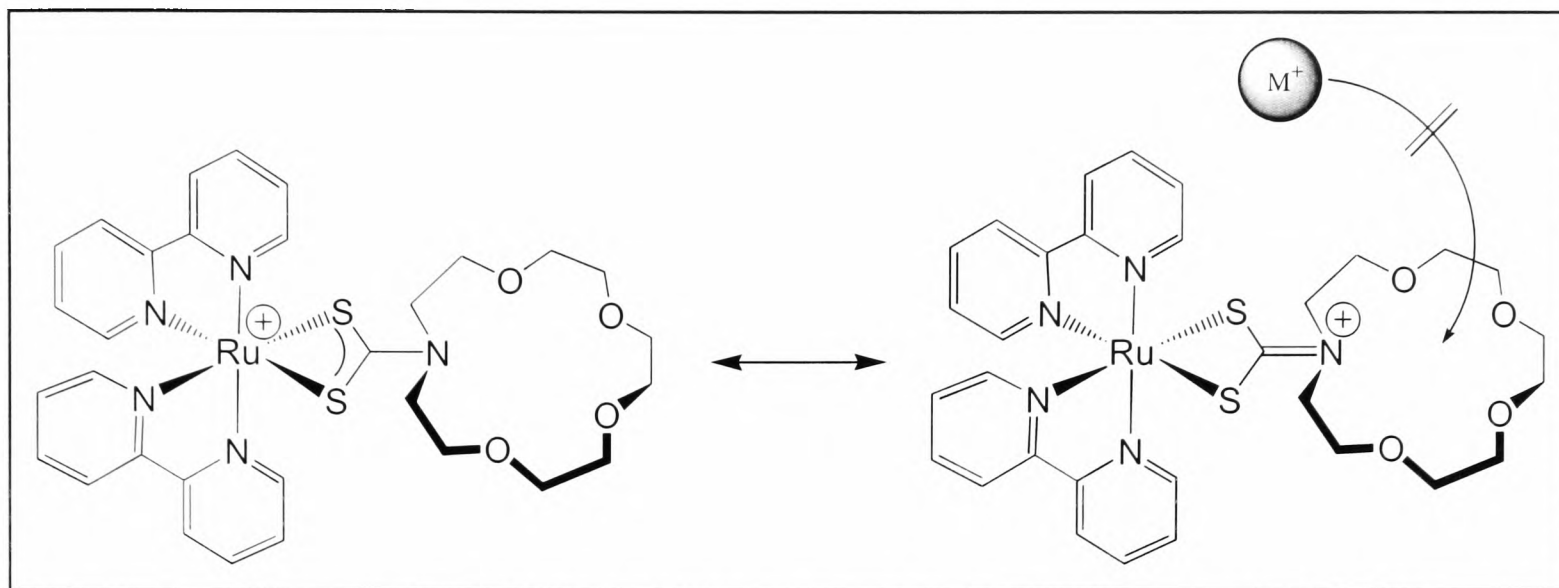


Figure 9 Delocalisation about the dithiocarbamate ligand restricting metal ion binding within aza-15-crown-5 moiety (112)

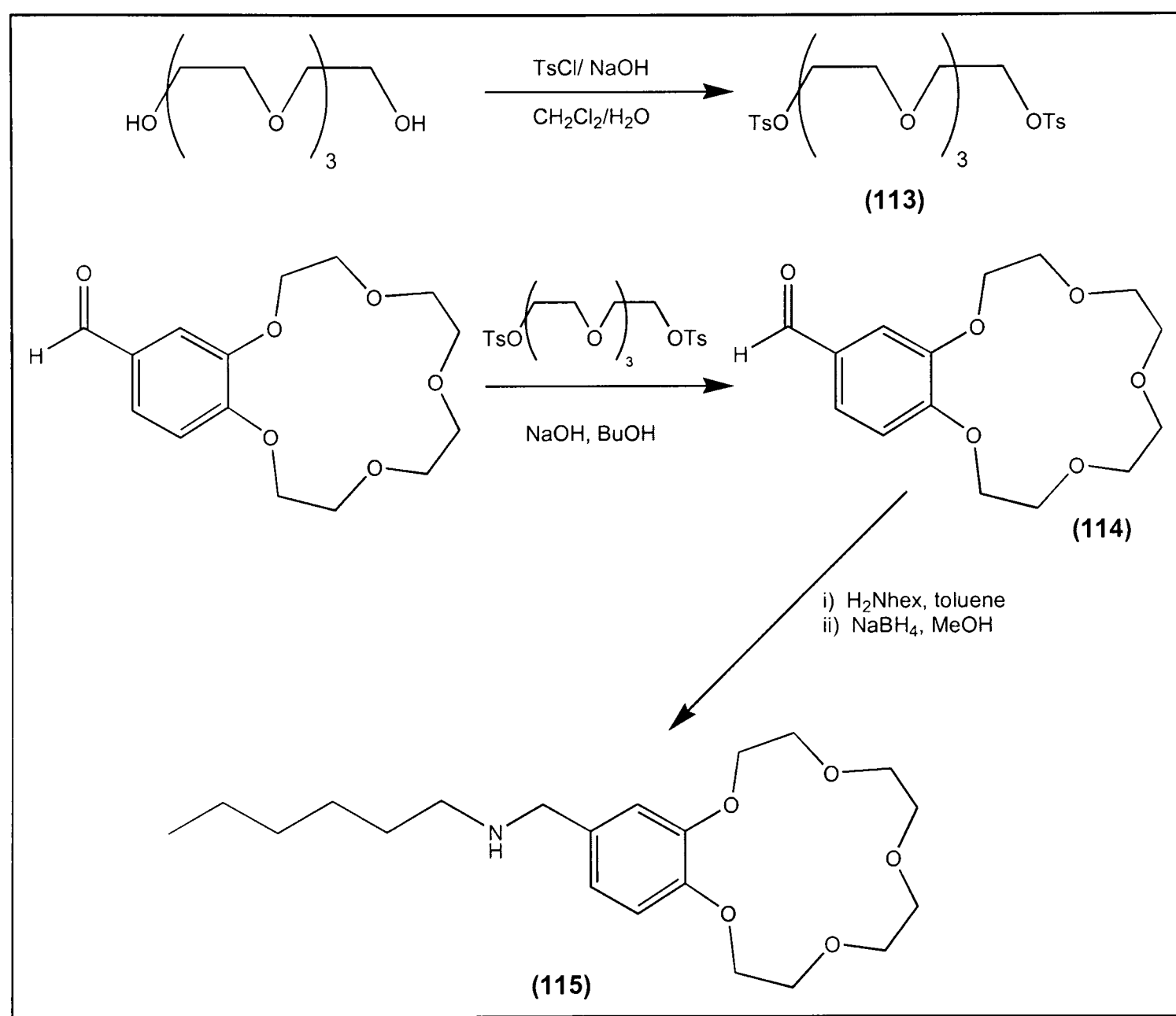
4.2 Benzo-15-Crown-5 Appended Ruthenium(II) bis(2,2'-Bipyridine)

Dithiocarbamate Complex (116)

It was apparent after the study of (112) that the positively charged ruthenium(II) bis(2,2'-bipyridine) dithiocarbamate-based reporter group is too close to the aza-15-crown-5 binding site to allow the coordination of cationic guests within this complex. An analogous complex was therefore designed, where the reporter group was moved away from the binding site, such that the binding of cationic guests would not be discouraged whilst still being close enough to be able to monitor the binding process. This was achieved by the preparation of a secondary amine functionalised benzo-15-crown-5 and its subsequent treatment to generate the ruthenium(II) bis(2,2'-bipyridine) dithiocarbamate complex.

Initially, a formyl-substituted crown ether was prepared via a templation synthesis (Scheme 6). Tetraethylene glycol was treated with *p*-toluenesulphonyl chloride using a phase transfer method, to afford the ditosylated product (113) in near quantitative yield²⁷. This was

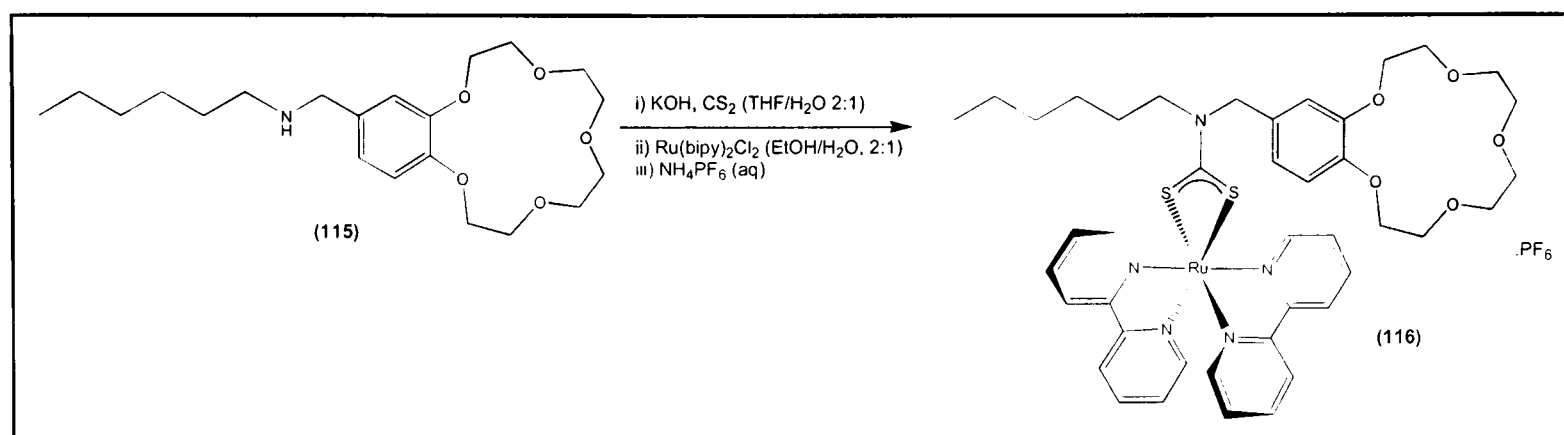
subsequently reacted with 3,4-dihydroxybenzaldehyde, templated by sodium hydroxide, to give the cyclised product formyl-4-benzo-15-crown-5 (**114**)²⁸. This was converted to a secondary amine via treatment with *n*-hexylamine in toluene. The formation of the corresponding imine, which was encouraged by azeotropic distillation using a Dean-Stark trap. The imine was reduced to the secondary amine (**115**) by the addition of sodium borohydride in methanol²⁹.



Scheme 6 Synthesis of amino-functionalised benzo-15-crown-5

The crown ether appended secondary amine (**115**) was converted to the corresponding potassium dithiocarbamate salt, by treatment with potassium hydroxide and carbon disulphide in a tetrahydrofuran/water (2:1) solvent system. The solvent was removed under reduced pressure and the salt, which was not isolated, redissolved in ethanol/water (2:1). Ruthenium(II) bis(2,2'-bipyridine) dichloride was added and the solution refluxed under

nitrogen for 18 hours. The purple solution was evaporated to dryness, redissolved in water and ammonium hexafluorophosphate added to yield **(116)** (Scheme 7).



Scheme 7 Synthesis of benzo-15-crown-5 Ru(II) bis(bipyridyl dithiocarbamate complex (116)

The desired receptor **(116)** was isolated as a purple solid and characterised via ^1H , ^{13}C , ^{31}P and ^{19}F NMR spectroscopy, electrospray mass spectrometry and elemental analysis.

4.2.1 Cation Binding

The cation binding properties of receptor **(116)** were studied using electrospray mass spectrometry, ^{13}C NMR spectroscopy and electrochemical techniques. The Group 1 cations lithium, sodium, potassium, rubidium and caesium were used for this.

4.2.2 Electrospray Mass Spectrometry

Electrospray mass spectrometry has previously been used for assessing the Group 1 cation binding affinity with crown ether complexes³⁰. This has demonstrated that the largest peaks observed in the spectra correlated with the known stability constants of the complexes. In contrast to **(112)** which did not exhibit any peaks corresponding to adducts with alkali metal cations in its electrospray spectrum, the characterisation of **(116)** reveal the formation of a $[\text{M}+\text{Na}]^{2+}$ peak (m/z 446.58) in its spectrum. The presence of Group 1 metal cations results from the alkali metal salts that are used to calibrate the spectrometer³¹. This observation of adduct formation, suggests that the moving of the positively-charged ruthenium(II) reporting

group away from the binding site, allows the coordination of alkali metal cations within the crown ether moiety.

An electrospray mass spectrometry competition experiment was performed upon receptor **(116)**. One equivalent each of sodium, potassium, rubidium and caesium cations (as their perchlorate salts) were coinjected into the electrospray mass spectrometer with an acetonitrile solution of **(116)**.

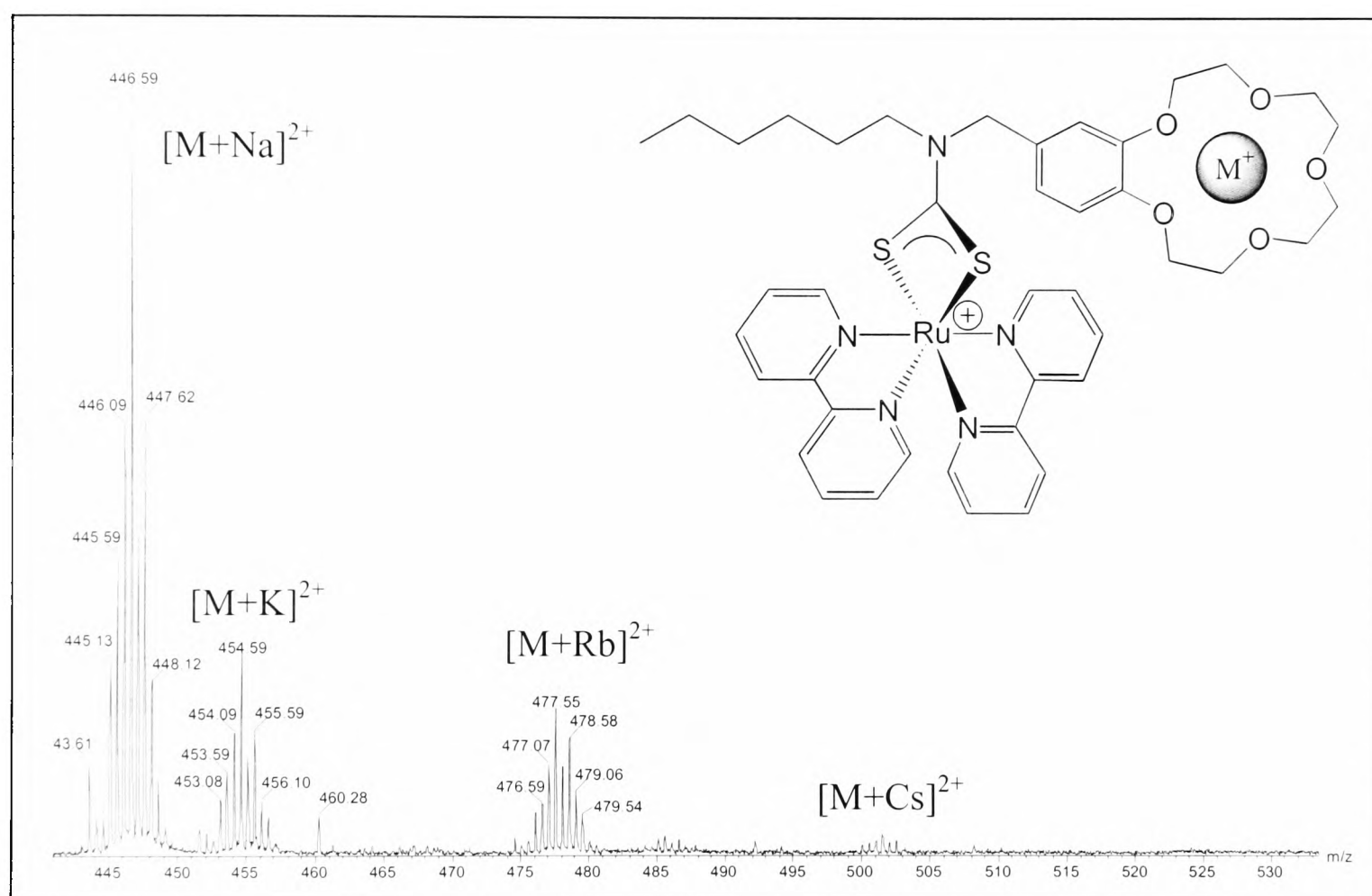


Figure 10 Electrospray mass spectrometry competition experiment for **(116)** in the presence of 1.0 equivalent of Na, K, Rb and Cs cations

The spectrum (Figure 10) shows that the receptor forms complexes with all of the coinjected alkali metals with the largest peak corresponding to the formation of a 1:1 complex with the sodium cation. This observed selectivity for sodium is due to the optimal spatial fit between the cationic guest and the macrocyclic cavity. Despite the well-documented formation of intramolecular sandwich complexes between benzo-15-crown-5 derivatives and larger alkali metal guests, there was no evidence of the formation of such tricationic complexes within this electrospray mass spectroscopic experiment.

4.2.3 Electrochemistry

The electrochemical properties of **(116)** were investigated using cyclic and square wave voltammetry in acetonitrile. These electrochemical characteristics are displayed in Table 5.

(116)	Ru(II/III)	bipyH1	bipyH2
$E_{1/2}$	0.26V	-1.85V	-2.10V
E_{pa}	0.30V	-1.82V	-2.06V
E_{pc}	0.23V	-1.89V	-2.14V

Table 5 Electrochemical data for benzo-15-crown-5-appended Ru(II) bis(2,2'-bipyridine) dithiocarbamate complexes **(116)** recorded in MeCN with TBABF₄ as the supporting electrolyte, Ag/AgNO₃ as the reference electrode and glassy carbon as the working electrode. Sample 1x10⁻³M, scan rate 100mVs⁻¹, frequency 5Hz, T = 293K, errors ±5mV

The properties of **(116)** are similar to those observed for **(104)**, with a quasi-reversible ruthenium(II/III) oxidation and two bipyridyl reductions couples being displayed. The cyclic and square wave voltammograms of **(116)** were re-recorded in the presence of ten equivalents of lithium, sodium, potassium hexafluorophosphate and rubidium and caesium perchlorate. The magnitude of the perturbations of the redox couples in the square wave voltammogram of **(116)**, upon the addition of ten equivalents of Group 1 metal ions, is highlighted in Table 6.

(116)	Ru(II/III)	bipyH1	bipyH2
$\Delta E(\text{Li}^+)$	+10mV	+10mV	+10mV
$\Delta E(\text{Na}^+)$	+10mV	+5mV	+10mV
$\Delta E(\text{K}^+)$	+5mV	0mV	0mV
$\Delta E(\text{Rb}^+)$	0mV	0mV	0mV
$\Delta E(\text{Cs}^+)$	0mV	0mV	0mV

Table 6 Perturbation in the square wave voltammogram upon the addition of 10.0 equivalents of given cation to a MeCN solution of the Ru(II) bis(2,2'-bipyridine) dithiocarbamate-based receptor **(116)** with TBABF₄ as the supporting electrolyte Ag/AgNO₃ as the reference electrode and glassy carbon as the working electrode. Sample 1x10⁻³M, frequency 5Hz, T = 293K

The addition of suitably-sized cationic guests to **(116)** leads only to a modest anodic shift in both the ruthenium(II/III) and bipyridyl redox couples, i.e. it is harder to oxidise the ruthenium centre, whilst being easier to reduce the bipyridyl-based centres, in the presence of the alkali metal ion. In the presence of the small cations which are able to strongly bind within the macrocyclic cavity, lithium and sodium, the largest shifts (10mV) are observed. For the larger cations, such as rubidium and caesium, no perturbation in electrochemical waves is noted.

4.2.4 ^{13}C NMR Spectroscopy

The binding of sodium cations with receptor **(116)** was investigated via ^{13}C NMR spectroscopy. This was achieved by the addition of ten equivalents of sodium perchlorate to an acetonitrile solution of **(116)**. The resulting spectrum was difficult to interpret due to a number of overlapping peaks, however, it could be seen that the ethylene signals of the crown ether were shifted upfield by up to 2 ppm. This indicates that the cation is, as expected, binding to the electron-rich oxygen moieties within the crown ether cavity.

4.2.5 UV-vis Spectroscopy

The UV-vis spectrum of **(116)** was recorded in an acetonitrile solution. This showed characteristic peaks for ruthenium(II) bis(2,2'-bipyridine) dithiocarbamate complex, with two metal to ligand charge transfer bands being displayed at 468nm ($\epsilon = 11500 \text{ M}^{-1}\text{cm}^{-1}(\pm 10\%)$) and 519nm ($\epsilon = 8300 \text{ M}^{-1}\text{cm}^{-1}(\pm 10\%)$). Unfortunately, the addition of a large excess of cationic guests to an acetonitrile solution of **(116)** did not result in any discernable perturbation within its electronic spectrum.

5 Anion Binding Ruthenium(II) bis(2,2'-Bipyridine) Dithiocarbamate-based Complexes

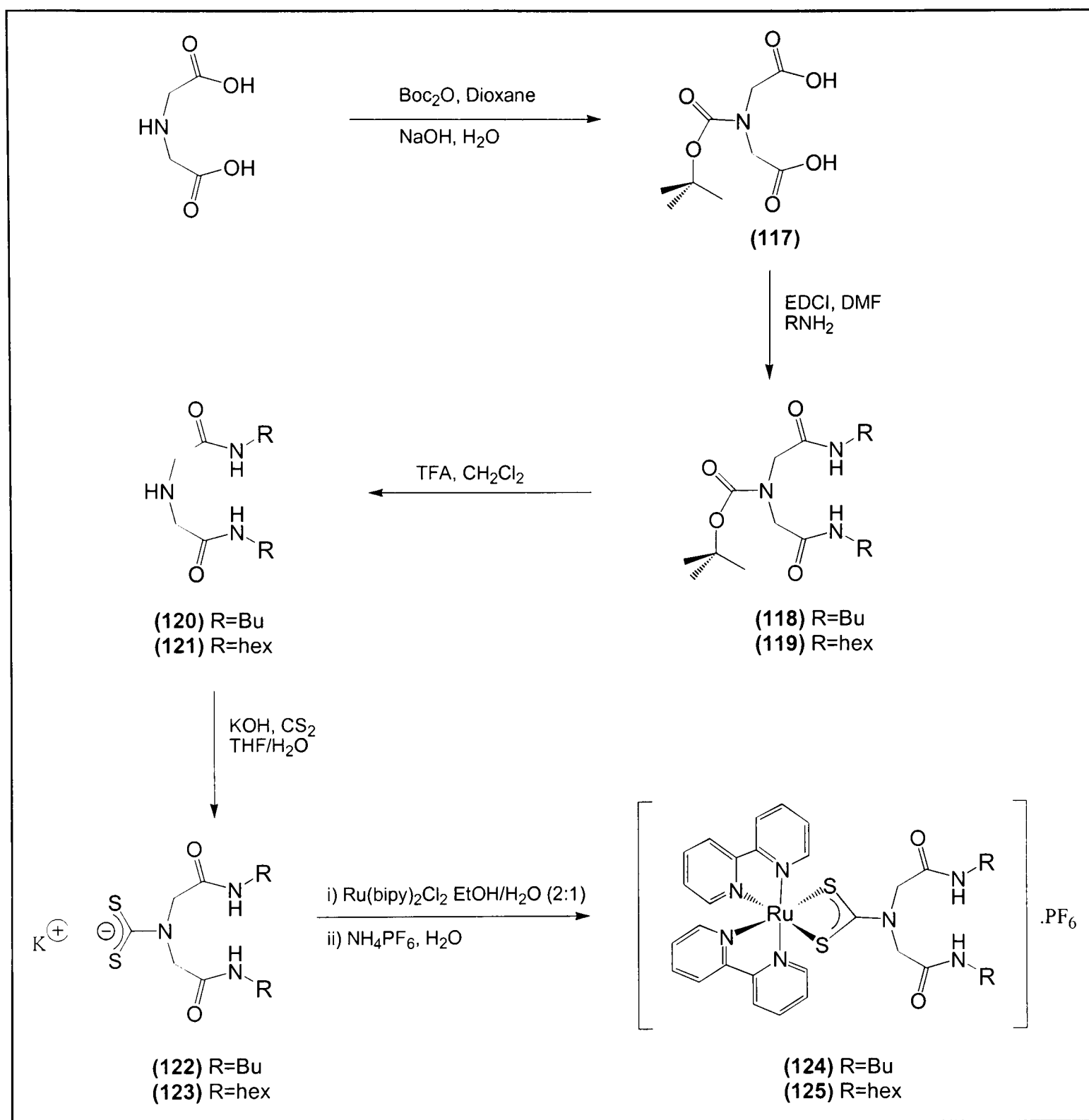
Chapter One has described the challenge in both binding and sensing anionic guests^{32,33}. One of the most exploited systems for achieving this goal has been the ruthenium(II) tris(2,2'-bipyridine) complex. Modification of the bipyridine groups has allowed the incorporation of well known anion binding units^{34,35}. This has allowed the complexation and subsequent optical, luminescent and electrochemical detection of anionic guests^{36,37,38,39}.

The analogous redox-active ruthenium(II) bis(2,2'-bipyridine) dithiocarbamate system also has the potential to act as an electrochemical anion sensor. In contrast, to the mutual electrostatic repulsions observed in cation-binding of positively-charged crown ether-based receptors, the ruthenium bis(2,2'-bipyridine) dithiocarbamate group has the potential to electrostatically encourage the association of anionic species. Here, the metal centre plays a key role, as a source of electrostatic interaction with the anion and also has the potential to act as a sensor. Hydrogen bond donor groups can be incorporated into the dithiocarbamate ligand framework to favour anionic binding.

5.1 Synthesis of Ruthenium(II) bis(2,2'-bipyridine) Dithiocarbamate

Amide-Functionalised Complexes

The synthetic procedure to produce ruthenium(II) bis(2,2'-bipyridine) dithiocarbamate-based receptors, with amide groups incorporated into lipophilic side-chains is outlined in Scheme 8. This involves the coupling of a primary amine with an amino-protected bis-acid to generate a bis-amide. Subsequent deprotection and treatment with carbon disulphide in basic solution affords the corresponding dithiocarbamate salt which is coordinated to the metal centre furnishing the desired receptors.



Scheme 8 Synthetic route for the generation of Ru(II) bis(2,2'-bipyridine) dithiocarbamate amide-functionalised complexes (124) and (125)

Initially, the secondary amine group of the commercially available iminodiacetic acid was protected, via the *t*-butyloxycarbonyl (Boc) group. This was achieved by the addition of di-*t*-butyldicarbonate to an alkaline aqueous dioxane solution. The product was recrystallised from ethyl acetate/hexane and isolated as colourless crystals in good yield. A crystal suitable for X-ray diffraction was grown and its structure solved by Dr A. R. Cowley and Dr R. L. Paul at the University of Oxford and its structure is displayed in Figure 11.



Figure 11 X-Ray crystal structure of (117) (right) packing diagram displaying intramolecular hydrogen bonding interactions (Key: C – grey, H – white, N – blue, O – red)

The structure shows the formation of the desired Boc-protected bis-acid (**117**). In the solid state, intramolecular hydrogen bonds are observed between acid and carbonyl groups.

Conversion of the protected bis-acid (**117**) to the bis-amides (**118**) and (**119**), was effected by the addition of EDCI (3-ethyl-1-[3-(dimethylamino)propyl]carbodiimide hydrogen chloride) in DMF (dry), possibly via a cyclic anhydride intermediate⁴⁰. Subsequent addition of two equivalents of *n*-butylamine and *n*-hexylamine generated the desired bis-amides (**118**) and (**119**) respectively, in good yields. The brown oils were characterised by ¹H and ¹³C NMR spectroscopy, electrospray mass spectrometry and elemental analysis. Interestingly, the ¹H and ¹³C NMR spectra of the bis-amides proved more complex than might be expected, with a doubling of many of the resonances. For example, in the ¹H NMR spectrum of (**119**) (Figure 12) displays two peaks for both the protons of the amide group and those adjacent to the amide carbonyl group.

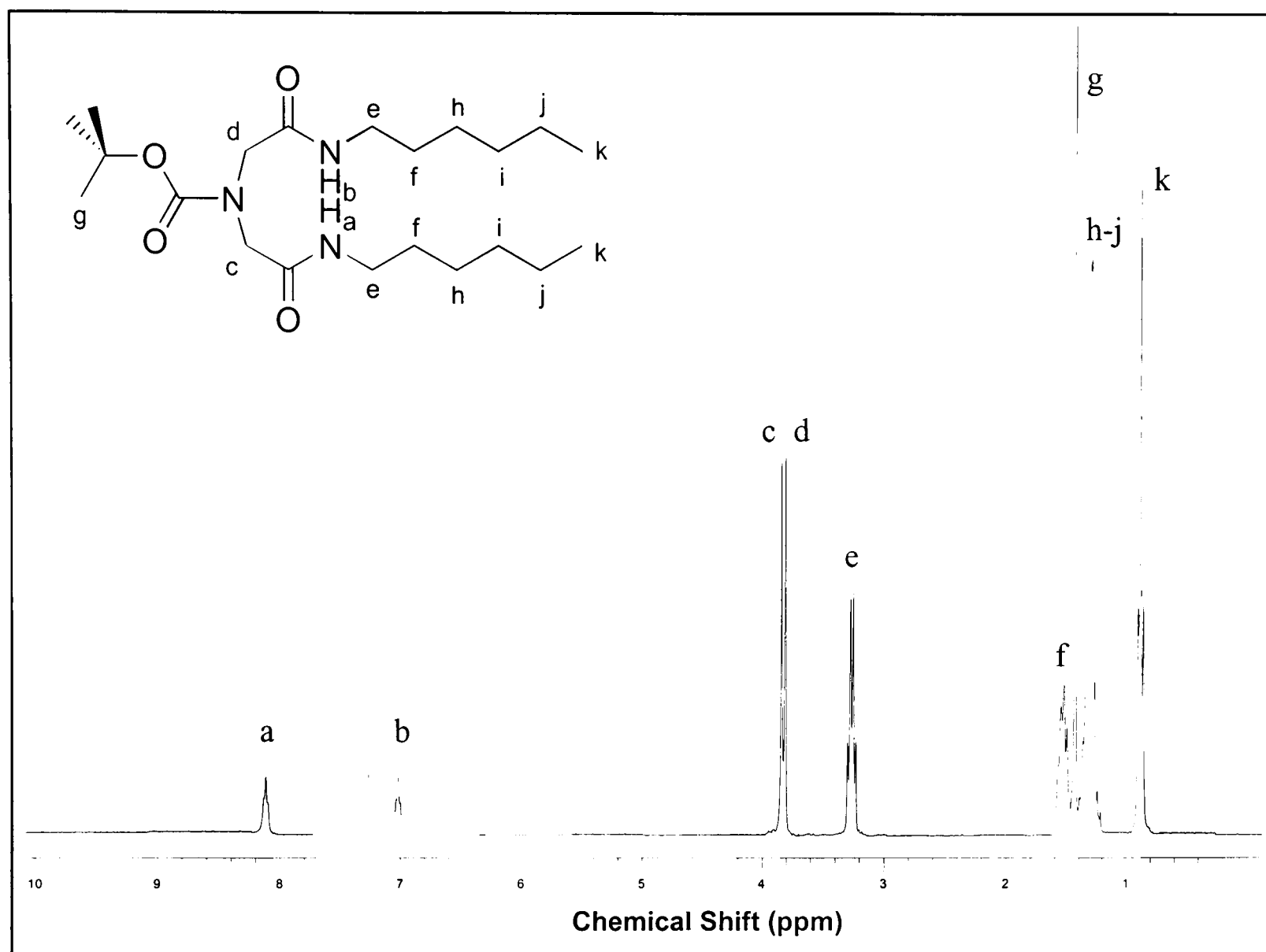


Figure 12 ^1H NMR spectrum of Boc-protected bis-amide (**119**) (300MHz, CDCl_3 , 293K)

This feature can be explained by the restricted rotation of the nitrogen-carbonyl bond of the Boc protecting group. The rotation of the bulky Boc group is slow on the NMR timescale resulting in the molecule losing an axis of symmetry and two rotamers are formed with differing NMR spectra (Figure 13). The formation of rotamers is also observed in the ^1H NMR spectrum of the bis-acid precursor (**117**) and this is also highlighted in the X-ray crystal structure (Figure 11), where the inequivalence of the two sides of the molecule, due to the Boc-protecting group, is clearly seen.

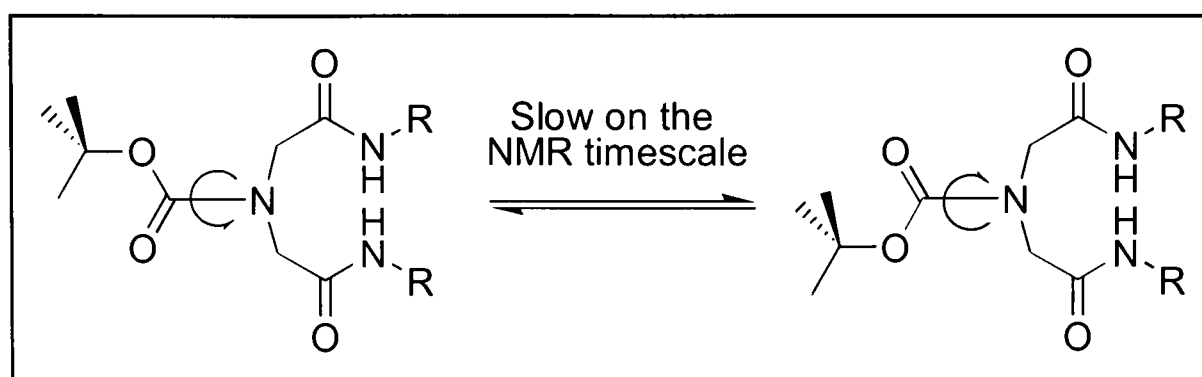


Figure 13 Two rotamers of the bis-amides (118) R=Bu and (119) R=hex

Dichloromethane solutions of the bis-amides (**118**) and (**119**) were treated with trifluoroacetic acid (TFA) to remove the Boc protecting group affording the secondary amines (**120**) and (**121**), in quantitative yield. These were characterised by ^1H and ^{13}C NMR spectroscopy, electrospray mass spectrometry and elemental analysis. The observed splitting in the NMR spectra of (**118**) and (**119**) is no longer seen in the spectra of (**120**) and (**121**) due to the, now symmetrical, nature of the molecule as a consequence of the removal of the Boc protecting group.

Treatment of the secondary amines (**120**) and (**121**) by addition of potassium hydroxide and carbon disulphide in a tetrahydrofuran/water (2:1) solvent system afforded the respective potassium dithiocarbamate salts (**122**) and (**123**) in high yields.

The potassium dithiocarbamate salts, (**122**) and (**123**) were refluxed with *cis*-dichlorobis(2,2'-bipyridine) ruthenium(II), in an analogous method to the preparation of (**104**) (Scheme 8).

The resulting receptors (**124**) and (**125**) were isolated as purple solids by the addition of ammonium hexafluorophosphate in yields of 54% and 66%, respectively. The products were characterised by ^1H , ^{13}C , ^{19}F , ^{31}P and ^1H - ^1H COSY NMR spectroscopy, electrospray mass spectrometry and elemental analysis.

The electrochemical properties of (**124**) and (**125**) were analysed via cyclic and square wave voltammetry. This was performed in an acetonitrile solution containing 0.1M tetra-*n*-butylammonium tetrafluoroborate as a background electrolyte. The resulting voltammograms

displayed peaks analogous to the mononuclear **(104)** with one ruthenium(II/III) oxidation and two bipyridine reduction couples being observed. The electrochemical data for the receptors **(124)** and **(125)** are displayed in Table 7. Interestingly, the presence of the amide functional groups adjacent to the dithiocarbamate ligand results in the ruthenium(II/III) oxidation couple occurring at a higher potential than the unfunctionalised analogue **(104)**.

		Ru(II/III)	bipyH1	bipyH2
(124)	$E_{1/2}$	0.32V	-1.84V	-2.09V
	E_{pa}	0.36V	-1.80V	-2.05V
	E_{pc}	0.28V	-1.88V	-2.14V
(125)	$E_{1/2}$	0.33V	-1.84V	-2.10V
	E_{pa}	0.36V	-1.80V	-2.06V
	E_{pc}	0.28V	-1.89V	-2.14V

Table 7 Electrochemical data for amide-functionalised Ru(II) bis(2,2'-bipyridine) dithiocarbamate complexes **(124)** and **(125)** recorded in MeCN with TBABF₄ as the supporting electrolyte, Ag/AgNO₃ as the reference electrode and glassy carbon as the working electrode. Sample 1x10⁻³M, scan rate 100mVs⁻¹, frequency 5Hz, T = 293K, errors ±5mV

5.2 Anion Binding

The effect of the addition of anions to the ruthenium(II) bis(2,2'-bipyridine) dithiocarbamate-based complexes **(124)** and **(125)** were investigated via a variety of spectroscopic and electrochemical techniques. This was undertaken by the addition of a variety of tetra-*n*-butylammonium salts.

5.2.1 ¹H NMR Spectroscopy

NMR spectroscopy has proved a useful tool for the examination of host:guest chemistry due to the sensitivity of various atomic nuclei to its surrounding electronic environment. This

perturbed chemical shift gives both a qualitative indication of the location of the recognition site and quantitative information of the magnitude of the interaction.

The anion binding capabilities of the amide-functionalised receptors **(124)** and **(125)** were investigated. The addition of a large excess of tetra-*n*-butylammonium chloride to a chloroform-*d* solution of **(125)** resulted in a large downfield perturbation ($\Delta\delta \sim 1.5$ ppm) of the amide resonance. This indicates that the anion forms favourable hydrogen bonds with the amide moiety within the molecular cleft.

The stoichiometry of anion binding was determined by Job's method of continued variation⁴¹. This was achieved by monitoring the chemical shift of the amide protons in the ¹H NMR spectrum of a chloroform-*d* solution of **(125)** and tetra-*n*-butylammonium chloride of changing concentrations⁴². The resulting Job plot is displayed in Figure 14.

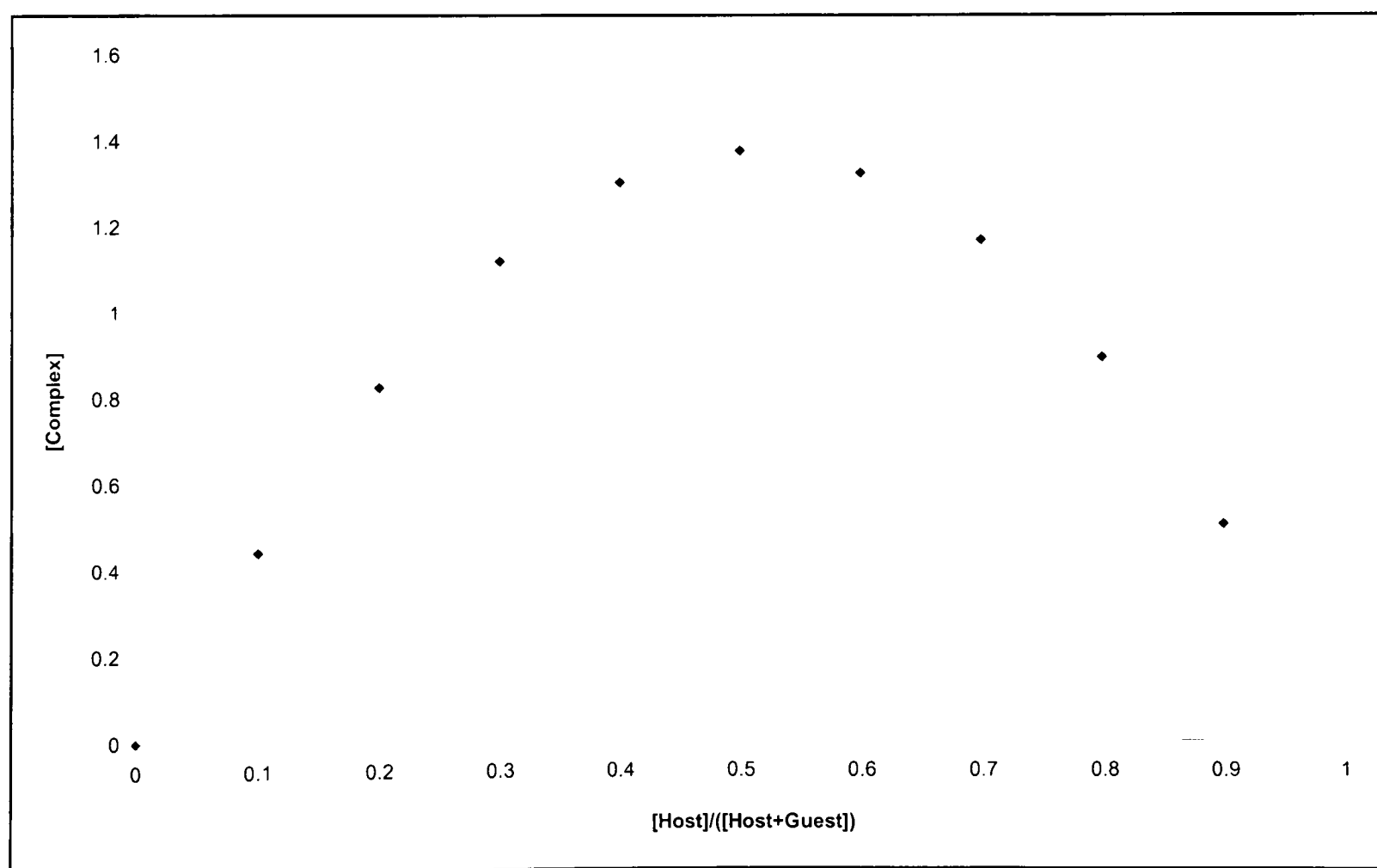


Figure 14 Job plot illustrating the binding stoichiometry of Ru(II) bis(2,2'-bipyridine) amide-functionalised dithiocarbamate receptor (125) upon the addition of chloride

The observation of a maximum in the graph at a mole fraction of 0.5 illustrates that the anion is binding in a 1:1 stoichiometry with the host. It is subsequently assumed that this binding

stoichiometry was maintained for all univalent anions.

Based upon a 1:1 binding model, stability constants were determined via the examination of the perturbation of the amide protons of the receptors **(124)** and **(125)** for a variety of anions. Initially this was undertaken by the addition of anions to a chloroform-d solution of **(125)**. Whilst this lead to the large perturbations in the amide proton upon the addition of chloride, nitrate and *N,N'*-diethyldithiocarbamate, the addition of dihydrogen phosphate, acetate and benzoate lead to the precipitation of a purple solid.

Due to these solubility constraints, analogous titration experiments were carried in the more competitive dimethyl sulphoxide-d₆/acetonitrile-d₃ (1:1) solvent mixture. As a result of the increased competitive nature of the solvent, the resulting perturbations (and subsequent stability constants) are significantly reduced in this solvent system. The perturbation of the ¹H NMR spectrum of **(125)** upon the addition of varying amounts of the dihydrogen phosphate anion is displayed in Figure 15. This shows that the amide proton is shifted 0.51 ppm downfield, indicating the anion forms hydrogen bonds with the receptor.

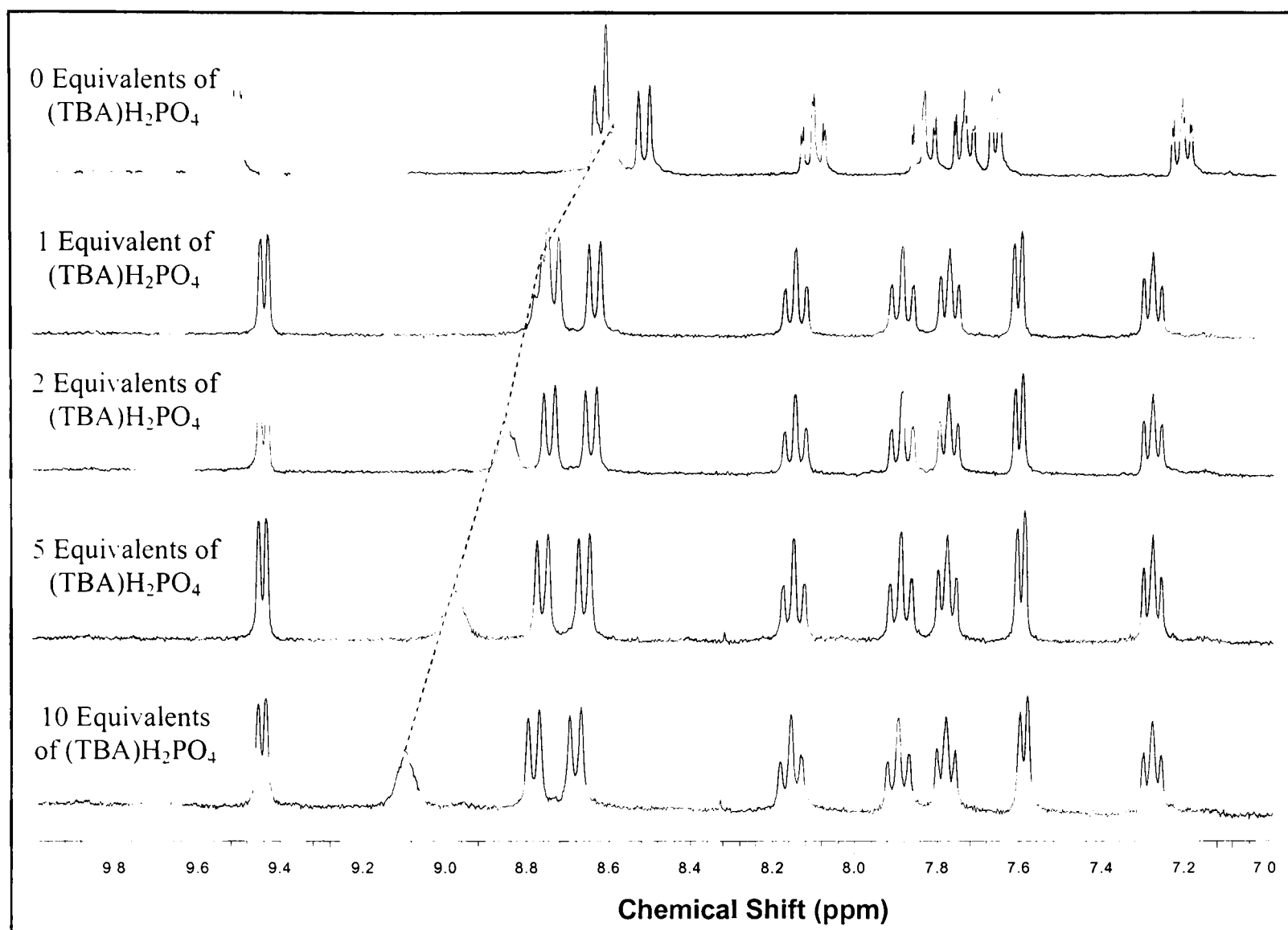


Figure 15 Change in ^1H NMR spectrum of (125) upon the addition given equivalents of $(\text{TBA})\text{H}_2\text{PO}_4$. Line represents perturbation of the amide proton of (125) (500MHz, DMSO- d_6 : CD_3CN (1:1), 293K)

Analysis of the data was undertaken by the least-squares computer-fitting program EQNMR⁴³ using a 1:1 binding model. The data and calculated binding curves for the addition of the chloride, nitrate and N,N' -diethyldithiocarbamate anions to (125) in chloroform- d are displayed in Figure 16. The analogous isotherms for the addition of the dihydrogen phosphate, acetate, benzoate and chloride anions to (124) and (125) in dimethyl sulphoxide- d_6 /acetonitrile- d_3 (1:1) are displayed in Figure 17. Unfortunately, addition of nitrate and N,N' -diethyldithiocarbamate failed to result in any perturbation of the amide protons in the more competitive solvent system. The determined stability constants from EQNMR are recorded in Table 8 (refer to Appendix One).

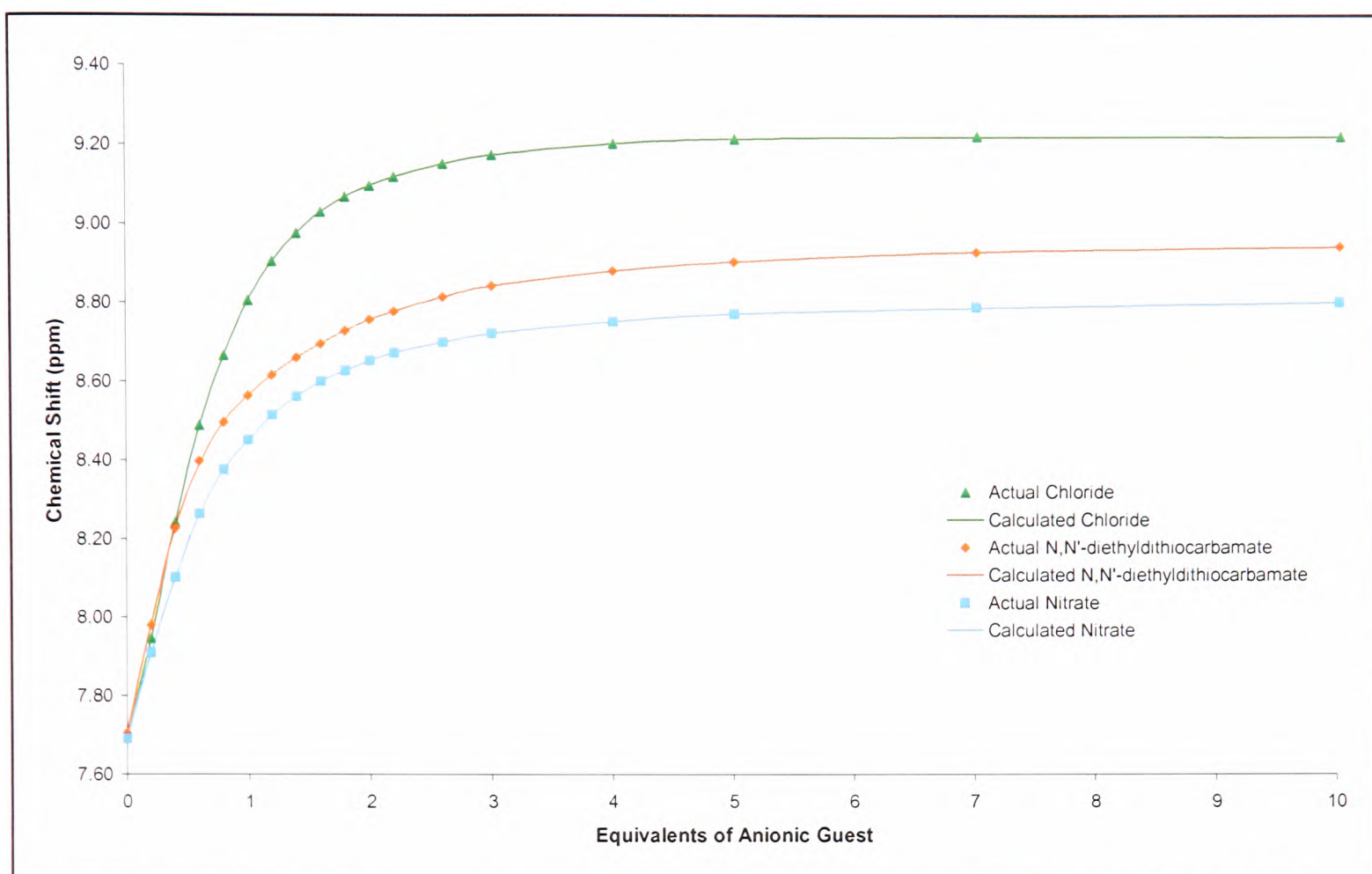


Figure 16 ^1H NMR titration experiment showing the perturbation of the amide proton of (125) upon addition of a range of anions (50MHz, CDCl_3 , 293K)

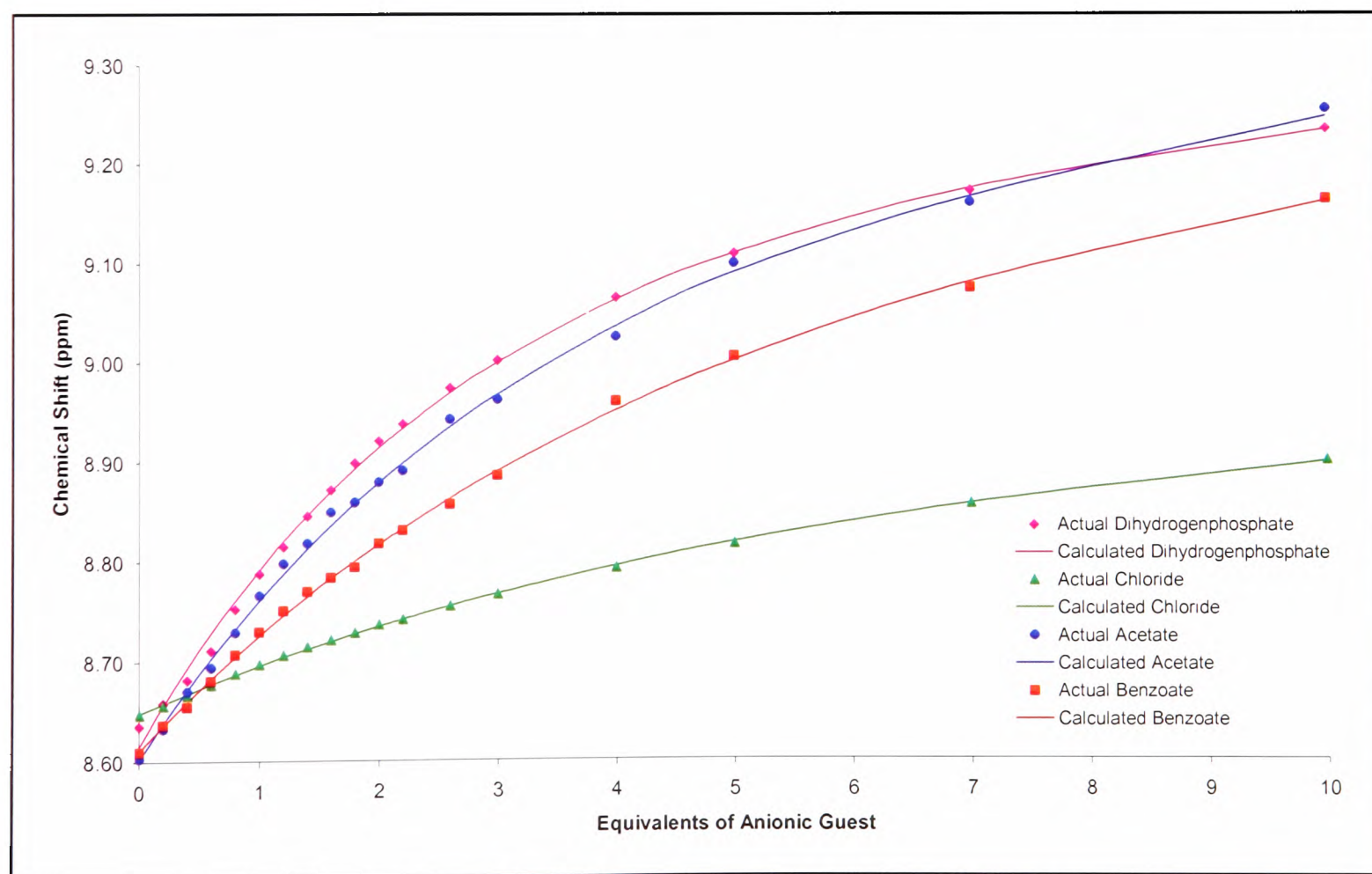


Figure 17 ^1H NMR titration experiment showing the perturbation of the amide proton of (125) upon addition of a range of anions (50MHz, $\text{DMSO-d}_6:\text{CD}_3\text{CN}$ (1:1), 293K)

	Solvent	H ₂ PO ₄ ⁻	AcO ⁻	C ₆ H ₅ CO ₂ ⁻	Cl ⁻	NO ₃	Et ₂ NCS ₂
(124)	DMSO-d ₆ / CD ₃ CN (1:1)	70	25	20	15	0	0
(125)	DMSO-d ₆ / CD ₃ CN (1:1)	45	30	20	15	0	0
	CDCl ₃	ppt	ppt	ppt	1000	700	500

**Table 8 Stability constants (*K*) for the Ru(II) bis(2,2'-bipyridine) amide functionalised dithiocarbamate receptors (124) and (125) upon the addition of anions as their TBA salts at 298K (Errors <10%)
ppt – precipitation occurred upon addition of the anionic guest**

Table 8 shows that the affinity of anions to the receptors followed the trend dihydrogen phosphate > acetate > benzoate > chloride > nitrate > *N,N'*-diethyldithiocarbamate. This may result from the dihydrogen phosphate anion being complementary with the receptors' cleft. Interestingly, the affinity for dihydrogen phosphate is significantly greater in the butyl-chained analogue (124) in contrast to the hexyl-chained (125). This is possibly a result of binding an anion in a receptor with greater steric bulk proving entropically disfavoured.

5.2.2 Electrochemistry

It was further examined whether the redox-active ruthenium centre may also be used as reporter group for detecting the binding of anionic guests. This was undertaken by measuring the square wave voltammograms of the receptors (124) and (125) both in the presence and absence of ten equivalents of anionic guests (Figure 18). This was performed in an acetonitrile solution containing 0.1M tetra-*n*-butylammonium tetrafluoroborate as a background electrolyte. Only the perturbations of the ruthenium(II/III) redox couple were recorded since the two bipyridine-based reductions were shown not to significantly change upon addition of anions.

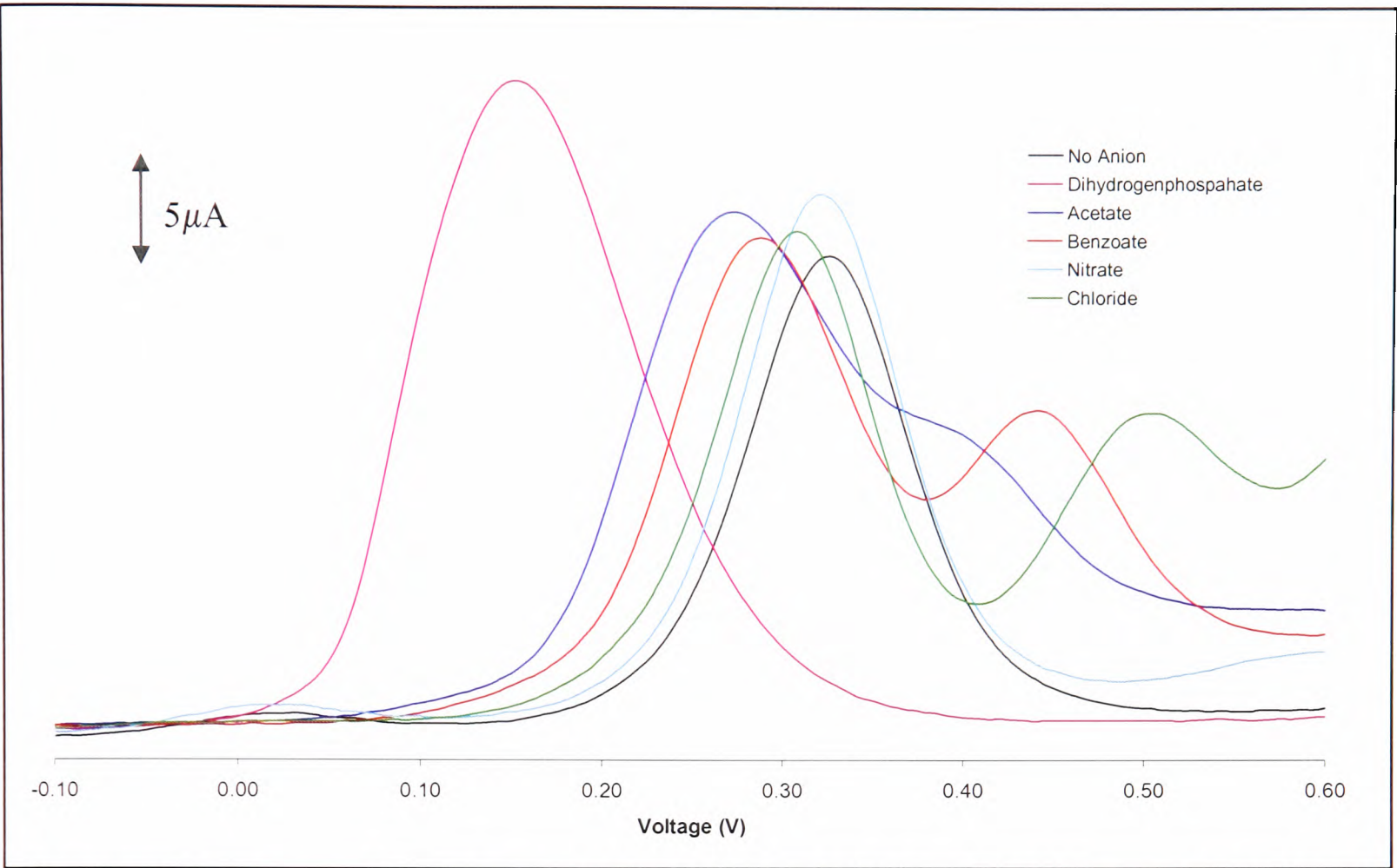


Figure 18 Square wave voltammograms of the Ru(II/III) oxidation couple of (125) upon the addition of 5.0 equivalents of given anions recorded in MeCN with TBABF₄ as the supporting electrolyte, Ag/AgNO₃ as the reference electrode and glassy carbon as the working electrode. Sample 1x10⁻³M, frequency 5Hz, T = 293K

	H ₂ PO ₄	AcO ⁻	C ₆ H ₅ CO ₂	Cl ⁻	NO ₃
(104)	ppt	-10	<-5	<-5	<-5
(124)	-180	-50	-40	-20	<-5
(125)	-170	-60	-40	-20	-10

Table 9 Perturbation of the Ru(II/III) oxidation couple in the square wave voltammogram upon the addition of 5.0 equivalents of given anions to a MeCN solution of the Ru(II) bis(2,2'-bipyridine) dithiocarbamate-based receptors (104), (124) and (125) with TBABF₄ as the supporting electrolyte, Ag/AgNO₃ as the reference electrode and glassy carbon as the working electrode. Sample 1x10⁻³M, frequency 5Hz, T = 293K, errors ±5mV

As Table 9 shows, in general, the presence of an excess amount of anions leads to significant cathodic shifts in the ruthenium(II/III) oxidation couple. This is a result of the bound anion making the oxidation of the ruthenium metal centre more facile, due to favourable electrostatic interactions. This effect is the result of the anion forming favourable hydrogen bonds with the amide groups, since in the absence of the amide groups (104) negligible shifts

were observed. The magnitudes of the electrochemical shifts mirror the observed stability constants as determined via ^1H NMR spectroscopic titrations. The largest shift ($\Delta E = 180\text{mV}$) was observed with the dihydrogen phosphate anion, with a slightly larger shift observed for the butyl-chained analogue with respect to the hexyl-chained derivative. This again suggests that the binding affinity of **(125)** suffers in comparison to **(124)** due to its increased steric bulk.

In the presence of acetate, chloride and benzoate, an additional peak emerges in the voltammogram at 0.4 - 0.5V (Figure 18). This is possibly due to the oxidation process labilising the complex and the incoming anions displacing one of the ligands. Unfortunately, attempts to observe these species via electrospray mass spectrometry has proved unsuccessful. The addition of dihydrogen phosphate to receptors **(124)** and **(125)** gave rise to the formation of an additional cathodically shifted peak, which increases to the detriment of the original wave. This is in contrast to the other anions which resulted in a gradual shifting wave. The formation of an additional wave suggests that the binding of dihydrogen phosphate is kinetically slow on the electrochemical timescale⁴⁴. As a result of this, it is possible to monitor the quantity of the anion added to the receptors. This is highlighted via the addition of successive 0.2 equivalent aliquots of dihydrogen phosphate to an acetonitrile solution of **(125)** and subsequently measuring its square wave voltammogram (Figure 19) thus enabling the monitoring the quantity of the anion in solution.

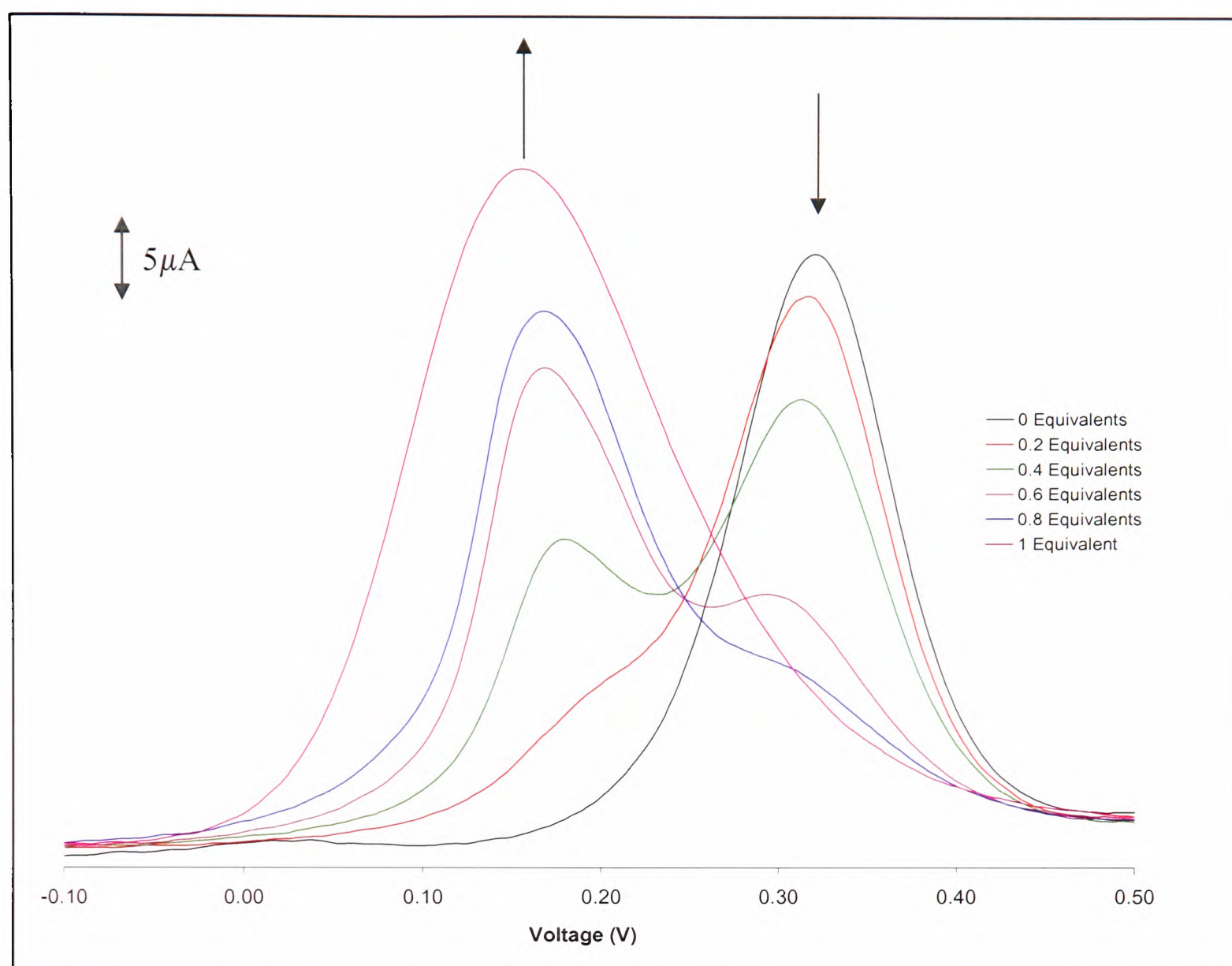


Figure 19 Variation in the square wave voltammogram of (125) upon the addition of given quantities of H_2PO_4^- to the Ru(II/III) oxidation couple recorded in MeCN with TBABF_4 as the supporting electrolyte, with glassy carbon as the working electrode. Sample $1 \times 10^{-3} \text{M}$, frequency 5Hz, $T = 293 \text{K}$

5.2.3 X-Ray Crystallography

In order to determine the nature of anion binding by the amide-appended ruthenium(II) bis(2,2'-bipyridine) dithiocarbamate receptors, a series of crystallisations were set up. A dimethyl sulphoxide/acetonitrile (1:1) solution of (124) was combined with an excess of tetra-*n*-butylammonium chloride and benzoate. Vapour diffusion of diethyl ether into these solutions afforded single crystals suitable for X-ray analysis. The structures of these complexes were solved by Professor M. Drew, University of Reading and by Dr R. Paul, University of Oxford. The resulting structures (Figure 20) turned out to be that of the same complex. The accompanying anion, in both cases, is believed to be sulphate, whose origin is thought to be from the use of magnesium sulphate as a drying agent in the synthetic protocol.

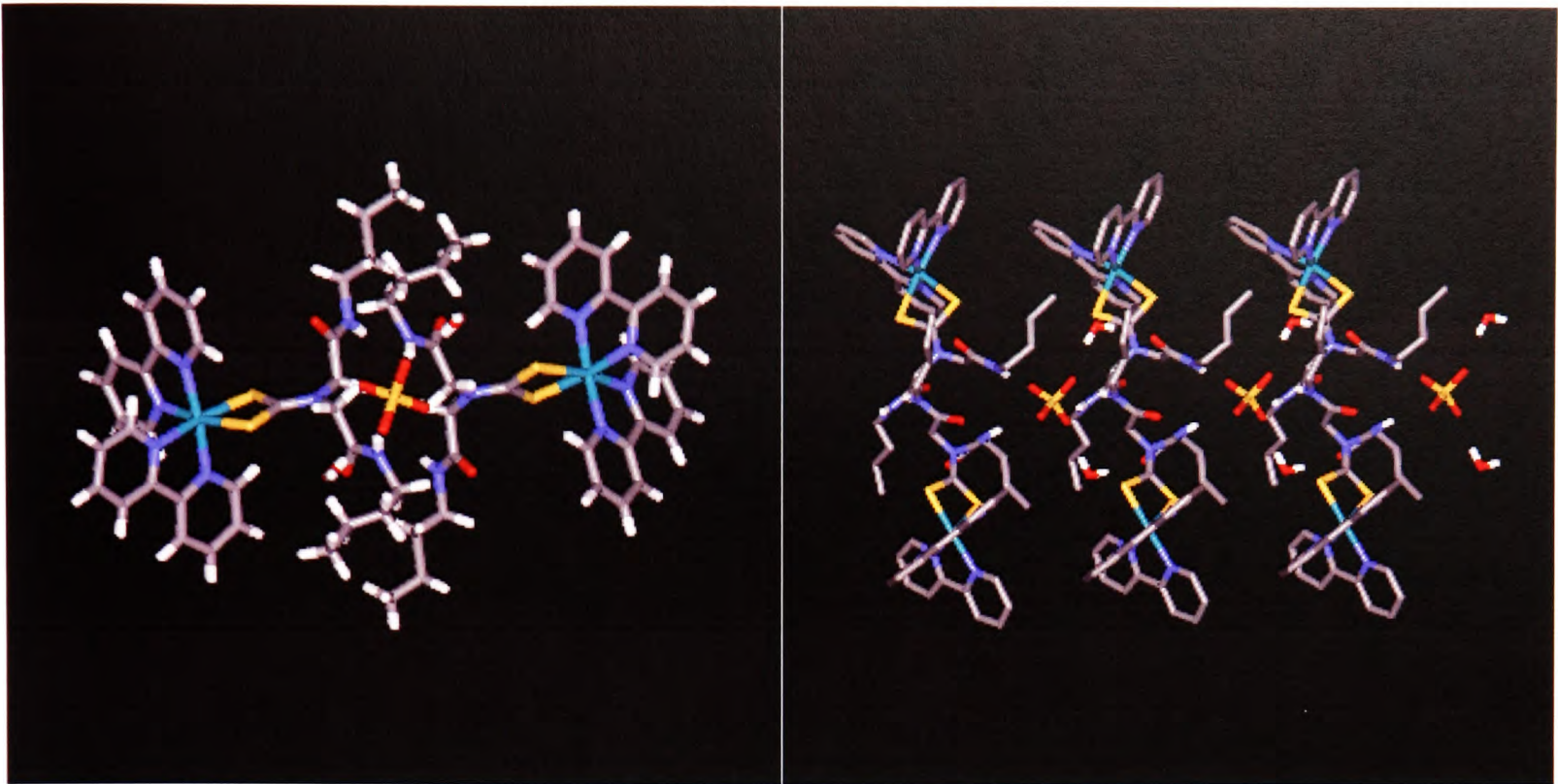


Figure 20 X-Ray crystal structure of 2{(124)}.SO₄.H₂O Right: Crystal packing structure illustrating anion binding mediated via hydrogen bonding to amide moieties and water molecules along the crystallographic *a*-axis (non-polar hydrogen atoms omitted for clarity) (Key: C – grey, H – white, N – blue, S – yellow, O – red, Ru – green)

	2(124).SO ₄
d(Ru-S) Å	2.39, 2.40
d(Ru-N) Å	2.04, 2.05 2.06, 2.07
d(N-C(S ₂)) Å	1.31, 1.32
θ(S-Ru-S) °	72.9
θ(N-Ru-N) °	78.4, 78.8
d(NH-O(SO ₃)) Å	2.16, 2.59
d(HOH-O(SO ₃)) Å	1.98
d(HOH-OC) Å	2.07

Table 10 Selected crystallographic parameters for 2(124).SO₄

The structure (Figure 20) shows that, similar to the functionalised analogue (104), the ruthenium centre adopts a pseudo-octahedral geometry due to the restricted bite angle of the

planar bipyridine and dithiocarbamate ligands. As predicted the anion (believed to be sulphate) is stabilised by the formation of hydrogen bonds to the amide protons. Due to the divalent nature of the anion, the sulphate forms hydrogen bonds with two different ruthenium(II)-based complexes. There are also interactions between the sulphate anions and the carbonyl oxygen's via the mediation of water molecules. The anion forms two short hydrogen bonds (2.21 Å) with two different ligands and two further hydrogen bonds between the sulphate oxygens and amide protons (2.59 Å). This illustrates that the anion binds to the receptor via hydrogen bonding interactions with the amide groups, as predicted from solution state studies. It is also worth noting that the sulphate anion is, like dihydrogen phosphate, tetrahedral, and this may reflect a preference by the receptor to bind guests of this geometry.

6 Second Sphere Complexation

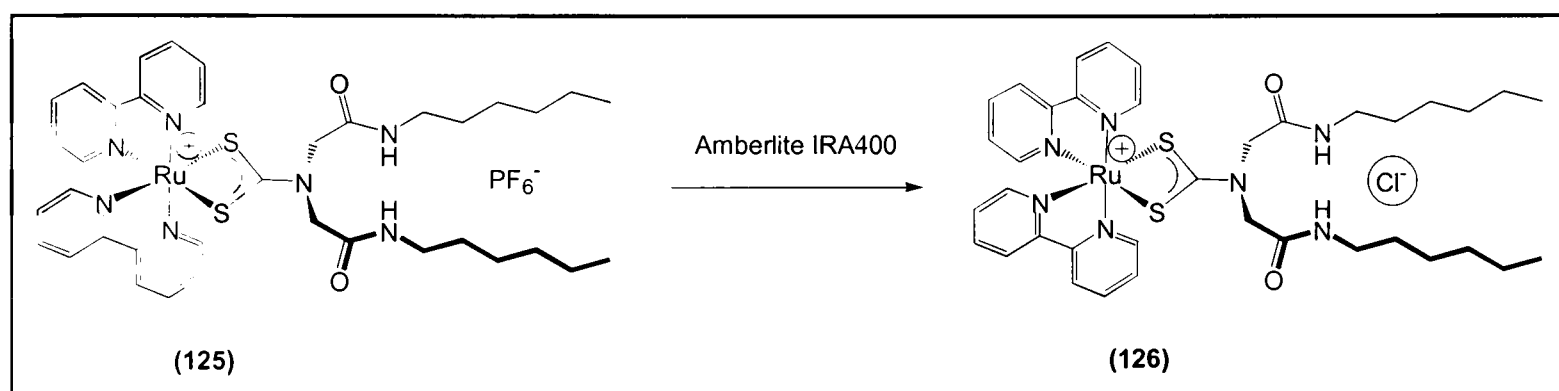
As discussed in Chapters One and Five, the generation of interlocked molecules is currently an area of intense research. The most common methodology for the synthesis of these architectures is via the templation of neutral or cationic components by the use of hydrogen bonding, π - π stacking, hydrophobic interactions and metal-directed self-assembly. In contrast, the use of anionic templates to generate interlocked architectures is a less well-developed area. There have been a handful of examples of anions playing a vital role in the templation of supramolecular architectures^{45,46,47}. More recently, Wisner *et. al.* have shown that the use of organic, pyridinium halide complexes are able to generate superstructures by coordination of the ion-pair to additional hydrogen bonding derivatives⁴⁸. Further functionalisation of these systems has lead to the development of a range of anion-templated pseudo-rotaxane and rotaxane structures^{49,50}.

The ruthenium bis(2,2'-bipyridine) dithiocarbamate-based amide-functionalised receptors (124) and (125) have been demonstrated to form strong complexes with anionic guests in

organic solvents. An investigation was undertaken as to whether these redox-active complexes could be utilised to generate analogous inorganic structures.

6.1 Synthesis and Characterisation

Initially, a coordinately unsaturated ion-pair complex was formed from the amide-functionalised ruthenium(II) bis(2,2'-bipyridine) dithiocarbamate complex (**125**). This was achieved via passing an acetonitrile solution of the hexafluorophosphate salt (**125**) down an Amberlite IRA-400 column loaded with sodium chloride to generate the corresponding chloride salt (**126**) (Scheme 9).



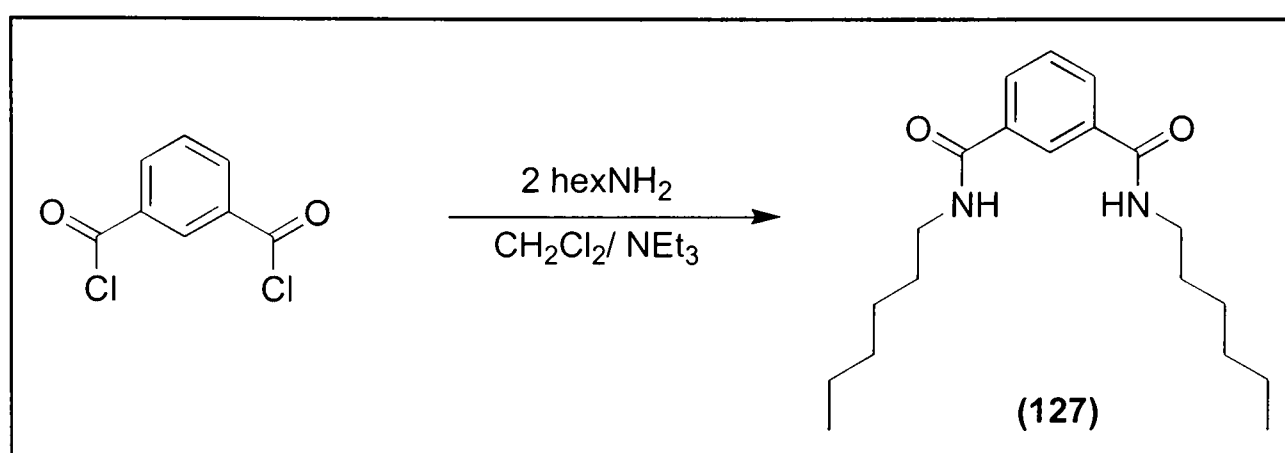
Scheme 9 Synthesis of chloride salt (**126**)

The chloride salt, generated in near quantitative yield, was characterised via elemental analysis and ^1H NMR spectroscopy. In the ^1H NMR spectrum, the amide signal had moved significantly downfield ($\Delta\delta = 1.53$ ppm), indicating the chloride anion is hydrogen bonding to the amide groups. This strong association is expected in chloroform solution as ^1H NMR experiments reveal tetra-*n*-butylammonium chloride forms a 1:1 complex with (**125**) with a stability constant of 10^3 , in this solvent system. The resulting tight ion-pair should leave the chloride anion with a vacant meridian that could bind another hydrogen bond donor in the absence of competitive solvents.

To test this theory, the isophthalamide (**127**) was prepared. Such molecules have been shown by Crabtree and co-workers to form strong complexes with chloride anions in noncompetitive solvents, due to its size complementarity and hydrogen bond donor cleft created by the amide

groups^{51,52}. The use of this structure may generate the desired ion-pair architecture.

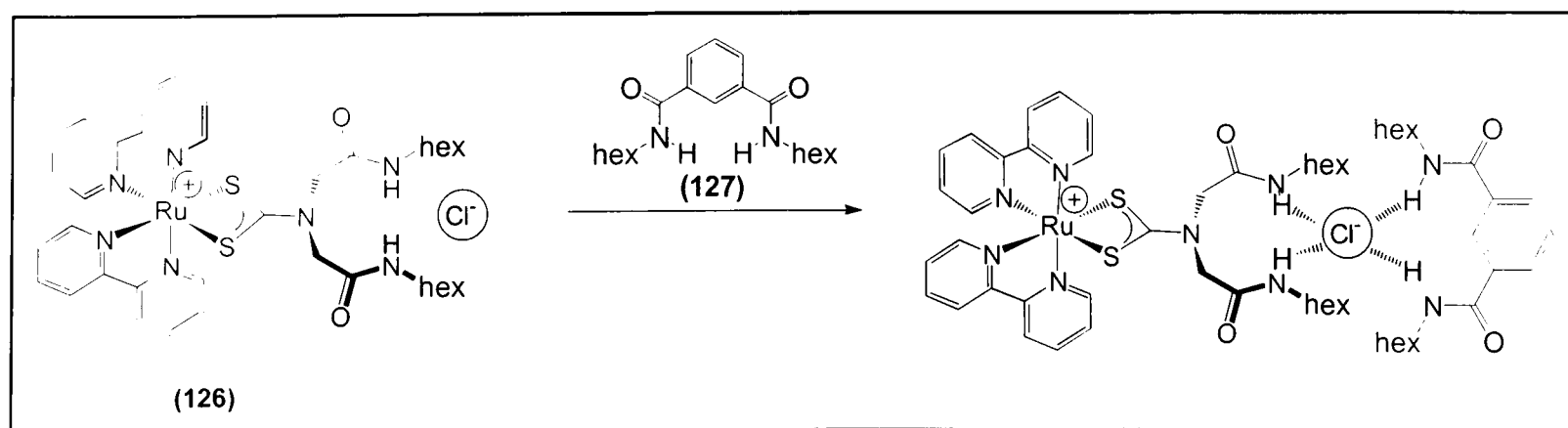
The synthesis of **(127)** was achieved by stirring the corresponding bis-acid chloride with *n*-hexylamine in dry dichloromethane, using triethylamine as a nucleophilic catalyst⁵³ (Scheme 10). The crude product was purified via the dropwise addition of diethyl ether to a stirred dichloromethane solution. The white solid was isolated in 54% yield and characterised by ¹H and ¹³C NMR spectroscopy, elemental analysis and electrospray mass spectrometry.



Scheme 10 Synthesis of isophthaloyl bis-amide (**127**)

6.2 Formation of Second Sphere Complex

The investigation into whether the ruthenium-based ion-pair complex **(126)** may form an ion-pair complex with the isophthalamide **(127)** was undertaken (Scheme 11). This was achieved by the study of a variety of spectroscopic and electrochemical techniques.



Scheme 11 Formation of secondary sphere complex

6.2.1 ^1H NMR Spectroscopy

^1H NMR spectroscopy was used to assess the affinity of the isophthalamide (**127**) for the chloride salt of the ruthenium(II) amide-appended receptor (**126**). This was achieved by the addition of (**126**) to a chloroform-d solution of (**127**). The hexafluorophosphate ruthenium(II) salt was also investigated to examine the effect the nature of the anion had in the coordination process. The ^1H NMR spectra of (**127**) upon the addition of the chloride salt (**126**) is displayed in Figure 21 and the perturbations of the isophthalamide protons are shown in Table 11.

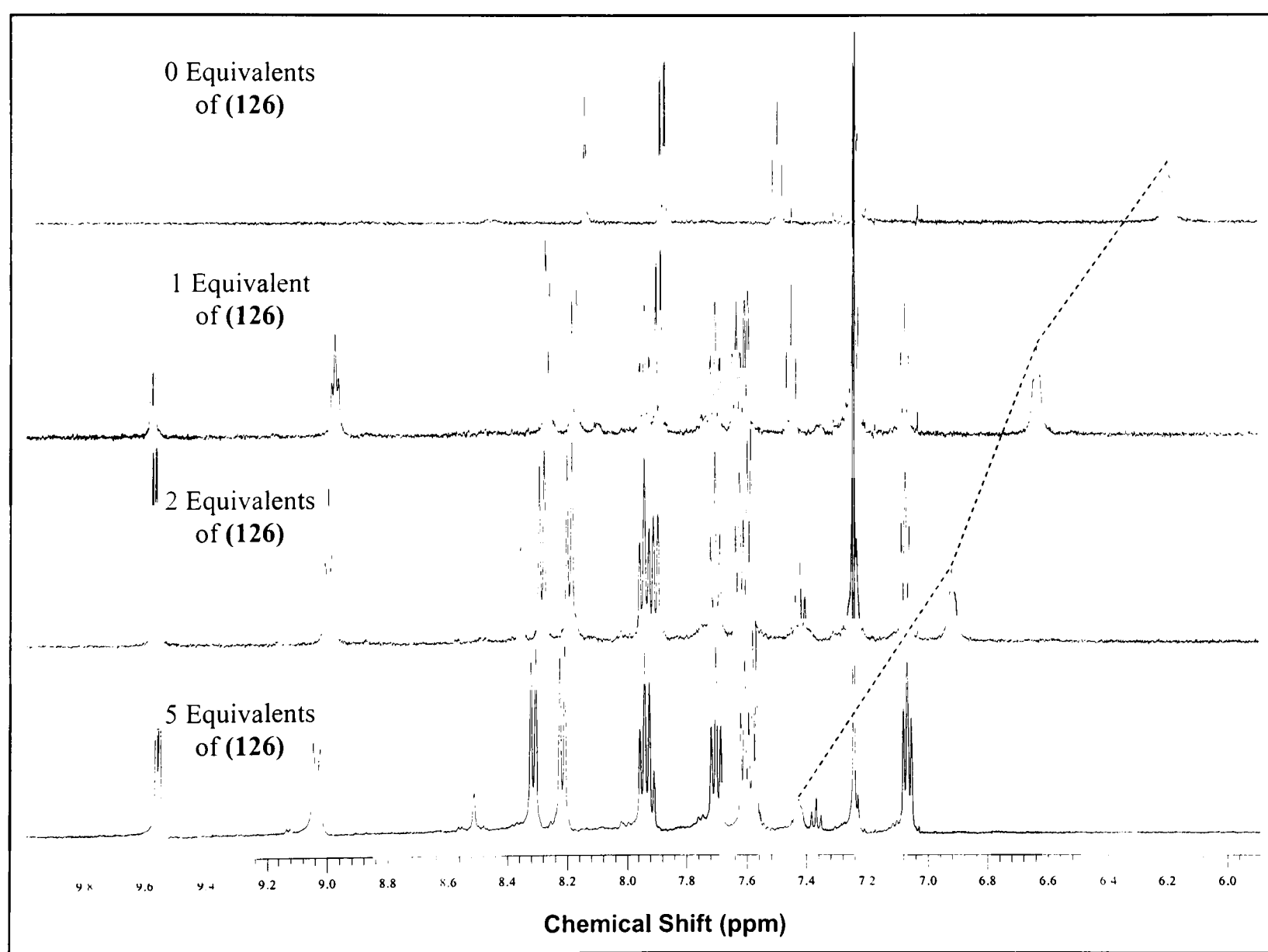


Figure 21 Change in ^1H NMR spectrum of (**127**) upon the addition of (**126**). Line represents perturbation of the amide proton of (**126**) (500MHz, CDCl_3 , 293K)

	ArH ²	ArH ⁵	ArH ^{4/6}	NH
$\Delta\delta$ (127) upon the Addition of 5.0 Equivalents of Cl ⁻ Salt (126)	+0.37 ppm	-0.13 ppm	#	+1.24 ppm
$\Delta\delta$ (127) upon the Addition of 5.0 Equivalents of PF ₆ ⁻ Salt (125)	-0.01 ppm	-0.02 ppm	0.00 ppm	+0.14 ppm

Table 11 Perturbation in the chemical shift of (**127**) upon the addition of 5.0 equivalents of Ru(II) bis(2,2'-bipyridine) amide-functionalised dithiocarbamate chloride complex (**126**) and hexafluorophosphate salt (**125**) (# indicates overlapping peaks)

Addition of the isophthalamide (**127**) to the chloride-based ion-pair (**126**) lead to a significant downfield perturbation of the amide resonance ($\Delta\delta = 1.24$ ppm) and the ArH² proton ($\Delta\delta = 0.37$ ppm). This illustrates that the ion-pair (**126**) is bound within the cleft of the isophthalamide via hydrogen bonding to the amide groups and the resultant close proximity of the aromatic proton. It is also noteworthy that the amide proton of the ruthenium(II) complex (**126**) is shifted downfield 0.07 ppm upon coordination with (**127**). This observation suggests that the filling of the second coordination site of the ion-pair also increases the affinity of the chloride anion for the ruthenium dithiocarbamate complex.

In contrast, addition of the hexafluorophosphate salt (**125**) leads to significantly smaller shifts in the protons of the isophthalamide. This shows that the nature of the anion dictates the formation of the desired host-guest complex.

In order to quantify this interaction, ¹H NMR titration experiments were undertaken in chloroform-d solution (Figure 22). Analysis of the generated data using the EQNMR curve fitting program yielded stability constants for this process and are displayed in Table 12.

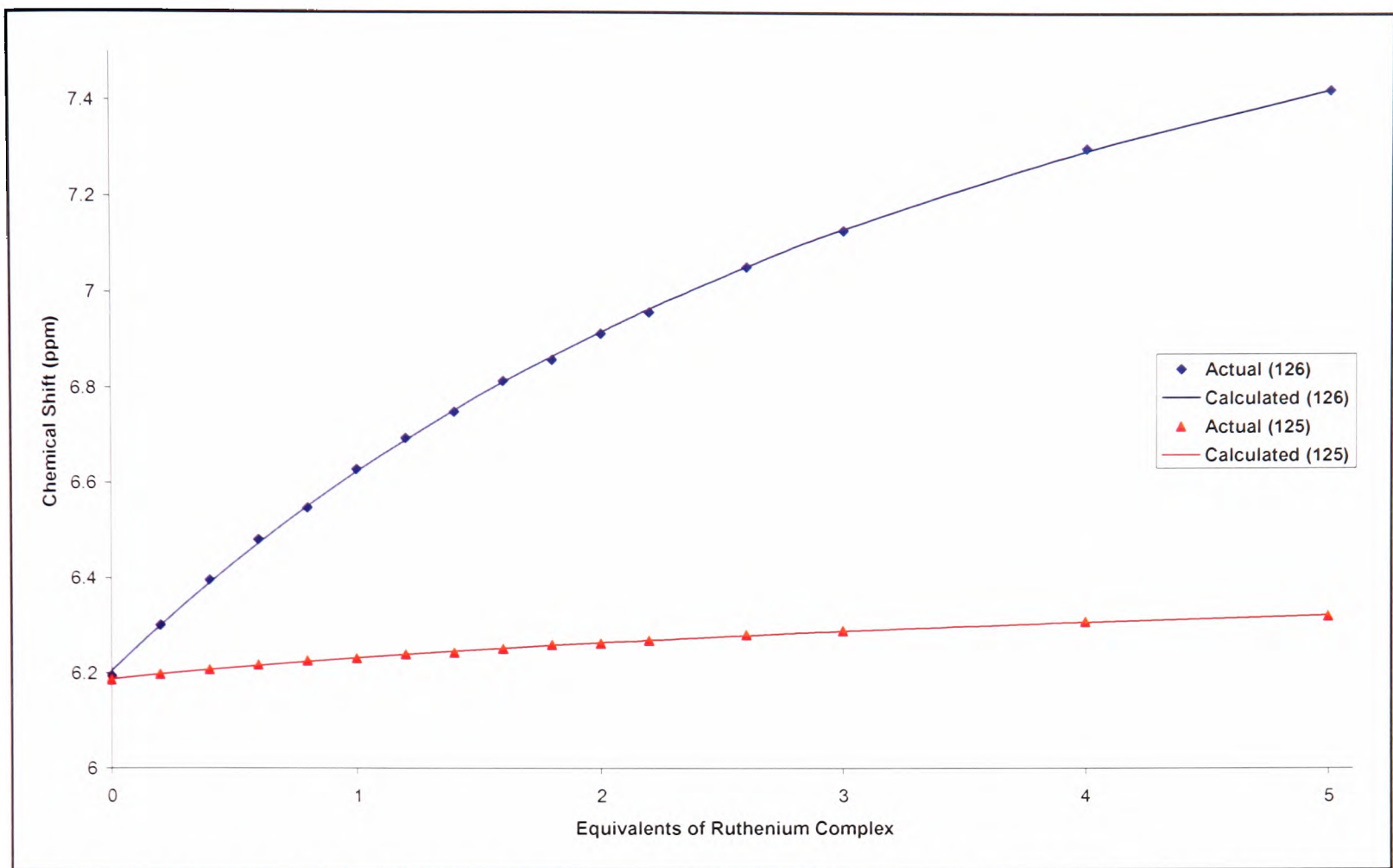


Figure 22 ¹H NMR titration experiment showing the perturbation of the amide proton of (127) upon addition of the chloride(126) and hexafluorophosphate (125) salts of Ru(II) bis(2,2'-bipyridine) dithiocarbamate amide complexes (50MHz, CDCl₃, 293K)

	(125)	(126)
<i>K</i>	#	100

Table 12 Stability constants (*K*) for the association of the bis-amide (127) upon the addition of the chloride and hexafluorophosphate salts of the Ru(II) bis(2,2'-bipyridine) amide functionalised dithiocarbamate receptors (126) and (125) respectively, in CDCl₃, 298K # indicates stability constant too small to accurately calculate (Errors <10%)

As expected, the chloride complex (126) displays a larger stability constant than the corresponding hexafluorophosphate salt. This result is analogous to the work performed by Wisner *et. al.* in which pyridinium bis-amide complexes (Figure 23) exhibited similar stability constants for binding the isophthalamide (127) (Table 13)⁵⁴.

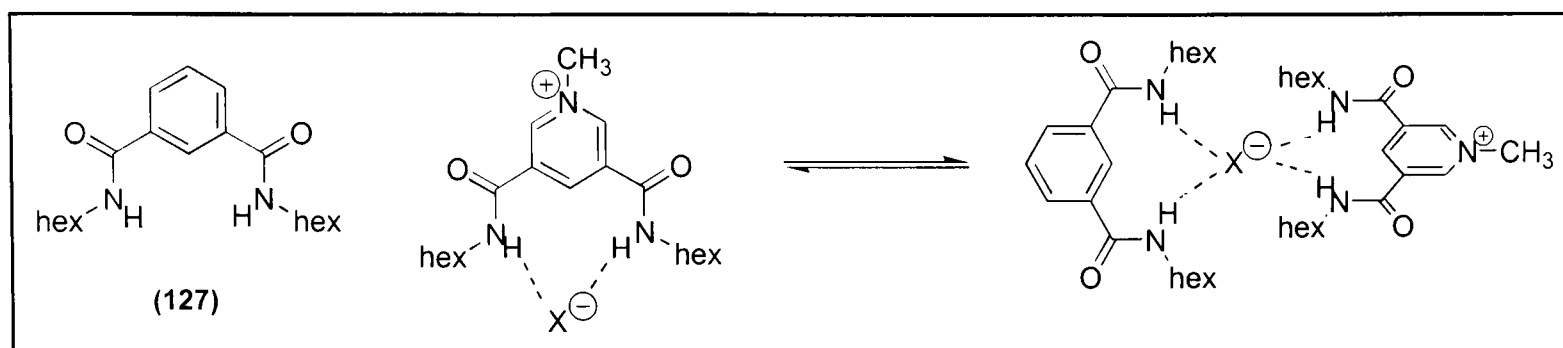


Figure 23 Ion-pair coordination of the organic pyridinium complexes with isophthalamide (127)

	$X = Cl^-$	$X = PF_6^-$
$\Delta\delta$ (Amide of (127))	+0.52 ppm	+0.18 ppm
K	60	25

Table 13 Change in the chemical shift in the amide protons of (127) upon the addition of 7.0 equivalents of the addition of chloride and hexafluorophosphate salts of pyridinium bis-amide complexes and calculated stability constants for these processes (300MHz, $CDCl_3$) Errors in $K < 10\%$

6.2.2 UV-vis Spectroscopy

The interaction between the ruthenium(II)-based ion-pair complexes (125) and (126) and the bis-amide (127) was also studied via UV-vis spectroscopy. Aliquots of the isophthalamide (127) was added to a dichloromethane solution of the ruthenium(II) bis(2,2'-bipyridine) dithiocarbamate-based complex (126). The changes in the UV-vis spectrum upon the addition of (127) are highlighted in Figure 24.

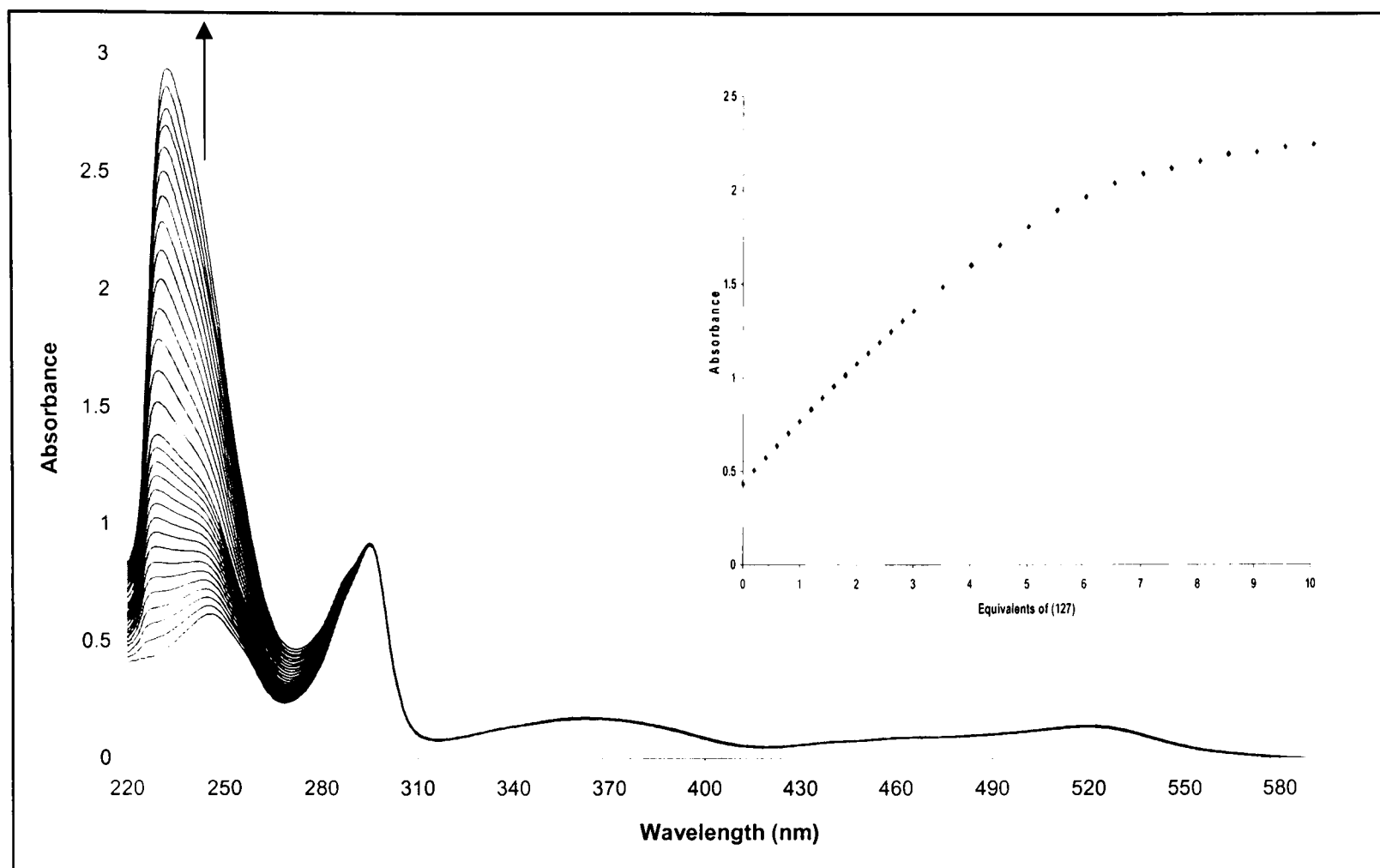


Figure 24 UV-vis titration experiment illustration the effect of the addition of (127) to (126) (inset) binding curve calculated from the data at 230nm

The addition of the aromatic bis-amide results in a significant change in the optical spectrum. Analysis of this data in order to obtain stability constants was undertaken using Specfit© global analysis software, a least-squares regression computer fitting program (refer to Appendix One). Unfortunately, the addition of the bis-amide to the hexafluorophosphate salt (**125**) did not allow the calculation of a stability constant for this process, but the addition of the analogous chloride salt (**126**) determined a stability constant of $\log\beta$ 3.54 (± 0.09) for this process. This large value illustrates the high affinity of the bis-amide for the coordinately unsaturated ion-pair (**126**) in forming a complex

6.2.3 Electrochemistry

The interaction between the ruthenium-based ion-pairs (**125**) and (**126**) and the isophthalamide (**127**) was examined further via cyclic and square wave voltammetry. This was achieved by monitoring the ruthenium(II/III) redox couple in a dichloromethane/

acetonitrile (9:1) solution containing 0.1M tetra-*n*-butylammonium tetrafluoroborate as a background electrolyte. In this solvent system, the ruthenium(II/III) couple occurs as a quasi-reversible wave at a half-potential of 0.34V.

Upon addition of 5.0 equivalents of the isophthalamide (**127**), a small cathodic shift of 10mV was observed in the voltammogram of the chloride salt (**126**). This implies that the isophthalamide is hydrogen bonding to the chloride anion and forming a tight ion-pair complex. This strong complex subsequently stabilises the ruthenium oxidation process.

The analogous experiment upon the hexafluorophosphate salt (**125**), gave no perturbation upon addition of 5.0 equivalents of the isophthalamide, showing the vital role of the chloride anion in forming the ion-pair complex.

6.2.4 Other Techniques

It has been shown via ¹H NMR and UV-vis spectroscopy and electrochemistry that the addition of the isophthalamide (**127**) results in the binding of the bis-amide by hydrogen bonding to the coordinately unsaturated chloride in the ion-pair (**126**). This interaction was further studied via electrospray mass spectrometry and molecular modelling.

An electrospray mass spectrum of a solution of (**126**) and (**127**) coinjected with potassium hexafluorophosphate afforded a peak corresponding to the formation of an adduct of the composition [(**126**).(**127**).K]⁺. This in combination with the aforementioned techniques suggest the anion is indeed templating the formation of a 1:1 complex between the ion-pair complex (**126**) and the bis-amide (**127**). The structure of such a complex was investigated using the CaChe molecular modelling computer program.

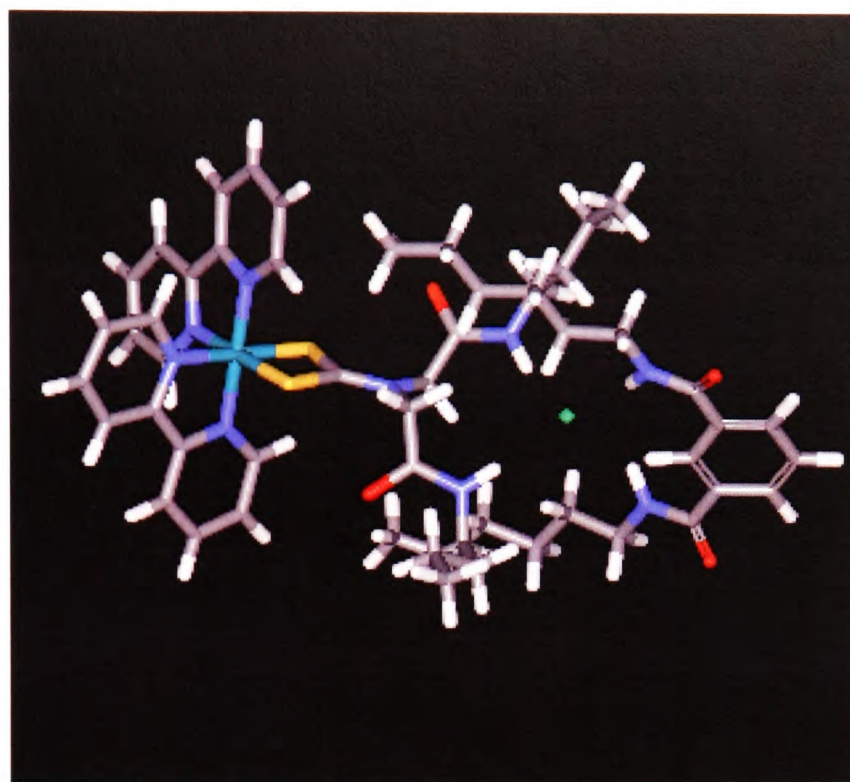


Figure 25 Cache molecular model for the association of (126) and (127) in forming an ion-pair complex

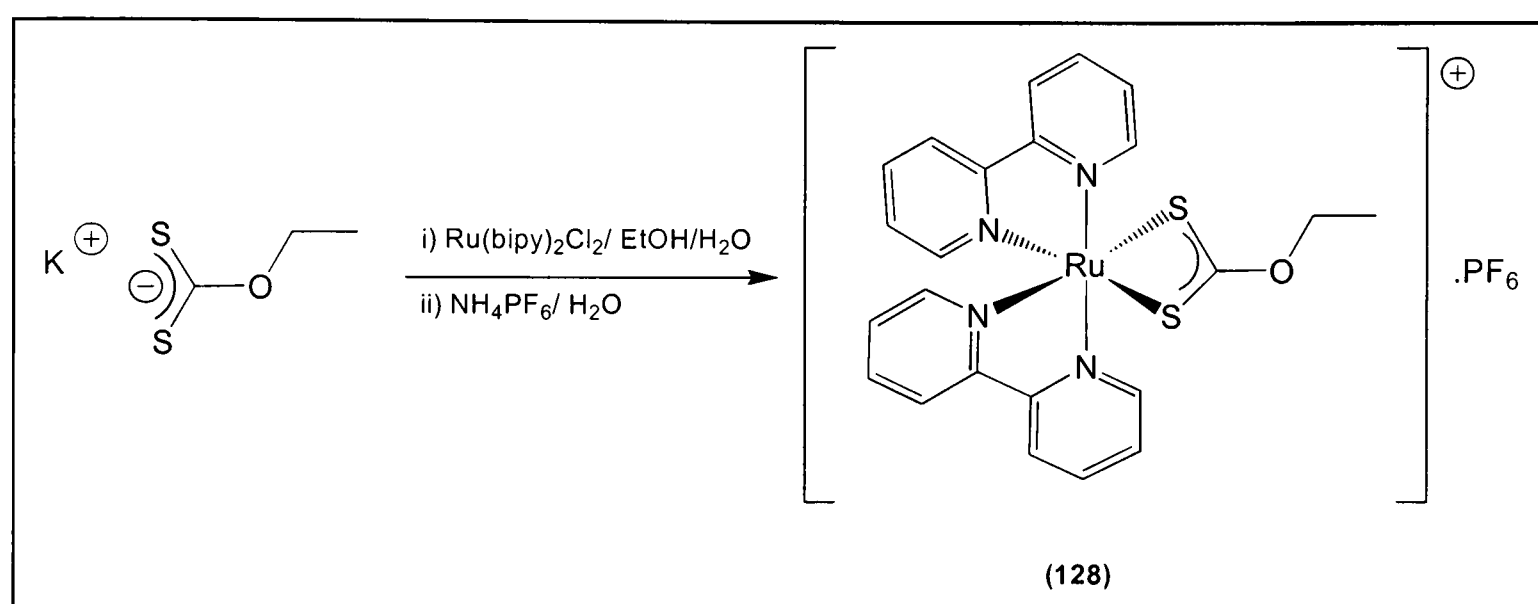
The resulting structure (Figure 25) suggests the formation of the predicted structure via the formation of favourable hydrogen bonding interactions about the tetrahedrally coordinated chloride anion. The generation of this structure offers the possibility of generating a range of interlocked redox-active anion-templated architectures.

7 Ruthenium(II) bis(2,2'-Bipyridine) Xanthate Complexes

Closely related to the dithiocarbamate ligand is the xanthate ligand, formed by the addition of carbon disulphide to a basic alcoholic solution⁵⁵. The use of the xanthate ligand has been problematic for the self-assembly of macrocyclic complexes⁵⁶, due to its propensity to form polymers and its lower stability in comparison to corresponding dithiocarbamate complexes. In the case of ruthenium(II) bis(2,2'-bipyridine) xanthate complexes, since only one metal centre is incorporated in a structure, the problem of polymerisation is alleviated.

7.1 Ruthenium(II) bis(2,2'-Bipyridine) *O*-Ethylxanthate (128)

Initially, a mononuclear, unfunctionalised ruthenium(II) bis(2,2'-bipyridine) xanthate complex was prepared. This was achieved through refluxing a slight excess of potassium *O*-ethylxanthate with *cis*-dichlorobis(2,2'-bipyridine) ruthenium(II), for 18 hours, in an ethanol/water (2:1) solvent system. Addition of ammonium hexafluorophosphate to an aqueous solution of the crude product afforded the elementally pure product (**128**) in 89% yield (Scheme 12).



Scheme 12 Synthesis of Ru(II) bis(2,2'-bipyridine) *O*-ethylxanthate hexafluorophosphate (**128**)

The resulting purple solid was characterised by ^1H , ^{13}C , ^{19}F , ^{31}P and ^1H - ^1H COSY NMR spectroscopy, electrospray mass spectrometry and elemental analysis. Similar to the analogous dithiocarbamate complex (**104**), the ^1H NMR spectrum shows a well-resolved aromatic region, and a multiplet (4.59 ppm) corresponding to the diastereotopic methylene group, adjacent to the chiral ruthenium centre. The ^{13}C NMR spectrum of (**128**) is displayed in Figure 26. The most interesting feature of this is the peak corresponding to the xanthate (CS_2) group, which is seen at 231.46 ppm. This is in contrast to the analogous dithiocarbamate complex (**104**), where the analogous peak is seen at much higher field (211.73 ppm).

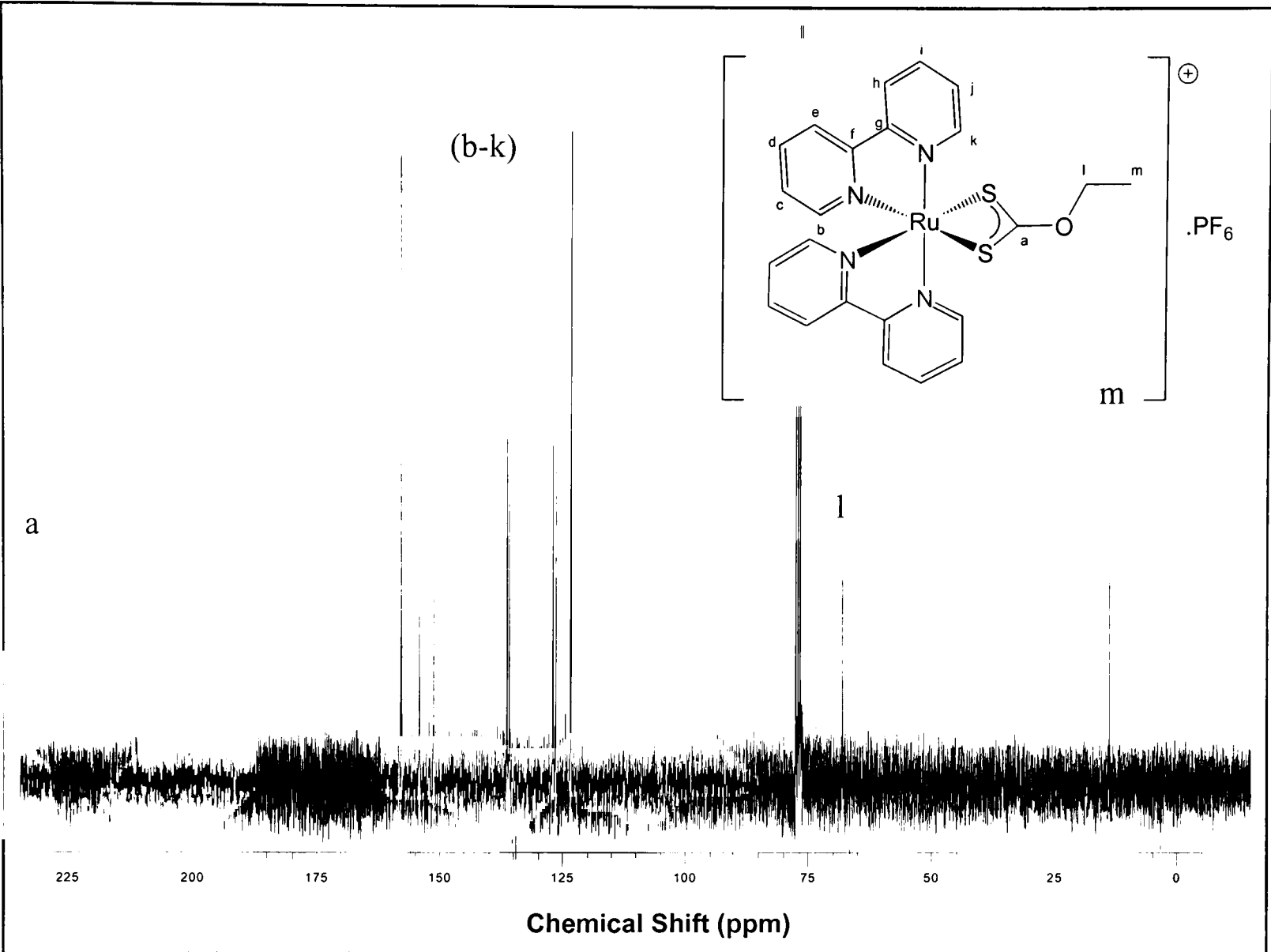


Figure 26 ¹³C NMR spectrum of Ru(II) bis(2,2'-bipyridine) *O*-ethylxanthate hexafluorophosphate (128) (75.4MHz, CDCl₃, 293K)

The electrochemical properties of the xanthate complex were investigation by the use of cyclic and square wave voltammetry. This was performed in an acetonitrile solution of the complex containing 0.1M tetra-*n*-butylammonium tetrafluoroborate as a background electrolyte. The electrochemical data of (128) is displayed in Table 14.

		Ru(II/III)	bipyH1	bipyH2
(128)	E _½	0.44V	1.80V	2.06V
	E _{pa}	0.48V	1.77V	2.00V
	E _{pc}	0.40V	1.85V	2.10V

Table 14 Electrochemical data for Ru(II) bis(2,2'-bipyridine) *O*-ethylxanthate hexafluorophosphate (128) in MeCN with TBABF₄ the supporting electrolyte, Ag/AgNO₃ the reference electrode and glassy carbon the working electrode. Sample 1x10⁻³M, scan rate 100mVs⁻¹, frequency 5Hz, T = 293K, errors ±5mV

The resulting voltammograms displayed peaks analogous to the dithiocarbamate complex **(104)** with one ruthenium(II/III) oxidation and two bipyridine reduction quasi-reversible couples being observed. However, in contrast to **(104)**, the peaks are significantly anodically shifted. This means that it is more difficult to oxidise the xanthate complex (by 0.20V), although it is still significantly easier to oxidise than tris(2,2'-bipyridine) ruthenium(II) hexafluorophosphate **(103)**.

The low oxidation potential of **(104)** is an example of the affinity of dithiocarbamate-based ligands in stabilising high oxidation state complexes. This is a result of the important resonance form (**R2**, Figure 27) which localises the formal negative charges on each of the coordinated sulphur donors⁵⁷. In contrast, the analogous resonance structure of the xanthate complex (**R4**) is less likely to contribute significantly, resulting in it being harder to oxidise^{58,59}. This feature is also highlighted in the ¹³C NMR spectra of the complexes. As has been seen, the resonance corresponding to the dithiocarbamate carbon of **(104)** is at a significantly lower chemical shift in comparison to the xanthate complex **(128)**. This is a result of the higher proportion of the more shielding resonance structure **R2** in comparison to **R4** resulting in a greatly increased electron density on the dithiocarbamate carbon.

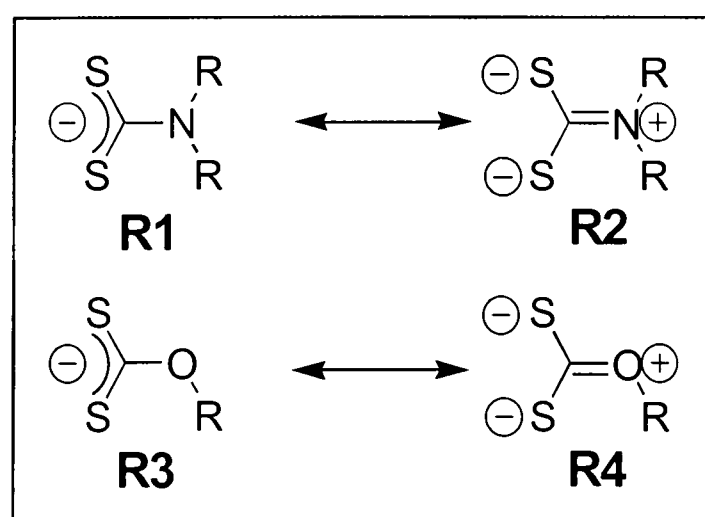
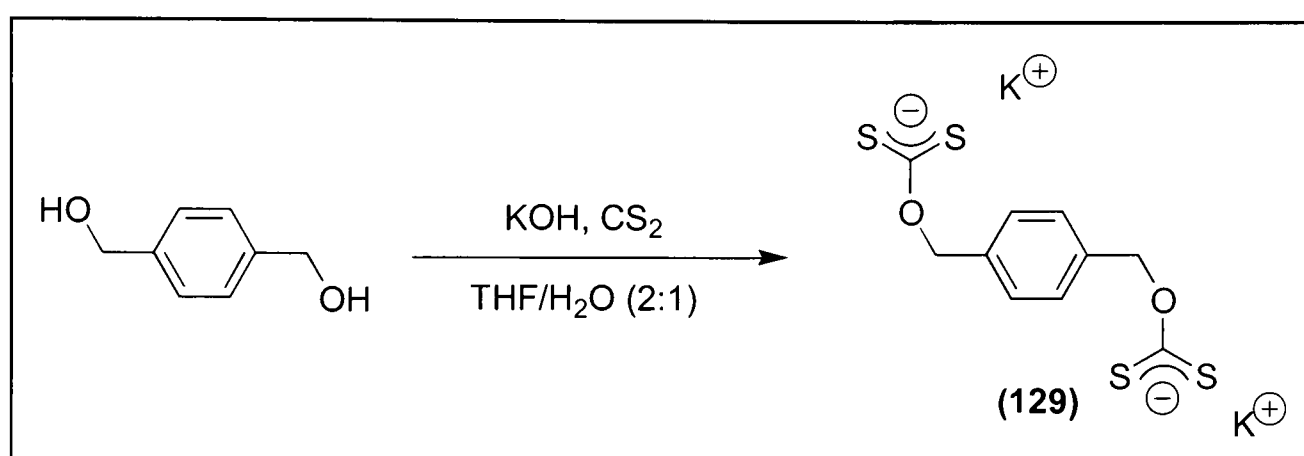


Figure 27 Delocalisation about (upper) dithiocarbamate and (lower) xanthate ligands

7.2 Attempted Synthesis of Multinuclear Ruthenium(II) bis(2,2'-bipyridine) Xanthate Complexes

In an attempt to synthesise dinuclear ruthenium(II) bis(2,2'-bipyridine) xanthate complex, a potassium bis-xanthate complex was prepared. This was achieved by the addition of potassium hydroxide and carbon disulphide to a tetrahydrofuran/water (4:1) solution of 1,4-benzenedimethanol, isolating an off-white solid (**129**) (Scheme 12).



Scheme 13 Synthesis of potassium bis-xanthate salt (**129**)

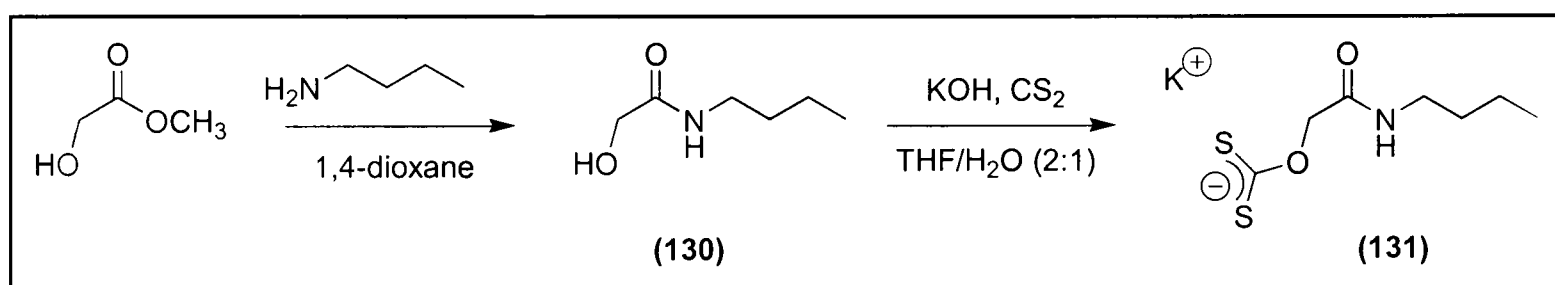
Unfortunately, the attempted coordination of the potassium bis-xanthate (**129**) to ruthenium(II) bis(2,2'-bipyridine) proved unsuccessful. It is possible that the weaker nature of the xanthate bond in comparison to that of the dithiocarbamate ligand may not be sufficiently strong enough to be stable in the presence of another positive charge in close proximity.

7.3 Attempted Synthesis of Anion Binding Ruthenium(II) bis(2,2'-bipyridine) Xanthate Complexes

It has been demonstrated that the ruthenium(II) bis(2,2'-bipyridine) dithiocarbamate group is able to act as an effective reporter group for the detection of anionic guests. This was encouraged by the incorporation of anion binding moieties such as amides into the dithiocarbamate framework. Since xanthates have similar properties to the analogous dithiocarbamate complexes, it was attempted to synthesise xanthate ligands appended with amide groups in order to observe whether such complexes would also offer effective anion

binding capabilities.

To this end, an alcohol-appended amide was prepared via refluxing a 1,4-dioxane solution of methyl glycolate and *n*-butylamine affording the amide **(130)**⁶⁰. The colourless oil was purified by dissolving in hexane and cooling the solution to -18°C, which resulted in the formation of a white crystalline solid that was collected by filtration. Warming to room temperature lead to re-formation of the oil, which was characterised by ¹H and ¹³C NMR spectroscopy, electrospray mass spectrometry and elemental analysis Treatment of the alcoholic group with potassium hydroxide and carbon disulphide resulted in the formation of the xanthate ligand **(131)**, which was characterised by ¹H and ¹³C NMR spectroscopy (Scheme 14).



Scheme 14 Synthesis of amide-functionalised potassium xanthate salt (131)

Unfortunately, attempts to coordinate **(131)** by refluxing it with *cis*-dichlorobis(2,2'-bipyridine) ruthenium(II), for 18 hours, in ethanol/water (2:1) did not generate the desired xanthate product. Analysis by electrospray mass spectrometry revealed the main product for the reaction was the ruthenium(II) bis(2,2'-bipyridine) *O*-xanthate complex **(128)**. This suggests that the xanthate moiety is considerably less stable than the analogous dithiocarbamate system, with it undergoing a ligand exchange reaction with the solvent. Attempts to perform the reaction in milder conditions and in a variety of non-alcoholic solvents also proved unsuccessful.

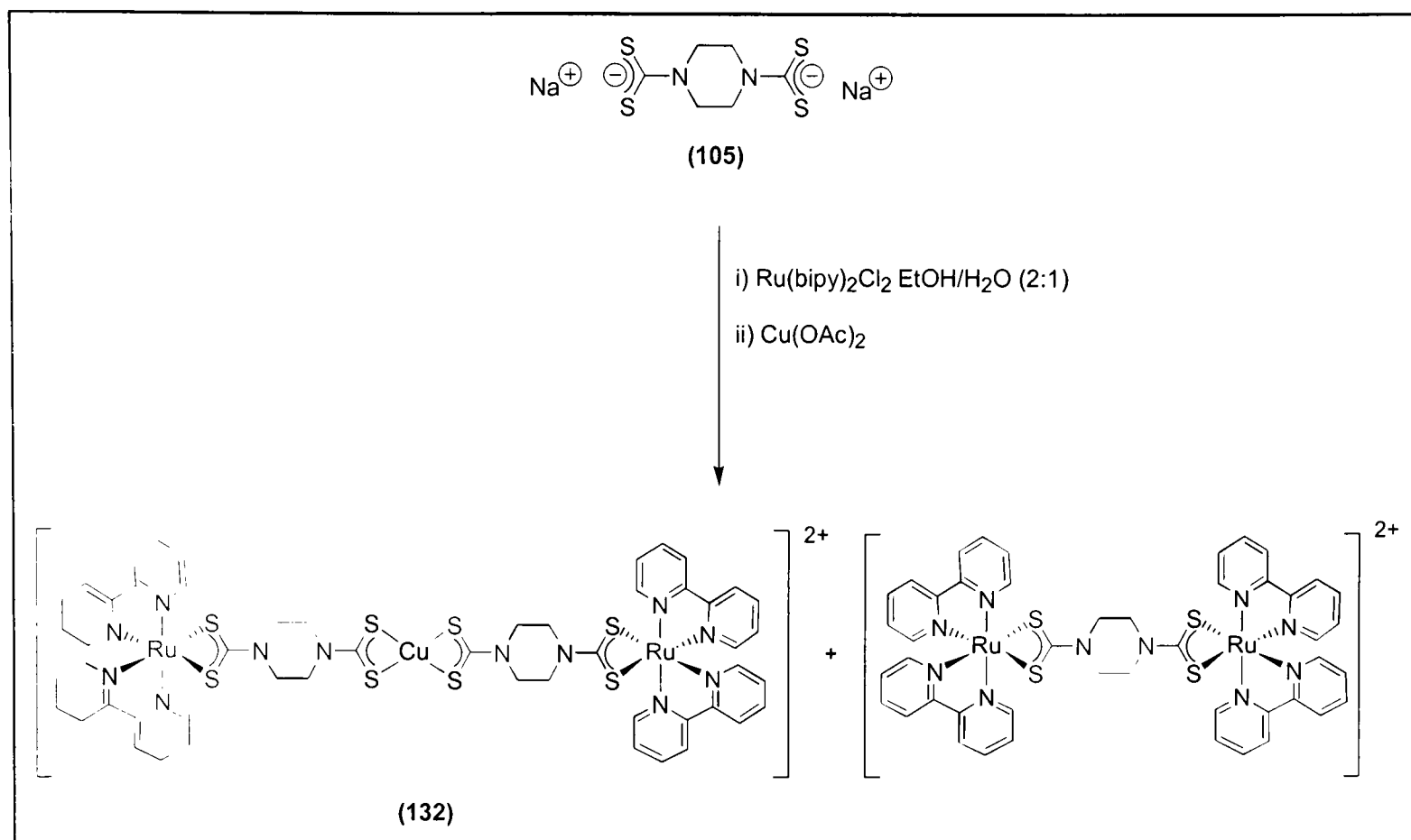
8 Attempted Synthesis of Mixed-Metal Dithiocarbamate Complexes

Since the metal centre within the ruthenium(II) bis(2,2'-bipyridine) dithiocarbamate-based complexes are low-spin d^6 complexes it would be expected that they would be kinetically inert. Even after seven days, a combination of the labile mononuclear copper(II) dithiocarbamate complex (**20**) with the dinuclear piperazine-spaced ruthenium(II) complex (**107**) showed no evidence of ligand scrambling by electrospray mass spectrometry. This suggests that the ruthenium(II) dithiocarbamate bond is indeed kinetically inert.

8.1 Multinuclear Mixed-Metal Dithiocarbamate Complexes

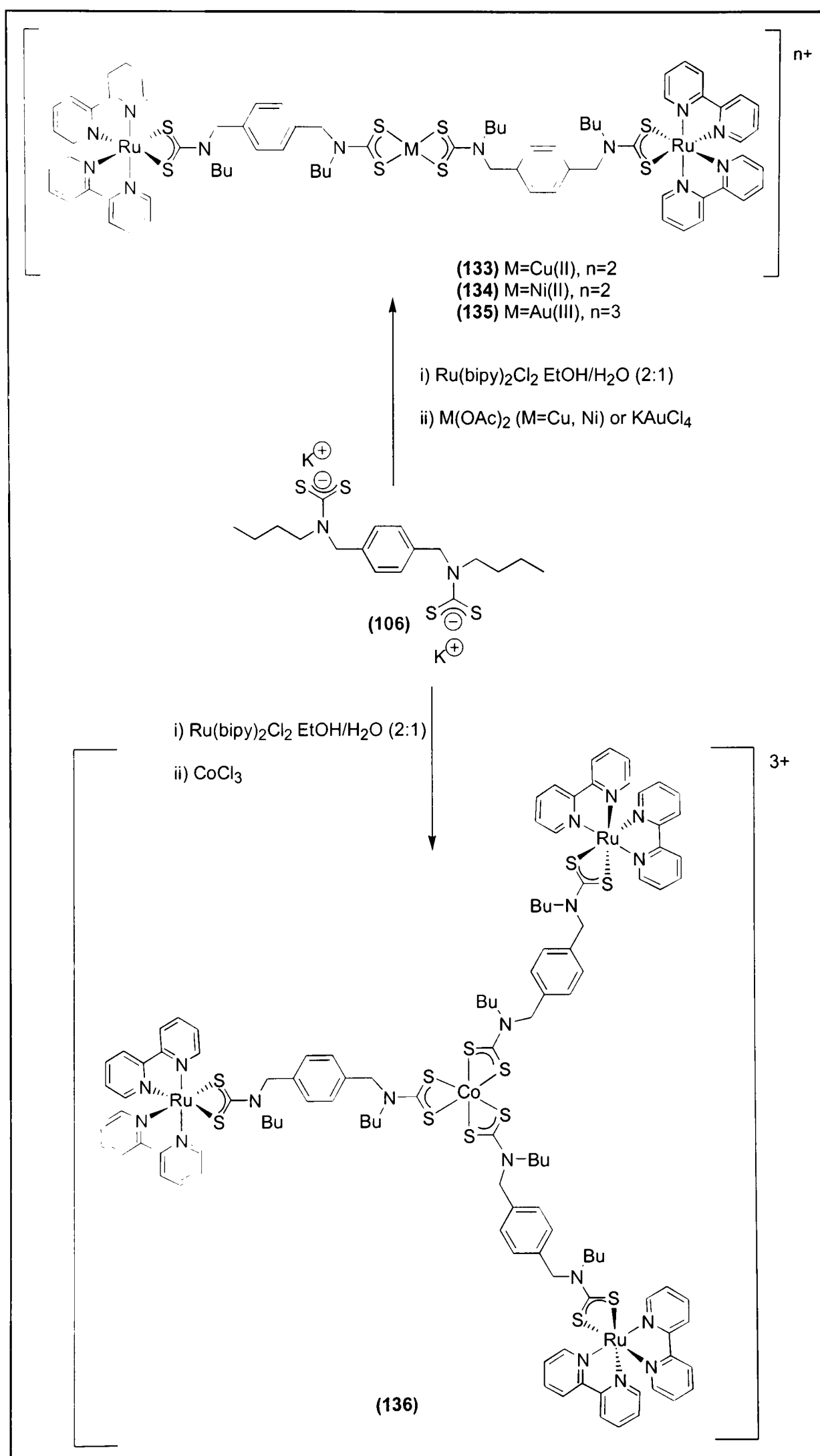
Due to the kinetically inert nature of the ruthenium bis(2,2'-bipyridine) dithiocarbamate linkage the synthesis of mixed-metal dithiocarbamate complexes was attempted. This was achieved by the combination of an equimolar solution of a potassium bis-dithiocarbamate salt and *cis*-dichlorobis(2,2'-bipyridine) ruthenium(II) and subsequent addition of a further equivalent of a different transition metal ion.

Initially, the piperazine-spaced bis-dithiocarbamate salt (**105**) was used for this purpose. This was refluxed in an ethanol/water (2:1) solvent system with one equivalent with *cis*-dichlorobis(2,2'-bipyridine) ruthenium(II) for 18 hours. The resultant solution was stirred for 18 hours with a further equivalent of copper(II) acetate (Scheme 15). Analysis of the solution by electrospray mass spectrometry revealed the formation of the desired dicationic mixed-metal complex (m/z 682.25). However, in addition to this, a large peak was also observed corresponding to the dinuclear ruthenium complex (**107**) (m/z 532.28). Unfortunately, numerous attempts to separate the two products did not prove possible via a variety of chromatographic techniques or recrystallisations.



Scheme 15 Synthesis of piperazine-spaced mixed-metal dithiocarbamate complex (132)

An analogous reaction was also performed with the *p*-xylene spaced bis-dithiocarbamate salt (106). Subsequent addition of copper(II), nickel(II), gold(III) and cobalt(III) salts aimed to generate a variety of novel architectures (Scheme 16).



Scheme 16 Synthesis of multi-nuclear mixed-metal dithiocarbamate complexes

The electrospray mass spectrum of the crude product of **(133)** is displayed in Figure 28 and shows the formation of the desired trinuclear product. However, the formation of the dinuclear product **(109)** is also clearly visible. The half-integer spacing of both of these peaks shows that they result from the generation of the dicationic species.

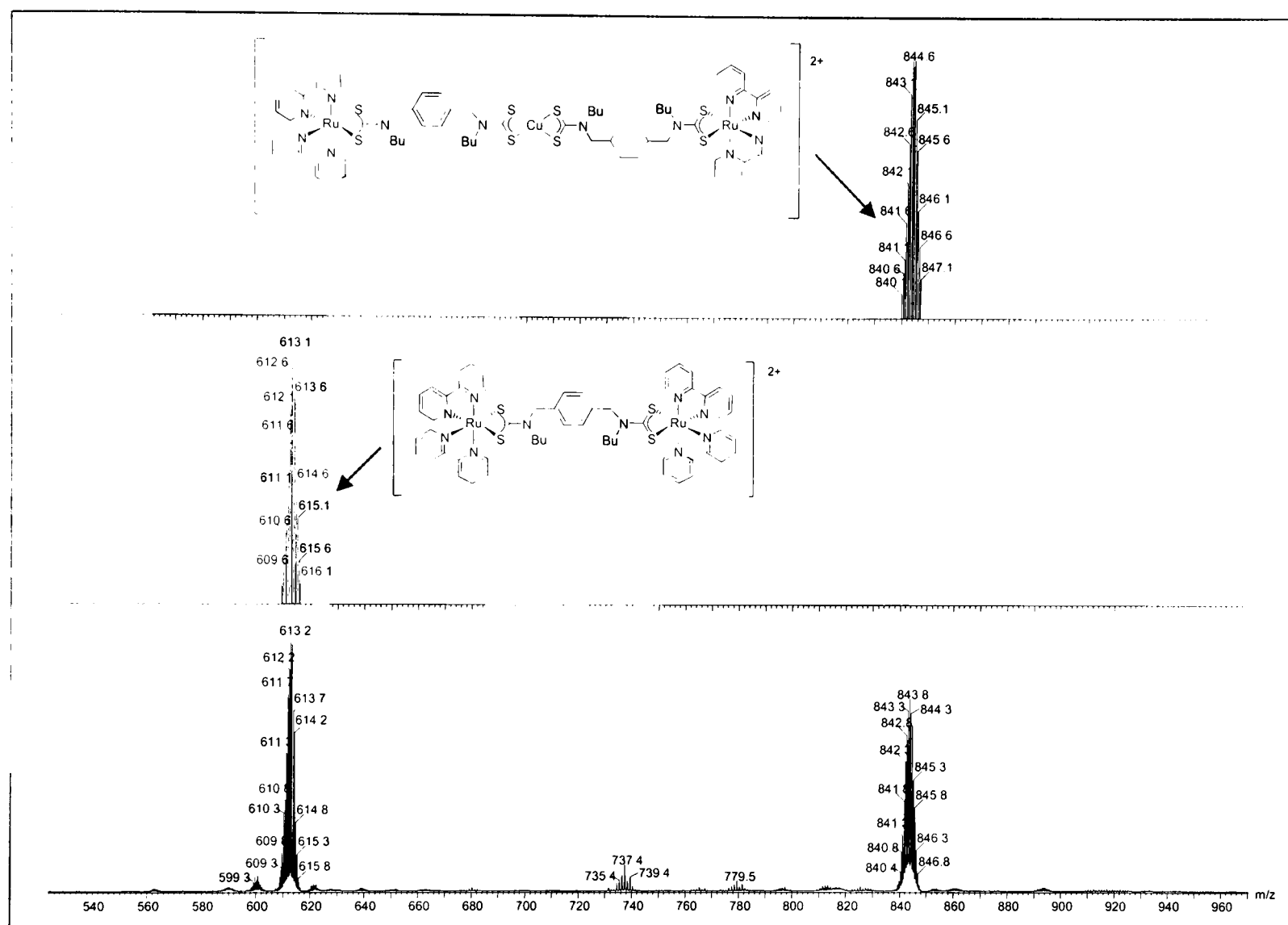


Figure 28 Electrospray mass spectrum of mixed-metal dithiocarbamate complex **(133)** (upper) predicted isotopic patterns for complexes

The addition of one equivalent of *cis*-dichlorobis(2,2'-bipyridine) ruthenium(II) to the *p*-xylene spaced bis-dithiocarbamate salt **(106)** followed by cobalt(III) chloride and potassium gold(III)tetrachloroaurate afforded the tricationic complexes **(135)** and **(136)**, respectively. The geometry of both of these complexes is, however, significantly different, with the square-planar gold(III) ion resulting in the formation of a linear trinuclear complex, while the octahedral cobalt(III) complex yields a trigonal planar tetranuclear structure (Scheme 16). This illustrates that architectures with a range of geometries may be synthesised, which in turn, may be regarded as the initial step in the preparation of heteropolymetallic inorganic

dendrimers.

Unfortunately, the formation of the multi-nuclear mixed-metal complexes **(133)** - **(136)** was also accompanied by the formation of dication bis-ruthenium complex **(109)**. Again, repeated attempts at purification of these novel multi-nuclear complexes have to date proved unsuccessful.

9 Conclusion

The use of the ruthenium(II) bis(2,2'-bipyridine) dithiocarbamate moiety has been expanded to generate a range of complexes. These complexes have been characterised by ^1H and ^{13}C NMR spectroscopy, electrospray mass spectrometry, elemental analysis and X-ray crystallography. The optical properties of the complexes were examined although they were shown not to luminesce at room temperature. The ruthenium(II) bis(2,2'-bipyridine) dithiocarbamate group is also shown to be redox-active, exhibiting a quasi-reversible ruthenium(II/III) oxidation and two bipyridine reduction potentials.

A number of multinuclear complexes have also been synthesised and their properties investigated. A tetranuclear resorcinarene dithiocarbamate complex was prepared, and electrospray mass spectrometry showed a peak corresponding to an adduct with chloride. Exchange of this anion resulted in the decomposition of the tetranuclear complex, possibly indicating that the chloride anion templates and stabilises this architecture.

Crown ether derivatised ruthenium(II) bis(2,2'-bipyridine) dithiocarbamate complexes have been synthesised. Unfortunately, due to the positively-charged nature of these hosts, only limited binding of Group 1 metal ions was observed.

Synthesis of amide functionalised dithiocarbamate ligands and subsequent coordination to the ruthenium(II) bis(2,2'-bipyridine) group has enabled the preparation of receptors capable of anion binding. Investigation into the binding properties of these complexes by ^1H NMR

spectroscopy demonstrated the binding stoichiometry and stability constants with a range of anionic guests. The receptors (**124**) and (**125**) show a preference for the binding of the dihydrogen phosphate over other anionic guests. The binding process may also be monitored by electrochemistry with large cathodic shifts observed upon the addition of anions. An X-ray crystal structure of (**124**) was obtained binding the sulphate anion via favourable hydrogen bonding interactions with the amide groups.

A coordinately unsaturated ruthenium-based chloride salt complex has been shown to form a second sphere complex in non-competitive solvent systems. The bis-amide (**127**) has been investigated via ^1H NMR and UV-vis spectroscopy, electrospray mass spectrometry, electrochemistry and molecular modelling. The generation of this complex acts as a prelude to the generation of redox- and photo-active interlocked structures.

Attempts have also been undertaken to utilise the kinetic inertness of the ruthenium(II) dithiocarbamate bond and generate mixed-metal dithiocarbamate complexes. Whilst the formation of a range of these architectures can be demonstrated via electrospray mass spectrometry, their subsequent purification has proved problematic.

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Chapter Eight

Experimental

Chapter Eight: Experimental

1 Solvent and Reagent Pre-treatment

Commercially available materials were used without further purification, unless otherwise stated. Acetonitrile and dichloromethane were distilled under nitrogen from calcium hydride. Tetrahydrofuran and toluene were distilled from sodium; in the former case using benzophenone as an indicator. Thionyl chloride was distilled from triphenyl phosphate, and triethylamine distilled and stored over potassium hydroxide. De-ionised water was used in all cases.

2 Instrumental Techniques

NMR spectra were recorded on a Varian Mercury 300 or a Varian Unity Plus 500 spectrometer. Electrospray mass spectrometry was recorded on a Micromass LCT instrument. Typical settings were as follows: Capillary Voltage 3.2kV, Sample Cone 40V, Extraction Cone 10V, RFLens 200, Desolvation Temperature 80°C, Source Temperature 60°C. In electrospray competition experiments the sample cone voltage is increased to 80V.

Where nitrosium tetrafluoroborate is added to the sample, milder conditions are used, i.e. Capillary Voltage 3.2kV, Sample Cone 20V, Extraction Cone 6V, Desolvation Temperature 60°C, Source Temperature 40°C.

Elemental analyses were performed at the Inorganic Chemistry Department Microanalysis Department, University of Oxford. For the synthesis of gold and silver nanoparticles, elemental analysis was used as a tool for calculating the proportion of metal:stabilising ligands. Details of stability constant determination and EPR and TEM procedures are highlighted in Appendices One to Three.

3 Synthetic Procedures

Syntheses from Chapter Two:

N,N'-Dibutyl-*m*-xylylenediamine (7)

α - α' -Dibromo-*m*-xylene (2.05g, 7.50mmol) was added portionwise to *n*-butylamine (40ml) and the solution stirred at room temperature for 1 hour. The excess amine was then removed under reduced pressure. The resulting yellow oil was dissolved in CH₂Cl₂ (100ml) and washed with water (2x100ml). The organic layer was dried over K₂CO₃ (anhydrous) and the solvent removed yielding a yellow oil. (1.69g, 90%)

¹H NMR (300MHz, CDCl₃) δ_{H} : 7.27 (1H, m, ArH⁵), 7.20 (2H, m, ArH^{4/6}), 7.18 (1H, s, ArH²), 3.77 (4H, s, ArCH₂), 2.61 (4H, t, J=7.2Hz, NHCH₂CH₂), 1.46 (4H, m, NHCH₂CH₂), 1.34 (4H, m, CH₂CH₃), 0.89 (6H, t, J=7.2Hz, CH₃)

¹³C NMR (75.5Hz, CDCl₃) δ_{C} : 140.56, 128.23, 127.67, 126.50 (ArC), 53.98, 49.15, 32.12, 20.35 (CH₂), 13.90 (CH₃)

ESIMS (m/z): 249.3 [M+H]⁺, 193.2 [M-Bu]⁺, 176.2 [M-NHBu]⁺

Elemental Analysis for C₁₆H₂₈N₂ · 1/10 H₂O:

Expected: C 76.80, H 11.36, N 11.20

Found: C 76.86, H 11.29, N 11.26

N,N'-Dicyclohexyl-*m*-xylylenediamine (8)

The reaction was undertaken in an identical manner to (7), using cyclohexylamine. (2.67g, 59%)

¹H NMR (300MHz, CDCl₃) δ_{H} : 7.18 (4H, m, ArH), 3.73 (4H, s, ArCH₂), 2.42 - 2.56 (4H, m, NH & CH), 1.65 - 1.88 (8H, m, CH₂), 1.14 (12H, m, CH₂)

¹³C NMR (75.5Hz, CDCl₃) δ_{C} : 140.75, 128.03, 127.44, 126.21 (ArC), 55.96 (ArCH₂), 50.75 (CH), 36.52, 33.23, 25.89, 25.37, 24.68 (CH₂)

ESIMS(*m/z*): 301.3 [M+H]⁺, 219.23 [MH-cyclohexyl]⁺

Elemental Analysis for C₂₀H₃₂N₂:

Expected: C 79.94, H 10.73, N 9.32

Found: C 79.73, H 10.98, N 9.27

1,3-Bis-bromomethyl-5-*tert*-butyl-benzene (9)

1-*tert*-Butyl-3,5-dimethyl-benzene (5.00g, 30.81mmol) was dissolved in of 1,2-dichloroethane (125ml) and a catalytic amount of AIBN was added. NBS (13.25g, 73.94mmol) was added portionwise over 30 minutes and the resulting solution refluxed for 20 hours. The mixture was allowed to cool and filtered to remove excess NBS. The solvent was removed under reduced pressure and the resulting solid dissolved in CH₂Cl₂ (100ml) and washed with water (2x100ml). The organic layer was dried over MgSO₄ and then layered with ethanol. The crystalline product was collected and dried *in vacuo*. (4.54g, 46%)

¹H NMR (300MHz, CDCl₃) δ_H: 7.33 (2H, s, ArH^{4/6}), 7.25 (1H, s, ArH²), 4.49 (4H, s, ArCH₂Br), 1.34 (9H, s, Bu^t)

ESIMS(*m/z*): 319.0 [M]⁺, 305.0 [M-CH₃]⁺, 239.0 [M-Br]⁺

Elemental Analysis for C₁₂H₁₆Br₂.½H₂O:

Expected: C 43.93, H 5.22, Br 48.72

Found: C 43.47, H 5.64, Br 48.74

N,N'-Dibutyl-(5-*tert*-butyl)-*m*-xylylenediamine (10)

Synthesised in an analogous manner to (7), through the addition of 1,3-bis-bromomethyl-5-*tert*-butylbenzene (9) (1.00g, 3.12 mmol) to *n*-butylamine, yielding a yellow oil. (0.77g, 94%)

^1H NMR (300MHz, CDCl_3) δ_{H} : 7.26 (2H, s, $\text{ArH}^{4/6}$), 7.20 (1H, s, ArH^2), 4.62 (4H, s(br), ArCH_2), 3.83 (4H, m, NHCH_2CH_2), 2.70 (4H, t, $J=7.2\text{Hz}$, NHCH_2CH_2), 1.57 (4H, m, CH_2CH_3), 1.16 (9H, s, Bu^t), 0.94 (6H, t, $J=7.2\text{Hz}$, CH_3)

^{13}C NMR (75.43MHz, CDCl_3) δ_{C} : 151.33, 140.13, 125.03, 123.73 (ArC), 54.36, 49.32 (CH_2), 34.60 ($\text{C}(\text{CH}_3)_3$), 32.16 (CH_2), 31.39 ($\text{C}(\text{CH}_3)_3$), 20.48 (CH_2), 14.01 (CH_3)

ESIMS(m/z): 304.49 $[\text{M}]^+$

Elemental Analysis for $\text{C}_{20}\text{H}_{36}\text{N}_2\cdot\text{H}_2\text{O}$:

Expected: C 74.48, H 11.88, N 8.69

Found: C 74.52, H 11.24, N 8.72

***N,N'*-Cyclohexyl-(5-*tert*-butyl)-*m*-xylylenediamine (11)**

Synthesised in an analogous method to (10), using cyclohexylamine. (1.00g, 90%)

^1H NMR (300MHz, CDCl_3) δ_{H} : 7.10 (2H, s, $\text{ArH}^{4/6}$), 7.02 (1H, s, ArH^2), 3.17 (4H, s, ArCH_2), 2.59 - 2.39 (4H, m, NH & CH), 1.24 (9H, s, Bu^t), 1.88 - 0.90 (20H, m, CH_2)

^{13}C NMR (75.43MHz, CDCl_3) δ_{C} : 152.20, 140.54, 124.93, 123.62 (ArC), 56.38 (ArCH_2), 51.37 (CH), 36.83 (CH_2), 34.55 ($\text{C}(\text{CH}_3)_3$), 33.48 (CH_2), 31.35 ($\text{C}(\text{CH}_3)_3$), 26.13, 25.61, 25.61, 25.10, 24.99 (CH_2)

ESIMS(m/z): 356.24 $[\text{M}]^+$

Elemental Analysis for $\text{C}_{24}\text{H}_{40}\text{N}_2\cdot\text{H}_2\text{O}$:

Expected: C 76.95, H 11.30, N 7.48

Found: C 76.64, H 11.13, N 7.87

3,3'-Bis-bromomethyl-biphenyl (12)

3,3'-Dimethylbiphenyl (5.00g, 27.33mmol) was stirred in 1,2-dichloromethane (40ml). AIBN (catalytic amount) and NBS (10.32g, 57.59mmol) were added portionwise to the mixture over

30 minutes. The solution was then heated at 80°C for 18 hours. The solution was allowed to cool to room temperature. A further 0.5g of NBS and a catalytic amount of AIBN were added and the solution heated again for 1 hour. The solvent was evaporated and the orange residue suspended in EtOH (100ml) and stirred for 1 hour. The resulting white precipitate was filtered, washed with cold EtOH and the residue recrystallised from CH₂Cl₂/EtOH to yield a white crystalline solid. (The product was stored in the dark, due to its light sensitive nature.) (8.11g, 87%)

¹H NMR (300MHz, CDCl₃) δ_H: 7.55 (2H, s, ArH^{2/2'}), 7.45 (2H, m, ArH^{5/5'}), 7.35 (4H, m, ArH^{4/4'} & H^{6/6'}), 4.60 (4H, s, CH₂Br)

ESIMS(m/z): 339.95 [M]⁺, 261.11 [M-Br]⁺

***N,N'*-Di-*n*-butyl-(3,3'-biphenylmethyldiamine) (13)**

3,3'-Bis-bromomethyl-biphenyl (**12**) (1.00g, 2.94mmol) was added portionwise over 30 minutes to *n*-butylamine (50ml) and the solution stirred for 2 hours. Excess amine was removed under reduced pressure. The resulting residue was extracted into CH₂Cl₂ (100ml) and washed with H₂O (2x100ml). The organic layer was then dried over anhydrous K₂CO₃ and the solvent removed to yield a yellow oil. (0.89g, 94%)

¹H NMR (300MHz, CDCl₃) δ_H: 7.55 (2H, t, J=1.5Hz, ArH^{2/2'}), 7.46 (2H, dt, J=7.5Hz, J'=1.5Hz, ArH^{6/6'}), 7.37 (2H, t, J=7.5Hz, ArH^{5/5'}), 7.29 (2H, dt, J=7.8Hz, J'=1.5Hz, ArH^{4/4'}), 3.88 (4H, s, ArCH₂), 2.66 (4H, t, J=7.2Hz, NHCH₂CH₂), 1.52 (4H, m, NHCH₂CH₂), 1.36 (4H, m, CH₂CH₃), 0.92 (6H, t, J=7.2 Hz, CH₃)

¹³C NMR (75.47MHz, CDCl₃) δ_c: 141.08, 140.59, 128.63, 126.98, 126.88, 125.66 (ArC), 54.08, 49.02, 32.17, 20.56 (CH₂), 14.11 (CH₃)

ESIMS(m/z): 325.3 [M+H]⁺, 252.2 [M-NHBu]⁺

Elemental Analysis for C₂₂H₃₂N₂·¼H₂O:

Expected: C 80.32, H 9.96, N 8.51

Found: C 80.25, H 10.42, N 8.40

***N,N'*-Di-*n*-cyclohexyl-(3,3'-biphenylmethyldiamine) (14)**

The product was synthesised in an identical method to *N,N'*-Di-*n*-butyl-(3,3'-biphenylmethyldiamine) (13) via the addition of cyclohexylamine, yielding a yellow oil. (1.05g, 95%)

^1H NMR (300MHz, CDCl_3) δ_{H} : 7.53 (2H, s, $\text{ArH}^{2/2'}$), 7.46 (2H, d, $J=7.5\text{Hz}$, $\text{ArH}^{6/6'}$), 7.36 (2H, t, $J=7.5\text{Hz}$, $\text{ArH}^{5/5'}$), 7.28 (2H, d, $J=7.5\text{Hz}$, $\text{ArH}^{4/4'}$), 3.86 (4H, s, ArCH_2), 2.48 - 1.04 (22H, m, CH_2)

ESIMS(m/z): 377.4 $[\text{M}]^+$, 295.3 $[\text{M}-\text{C}_6\text{H}_{11}]^+$

***N,N'*-Di-*n*-butyl-(4,4'-biphenylmethyldiamine) (15)**

NaI (6.00g, 40.0mmol) was dissolved in the minimum volume of water was added to a stirred solution of *n*-butylamine (100ml) at 60°C. 4,4'-Bis(chloromethyl)-1-1'-biphenyl (5.00g, 20.0mmol) was added portionwise over 2 hours. The mixture was stirred for a further 3 hours when the excess *n*-butylamine was removed under reduced pressure. CH_2Cl_2 (125ml) was added to the white solid and the mixture filtered. The filtrate was washed with H_2O (4x100ml) and dried over K_2CO_3 . The solvent was evaporated and the resulting oil dried *in vacuo*. (4.20g, 65%)

^1H NMR (300MHz, CDCl_3) δ_{H} : 7.45 (4H, d, $J=6.9\text{Hz}$, ArH), 7.27 (4H, d, $J=7.2\text{Hz}$, ArH), 3.73 (4H, s, ArCH_2), 2.57 (4H, t, $J=7.2\text{Hz}$, NHCH_2CH_2), 1.43 (4H, m, NHCH_2CH_2), 1.29 (4H, m, CH_2CH_3), 0.89 (6H, t, $J=6.9\text{Hz}$, CH_3)

^{13}C NMR (75.47MHz, CHCl_3) δ_{C} : 139.41, 129.15, 127.69, 125.99 (ArC), 53.80, 49.28, 32.33, 20.59 (CH_2), 14.34 (CH_3)

ESIMS(m/z): 324.5 $[\text{M}]^+$, 253.3 $[\text{M}-\text{NHBu}]^+$

2,7-Dimethyl naphthalene (16)

Magnesium turnings (2.67g) were added to an oven-dried three-necked round-bottomed flask containing THF (55ml, dry) and stirred, under N₂, at 4°C. 3-Methylbenzyl chloride (12.50g, 88.9mmol) was added gradually to the flask. Acetylacetaldehyde dimethyl acetal (11.9ml, 90.4mmol) in THF (33ml, dry) was added dropwise and the reaction colour turned from green to yellow. The mixture was refluxed for 30 minutes at 150°C during which time the mixture turned to a burnt orange colour. The mixture was stirred for 12 hours. H₂O (3ml) was added to the reaction mixture, the THF was removed under reduced pressure and diethyl ether (100ml) added to the remainder. The mixture was poured over ice-cold saturated NH₄Cl (180ml) and left to settle for two hours. The ether layer was collected and washed with H₂O (3x50ml) and dried over MgSO₄. The solvent was removed to give a red oil.

The hydroxy acetal was heated at 100°C in glacial acetic acid (70ml) and 48% hydrobromic acid (50ml) for 1 hour. Initially, a white suspension formed, but on heating the mixture turned dark brown. The solution was placed in an ice bath allowing the solids to separate. The solid was filtered by suction and washed with H₂O. The crude product was purified by vacuum sublimation collecting a white solid. (7.37g, 66%)

¹H NMR (300MHz, CDCl₃) δ_{H} : 7.67 (2H, d, J=8.4Hz, ArH^{4/5}), 7.50 (2H, s, ArH^{1/8}), 7.22 (2H, dd, J=8.4Hz, J'=1.8Hz, ArH^{3/6}), 2.49 (6H, s, ArCH₃)

ESIMS(m/z): 156.20 [M]⁺

Elemental Analysis for C₁₂H₁₂:

Calculated: C 89.67, H 7.84

Found: C 89.52, H 7.85

α - α' -Dibromo-2,7-naphthalene (17)

2,7-Dimethylnaphthalene (**16**) (1.00g, 6.41mmol) was dissolved in CCl₄ (100ml) (Caution-Very Toxic!). A catalytic amount of AIBN was added and NBS (2.51g, 14.10mmol) was added portionwise over 30 minutes and the solution was refluxed for 12 hours. The mixture was allowed to cool and the mixture filtered through Celite®, to remove excess NBS, and washed through with CH₂Cl₂ (20ml). The solvent was removed under reduced pressure and the residue recrystallised from a minimum volume of hot ethanol, yielding a white crystalline solid. (0.66g, 33%)

¹H NMR (300MHz, CDCl₃) δ_{H} : 7.80 (2H, d, J=8.1Hz, ArH^{4/5}), 7.80 (2H, s, ArH^{1/8}), 7.50 (2H, d, J=8.1Hz, ArH^{3/6}), 4.65 (4H, s, CH₂Br)

¹³C NMR (75.43MHz, CDCl₃) δ_{C} : 135.56, 132.68, 132.41, 128.35, 127.64, 127.27 (ArC), 33.91 (CH₂Br)

ESIMS(m/z): 235.2 [M-Br+H]⁺

EIMS(m/z): 312.1 [M]⁺

Elemental Analysis for C₁₂H₁₀Br₂·¹/₄H₂O:

Calculated: C 45.25, H 3.32

Found: C 45.27, H 3.25

***N,N'*-Di-*n*-butyl-(2,7-naphenylmethyldiamine) (18)**

2,7-Dibromonaphthalene (**17**) (0.50g, 1.60mmol) was added portionwise over 15 minutes to a stirred solution of *n*-butylamine. The solution was stirred at room temperature for 4 hours. After this time, the excess amine was removed under reduced pressure and the residue dissolved in CH₂Cl₂ (100ml), washed with H₂O (3x100ml) and the organic layer dried over K₂CO₃. Evaporation of the solvent afforded a brown oil that was dried *in vacuo*. (0.45g, 96%)

^1H NMR (300MHz, CDCl_3) δ_{H} : 7.76 (2H, d, $J=8.4\text{Hz}$, $\text{ArH}^{4/5}$), 7.70 (2H, s, $\text{ArH}^{1/8}$), 7.41 (2H, d, $J=8.7\text{Hz}$, $\text{ArH}^{3/6}$), 3.94 (4H, s, ArCH_2), 2.66 (4H, t, $J=7.2\text{Hz}$, NHCH_2CH_2), 1.53 (4H, m, NHCH_2CH_2), 1.36 (4H, m, CH_2CH_3), 0.91 (6H, t, $J=7.2\text{Hz}$, CH_3)

^{13}C NMR (75.47MHz, CDCl_3) δ_{C} : 137.75, 133.29, 131.68, 128.37, 127.04, 125.61 (ArC), 54.10, 49.11, 32.20, 20.57 (CH_2), 14.11 (CH_3)

ESIMS(m/z): 298.6 $[\text{M}]^+$, 227.2 $[\text{M}-\text{NHBu}]^+$

Naphthyl-Spaced Bis-Potassium Dithiocarbamate Salt ($\text{R} = n\text{-butyl}$) (19)

Bis-amine (18) (0.25g, 0.84mmol) was dissolved in THF/ H_2O (2:1, 100ml) and stirred at room temperature. KOH (0.11g, 2.10mmol) was added and the solution stirred for 10 minutes. Addition of CS_2 (0.16g, 2.10mmol) resulted in a yellow solution which was stirred for a further 18 hours. The solvent was then removed under reduced pressure and the resulting residue dissolved in MeOH (50ml). The suspension was filtered and the solvent reduced in volume to 5ml. Et_2O (200ml) was added and the resulting solution was stored at -18°C for 18 hours. The resulting white solid was filtered off, washed with Et_2O (100ml) and dried *in vacuo*. (0.33g, 75%)

^1H NMR (500MHz, D_2O) δ_{H} : 7.77 (2H, d, $J=8.5\text{Hz}$, $\text{ArH}^{4/5}$), 7.54 (2H, s, $\text{ArH}^{1/8}$), 7.41 (2H, d, $J=8.5\text{Hz}$, $\text{ArH}^{3/6}$), 5.39 (4H, s, ArCH_2), 3.81 (4H, t, $J=8.0\text{Hz}$, NCH_2CH_2), 1.50 (4H, m, NCH_2CH_2), 1.06 (4H, m, CH_2CH_3), 0.66 (6H, t, $J=7.5\text{Hz}$, CH_3)

^{13}C NMR (75.40MHz, D_2O) δ_{C} : 209.89 (CS_2), 135.24, 133.29, 131.70, 128.30, 125.27 (ArC), 57.26, 54.10, 28.46, 19.71 (CH_2), 13.29 (CH_3)

Elemental Analysis for $\text{C}_{22}\text{H}_{28}\text{N}_2\text{S}_4\text{K}_2 \cdot \frac{3}{2}\text{H}_2\text{O}$:

Expected: C 47.70, H 5.64, N 5.06

Found: C 47.89, H 5.60, N 4.96

***m*-Xylyl-Spaced Bis-Potassium Dithiocarbamate Salt (R = cyclohexyl) (24)**

Bis-amine (**8**) (0.50g, 1.66mmol) was dissolved in MeCN (100ml) and stirred at room temperature. KOH (0.22g, 4.20mmol) was dissolved in the minimum amount of H₂O and added to the stirred solution. After 10 minutes, CS₂ (0.32g, 4.20mmol) was added, resulting initially in the formation of a white suspension, which cleared to a yellow solution upon stirring for a further 18 hours. The solvent was then reduced in volume to 10ml and Et₂O (200ml) was added dropwise to the solution. The resulting white solid was filtered off, washed with Et₂O (100ml) and dried *in vacuo*. (0.74g, 84%)

¹H NMR (300MHz, DMSO-d₆) δ_{H} : 7.77 (1H, s, ArH²), 7.29 (3H, m, ArH), 4.51 (4H, s, ArCH₂), 3.59 (2H, m, CH), 1.89 - 1.25 (20H, m, CH₂)

Elemental Analysis for C₂₂H₃₀N₂S₄K₂·2H₂O:

Expected: C 46.77, H 6.07, N 4.96

Found: C 46.51, H 5.78, N 4.92

Macrocyclic Syntheses:

In general, dinuclear dithiocarbamate-based macrocyclic complexes were synthesised via a one-pot reaction. These reactions were undertaken using one of the four methods described below:

Method A: One equivalent of bis-amine was dissolved in a THF/H₂O (2:1, 100ml) solvent system and stirred at room temperature. 2.5 equivalents of KOH were added and the solution stirred for 10 minutes. 2.5 equivalents of CS₂ were then added and the solution stirred for a further 10 minutes, generating a yellow solution. 1.25 equivalents of the appropriate transition metal salt (Cu(OAc)₂·H₂O, Ni(OAc)₂·4H₂O, K₂PdCl₄ or K₂PtCl₄) were then added and the solution stirred at room temperature for 18 hours. The solution was filtered and the residue

dissolved in CH_2Cl_2 (100ml), dried over K_2CO_3 and layered with ethanol (150ml) in order to induce crystallisation. The resulting solid was dried in *vacuo*.

Method B: As Method A. The crude product was further purified by column chromatography on silica gel 60 eluted with CHCl_3 . The forerunning band was isolated, the solvent removed under reduced pressure and recrystallised from $\text{CH}_2\text{Cl}_2/\text{EtOH}$. The resulting solid was dried in *vacuo*.

Method C: As Method A. The crude product was further purified by the dropwise addition of hexane into a rapidly stirred CH_2Cl_2 solution of the macrocycle. The resulting solid was dried in *vacuo*.

Method D: One equivalent of the bis-potassium dithiocarbamate salt was dissolved in $\text{THF}/\text{H}_2\text{O}$ (2:1, 100ml). One equivalent of the appropriate transition metal salt was then added and the solution stirred at room temperature for 18 hours. The solution was filtered and the residue dissolved in CH_2Cl_2 (100ml), dried over K_2CO_3 and layered with ethanol (150ml) in order to induce crystallisation. The resulting solid was dried in *vacuo*.

(7-Cu)

Method A: Bis-amine (7) (1.20g, 4.83mmol) was reacted via Method A yielding a black crystalline solid. (1.14g, 51%)

ESIMS(m/z): 924.05 $[\text{M}]^+$

ESIMS(m/z) with NOBF_4 : 462.04 $[\text{M}]^{2+}$, 1011.02 $[\text{M}+\text{BF}_4]^+$

Elemental Analysis for $\text{C}_{36}\text{H}_{52}\text{N}_4\text{S}_8\text{Cu}_2$:

Expected: C 46.77, H 5.67, N 6.06

Found: C 46.72, H 5.65, N 6.08

(7-Ni)

Bis-amine **(7)** (1.20g, 4.83mmol) was reacted via Method A yielding a green crystalline solid.
(0.68g, 31%)

^1H NMR (300MHz, CDCl_3) δ_{H} : 7.33 (8H, m, ArH), 4.77 (8H, s, ArCH_2), 2.62 (8H, m, NCH_2CH_2), 1.51 (8H, m, NCH_2CH_2), 1.28 (8H, m, CH_2), 0.87 (12H, t, $J=6.6\text{Hz}$, CH_3)

^{13}C NMR (75.43MHz, CDCl_3) δ_{C} : 208.26 (CS_2), 135.10, 129.63, 128.43, 127.83 (ArC), 51.56, 48.54, 28.85, 19.95 (CH_2), 13.72 (CH_3)

ESIMS(m/z): 914.6 $[\text{M}+\text{H}]^+$, 937.5 $[\text{M}+\text{Na}]^+$

Elemental Analysis for $\text{C}_{36}\text{H}_{52}\text{N}_4\text{S}_8\text{Ni}_2 \cdot \frac{1}{2}\text{CH}_2\text{Cl}_2$:

Expected: C 45.80, H 5.58, N 5.85

Found: C 45.76, H 5.62, N 5.89

(8-Cu)

Bis-amine **(8)** (0.55g, 1.83mmol) was reacted via Method A yielding a black crystalline solid.
(0.21g, 28%)

ESIMS(m/z): 1028.3 $[\text{M}]^+$

ESIMS(m/z) with NOBF_4 : 514.3 $[\text{M}]^{2+}$, 1028.3 $[\text{M}]^+$, 1115.7 $[\text{M}+\text{BF}_4]^+$

Elemental Analysis for $\text{C}_{44}\text{H}_{60}\text{N}_4\text{S}_8\text{Cu}_2 \cdot \frac{3}{2}\text{H}_2\text{O}$:

Expected: C 50.09, H 6.02, N 5.35

Found: C 49.71, H 6.07, N 5.98

(8-Ni)

Bis-amine **(8)** (0.55g, 1.83mmol) was reacted via Method A yielding a green crystalline solid.
(0.56g, 60%)

^1H NMR (300MHz, CDCl_3) δ_{H} : 8.00 (2H, s, ArH^2), 7.17 (2H, t, $J=7.5\text{Hz}$, ArH^5), 7.02 (4H, d, $J=7.5\text{Hz}$, $\text{ArH}^{4/6}$), 5.49 ((0.33)8H, d, $J=15.6\text{Hz}$, ArCH_2), 4.79 ((0.33)8H, s(br), ArCH_2), 4.50 (4H, m(br), CH), 3.98 ((0.33)8H, d, $J=15.6\text{Hz}$, ArCH_2), 1.91-0.74 (40H, m, CH_2)

^{13}C NMR (75.43MHz, CDCl_3) δ_{C} : 210.22 (CS_2), 137.25, 128.38, 127.95, 125.99 (ArC), 58.92 (ArCH_2), 48.01 (CH), 31.31, 29.74, 25.51, 25.22 (CH_2)

ESIMS(m/z): 1018.44 $[\text{M}]^+$

Elemental Analysis for $\text{C}_{44}\text{H}_{60}\text{N}_4\text{S}_8\text{Ni}_2\cdot\text{H}_2\text{O}$:

Expected: C 51.00, H 6.03, N 5.41

Found: C 50.98, H 5.79, N 5.21

(8-Pd)

Bis-amine **(8)** (0.55g, 1.83mmol) was reacted via Method A yielding an orange crystalline solid. (0.49g, 45%)

^1H NMR (300MHz, CDCl_3) δ_{H} : 8.13 (2H, s, ArH^2), 7.19-7.04 (6H, m, ArH^{4-6}), 5.56 ((0.15)8H, d, $J=15.6\text{Hz}$, ArCH_2), 4.88 ((0.7)8H, s(br), ArCH_2), 4.62 (4H, m(br), CH), 4.06 ((0.15)8H, d, $J=15.6\text{Hz}$, ArCH_2), 2.03 - 0.82 (40H, m, CH_2)

^{13}C NMR (75.43MHz, CDCl_3) δ_{C} : 212.35 (CS_2), 137.42, 136.55, 128.97, 126.29, 126.00 (ArC), 59.97, 59.20 (ArCH_2), 48.96, 48.50 (CH), 32.12, 31.37, 30.50, 29.72, 25.58, 25.13, 24.44 (CH_2)

ESIMS(m/z): 1115.41 $[\text{M}+\text{H}]^+$, 1153.40 $[\text{M}+\text{K}]^+$

Elemental Analysis for $\text{C}_{44}\text{H}_{68}\text{N}_4\text{S}_8\text{Pd}_2$:

Expected: C 47.45, H 5.43, N 5.03

Found: C 47.19, H 5.41, N 4.96

(8-Pt)

Bis-amine **(8)** (0.55g, 1.83mmol) was reacted via Method A yielding a yellow solid. (0.39g, 33%)

^1H NMR (300MHz, CDCl_3) δ_{H} : 7.21 - 7.04 (8H, m, ArH), 5.34 ((0.05)8H, d, $J=15.6\text{Hz}$, ArCH_2), 4.75 ((0.9)8H, s(br), ArCH_2), 4.36 (4H, m(br), CH), 3.97 ((0.05)8H, d, $J=15.6\text{Hz}$, ArCH_2), 1.77-0.85 (40H, m, CH_2)

^{13}C NMR (75.43MHz, CDCl_3) δ_{C} : 213.71 (CS_2), 136.38, 129.10, 126.51, 125.73 (ArC), 60.21, (ArCH_2), 48.66 (CH), 30.41, 25.56, 25.03, 23.20 (CH_2)

ESIMS(m/z): 1292.84 $[\text{M}+\text{H}]^+$, 1330.83 $[\text{M}+\text{K}]^+$

Elemental Analysis for $\text{C}_{44}\text{H}_{68}\text{N}_4\text{S}_8\text{Pt}_2$:

Expected: C 40.94, H 4.68, N 4.34

Found: C 40.60, H 5.14, N 4.81

(8-Pb)

The potassium bis-dithiocarbamate salt **(24)** (0.50g, 0.95mmol) was combined with lead(II) acetate (0.36g, 0.95mmol) and reacted via Method D. (0.25g, 40%)

^1H NMR (300MHz, CDCl_3 , 293K) δ_{H} : 7.62 (2H, s(br), ArH^2), 7.22 (2H, m, ArH^5), 7.03 (4H, d, $J=7.2\text{Hz}$, $\text{ArH}^{4/6}$), 5.62 ($\sim 4\text{H}$, m(br), ArCH_2), 5.36 (4H, m(br), CH), 4.38 (4H, m(br), ArCH_2), 1.98 - 0.99 (40H, m, CH_2)

^{13}C NMR (75.43MHz, CDCl_3) δ_{C} : 203.65 (CS_2), 136.36, 127.88, 126.15, 124.18 (ArC), 62.73, (ArCH_2), 50.15 (CH), 30.90, 26.02, 25.59 (CH_2)

ESIMS(m/z): 1316.98 $[\text{M}+\text{H}]^+$, 1339.06 $[\text{M}+\text{Na}]^+$, 1356.11 $[\text{M}+\text{K}]^+$

Elemental Analysis for $\text{C}_{44}\text{H}_{60}\text{N}_4\text{S}_8\text{Pb}_2 \cdot \frac{1}{2}\text{CH}_2\text{Cl}_2$:

Expected: C 39.35, H 4.53, N 4.12

Found: C 39.30, H 4.04, N 4.33

(10-Cu)

Bis-amine **(10)** (0.17g, 0.57mmol) was reacted via Method B yielding a black crystalline solid. (0.10g, 17%)

ESIMS(m/z): 1036.78 [M]⁺, 1059.76 [M+Na]⁺

Elemental Analysis for C₄₄H₆₈N₄S₈Cu₂.⁷/₄CH₂Cl₂:

Expected: C 46.36, H 6.08, N 4.73

Found: C 46.01, H 6.08, N 5.04

(10-Ni)

Bis-amine **(10)** (0.17g, 0.57mmol) was reacted via Method A yielding a green crystalline solid. (0.16g, 53%)

¹H NMR (300MHz, CDCl₃) δ_H: 7.23 (2H, s, ArH²), 7.08 (4H, m, ArH^{4/6}), 4.79 (8H, s, ArCH₂), 3.50 (8H, s(br), NCH₂CH₂), 1.57 (8H, s(br), NCH₂CH₂), 1.32 (26H, m(br), CH₂CH₃ & Bu¹), 0.88 (12H, s, CH₃)

¹³C NMR (75.43MHz, CDCl₃) δ_C: 207.58, 206.96 (CS₂), 152.73, 151.49, 135.17, 134.45, 124.90, 123.78 (ArC), 52.00, 48.61 (NCH₂), 34.77 (C(CH₃)₃), 31.46 (C(CH₃)₃), 29.05, 20.19 (CH₂), 13.98 (CH₃)

ESIMS(m/z): 1027.6 [M]⁺, 1049.7 [M+Na]⁺, 1065.6 [M+K]⁺

Elemental Analysis for C₄₄H₆₈N₄S₈Ni₂.CH₂Cl₂:

Expected: C 48.61, H 6.35, N 5.04

Found: C 48.34, H 6.27, N 5.11

(10-Pd)

Bis-amine **(10)** (0.35g, 1.15mmol) was reacted via Method B yielding fine orange crystals. (0.22g, 34%)

^1H NMR (300MHz, CDCl_3) δ_{H} : 7.58 (2H, m, ArH^2), 7.11 - 7.00 (4H, m, $\text{ArH}^{4/6}$), 4.88 (8H, s, ArCH_2), 3.59 (8H, s(br), NCH_2CH_2), 1.59 (8H, m, NCH_2CH_2), 1.31 (26H, m(br), CH_2CH_3 & Bu^t), 0.88 (12H, m(br), CH_3)

^{13}C NMR (75.43MHz, CDCl_3) δ_{C} : 211.19 (CS_2), 152.76, 135.64, 134.55, 124.90 (ArC), 52.35, 48.96 (NCH_2), 34.88 ($\text{C}(\text{CH}_3)_3$), 31.44 ($\text{C}(\text{CH}_3)_3$), 29.07, 20.24 (CH_2), 14.00 (CH_3)

ESIMS(m/z): 1122.51 $[\text{M}+\text{H}]^+$, 1145.58 $[\text{M}+\text{Na}]^+$

Elemental Analysis for $\text{C}_{44}\text{H}_{68}\text{N}_4\text{S}_8\text{Pd}_2 \cdot 2\text{CHCl}_3$:

Expected: C 40.59, H 5.18, N 4.12

Found: C 40.38, H 5.32, N 4.35

(10-Pt)

Bis-amine (**10**) (0.35g, 1.15mmol) was reacted via Method A yielding an orange powder (0.51g, 35%)

^1H NMR (300MHz, CDCl_3) δ_{H} : 7.25 (4H, m, $\text{ArH}^{4/6}$), 7.02 (2H, m, ArH^2), 4.74 (8H, s, ArCH_2), 3.46 (8H, t(br), $J=6.9$ Hz, NCH_2CH_2), 1.65 (8H, m, NCH_2CH_2), 1.36 - 1.25 (26H, m(br), CH_2CH_3 & Bu^t), 0.91 (12H, t, $J=6.9$ Hz, CH_3)

^{13}C NMR (75.43MHz, CDCl_3) δ_{C} : 212.45 (CS_2), 157.02, 134.37, 133.55, 125.97 (ArC), 52.37, 48.90 (NCH_2), 34.91 ($\text{C}(\text{CH}_3)_3$), 31.44 ($\text{C}(\text{CH}_3)_3$), 29.00, 20.21 (CH_2), 13.96 (CH_3)

ESIMS(m/z): 1298.63 $[\text{M}]^+$, 1299.90 $[\text{M}+\text{H}]^+$, 1321.84 $[\text{M}+\text{Na}]^+$

Elemental Analysis for $\text{C}_{44}\text{H}_{68}\text{N}_4\text{S}_8\text{Pt}_2$:

Expected: C 40.66, H 5.27, N 4.33

Found: C 40.45, H 5.21, N 4.33

(11-Cu)

Bis-amine (**11**) (0.50g, 1.41mmol) was reacted via Method A yielding a black powder. (0.37g, 46%)

ESIMS(m/z): 1138.20 [M]⁺, 1177.90 [M+K]⁺

Elemental Analysis for C₅₂H₇₆N₄S₈Cu₂:

Expected: C 54.75, H 6.71, N 4.91

Found: C 54.52, H 6.70, N 4.95

(11-Ni)

Bis-amine (**11**) (0.50g, 1.41mmol) was reacted via Method A yielding a green powder. (0.40g, 51%)

¹H NMR (300MHz, CDCl₃) δ_H: 7.83 (2H, s, ArH²), 7.31-6.98 (4H, m, ArH^{4/6}), 5.56 ((0.25)8H, d, J=14.4Hz, ArCH₂), 4.86 ((0.5)8H, s, ArCH₂), 4.56 (4H, s(br), CH), 4.06 ((0.25)8H, d, J=14.7Hz, ArCH₂), 1.85-0.79 (40H, m, CH₂), 1.38 (18H, s, Bu^t)

¹³C NMR (75.43MHz, CDCl₃) δ_C: 209.40, 208.08 (CS₂), 151.77, 150.80, 136.45, 135.67, 125.23, 122.81 (ArC), 59.81, 58.98, 48.96, 48.47 (NCH₂), 34.77 (C(CH₃)₃), 31.50 (C(CH₃)₃), 31.28, 30.68, 29.95, 25.76, 25.50 (CH₂)

ESIMS(m/z): 1132.17 [M+H]⁺

Elemental Analysis for C₅₂H₇₆N₄S₈Ni₂:

Expected: C 53.51, H 6.91, N 4.80

Found: C 53.42, H 6.88, N 4.80

(11-Pd)

Bis-amine (**11**) (0.43g, 1.19mmol) was reacted via Method B yielding a yellow powder. (0.08g, 11%)

^1H NMR (300MHz, CDCl_3) δ_{H} : 7.89 (2H, s, ArH^2), 7.32 - 7.03 (4H, m, $\text{ArH}^{4/6}$), 5.56 ((0.2)8H, d, $J=15.6\text{Hz}$, ArCH_2), 4.88 ((0.6)8H, s(br), ArCH_2), 4.62 (4H, t(br), $J=11.4\text{Hz}$, CH), 4.06 ((0.2)8H, d, $J=15.3\text{Hz}$, ArCH_2), 1.93-0.76 (40H, m, CH_2), 1.33 (18H, s, Bu^t)

^{13}C NMR (75.43MHz, CDCl_3) δ_{C} : 212.84 (CS_2), 150.87, 136.66, 125.64, 122.85 (ArC), 59.28, 48.98 (NCH_2), 34.85 ($\text{C}(\text{CH}_3)_3$), 31.57 ($\text{C}(\text{CH}_3)_3$), 31.36, 30.66, 29.96, 29.86, 25.94, 25.84, 25.59 (CH_2)

ESIMS(m/z): 1227.38 $[\text{M}]^+$, 1251.44 $[\text{M}+\text{Na}]^+$

Elemental Analysis for $\text{C}_{52}\text{H}_{76}\text{N}_4\text{S}_8\text{Pd}_2\cdot\text{H}_2\text{O}$:

Expected: C 50.18, H 6.32, N 4.50

Found: C 50.30, H 6.37, N 4.22

(11-Pt)

Bis-amine (11) (0.43g, 1.19mmol) was reacted via Method C yielding a yellow powder. (0.33g, 39%)

^1H NMR (300MHz, CDCl_3) δ_{H} : 7.20 (4H, m, $\text{ArH}^{4/6}$), 6.95 (2H, m, ArH^2), 4.74 (8H, s, ArCH_2), 4.36 (4H, s, CH), 1.79-1.03 (58H, m, CH_2 & Bu^t)

^{13}C NMR (75.43MHz, CDCl_3) δ_{C} : 213.09 (CS_2), 152.04, 136.63, 135.61, 123.43, (ArC), 60.33, 49.12 (CH_2N), 34.86 ($\text{C}(\text{CH}_3)_3$), 31.46 ($\text{C}(\text{CH}_3)_3$), 30.52, 30.44, 25.80, 25.25 (CH_2)

ESIMS(m/z): 1403.86 $[\text{M}]^+$, 1404.84 $[\text{M}+\text{H}]^+$

Elemental Analysis for $\text{C}_{52}\text{H}_{76}\text{N}_4\text{S}_8\text{Pd}_2\cdot\frac{1}{2}\text{CH}_2\text{Cl}_2$:

Expected: C 43.60, H 5.37, N 3.87

Found: C 43.22, H 5.35, N 3.92

(13-Cu)

Bis-amine (**13**) (0.25g, 0.77mmol) was reacted via Method B (silica gel 60 column eluted with hexane:CHCl₃ (2:1)). A brown powder was isolated. (0.23g, 55%)

ESIMS(m/z) (with NOBF₄): 537.2 [M]²⁺, 1076.4 [M]⁺

Elemental Analysis for C₄₈H₆₀N₄S₈Cu₂·½H₂O:

Expected: C 52.27, H 5.08, N 5.08

Found: C 52.26, H 5.68, N 5.11

(13-Ni)

Bis-amine (**13**) (0.25g, 0.77mmol) was reacted via Method A yielding a green crystalline solid. (0.32g, 72%)

¹H NMR (300MHz, CDCl₃) δ_H: 7.51-7.44 (12H, m, ArH), 7.30 (4H, s, ArH), 4.88 (8H, s, ArCH₂), 3.53 (8H, s, NCH₂CH₂), 1.63 (8H, m, NCH₂CH₂), 1.31 (8H, m, CH₂CH₃), 0.92 (12H, m, CH₃)

¹³C NMR (75.43MHz, CDCl₃) δ_C: 207.58 (CS₂), 140.93, 134.71, 129.31, 127.02, 126.95, 126.61 (ArC), 51.82, 48.50, 29.02, 20.16, (CH₂) 13.96 (CH₃)

ESIMS(m/z): 1166.4 [M]⁺, 1089.4 [M+Na]⁺, 1105.4 [M+K]⁺, 1129.4 [M+Cu]⁺, 2197.9 [M₂+Cu]⁺

Elemental Analysis for C₄₈H₆₀N₄S₈Ni₂·3CHCl₃:

Expected: C 42.74, H 4.46, N 3.93

Found: C 42.98, H 4.38, N 4.11

(13-Pd)

Bis-amine (**13**) (0.25g, 0.77mmol) was reacted via Method B yielding a yellow solid. (0.013g, 3%)

^1H NMR (300MHz, CDCl_3) δ_{H} : 7.49 - 7.40 (12H, m, ArH), 7.28 (4H, s, ArH), 4.91 (8H, s, ArCH₂), 3.53 (8H, s, NCH₂CH₂), 1.65 (8H, m, NCH₂CH₂), 1.29 (8H, m, CH₂CH₃), 0.90 (12H, m, CH₃)

ESIMS(m/z): 1163.8 $[\text{M}]^+$, 1186.0 $[\text{M}+\text{Na}]^+$, 1201.6 $[\text{M}+\text{K}]^+$, 2347.2 $[2\text{M}+\text{K}]^+$

(13-Pt)

Bis-amine (**13**) (0.25g, 0.77mmol) was reacted via Method C yielding an orange powder. (0.17g, 33%)

^1H NMR (300MHz, CDCl_3) δ_{H} : 7.51 - 7.40 (12H, m, ArH), 7.30 (4H, d, $J=6.9\text{Hz}$, ArH⁴), 4.84 (8H, s, ArCH₂), 3.51 (8H, t(br), $J=6.9\text{Hz}$, NCH₂CH₂), 1.68 (8H, m, NCH₂CH₂), 1.35 (8H, m, CH₂CH₃), 0.90 (12H, t, $J=7.2\text{Hz}$, CH₃)

^{13}C NMR (75.43MHz, CDCl_3) δ_{C} : 212.42 (CS_2), 140.99, 134.54, 129.37, 127.08, 126.61 (ArC), 52.15, 48.81, 29.00, 20.21 (CH₂), 13.99 (CH₃)

ESIMS(m/z): 1338.1 $[\text{M}]^+$, 1351.1 $[\text{M}+\text{Na}]^+$

Elemental Analysis for $\text{C}_{48}\text{H}_{60}\text{N}_4\text{S}_8\text{Pt}_2 \cdot 2\text{CH}_2\text{Cl}_2$:

Expected: C 41.31, H 4.39, N 3.93

Found: C 41.55, H 4.36, N 3.76

(14-Cu)

Bis-amine (**14**) (0.25g, 0.66mmol) was reacted via Method A yielding a brown solid. (0.30g, 78%)

ESIMS(m/z) with NOBF_4 : 590.5 $[\text{M}]^{2+}$, 1178.9 $[\text{M}]^+$, 1199.9 $[\text{M}+\text{F}]^+$, 1268.0 $[\text{M}+\text{BF}_4]^+$

Elemental Analysis for $\text{C}_{56}\text{H}_{68}\text{N}_4\text{S}_8\text{Cu}_2 \cdot 2\text{CH}_2\text{Cl}_2$:

Expected: C 51.58, H 5.37, N 4.48

Found: C 50.68, H 5.76, N 4.44

(14-Ni)

Bis-amine (**14**) (0.25g, 0.66mmol) was reacted via Method A yielding a green solid. (0.36g, 94%)

^1H NMR (300MHz, CDCl_3) δ_{H} : 7.47 - 7.26 (16H, m, ArH), 4.92 (8H, s, ArCH_2), 4.53 (4H, s(br), CH), 1.97 - 1.07 (40H, m, CH_2)

^{13}C NMR (75.43MHz, CDCl_3) δ_{C} : 208.31 (CS_2), 140.69, 136.39, 128.93, 126.23, 125.86, 125.40 (ArC), 59.79 (ArCH_2), 48.86 (CH), 30.69, 25.72, 25.26, 24.98 (CH_2)

ESIMS(m/z): 1172.9 $[\text{M}]^+$, 1193.7 $[\text{M}+\text{Na}]^+$, 1208.9 $[\text{M}+\text{K}]^+$

Elemental Analysis for $\text{C}_{56}\text{H}_{68}\text{N}_4\text{S}_8\text{Ni}_2 \cdot \frac{1}{2}\text{H}_2\text{O}$:

Expected: C 57.00, H 5.89, N 4.75

Found: C 59.96, H 5.64, N 5.69

(14-Pd)

Bis-amine (**14**) (0.25g, 0.66mmol) was reacted via Method A yielding an orange powder. (0.18g, 43%)

^1H NMR (300MHz, CDCl_3) δ_{H} : 7.44 - 7.36 (12H, m, ArH), 7.21 (4H, s, ArH), 4.99 (8H, s, ArCH_2), 4.66 (4H, s(br), CH), 1.79 - 1.05 (40H, m, CH_2)

^{13}C NMR (75.43MHz, CDCl_3) δ_{C} : 211.90 (CS_2), 140.70, 136.45, 128.92, 126.18, 125.81, 125.37 (ArC), 59.99 (ArCH_2), 49.29 (CH), 30.67, 25.79, 25.33 (CH_2)

ESIMS(m/z): 1289.5 $[\text{M}+\text{Na}]^+$, 1306.5 $[\text{M}+\text{K}]^+$

Elemental Analysis for $\text{C}_{56}\text{H}_{68}\text{N}_4\text{S}_8\text{Pd}_2$:

Expected: C 57.43, H 5.41, N 4.78

Found: C 57.29, H 5.71, N 4.64

(14-Pt)

Bis-amine **(14)** (0.25g, 0.66mmol) was reacted via Method A giving yellow needle-like crystals. (0.08g, 16%)

^1H NMR (300MHz, CDCl_3) δ_{H} : 8.09 (2H, s, $\text{ArH}^{2/2'}$), 7.45 (2H, d, $J=7.5\text{Hz}$, $\text{ArH}^{6/6'}$), 7.34 (2H, t, $J=7.5\text{Hz}$, $\text{ArH}^{5/5'}$), 7.16 (2H, d, $J=7.5\text{Hz}$, $\text{ArH}^{4/4'}$), 4.83 (4H, s, ArCH_2), 4.30 (2H, t, $J=11.2\text{Hz}$, CH), 1.74-1.71 (8H, m, CH_2), 1.57 (8H, m, CH_2), 1.25 (4H, m, CH_2)

^{13}C NMR (75.45MHz CDCl_3) δ_{H} : 213.47 (CS_2), 141.59, 137.75, 128.85, 128.32, 126.87, 126.10 (ArC), 60.06 (ArCH_2), 48.98 (CH), 30.69, 29.78, 25.74, 25.30 (CH_2)

ESIMS(m/z): 1443.5 $[\text{M}]^+$, 1466.6 $[\text{M}+\text{Na}]^+$, 1482.2 $[\text{M}+\text{K}]^+$

Elemental Analysis for $\text{C}_{56}\text{H}_{68}\text{N}_4\text{S}_8\text{Pt}_2$:

Expected: C 46.58, H 4.75, N 3.88

Found: C 46.57, H 4.88, N 3.97

(15-Cu)

Bis-amine **(15)** (0.25g, 0.77mmol) was reacted via Method B to generate a brown solid. (0.27g, 64%)

ESIMS(m/z): 1075.0 $[\text{M}]^+$, 1114.3 $[\text{M}+\text{K}]^+$

Elemental Analysis for $\text{C}_{48}\text{H}_{60}\text{N}_4\text{S}_8\text{Cu}_2$:

Expected: C 53.55, H 5.63, N 5.20

Found: C 55.64, H 5.63, N 5.31

(15-Ni)

Bis-amine **(15)** (0.25g, 0.77mmol) was reacted via Method B to generate a green solid. (0.09g, 23%)

^1H NMR (300MHz, CDCl_3) δ_{H} : 7.51 (8H, d, $J=7.2\text{Hz}$, $\text{ArH}^{2/6}$), 7.36 (8H, d, $J=6.9\text{Hz}$, $\text{ArH}^{3/5}$), 4.91 (8H, s, ArCH_2), 3.62 (8H, s(br), NCH_2CH_2), 1.60 (8H, m, NCH_2CH_2), 1.36 (8H, m, CH_2CH_3), 0.89 (12H, t, $J=6.9\text{Hz}$, CH_3)

^{13}C NMR (75.43MHz, CDCl_3) δ_{C} : 208.53 (CS_2), 140.84, 134.31, 128.76, 127.73 (ArC), 52.22, 48.94, 29.13, 20.21 (CH_2), 14.01 (CH_3)

ESIMS(m/z): 1066.3 $[\text{M}+\text{H}]^+$

Elemental Analysis for $\text{C}_{48}\text{H}_{60}\text{N}_4\text{S}_8\text{Ni}_2 \cdot \frac{1}{2}\text{CH}_2\text{Cl}_2$:

Expected: C 52.51, H 5.54, N 5.05

Found: C 52.37, H 5.73, N 5.20

(15-Pd)

Bis-amine (**15**) (0.25g, 0.77mmol) was reacted via Method B to generate an orange solid. (0.09g, 20%)

^1H NMR (300MHz, CDCl_3) δ_{H} : 7.53 (8H, d, $J=6.9\text{Hz}$, $\text{ArH}^{2/6}$), 7.38 (8H, d, $J=6.9\text{Hz}$, $\text{ArH}^{3/5}$), 4.95 (8H, s, ArCH_2), 3.63 (8H, t(br), $J=7.5\text{Hz}$, NCH_2CH_2), 1.66 (8H, m, NCH_2CH_2), 1.35 (8H, s, CH_2CH_3), 0.92 (12H, t, $J=6.9\text{Hz}$, CH_3)

^{13}C NMR (75.43MHz, CDCl_3) δ_{C} : 211.17 (CS_2), 140.16, 133.36, 128.41, 127.36 (ArC), 51.87, 48.81, 29.06, 20.23 (CH_2), 13.97 (CH_3)

ESIMS(m/z): 1163.1 $[\text{M}]^+$

Elemental Analysis for $\text{C}_{48}\text{H}_{60}\text{N}_4\text{S}_8\text{Pd}_2 \cdot 2\frac{1}{2}\text{H}_2\text{O}$:

Expected: C 47.75, H 5.43, N 4.64

Found: C 47.64, H 5.72, N 4.64

(18-Cu)

Bis-amine **(18)** (0.10g, 0.33mmol) was reacted both via Method B yielding a brown powder. (0.06g, 35%)

The reaction was also undertaken by Method D, using the potassium bis-dithiocarbamate salt **(19)** (0.25g, 0.47mmol) affording a black crystalline solid. (0.19g, 78%)

ESIMS(m/z): 1025.5 [M+H]⁺, 1063.4 [M+K]⁺

ESIMS(m/z) with NOBF₄: 512.1 [M]²⁺

Elemental Analysis for C₄₄H₅₆N₄S₈Cu₂·½CH₂Cl₂:

Expected: C 50.09, H 5.38, N 5.25

Found: C 49.84, H 5.31, N 5.54

Bis-amide (26)

1,5-Diaminonaphthalene (2.00g, 12.64mmol) and NEt₃ (2.68g, 26.54mmol) were dissolved in CH₂Cl₂ (50ml, dry) and stirred at room temperature under N₂. Propionyl chloride (2.44g, 26.54mmol) was added dropwise to the solution and the resulting mixture stirred for a further 18 hours. The resulting white solid was filtered off, washed with water (250ml), precipitated from DMSO(hot)/H₂O and dried *in vacuo*. The product had very poor solubility and only dissolved in hot DMSO (1.61g, 94%)

¹H NMR (300MHz, DMSO-d₆(hot)) δ_H: 9.87 (2H, s, NH), 7.88 (2H, d, J=8.4Hz, ArH^{2/6}), 7.64 (2H, d, J=7.5Hz, ArH^{4/8}), 7.48 (2H, t, J=8.1Hz, ArH^{3/7}), 2.48 (4H, m, CH₂), 1.17 (6H, t, J=6.9Hz, CH₃)

ESIMS(m/z): 271.3 [M+H]⁺, 293.4 [M+Na]⁺, 541.6 [2M+H]⁺, 563.6 [2M+Na]⁺

Bis-amide (27)

1,5-Diaminonaphthalene (2.50g, 15.81mmol) and NEt₃ (3.36g, 33.19mmol) were dissolved in CH₂Cl₂ (50ml, dry) and stirred at room temperature under N₂. Octanoyl chloride (10.28g, 31.61mmol) was added dropwise to the solution and the resulting mixture stirred for a further 18 hours. The residue was filtered off, washed with water (250ml), recrystallised from DMSO and the resulting white crystalline solid was dried *in vacuo*. (5.89g, 91%)

¹H NMR (500MHz, DMSO-d₆) δ_H: 10.09 (2H, s(br), NH), 8.07-7.57 (6H, m, ArH), 1.61 (4H, m, COCH₂), 1.25 (20H, m(br), CH₂) 1.17 (6H, m, CH₃)

ESIMS(m/z): 411.6 [M+H]⁺, 433.6 [M+Na]⁺, 449.6 [M+K]⁺

Elemental Analysis for C₂₆H₃₈N₂O₂.H₂O:

Expected: C 72.86, H 9.41, N 6.53

Found: C 72.65, H 9.53, N 7.63

Bis-amide (28)

1,8-Diaminonaphthalene (1.00g, 6.32mmol) and NEt₃ (1.34g, 13.27mmol) were dissolved in CH₂Cl₂ (50ml, dry) and stirred at room temperature under N₂. Propionyl chloride (1.22g, 13.27mmol) was added dropwise to the solution and the resulting mixture stirred for a further 18 hours. The solvent was reduced in volume and the resulting white solid was filtered off and washed with water. The solid was redissolved in CH₂Cl₂ (100ml) and washed with H₂O (3x50ml) and 1M KOH (3x50ml). The organic layer was then dried over K₂CO₃, filtered and the solvent removed under reduced pressure yielding a white solid. (1.61g, 94%)

¹H NMR (500MHz, DMSO-d₆) δ_H: 9.88 (2H, s, NH), 7.82 (2H, d, J=8.0 Hz, ArH^{2/7}), 7.54 (2H, d, J=7.5 Hz, ArH^{4/5}), 7.49 (2H, t, J=8.0 Hz, ArH^{3/6}), 2.39 (4H, q, J=7.5Hz, CH₂), 1.09 (6H, t, J=7.5Hz, CH₃)

^{13}C NMR (125.7MHz, DMSO- d_6) δ_{C} : 172.03 (CO), 135.52, 132.83, 126.83, 125.30, 124.92, 124.05 (ArC), 29.07 (CH_2), 9.49 (CH_3)

ESIMS(m/z): 271.3 $[\text{M}+\text{H}]^+$, 541.6 $[2\text{M}+\text{H}]^+$

Bis-amide (29)

4,4'-Methylenedianiline (1.00g, 5.04mmol) was dissolved in CH_2Cl_2 (50ml). *tert*-Butylacetylchloride (1.36g, 10.08mmol) and NEt_3 (1.12g, 11.09mmol) were added. The mixture was stirred overnight under N_2 . The white precipitate was filtered off and recrystallised from MeOH generating a white crystalline solid. (1.35g, 68%)

^1H NMR (300MHz, CDCl_3) δ_{H} : 9.64 (2H, m(br), NH), 7.42 (4H, d, $J=8.1\text{Hz}$, ArH), 7.12 (4H, d, $J=8.1\text{Hz}$, ArH), 3.91 (2H, s, CH_2Ar_2), 2.23 (4H, s, COCH_2), 1.12 (18H, s, Bu^t)

^{13}C NMR (75.47MHz, CDCl_3) δ_{C} : 170.38 (CO), 137.88, 136.75, 129.40, 119.40 (ArC), 50.39, 31.70 (CH_2), 31.57 ($\text{C}(\text{CH}_3)_3$), 30.48 ($\text{C}(\text{CH}_3)_3$)

ESIMS(m/z): 395.4 $[\text{M}+\text{H}]^+$, 412.6 $[\text{M}+\text{NH}_4]^+$, 417.4 $[\text{M}+\text{Na}]^+$, 433.4 $[\text{M}+\text{K}]^+$

Elemental Analysis for $\text{C}_{25}\text{H}_{34}\text{N}_2\text{O}_2$:

Expected: C 76.10, H 8.69, N 7.10

Found: C 76.03, H 8.56, N 6.90

Bis-amide (30)

2,7-Diaminoflourene (1.00g, 5.10 mmol) was dissolved in CH_2Cl_2 (50ml). *tert*-Butylacetylchloride (1.37g, 10.20mmol) and NEt_3 (1.14g, 11.22mol) were then added and the mixture was stirred under N_2 for 18 hours. The white precipitate was filtered off and recrystallised from MeOH to yield a white crystalline solid. (1.32g, 63%)

^1H NMR (300MHz, CDCl_3) δ_{H} : 9.82 (2H, s, NH), 7.88 (2H, s, ArH^2), 7.64 (2H, d, $J=8.1\text{Hz}$, ArH), 7.40 (2H, d, $J=7.8\text{Hz}$, ArH), 3.86 (2H, s, CH_2Ar_2), 2.21 (4H, s, COCH_2), 1.04 (18H, s, Bu^t)

ESIMS(m/z): 392.27 $[\text{M}+\text{H}]^+$, 415.38 $[\text{M}+\text{Na}]^+$

Bis-amine (31)

LiAlH_4 (0.31g, 8.12mmol) and THF (200ml, dry) were placed in a three-necked round bottomed flask and stirred under N_2 . AlCl_3 (2.70g, 20.3mmol) was dissolved in THF (300ml, dry) at 4°C and added dropwise to the stirred LiAlH_4 suspension over 30 minutes.

Bis-amide (**29**) (0.80g, 2.03mmol) was then added to the flask and the mixture stirred for 15 minutes. The mixture was refluxed at 150°C for 72 hours under N_2 . The reaction mixture was left to cool. 0.5M H_2SO_4 solution was added until the reaction mixture reached pH 0 (to deactivate excess LiAlH_4). NaOH solution was then added until the mixture was of approximately pH 9. The solvent was removed under reduced pressure and the aqueous layer extracted with CHCl_3 (2x50ml). The combined organic extracts were dried over MgSO_4 and the solvent removed under reduced pressure to leave a white solid which was then recrystallised from hot methanol. (0.72g, 85%)

^1H NMR (300MHz, CDCl_3) δ_{H} : 6.97 (4H, d, $J=8.4\text{Hz}$, ArH), 6.52 (4H, d, $J=8.1\text{Hz}$, ArH), 3.77 (2H, s, ArCH_2N), 3.09 (4H, t, $J=8.1\text{Hz}$, NHCH_2), 1.51 (4H, t, $J=8.1\text{Hz}$, NHCH_2CH_2), 0.97 (18H, s, Bu^t)

ESIMS(m/z) 367.43 $[\text{M}+\text{H}]^+$

Bis-amine (32)

Bis-amide (**30**) (0.80g, 2.04mmol) was reacted in an analogous method to (**31**), yielding a white solid. (0.64g, 85%)

^1H NMR (300MHz, CDCl_3) δ_{H} : 7.42 (2H, d, $J=8.4\text{Hz}$, ArH^5), 6.71 (2H, s, ArH^2), 6.54 (2H, d, $J=8.4\text{Hz}$, ArH^6), 3.72 (2H, s, ArCH_2), 3.10 (4H, t, $J=8.1\text{Hz}$, NHCH_2), 1.49 (4H, m, NHCH_2CH_2), 0.91 (18H, s, Bu^1)

ESIMS(m/z) 365.27 $[\text{M}+\text{H}]^+$, 386.25 $[\text{M}]^+$

***N,N'*-di-*n*-butyl-*p*-xylenediamine (33)**

α - α' -Dibromo-*p*-xylene (2.00g, 7.58mmol) was added portionwise to *n*-butylamine (40ml) and the solution stirred at room temperature for 1 hour. The excess amine was then removed under reduced pressure. The resulting yellow oil was dissolved in CH_2Cl_2 (100ml) and washed with water (2x100ml). The organic layer was dried over K_2CO_3 (anhydrous) and the solvent removed yielding a yellow oil. (1.65g, 88%)

^1H NMR (300MHz, CDCl_3) δ_{H} : 7.25 (4H, s, ArH), 3.71 (4H, s, ArCH_2), 2.58 (4H, m, NCH_2), 1.48 (4H, m, CH_2), 1.34 (4H, m, CH_2), 1.22 (2H, s(br), NH), 0.92 (6H, t, $J=6.9\text{Hz}$, CH_3)

^{13}C NMR (75.48MHz, CDCl_3) δ_{C} : 138.93, 127.95 (ArC), 53.64, 48.98, 32.04, 20.30 (CH_2), 13.85 (CH_3)

ESIMS(m/z): 249.25 $[\text{M}+\text{H}]^+$, 176.18 $[\text{M}-\text{NHBu}]^+$

Elemental Analysis for $\text{C}_{16}\text{H}_{28}\text{N}_2 \cdot \frac{1}{4}\text{H}_2\text{O}$:

Expected: C 75.98, H 11.36, N 11.08

Found: C 75.72, H 10.94, N 11.10

Tris-amine (35)

2,4,6-Tris(bromomethyl)mesitylene (1.00g, 2.50mmol) was added portionwise to *n*-butylamine (50ml) and the mixture was stirred at room temperature for 2 hours. The solvent was then removed under reduced pressure, the resulting residue dissolved in CH_2Cl_2 (100ml)

and washed with H₂O (3x100ml). The organic layer was collected, dried over K₂CO₃, the solvent removed under reduced pressure and the resulting oil dried *in vacuo*. (0.92g, 98%)

¹H NMR (300MHz, CDCl₃) δ_H: 3.72 (6H, s, ArCH₂), 2.69 (6H, t, J=6.9Hz, NHCH₂CH₂), 2.39 (9H, s, ArCH₃), 1.49 (6H, quintet, J=6.6Hz, NHCH₂CH₂), 1.38 (6H, m, CH₂CH₃), 0.90 (9H, t, J=7.2Hz, CH₃)

¹³C NMR (75.43MHz, CDCl₃) δ_C: 135.13, 134.81 (ArC), 50.11, 48.69, 32.12, 20.46, 15.39 (CH₂), 13.92 (CH₃)

ESIMS(m/z): 376.4 [M+H]⁺, 303.8 [M-NHBu]⁺, 230.2 [M-2NHBu]⁺, 157.1 [M-3NHBu]⁺

Elemental Analysis for C₂₄H₄₅N₃·¹/₁₀H₂O:

Expected: C 76.37, H 12.07, N 11.13

Found: C 76.19, H 11.60, N 10.97

Tris-amine (36)

Prepared in an analogous method to (35) via the addition of 2,4,6-tris(bromomethyl) mesitylene (1.00g, 2.50mmol) to *n*-hexylamine (50ml). (1.10g, 96%)

¹H NMR (300MHz, CDCl₃) δ_H: 3.72 (6H, s, ArCH₂), 2.70 (6H, t, J=6.9Hz, NHCH₂CH₂), 2.50 (9H, s, ArCH₃), 1.55 (6H, m, NHCH₂CH₂), 1.40 (18H, m, CH₂CH₃), 0.89 (9H, t, J=6.9Hz, CH₃)

ESIMS(m/z): 460.61 [M+H]⁺, 359.38 [M-NHhex]⁺

Elemental Analysis for C₃₀H₅₇N₃·¹/₄H₂O:

Expected: C 77.61, H 12.48, N 9.05

Found: C 77.30, H 12.88, N 9.51

Tris-amine (37)

Prepared in an analogous method to **(35)** by the addition of 1,3,5-tris(bromomethyl)benzene (1.00g, 2.80mmol) to *n*-hexylamine (50ml). (1.12g, 96%)

^1H NMR (300MHz, CDCl_3) δ_{H} : 7.11 (3H, s, ArH), 3.73 (6H, s, ArCH_2), 2.59 (6H, t, $J=6.9\text{Hz}$, NHCH_2CH_2), 1.48 (6H, m, NHCH_2CH_2), 1.27 (18H, m, CH_2), 0.87 (9H, t, $J=6.6\text{Hz}$, CH_3)

^{13}C NMR (75.43MHz, CDCl_3) δ_{C} : 140.53, 126.30 (ArC), 54.01, 49.65, 31.78, 30.06, 27.07, 22.64 (CH_2), 14.10 (CH_3)

ESIMS(m/z): 418.6 $[\text{M}+\text{H}]^+$, 332.9 $[\text{M}-\text{NHhex}]^+$

Elemental Analysis for $\text{C}_{27}\text{H}_{51}\text{N}_3$:

Expected: C 77.64, H 12.31, N 10.06

Found: C 77.29, H 11.81, N 9.63

Trinuclear Cu(II) Dithiocarbamate-based Cage Complex (38)

The tris-amine **(37)** (0.45, 1.08mmol) was dissolved in THF:H₂O (2:1, 50ml) and KOH (0.18g, 3.23mmol) was added and the solution stirred at room temperature. CS₂ (0.24g, 3.23mmol) was then added and the solution stirred for a further 30 minutes. Cu(CH₃CO₂)₂·H₂O (0.32g, 1.62mmol) was added to the yellow solution and the mixture stirred for 18 hours. The resulting brown solid was filtered off, extracted into CH₂Cl₂ (200ml) and recrystallised from CH₂Cl₂/EtOH yielding a black solid, which was dried in *vacuo* (0.34g, 43%).

ESIMS(m/z) with NOBF₄: 1475.3 $[\text{M}]^+$, 737.7 $[\text{M}]^{2+}$, 491.8 $[\text{M}]^{3+}$ (very weak)

Elemental Analysis for $\text{C}_{60}\text{H}_{96}\text{N}_6\text{S}_{12}\text{Cu}_3\cdot\text{THF}$:

Expected: C 49.63, H 6.77, N 5.43

Found: C 49.59, H 6.81, N 6.30

Syntheses from Chapter Three:

Tetramethylresorcinarene (40)

2-Methylresorcinol (124.2g, 1.00mol) was dissolved in EtOH (500ml) and water (500ml) and conc. HCl (250ml) were added to a solution. Hexanal (100g, 120ml, 1.00mol) was then added dropwise over a period of thirty minutes. The resulting mixture was stirred overnight leading to the formation of a sticky brown solid. The solvent was decanted off and 500ml of EtOH was added. The mixture was heated under N₂ to 65°C with stirring, in order to aid rearrangement. Water (~250ml) was added dropwise to the hot solution with stirring, until precipitation was observed. The solution was allowed to cool overnight, without stirring. The resulting cream precipitate was filtered off under suction and oven dried. (174.6g, 52%)

¹H NMR (300MHz, (CD₃)₂CO) δ_{H} : 7.93 (8H, s(br), OH), 7.42 (4H, s, ArH), 4.37 (4H, t, J=7.8Hz, ArCH), 2.28 (8H, m, CHCH₂), 1.98 (12H, m, ArCH₃), 1.37 (24H, m, CH₂), 0.89 (12H, t, J=7.2Hz, CH₃)

Elemental analysis for C₅₂H₇₂O₈:

Expected: C 75.69, H 8.80

Found: C 75.72, H 8.76

Tetramethyl-resorcinarene cavitand (41)

Tetramethylresorcinarene (40) (10.0g, 12.2mmol), BrCH₂Cl (14ml, 215mmol) and K₂CO₃ (40g, 670mmol) were stirred in DMF (400ml) at 80°C under N₂ for 18 hours, yielding a brown suspension. The solvent was removed under reduced pressure, CH₂Cl₂ (400ml) was added, followed by careful addition of water:HCl (conc) (4:1, 250ml) to the solution, which was stirred for a further 30 minutes. The phases were separated and the dark organic layer washed with brine (2x400ml) before being dried over MgSO₄. Removal of the solvent under reduced pressure yields a red-brown solid. The solid was redissolved in CH₂Cl₂ and purified

by column chromatography on silica gel 60 eluted with CH_2Cl_2 . Removal of the solvent of the fractions of the forerunning band afforded a cream-coloured solid which was dried *in vacuo*. (8.05g, 76%)

^1H NMR (300MHz, CDCl_3) δ_{H} : 6.95 (4H, s, ArH), 5.86 (4H, d, $J=6.9\text{Hz}$, $\text{OCH}_2[\text{H}_{\text{outer}}]$), 4.73 (4H, t, $J=8.1\text{Hz}$, ArCH), 4.25 (4H, d, $J=6.9\text{Hz}$, $\text{OCH}_2[\text{H}_{\text{inner}}]$), 2.21-2.16 (8H, m, CH_2), 1.95 (12H, s, ArCH_3), 1.37 - 1.28 (24H, m, CH_2), 0.89 (12H, t, $J=6.9\text{Hz}$, CH_3)

Elemental analysis for $\text{C}_{56}\text{H}_{72}\text{O}_8$:

Expected: C 77.03, H 8.31

Found: C 77.20, H 8.36

Tetra(bromomethyl)-resorcinarene cavitand (42)

Tetramethyl-resorcinarene cavitand (**41**) (7.00g, 8.02mmol) and a catalytic amount of AIBN were dissolved in 1,2-dichloroethane (150ml). NBS (7.00g, 38.99mmol) was added portionwise to the solution which was stirred at 80°C under N_2 for 3 hours. Additional NBS (1.00g) and AIBN (catalytic amount) were added at this stage, as this was found to increase the yield. The orange solution was stirred for a further 18 hours, after which the solvent was removed under reduced pressure. The resulting solid was stirred in EtOH (150ml) for 2 hours and the resulting precipitate filtered off. The solid was dissolved in CH_2Cl_2 and layered with EtOH in order to induce crystallisation. The resulting cream crystals were collected and dried *in vacuo*. (8.05g, 84%)

^1H NMR (300MHz, CDCl_3) δ_{H} : 7.11 (4H, s, ArH), 6.01 (4H, d, $J=6.6\text{Hz}$, $\text{OCH}_2[\text{H}_{\text{outer}}]$), 4.75 (4H, t, $J=7.8\text{Hz}$, ArCH), 4.53 (4H, d, $J=6.9\text{Hz}$, $\text{OCH}_2[\text{H}_{\text{inner}}]$), 4.40 (8H, s, CH_2Br), 2.17 (8H, m, ArCHCH_2), 1.33 (24H, m, CH_2), 0.89 (12H, t, $J=6.9\text{Hz}$, CH_3)

Elemental analysis for $C_{56}H_{68}Br_4O_8 \cdot \frac{1}{2}H_2O$:

Expected: C 56.16, H 5.81

Found: C 56.06, H 5.68

{Tetrakis[(butylamino)methyl]resorcinarene}cavitand (43)

{Tetra(bromomethyl)resorcinarene}cavitand (**42**) (1.00g, 0.84mmol) was added over 15 minutes to a stirred solution of *n*-butylamine (30ml). The solution was stirred for 30 minutes, after which excess *n*-butylamine was removed under reduced pressure. The resulting residue was dissolved in CH_2Cl_2 (100ml), washed with water (2x100ml) and the organic layer dried over K_2CO_3 . The CH_2Cl_2 was removed under reduced pressure affording a cream powder. (0.64g, 66%)

1H NMR (300MHz, $CDCl_3$) δ_H : 7.02 (4H, s, ArH), 5.84 (4H, d, $J=6.9Hz$, $OCH_2[H_{outer}]$), 4.72 (4H, t, $J=7.8Hz$, $ArCHCH_2$), 4.29 (4H, d, $J=6.6Hz$, $OCH_2[H_{inner}]$), 3.51 (8H, s, CH_2), 2.54 (8H, t, $J=6.9Hz$, CH_2), 2.17 (8H, m, CH_2), 1.50 - 1.26 (32H, m, CH_2), 0.87 (24H, m, CH_3)

ESIMS(m/z): 1158.4 $[M+H]^+$, 1100.3 $[M-Bu]^+$, 1085.3 $[M-NHBu]^+$, 1071.3 $[M-CH_2NHBu]^+$

Elemental Analysis for $C_{72}H_{108}N_4O_8$:

Expected: C 74.74, H 9.34, N 4.84

Found: C 74.27, H 9.24, N 4.45

{Tetrakis[(hexylamino)methyl]resorcinarene}cavitand (44)

Prepared using an analogous method as for {tetrakis[(butylamino)methyl]resorcinarene}cavitand using *n*-hexylamine. (0.98g, 92%)

1H NMR (300MHz, $CDCl_3$) δ_H : 7.02 (4H, s, ArH), 5.83 (4H, d, $J=6.9Hz$, $OCH_2[H_{outer}]$), 4.70 (4H, t, $J=7.8Hz$, $ArCH$), 4.29 (4H, d, $J=6.9Hz$, $OCH_2[H_{inner}]$), 3.49 (8H, s, CH_2), 2.50 (8H, t, $J=6.9Hz$, NCH_2), 2.12 (8H, m, CH_2), 1.47 - 1.06 (56H, m, CH_2), 0.86 (24H, m, CH_3)

^{13}C NMR (75.48MHz, CDCl_3) δ_{C} : 153.47, 138.00, 126.42, 119.13 (ArC), 99.36 (OCH_2), 56.86, 43.14, 36.90, 32.00, 31.67, 30.08, 29.81, 27.58, 26.91, 22.67, 22.58 (CH_2 & CH), 14.09, 14.04 (CH_3)

ESIMS(m/z): 1270.6 $[\text{M}+\text{H}]^+$, 1170.3 $[\text{M}-\text{NHhex}]^+$, 1156.4 $[\text{M}-\text{CH}_2\text{NHhex}]^+$

Elemental Analysis for $\text{C}_{80}\text{H}_{124}\text{N}_4\text{O}_8 \cdot \frac{1}{3}\text{CH}_2\text{Cl}_2$:

Expected: C 74.32, H 9.68, N 4.32

Found: C 74.70, H 9.29, N 3.80

{Tetrakis[(cyclohexylamino)methyl]resorcinarene}cavitand (45)

Prepared using an analogous method as for {tetrakis[(butylamino)methyl]resorcinarene}cavitand using cyclohexylamine. (0.97g, 92%)

^1H NMR (300MHz, CDCl_3) δ_{H} : 7.00 (4H, s, ArH), 5.83 (4H, d, $J=6.6\text{Hz}$, $\text{OCH}_2[\text{H}_{\text{outer}}]$), 4.72 (4H, t, $J=8.4\text{Hz}$, ArCH), 4.31 (4H, d, $J=6.9\text{Hz}$, $\text{OCH}_2[\text{H}_{\text{inner}}]$), 3.54 (8H, s, CH_2), 2.37 (4H, m, CH), 2.19 (8H, m, CH_2), 1.87 (8H, m, CH_2), 1.73 - 1.00 (44H, m, CH_2), 0.90 (24H, m, CH_3)

^{13}C NMR (75.48MHz, CDCl_3) δ_{C} : 153.49, 137.91, 126.45, 119.14 (ArC), 99.45 (OCH_2), 56.46, 40.37, 36.89, 33.52, 31.97, 30.09, 27.56, 26.07, 24.95, 22.66 (CH_2 & CH), 14.07 (CH_3)

Elemental Analysis for $\text{C}_{80}\text{H}_{116}\text{N}_4\text{O}_8$:

Expected: C 76.15, H 9.27, N 4.44

Found: C 77.79, H 9.03, N 4.68

{Tetrakis[(benzylamino)methyl]resorcinarene}cavitand (46)

Prepared using an analogous method as for {tetrakis[(butylamino)methyl]resorcinarene}cavitand using benzylamine. (1.05g, 97%)

^1H NMR (300MHz, CDCl_3) δ_{H} : 7.27 (20H, m, BzH), 7.00 (4H, s(br), ArH), 5.53 (4H, d, $J=6.9\text{Hz}$, $\text{OCH}_2[\text{H}_{\text{outer}}]$), 4.69 (4H, t, $J=7.8\text{Hz}$, ArCH), 4.12 (4H, d, $J=6.9\text{Hz}$, $\text{OCH}_2[\text{H}_{\text{inner}}]$),

3.71 (8H, s, CH₂Ph), 3.48 (8H, s, CH₂NH), 2.57 (8H, s(br), CH₂), 2.17 (8H, m, CH₂), 1.35 (16H, m, CH₂), 0.89 (12H, t, J=7.2Hz, CH₃)

¹³C NMR (75.48MHz, CDCl₃) δ_H: 153.46, 139.27, 138.04, 128.48, 128.41, 127.23, 125.42, 119.47 (ArC), 99.18, 53.23, 42.11, 36.86, 31.99, 30.00, 27.58, 22.68 (CH₂), 14.11 (CH₃)

ESIMS(m/z): 1294.53 [M+H]⁺, 1174.48 [M-BzNHCH₂]⁺

Elemental Analysis for C₈₄H₁₀₀N₄O₈.6H₂O:

Expected: C 71.97, H 8.05, N 4.00

Found: C 71.75, H 8.27, N 4.21

Cu(II) Dithiocarbamate-based (Butylamino)resorcinarene Octanuclear Complex (47)

{Tetrakis[(butylamino)]methylresorcinarene}cavitand (**43**) (1.00g, 0.86mmol) was dissolved in a THF/H₂O (2:1, 100ml) solution and KOH (0.22g, 3.96mmol) and CS₂ (0.29g, 4.00mmol) added sequentially. Cu(OAc)₂ (0.41g, 2.20mmol) was then added to the yellow solution and the reaction mixture stirred at room temperature for 18 hours. The resulting fine, dark brown powder was filtered and recrystallised from CH₂Cl₂/EtOH yielding black crystals, which were collected and dried *in vacuo*. (0.50g, 38%)

ESIMS(m/z) with NOBF₄: 792.6 [M]⁸⁺, 918.4 [M.BF₄]⁷⁺, 1085.6 [M.2BF₄]⁶⁺, 1320.3 [M.3BF₄]⁵⁺, 1671.9 [M.4BF₄]⁴⁺, 2258.1 [M.5BF₄]³⁺,

Elemental Analysis for C₃₀₄H₄₁₆N₁₆O₃₂S₃₂Cu₈.2CH₂Cl₂:

Expected: C 56.45, H 6.50, N 3.44

Found: C 56.53, H 6.28, N 3.42

Zn(II) Dithiocarbamate-based (Hexylamino)resorcinarene Hexanuclear Complex (48)

Synthesised using an analogous method to (**47**) using {Tetrakis[(hexylamino)]methylresorcinarene}cavitand (**44**) (1.00g, 0.86mmol) by the addition of Zn(OAc)₂ (0.41g,

2.0mmol). The resulting cream solid was redissolved in pyridine and precipitated by the addition of water and recrystallised from $\text{CHCl}_3/\text{EtOH}$. (0.62g, 52%)

^1H NMR (300MHz, CDCl_3) δ_{H} : 8.85 (12H, s, pyH), 7.80 (6H, s, pyH), 7.44 (12H, s, pyH), 7.12 (12H, s, ArH), 5.85 (12H, m(br), $\text{OCH}_2[\text{H}_{\text{outer}}]$), 4.76 (12H, s, ArCHCH_2) 4.35 - 3.54 (36H, m(br), $\text{OCH}_2[\text{H}_{\text{inner}}]$ & ArCH_2), 2.21 (24H, s, CH_2), 1.71 - 1.23 (192H, m, CH_2), 0.90 (72H, m, CH_3)

Elemental Analysis for $\text{C}_{282}\text{H}_{390}\text{N}_{18}\text{O}_{24}\text{S}_{24}\text{Zn}_6 \cdot 8\text{CHCl}_3 \cdot 8\frac{1}{2}\text{H}_2\text{O}$:

Expected: C 52.52, H 6.22, N 3.80

Found: C 52.76, H 6.47, N 3.50

Cd(II) Dithiocarbamate-based (Hexylamino)resorcinarene Hexanuclear Complex (49)

Synthesised by an analogous method to (47) using {Tetrakis[(hexylamino)]methylresorcinarene}cavitand (44) (1.00g, 0.86mmol) by the addition of $\text{Cd}(\text{OAc})_2$ (0.41g, 2.0mmol). The resulting cream solid was redissolved in pyridine and precipitated by the addition of water and recrystallised from $\text{CHCl}_3/\text{EtOH}$. (0.72g, 62%)

^1H NMR (300MHz, CDCl_3) δ_{H} : 8.65 (12H, s, pyH), 7.69 (6H, s, pyH), 7.30 (12H, s, pyH), 7.08 (12H, s, ArH), 5.85 (12H, m(br), $\text{OCH}_2[\text{H}_{\text{outer}}]$), 4.72 - 3.80 (48H, m(br), ArCHCH_2 & $\text{OCH}_2[\text{H}_{\text{inner}}]$ & ArCH_2), 2.16 (24H, s, CH_2), 1.69 (48H, m, CH_2), 1.33 (144H, s(br), CH_2), 0.89 (72H, m, CH_3)

Elemental Analysis for $\text{C}_{282}\text{H}_{390}\text{N}_{18}\text{O}_{24}\text{S}_{24}\text{Cd}_6 \cdot 8\text{CHCl}_3 \cdot 4\text{H}_2\text{O}$:

Expected: C 50.57, H 5.94, N 3.65

Found: C 50.55, H 5.94, N 3.35

Ni(II) Dithiocarbamate-based (Butylamino)resorcinarene Octanuclear Complex (50)

Synthesised using an analogous method to (47) using {Tetrakis[(butylamino)]methylresorcinarene}cavitand (43) (0.25g, 0.22mmol) by the addition of Ni(OAc)₂ (0.13g, 0.5mmol) forming a green crystalline solid. (0.04g, 12%)

¹H NMR (300MHz, CDCl₃) δ_H: 7.12 (16H, m, ArH), 6.30 - 5.86 (16H, m, OCH₂[H_{outer}]), 5.22 - 4.98 (16H, m, OCH₂[H_{inner}]), 4.73 (16H, m, CH), 4.12 (32H, m, CH₂), 3.42 (32H, m, CH₂), 2.21 (32H, s, CH₂), 1.32 - 1.15 (160H, m, CH₂), 0.91 - 0.72 (96H, m, CH₃)

¹³C NMR (75.48MHz, CDCl₃) δ_H: 207.57 (CS₂), 154.41, 153.71, 148.31, 138.97, 138.16 (ArC), 121.05, 119.52, 46.87, 36.50, 31.81, 29.66, 28.46, 27.37, 22.67, 19.94, 19.71 (CH₂), 14.04, 13.57 (CH₃)

Elemental Analysis for C₃₀₄H₄₁₆N₁₆O₃₂S₃₂Ni₈.4CH₂Cl₂.7H₂O:

Expected: C 54.66, H 6.52, N 3.31

Found: C 54.80, H 6.29, N 3.32

Pd(II) Dithiocarbamate-based (Butylamino)resorcinarene Octanuclear Complex (51)

Synthesised by an analogous method to (47) using {Tetrakis[(butylamino)]methylresorcinarene}cavitand (43) (0.56g, 0.48mmol) by the addition of K₂PdCl₄ (0.41g, 1.23mmol) forming a yellow crystalline solid.

¹H NMR (300MHz, CDCl₃) δ_H: 7.19 (16H, m, ArH), 6.18 - 5.90 (16H, m, OCH₂[H_{outer}]), 5.33 - 5.10 (16H, m, OCH₂[H_{inner}]), 4.82 - 4.71 (16H, m, CH), 4.34 - 4.21 (32H, m, CH₂), 3.14 (32H, m, CH₂), 2.21 (32H, s, CH₂), 1.39 - 1.13 (160H, m, CH₂), 0.89 (96H, m, CH₃)

Elemental Analysis for C₃₀₄H₄₁₆N₁₆O₃₂S₃₂Pd₈:

Expected: C 54.63, H 6.27, N 3.35

Found: C 55.03, H 6.54, N 3.24

Tetrabutylammonium Hexamolybdate

Na_2MoO_4 (58.0g, 282mmol) was stirred in DMF (100ml). Acetic anhydride (48ml) was then slowly added dropwise, forming a white suspension, which was stirred for an hour. Addition of concentrated HCl (33ml) (Caution Very Exothermic!), resulted in a green/yellow solution. The hot solution was filtered and the lime green filtrate precipitated by the addition of a solution of TBABr (1M, 32.24g in DMF (100ml)). The solution was refrigerated in order to encourage precipitation. The resulting yellow salt was collected, washed with ethanol (100ml), diethyl ether (100ml) and recrystallised from acetone yielding yellow crystals. (24.0g, 38%)

ESIMS(m/z) (+ve): 242.4 $[\text{C}_{16}\text{H}_{36}\text{N}]^+$; (-ve): 441.4 $[\text{Mo}_6\text{O}_{19}]^{2-}$

Elemental Analysis for $\text{C}_{32}\text{H}_{72}\text{N}_2\text{Mo}_6\text{O}_{19}$:

Expected: C 28.15, H 5.28, N 2.05, Mo 42.20

Found: C 28.20, H 5.25, N 2.01, Mo 42.67

Tetrabutylammonium Hexatungstate

A suspension of $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ (33.0g, 0.100mmol) was stirred in an acetic anhydride (40ml) and DMF (30ml) mixture for 3 hours at 100°C until a fluid paste was obtained. A mixture of acetic anhydride (20ml), DMF (50ml) and concentrated HCl (18ml) was then added and was continued to be heated at 100°C for a further 2 hours. The solution was cooled and the white residue collected. The filtrate was precipitated by a methanolic solution of TBABr (15g in 50ml of MeOH). The white solid was recrystallised from DMSO. (14.5g, 46%)

ESIMS(m/z) (+ve): 242.2 $[\text{C}_{16}\text{H}_{36}\text{N}]^+$; (-ve): 706.3 $[\text{W}_6\text{O}_{19}]^{2-}$

Elemental Analysis for $\text{C}_{32}\text{H}_{72}\text{N}_2\text{W}_6\text{O}_{19}$:

Expected: C 20.31, H 3.84, N 1.48, W 58.30

Found: C 20.34, H 4.75, N 1.48, W 58.57

Tetra-piperazine-derivatised Methylresorcinarene (52)

Piperazine (1.45g, 16.82mmol) was dissolved in CH₂Cl₂ (100ml) and {tetra(bromomethyl)resorcinarene}cavitand (**42**) (0.50g, 0.42mmol) was added portionwise to the stirred solution. This was stirred at room temperature for a further 18 hours. After this time the solvent was removed under reduced pressure and the residue was heated *in vacuo* to sublime excess piperazine into a secondary trap. The crude produce was dissolved in CH₂Cl₂ (100ml), washed with H₂O (3x100ml) and dried over K₂CO₃. The solvent was evaporated affording a white solid. (0.43g, 84%)

¹H NMR (300MHz, CDCl₃) δ_H: 7.07 (4H, s, ArH), 5.83 (4H, d, J=6.9Hz, OCH₂O[H_{outer}]), 4.75 (4H, t, J=7.5Hz, ArCH), 4.23 (4H, d, J=7.2Hz, OCH₂O[H_{inner}]), 3.57 (8H, s, ArCH₂), 2.81 (16H, m, NCH₂), 2.44 (20H, s(br), CH₂NH), 1.37 (24H, m, CH₂), 0.90 (12H, t, J=6.6Hz, CH₃)

ESIMS(m/z):1210.4 [M+H]⁺, 1124.3 [M-C₄H₉N₂]⁺

Elemental Analysis for C₇₂H₁₀₄N₈O₈·½CH₂Cl₂:

Expected: C 69.54, H 8.54, N 8.95

Found: C 69.46, H 8.12, N 8.67

Ethylene-Spaced Resorcinarene Cavitand (53)

Tetramethylresorcinarene cavitand (**40**) (1.00g, 1.21mmol), ethane-1,2-ditosylate (4.93g, 13.32mmol) and K₂CO₃ (anhydrous, 5.00g, 36.10mmol) were stirred in at 100°C DMA (dry, 100ml) for 4 days. The mixture was cooled to room temperature, filtered through Celite® and the solvent removed under reduced pressure. The residue was extracted into hexane (100ml), filtered and evaporated to dryness. It was then re-dissolved in CH₂Cl₂ (100ml), washed with H₂O (3x100ml) and dried over MgSO₄. The solvent was reduced in volume and filtered

through silica gel 60. Solvent removal from the forerunning band yielded a yellow solid that was dried *in vacuo*. (0.18g, 16%)

^1H NMR (300MHz, CDCl_3) 7.19 (4H, s, ArH), 5.18 (4H, t, $J=7.5\text{Hz}$, ArCH), 4.26 (8H, m, AB_2X_2 system, $\text{OCH}_2\text{O}[\text{H}_{\text{outer}}]$), 3.49 (8H, m, AB_2X_2 system, $\text{OCH}_2\text{O}[\text{H}_{\text{inner}}]$), 2.18 (12H, s, ArCH_3), 2.06 (8H, m, CHCH_2), 1.34 - 1.21 (24H, m, CH_2), 0.86 (12H, t, $J=6.9\text{Hz}$, CH_3)

^{13}C NMR (75.48Hz, CDCl_3) δ_{C} : 152.04, 135.51, 123.84, 121.76(br) (ArC), 70.40(br) (OCH_2), 34.60, 33.97, 33.42, 32.12, 27.71, 22.71 (CH_2), 14.36 (CH_3)

ESIMS(m/z): 929.7 $[\text{M}+\text{H}]^+$, 946.8 $[\text{M}+\text{NH}_4]^+$, 951.7 $[\text{M}+\text{Na}]^+$, 967.7 $[\text{M}+\text{K}]^+$

Elemental Analysis for $\text{C}_{60}\text{H}_{80}\text{O}_8 \cdot \frac{1}{2}\text{H}_2\text{O}$:

Expected: C 76.81, H 8.70

Found: C 76.52, H 8.32

Tetramethylbromo-Ethylene-Spaced Resorcinarene Cavitand (**54**)

Ethyl-spaced-resorcinarene cavitand (**55**) (0.50g, 0.54mmol) was dissolved in 1,2-dichloroethane (100ml) and a catalytic amount of AIBN was added. NBS (0.50g, 2.81mmol) was added portionwise to the stirred solution which was then heated to 80°C under N_2 and stirred for 3 hours. The orange solution was left to stir under N_2 for 18 hours at room temperature, after which the solvent was removed under reduced pressure. The residue was suspended in EtOH (150ml) and stirred for 3 hours with the resulting cream precipitate filtered off under suction. The solid recrystallised from $\text{CH}_2\text{Cl}_2/\text{EtOH}$ to yield a colourless crystalline solid which was dried *in vacuo*. (0.40g, 60%)

^1H NMR (300MHz, CDCl_3) δ_{H} : 7.04 (4H, s, ArH), 4.75 (4H, m, ArCH), 4.42, (8H, s, CH_2Br), 4.24 (4H, m, $\text{OCH}_2\text{O}[\text{H}_{\text{outer}}]$), 3.74 (4H, m, $\text{OCH}_2\text{O}[\text{H}_{\text{inner}}]$), 2.17 (8H, m, ArCHCH_2), 1.50 - 1.02 (24H, m, CH_2), 0.89 (12H, m, CH_3)

ESIMS(m/z): 1245.1 $[\text{M}+\text{H}]^+$, 1294.0 $[\text{M}+\text{K}]^+$, 1150.9 $[\text{M}-\text{CH}_2\text{Br}]^+$

Syntheses from Chapter Four:

General Synthesis for Dinuclear Gold(III) Dithiocarbamate-based Macrocycles (55) – (57)

Potassium bis-dithiocarbamate salts (0.10g, 1 equivalent) were suspended in MeCN (100ml) and stirred at room temperature. HAuCl_4 (2 equivalents) was added to the solutions and stirred for 18 hours. The golden solutions were filtered, reduced in volume to 10ml and the filtrates precipitated via the addition of Et_2O (100ml). The orange solids were dried *in vacuo*.

(55): (58mg, 25%)

^1H NMR (300MHz, DMSO-d_6 : CD_3CN (1:1)) δ_{H} : 7.51 (2H, m, ArH^5), 7.43 (2H, s, ArH^2), 7.38 (4H, d, $J=8.1\text{Hz}$, $\text{ArH}^{4/6}$), 5.09 (8H, s, ArCH_2), 3.71 (8H, m, NCH_2CH_2), 1.59 (8H, m, NCH_2CH_2), 1.26 (8H, m, CH_2CH_3), 0.85 (12H, t, $J=7.2\text{Hz}$, CH_3)

ESIMS(m/z): 595.34 $[\text{M}]^{2+}$

Elemental Analysis for $\text{C}_{36}\text{H}_{52}\text{N}_4\text{S}_8\text{Au}_2 \cdot 2\text{Cl} \cdot \text{H}_3\text{OCl} \cdot \text{H}_2\text{O}$:

Expected: C 32.40, H 4.30, N 4.20

Found: C 32.30, H 4.12, N 4.51

(56): (87mg, 40%)

^1H NMR (300MHz, DMSO-d_6) δ_{H} : 7.82-7.61 (16H, m, ArH), 5.01 (8H, s, ArCH_2), 3.49 (8H, m, NCH_2CH_2), 1.77 (8H, m, NCH_2CH_2), 1.29 (8H, m, CH_2CH_3), 0.90 (12H, m, CH_3)

ESIMS(m/z): 671.41 $[\text{M}]^{2+}$

(57): (76mg, 29%)

^1H NMR (300MHz, DMSO-d_6) δ_{H} : 7.99 (4H, m, ArH), 7.67-7.46 (8H, m, ArH), 5.03 (8H, s, ArCH_2), 3.50 (8H, m, NCH_2CH_2), 1.77 (8H, m, NCH_2CH_2), 1.31 (8H, m, CH_2CH_3), 0.91 (12H, m, CH_3)

ESI-MS(*m/z*): 644.88 $[M]^{2+}$, 1326.87 $[M+Cl]^+$

Elemental Analysis for $C_{44}H_{56}N_4S_8Au_2 \cdot 2Cl \cdot 2H_3OCl \cdot Et_2O \cdot \frac{1}{2}Et_2O \cdot \frac{5}{2}H_2O$:

Expected: C 37.81, H 4.89, N 4.05

Found: C 37.76, H 5.11, N 4.21

Gold(III) Bis-(diethylenediamine) Tris-hexafluorophosphate (58)

Ethylenediamine (1.80g, 2ml, 29.9mmol) was dissolved in Et_2O (10ml). This was added to a solution of $HAuCl_4$ (2.00g, 5.89mmol) in Et_2O (20ml), forming a gummy yellow precipitate. The crude product was dissolved in H_2O (5ml), filtered and precipitated via the addition of $EtOH$ (40ml). The white precipitate was filtered and reprecipitated from $EtOH/H_2O$.

The solid was dissolved in H_2O (10ml) and $AgPF_6$ (3.58g, 14.2mmol), dissolved in H_2O (20ml) and added to the colourless solution. The cloudy solution was left to stand for 1 hour after which, the grey $AgCl$ precipitate was filtered. The filtrate was evaporated to dryness and dried *in vacuo*. (3.42g, 80%)

1H NMR (300MHz, $CDCl_3$) δ_H : 3.17 (8H, s, CH_2)

^{19}F NMR (282.45MHz, $CDCl_3$) δ_F : 72.26 (d, $J=708Hz$, PF_6)

^{31}P NMR (121.51MHz, $CDCl_3$) δ_P : -143.96 (septet, $J=709Hz$, PF_6)

Elemental Analysis for $C_4H_{16}N_4AuPF_6 \cdot H_2O$:

Expected: C 6.24, H 2.36, N 7.28, Au 25.58, P 12.07

Found: C 6.28, H 2.28, N 7.43, Au 25.65, P 12.10

Gold(III) Bis-(*N,N'*-diethyldithiocarbamate) Tetraphenylborate (60)

Sodium *N,N'*-diethyldithiocarbamate (0.63g, 2.78mmol) was suspended in MeCN (100ml) and $HAuCl_4$ (0.47g, 1.39mmol) added to the stirred solution. The golden solution was stirred

at room temperature for 18 hours. The solvent was removed under reduced pressure and redissolved in CHCl_3 (100ml). This was washed with brine (2x100ml) and dried over K_2CO_3 . NaBPh_4 (1.20g, 3.48mmol) was dissolved in EtOH (50ml) and added to the golden solution. The yellow precipitate that formed was collected, recrystallised from CHCl_3 (hot) and dried *in vacuo*. (0.48g, 42%)

^1H NMR (300MHz, CDCl_3) δ_{H} : 7.17 (8H, m, $\text{ArH}^{2\&6}$), 6.91 (8H, t, $J=7.5\text{Hz}$, $\text{ArH}^{3\&5}$), 6.78 (4H, t, $J=7.5\text{Hz}$, ArH^4), 3.75 (8H, q, $J=6.9\text{Hz}$, CH_2), 1.28 (12H, t, $J=7.2\text{Hz}$, CH_3)

ESIMS(m/z): 492.96 $[\text{M}]^+$

Elemental Analysis for $\text{C}_{34}\text{H}_{40}\text{N}_2\text{S}_4\text{BAu}\cdot 2\text{CHCl}_3\cdot \text{H}_2\text{O}$:

Expected: C 40.43, H 4.15, N 2.62

Found: C 40.41, H 4.41, N 2.90

Gold(I) Bis-(*N,N'*-diethyldithiocarbamate)

HAuCl_4 (0.78g, 1.34mmol) was stirred in NaCl (25ml, saturated) at 4°C . Na_2SO_3 (0.22g, 1.74mmol) was added to the solution. The golden solution changed through pale green to colourless, indicative of Au(I) being formed. Immediately, an aqueous solution of sodium *N,N'*-diethyldithiocarbamate (0.84g, 3.71mmol, 20ml) was added to the solution. The gummy yellow precipitate was collected, washed with acetone and recrystallised from DMSO(hot) to afford yellow needles, which were stirred in acetone and dried *in vacuo*. (0.21g, 23%)

Elemental Analysis for $\text{C}_{10}\text{H}_{20}\text{N}_2\text{S}_4\text{Au}_2$:

Expected: C 17.39, H 2.92, N 4.06

Found: C 17.68, H 3.27, N 4.00

General Synthesis for Dinuclear Gold(III) Dithiocarbamate-based Macrocycles via Transmetallation (68) – (76)

Copper(II) and nickel(II) dithiocarbamate complexes (0.10g, 1 equivalent) were dissolved in CH_2Cl_2 (50ml) and stirred at room temperature. KAuCl_4 (2 equivalents) was dissolved in MeCN (50ml) and added to the solutions, which were stirred for 18 hours. The golden solutions were filtered, reduced in volume to 10ml and the filtrates precipitated through the addition of Et_2O (100ml). The resulting orange solids were dried *in vacuo*.

(Yields calculated assuming copper(II) dithiocarbamate-based macrocycles form $\text{Cu}_2\text{Cl}_6^{2-}$ and nickel(II) dithiocarbamate-based macrocycles form NiCl_4^{2-} complexes.)

(68): (92mg, 55%)

ESIMS(m/z): 595.65 $[\text{M}]^{2+}$

(69): (86mg, 57%)

ESIMS(m/z): 595.77 $[\text{M}]^{2+}$

(70): (54mg, 40%)

ESIMS(m/z): 647.52 $[\text{M}]^{2+}$

(71): (110mg, 69%)

ESIMS(m/z): 651.15 $[\text{M}]^{2+}$

(72): (98mg, 63%)

ESIMS(m/z): 671.57 $[\text{M}]^{2+}$, 1378.49 $[\text{M}.\text{Cl}]^+$

(73): (79mg, 52%)

ESIMS(m/z): 723.39 $[M]^{2+}$, 1482.81 $[M.Cl]^+$, 1579.38 $[M.CuCl_2]^+$, 1785.80 $[M.AuCl_4]^+$

(75): (51mg, 32%)

ESIMS(m/z): 645.23 $[M]^{2+}$

(76): (36mg, 24%)

ESIMS(m/z): 701.20 $[M]^{2+}$, 1270.30 $[M-Au+Cu]^+$, 1534.78 $[M.CuCl_2]^+$, 1741.22 $[M.AuCl_4]^+$

Syntheses from Chapter Five:

Cu(II)/Cu(III) Dithiocarbamate-based Naphthyl-Spaced [2]Catenane (78)

Cu(II) dithiocarbamate-based naphthyl-spaced macrocyclic complex (**18-Cu**) (0.021g, 0.02mmol) was dissolved in CH₂Cl₂/MeCN (12:1, 50ml). FeCl₃ (anhydrous, 0.007g, 0.04mmol) was dissolved in MeCN (3ml), added to the solution and stirred for 12 hours. After this time, the solvent was removed under reduced pressure, the product extracted into CH₂Cl₂ (50ml) and recrystallised by layering with Et₂O. (0.024g, 91%)

ESIMS(m/z): 1024.61 [M]²⁺, 2048.87 [M]⁺

ESIMS(m/z) (with NOBF₄): 512.1 [M]⁴⁺ 712.2 [M.BF₄]³⁺, 1110.6 [M.2BF₄]²⁺

Elemental Analysis for C₈₈H₁₁₂N₈S₁₆Cu₄.Fe₂Cl₈.³/₂.CH₃CN:

Expected: C 43.61, H 4.69, N 5.31

Found: C 43.75, H 5.10, N 5.42

Mixed-Spacer Cu(II)/Cu(III) [2]Catenane (80)

Cu(II) dithiocarbamate-based macrocycles (**18-Cu**) (10mg, 9.8μmol) and (**13-Cu**) (10.5mg, 9.8μmol) were combined in CH₂Cl₂/MeCN (12:1, 50ml). FeCl₃ (anhydrous, 6.6mg, 19.6μmol) was added to the solution and stirred for 12 hours. The solvent was removed and the product extracted into CH₂Cl₂ and the solution analysed by electrospray mass spectrometry.

ESIMS(m/z): 683.32 [NN-NN]³⁺, 692.01 [NB-NN]³⁺, 1037.53 [NB-NN]²⁺

Mixed-Metal Au(III)/Cu(II) Dithiocarbamate-based Naphthyl-Spaced [2]Catenane (84)

(**18-Cu**) (10mg, 9.8μmol) and (**57**) (10.5mg, 13.4μmol) were combined in CH₂Cl₂/MeCN (1:1, 50ml) solution and stirred at room temperature for 18 hours. After this time, the solution was analysed by electrospray mass spectrometry.

ESIMS(m/z): 1158.03 [M]²⁺

Syntheses from Chapter Six:

General Preparation of Thiol Stabilised Gold Nanoparticles:

An aqueous solution of HAuCl_4 (1 equivalent) was rapidly stirred with a toluene solution of the phase transfer reagent Aliquat[®]336 (1.8 equivalents) until complete transfer of the AuCl_4 anion had occurred.

The organic layer was collected, washed with H_2O (2x500ml) and the stabilising thiol ligand (0.60 equivalents) was added and the solution stirred at 4°C for 15 minutes. Initially the solution turned green in colour before returning to orange. An aqueous solution (50ml) of NaBH_4 (large excess) was prepared and added dropwise to the stirred solution. A dark purple solution was formed instantaneously and this was stirred for 2 hours maintaining the temperature below 10°C . The organic layer was isolated and washed with H_2O (3x100ml) and then concentrated ($\sim 5\text{ml}$) under reduced pressure. MeOH (200ml) was added and the mixture stored at -18°C for 18 hours. The black solid was filtered off, washed with MeOH and dried *in vacuo*.

1-Dodecylthiol Stabilised Gold Nanoparticles (85)

HAuCl_4 (0.86g, 1.37mmol, 50ml aq), Aliquat[®]336 (1.00g, 2.47mmol), 1-dodecylthiol (0.17g, 0.84mmol) and NaBH_4 (0.32g, 8.41mmol) were reacted as described. (0.30g, 51%)

^1H NMR (300MHz, CDCl_3) δ_{H} : 1.23 (s(br), CH_2), 0.86 (s(br), CH_3)

^{13}C NMR (75.48MHz, CDCl_3) δ_{C} : 32.04, 30.15 (v br), 22.77 (CH_2), 14.11 (CH_3)

Elemental Analysis for $\text{Au}_{11}(\text{C}_{12}\text{H}_{25}\text{SH})_3$:

Expected: C 15.59, H 2.83, Au 78.11

Found: C 15.39, H 2.95, Au 76.06

Ethyl-2-mercaptopropionate Stabilised Gold Nanoparticles (86)

HAuCl₄ (10.8g, 31.7mmol, 200ml aq), Aliquat[®]336 (19.30g, 47.6 mmol), ethyl-2-mercaptopropionate (7.67 g, 57.0mmol) and NaBH₄ (48.0g, 1.27mol) were combined as previously described. (3.18g)

¹H NMR (300MHz, CDCl₃) δ_{H} : 3.35 (s(br), CH₂), 1.86-1.34 (s(br), CH₂), 0.87 (s(br), CH₃)

Elemental Analysis:

Found: C 3.51, H 0.63

Methyl-3-mercaptopropionate Stabilised Gold Nanoparticles (87)

HAuCl₄ (1.57g, 4.62mmol), Aliquat[®]336 (2.83g, 6.93mmol), methyl-3-mercaptopropionate (1.00g, 8.32mmol) and NaBH₄ (5.00g, 132mmol) were combined as previously described. (0.61g)

Elemental Analysis for Au₆.(C₄H₇O₂SH).(C₂₅H₆₀NCl):

Expected: C 20.34, H 4.00, N 0.82, Au 69.02

Found: C 19.17, H 3.83, N 0.76, Au 66.47

Aliquat[®]336 Stabilised Gold Nanoparticles (88)

An aqueous solution (100ml) of HAuCl₄ (1.00g, 2.94mmol) was rapidly stirred at room temperature with a toluene solution (50ml) of the phase transfer reagent Aliquat[®]336 (1.78g, 4.41mmol) until complete transfer of the AuCl₄ anion had occurred.

The organic layer was collected and more Aliquat[®]336 (4.76g, 14.71mmol) was added and the solution stirred at 4°C for 15 minutes. An aqueous solution (50ml) of NaBH₄ (3.33g, 88.0mmol) was prepared and added dropwise to the stirred solution. A dark purple solution was formed instantaneously and this was stirred for 2 hours maintaining the temperature below 10°C. The organic layer was isolated and washed with H₂O (3x100ml) and then

concentrated (~5ml) under reduced pressure. MeOH (200ml) was added and the mixture stored at -18°C for 18 hours. The black solid was filtered off, washed with MeOH and dried *in vacuo*. (0.21g)

Elemental Analysis for Au₂(C₂₅H₆₀NCl):

Expected: C 59.03, H 11.89, N 2.75, Au 19.36

Found: C 50.70, H 6.70, N 2.98, Au 19.80

Indirect Synthesis of 1-Dodecylthiol Stabilised Gold Nanoparticles (89)

Aliquat stabilised gold nanoparticles were prepared as described in (88). After stirring for 2 minutes, 1-dodecylthiol (0.11g, 0.54mmol) was added to the solution which was stirred for a further 4 hours. After this time, the purple organic layer was collected, washed with H₂O (3x100ml) and then concentrated (~5ml) under reduced pressure. MeOH (200ml) was added, and the mixture stored at -18°C for 18 hours. The black solid was filtered off, washed with MeOH and dried *in vacuo*. (0.04g)

Elemental Analysis:

Found: C 7.15, H 1.24

Potassium *N,N'*-Di-*n*-hexyldithiocarbamate (90)

Di-*n*-hexylamine (5.00g, 26.97mmol) and KOH (1.52g, 26.97mmol) were combined in THF/H₂O (2:1, 100ml) and stirred at room temperature. CS₂ (2.06g, 26.97mmol) was added resulting in the formation of a yellow solution, which was stirred for a further 2 hours. The solvent was removed under reduced pressure and the residue recrystallised from hexane (hot) affording a white waxy solid which was dried *in vacuo*. (5.46g, 68%)

¹H NMR (300MHz, D₂O) δ_H: 3.83 (4H, m, NCH₂), 1.61 (4H, m, NCH₂CH₂), 1.21 (12H, s, CH₂), 0.79 (6H, t, J=6.9Hz, CH₃)

^{13}C NMR (75.48Hz, D_2O) δ_{C} : 207.85 (CS_2), 54.72, 31.62, 26.85, 26.68, 22.73 (CH_2), 14.04 (CH_3)

Elemental Analysis for $\text{C}_{13}\text{H}_{26}\text{NS}_2\text{K} \cdot \frac{2}{3}\text{H}_2\text{O}$:

Expected: C 50.11, H 8.84, N 4.50

Found: C 50.07, H 8.66, N 4.63

Potassium *N,N'*-Di-*n*-hexyldithiocarbamate Stabilised Gold Nanoparticles (91)

An aqueous solution (50ml) of HAuCl_4 (1.05g, 3.10mmol) was rapidly stirred with a toluene solution (50ml) of the phase transfer reagent Aliquat[®]336 (1.88g, 6.65mmol) until complete transfer of the AuCl_4^- anion had occurred.

The organic layer was collected and an aqueous solution of potassium *N,N'*-di-*n*-hexyldithiocarbamate (1.67g, 5.58mmol) (25ml) was added forming a yellow precipitate which stirred at 4°C for 10 minutes. An aqueous solution (50ml) of NaBH_4 (4.70g, 124.2mmol) was prepared and added dropwise over 10 minutes to the stirred solution. A dark purple solution was formed instantaneously and this was stirred for 2 hours maintaining the temperature below 10°C. The organic layer was isolated and washed with H_2O (3x100ml) and then concentrated (~5ml) under reduced pressure. MeOH (200ml) was added and the mixture stored at -18°C for 18 hours. The black solid was filtered off, washed with MeOH and dried *in vacuo*. (0.91g)

^1H NMR (300MHz, CDCl_3) δ_{H} : 3.78 (4H, m, NCH_2), 1.77 (4H, m, NCH_2CH_2), 1.28 (12H, s, CH_2), 0.87 (6H, m, CH_3)

^{13}C NMR (75.48Hz, D_2O) δ_{C} : 202.96 (CS_2), 57.66, 31.32, 26.44(x2), 22.52 (CH_2), 13.99 (CH_3)

Elemental Analysis for Au.(C₁₃H₂₆NS₂K):

Expected: C 31.45, H 5.28, N 2.82, Au 39.67

Found: C 28.19, H 4.78, N 2.41, Au 37.56

Tetra-Potassium {(butylaminodithiocarbamate)methyl Resorcinarene} Cavitand (92)

{Tetrakis[(butylamino)methyl]resorcinarene}cavitand (**43**) (1.00g, 0.86mmol) was dissolved in a THF/H₂O (2:1) solution and stirred at room temperature. KOH (0.24g, 4.32mmol) and CS₂ (0.33g, 4.32mmol) were sequentially added and the yellow solution stirred for a further 4 hours. The solvent was then removed under reduced pressure and the crude product redissolved in MeOH (100ml). The solution was filtered, reduced in volume (10ml) and added dropwise to rapidly stirred Et₂O (200ml). The white precipitate was collected and dried *in vacuo*. (0.86g, 62%)

¹H NMR (300MHz, DMSO-d₆(100°C)) δ_H: 7.49 (4H, s, ArH), 5.85 (4H, d, J=7.2Hz, OCH₂[H_{outer}]), 4.68 (4H, t, J=7.8Hz, ArCH₂CH₂), 4.42 (4H, d, J=7.5Hz, OCH₂[H_{inner}]), 3.52 (8H, s, CH₂), 2.37 (8H, m, CH₂), 2.17 (8H, m, CH₂), 1.41 - 1.30 (40H, m, CH₂), 0.87 (24H, m, CH₃)

Tetra-Potassium {(butylaminodithiocarbamate)methyl Resorcinarene} Cavitand Stabilised Gold Nanoparticles (93)

Prepared by an analogous method to (**91**) using HAuCl₄ (10mg, 0.030mmol) Aliquat (22mg, 0.056mmol), tetra-potassium {(butylaminodithiocarbamate)methyl resorcinarene} cavitand (**92**) (22.6mg, 0.014mol) and NaBH₄ (0.68g, 0.180mmol).

Tetra-Potassium {(butylaminodithiocarbamate)methyl Resorcinarene} Cavitand Stabilised Gold Nanoparticles Synthesised via an Indirect Method (94)

Aliquat stabilised gold nanoparticles were prepared from HAuCl_4 (0.10g, 0.29mmol) as described in (88). After stirring for 2 minutes tetra-potassium {(butylaminodithiocarbamate)methylresorcinarene} cavitand (92) (0.21g, 0.13mmol) was added to the solution which was stirred for a further 4 hours. After this time, the purple organic layer was collected washed with H_2O (3x100ml) and then concentrated (~5ml) under reduced pressure. MeOH (200ml) was added and the mixture stored at -18°C for 18 hours. The black solid was filtered off, washed with MeOH and dried *in vacuo*. (0.03g)

^1H NMR (300MHz, CDCl_3) δ_{H} : 7.09 (4H, s(br), ArH), 5.84 (4H, s(br), $\text{OCH}_2[\text{H}_{\text{outer}}]$), 4.71 (4H, m, ArCHCH_2), 4.30 (4H, m, $\text{OCH}_2[\text{H}_{\text{inner}}]$), 3.31 (8H, s, CH_2), 2.14 (8H, m, CH_2), 1.58 - 1.18 (48H, m, CH_2), 0.84 (24H, m, CH_3)

Thio-Amide (95)

Methyl 3-mercaptopropionate (10.00g, 83.2mmol) was combined with dioxane (50ml) and *n*-hexylamine (50ml) and refluxed for 18 hours under N_2 . The solvent was removed under reduced pressure and the resulting residue recrystallised from CH_2Cl_2 (hot) to yield a white crystalline solid. (12.82g, 81%)

^1H NMR (300MHz, DMSO-d_6) δ_{H} : 7.84 (1H, t(br), $J=6.9\text{Hz}$, NH), 2.99 (2H, m, NCH_2), 2.62 (2H, t, $J=7.2\text{Hz}$, SCH_2CH_2), 2.30 (2H, t, $J=7.2\text{Hz}$, SCH_2CH_2), 1.35 (2H, m, NCH_2CH_2), 1.26 (6H, s, CH_2), 0.84 (3H, t, $J=6.6\text{Hz}$, CH_3)

^{13}C NMR (75.48Hz, DMSO-d_6) δ_{C} : 170.25 (CO), 38.52, 35.74, 31.05, 29.10, 27.05, 26.13, 22.13 (CH_2), 13.99 (CH_3)

ESIMS(m/z): 345.4 $[2\text{M}+\text{H}]^+$, 367.5 $[2\text{M}+\text{Na}]^+$, 377.4 $[2\text{M}+\text{K}]^+$

Elemental Analysis for C₉H₁₉NOS:

Expected: C 57.10, H 10.12, N 7.40

Found: C 58.57, H 10.54, N 7.73

Thio-amide Stabilised Gold Nanoparticle (96)

Synthesised as previously discussed using H₂SO₄ (1.00g, 2.93mmol), Aliquat[®]336 (2.00g, 4.69mmol), thio-amide ligand (**95**) (1.00g, 5.28mmol) and NaBH₄ (1.80g, 47.6mmol). (0.46g)

Elemental Analysis:

Found: C 8.51, H 1.57, N 1.14

Bis-amide (97)

Cystamine dihydrogenchloride (5.00g, 22.2mmol) was dissolved in H₂O (100ml) and KOH (10.0g, 178mmol) was added and the solution stirred vigorously for 2 hours. The amine was extracted by the addition of CH₂Cl₂ (3x100ml). The organic layer was dried over K₂CO₃ and evaporated to dryness. The resulting oil was redissolved in CH₂Cl₂ (dry, 100ml) and NEt₃ (4.72g, 46.6mmol) was added. Octanoyl chloride (7.58g, 46.6mmol) was added dropwise to the stirred solution, which was stirred for a further 18 hours under N₂. The solution was washed with H₂O (3x100ml) and the organic layer evaporated under reduced pressure. The residue was recrystallised from DMSO/H₂O yielding a white powder which was washed with H₂O (3x50ml) and dried *in vacuo*. (1.52g, 17%)

¹H NMR (300MHz, CDCl₃) δ_H: 6.35 (2H, s(br), NH), 3.56 (4H, m, NHCH₂), 2.82 (4H, t, J=6.3Hz, CH₂S), 2.21 (4H, t, J=7.5Hz, COCH₂), 1.63 (4H, m, CH₂), 1.28 (16H, s, CH₂), 0.87 (6H, t, J=6.9Hz, CH₃)

¹³C NMR (75.48MHz, CDCl₃) δ_C: 173.78 (CO), 38.31, 37.79, 36.60, 31.69, 29.24, 29.02, 25.69, 22.60 (CH₂), 14.06 (CH₃)

ESIMS(m/z): 405.5 $[M+H]^+$, 427.6 $[M+Na]^+$, 810.0 $[2M+H]^+$

Elemental Analysis for $C_{20}H_{40}N_2O_2S_2$:

Expected: C 59.36, H 9.96, N 6.92

Found: C 59.33, H 9.93, N 6.96

Thio-Amine (98)

Bis-amide (97) (0.25g, 0.62mmol) was dissolved in THF (dry, 25ml) and added dropwise to a stirred solution of $LiAlH_4$ (0.06g, 1.55mmol) in THF (dry, 50ml) under N_2 . The mixture was then refluxed for 2 hours, allowed to cool to room temperature and stirred at room temperature for 18 hours. HCl (1M) was carefully added dropwise to the solution until pH=1 and then KOH (1M) was added until pH=7. The product was extracted with CH_2Cl_2 (3x50ml) and the organic layer dried over K_2CO_3 . The resulting oil was dried *in vacuo*. (0.20g, 87%)

1H NMR (300MHz, $CDCl_3$) δ_H : 2.90 (4H, t, $J=5.7Hz$, SCH_2CH_2), 2.80 (4H, t, $J=5.4Hz$, CH_2S), 2.58 (4H, t, $J=6.9Hz$, $NHCH_2$), 1.85 (2H, s(br), SH & NH) 1.46 (4H, m, CH_2), 1.25 (10H, s, CH_2), 0.85 (3H, t, $J=7.2Hz$, CH_3)

^{13}C NMR (75.48MHz, $CDCl_3$) δ_C : 49.59, 47.96, 38.70, 31.81, 30.06, 29.50, 29.25, 27.32, 22.65 (CH_2), 14.09 (CH_3)

ESIMS(m/z): 189.3 $[M]^+$, 230.4 $[M+K]^+$, 377.5 $[M_2-H]^+$

Elemental Analysis for $C_{10}H_{23}NS \cdot \frac{1}{6}CH_2Cl_2$:

Expected: C 61.97, H 11.43, N 7.17

Found: C 62.47, H 10.93, N 6.66

Partially Thio-amine Substituted 1-Dodecylthiol Stabilised Gold Nanoparticles (99)

1-Dodecylthiol stabilised gold nanoparticle (85) (0.10g) was dissolved in CH_2Cl_2 (100ml) and stirred at room temperature with thio-amine (98) (0.05g, 0.26mmol) for 18hours. The solvent

was removed under reduced pressure and the residue precipitated three times from toluene/MeOH. The black solid was filtered off and washed thoroughly with MeOH and Et₂O (0.07g).

Elemental Analysis for Au₄₆(C₁₂H₂₅SH)₁₂(C₈H₁₇NHC₂H₄SH):

Expected: C 15.84, H 2.89, N 0.12, Au 77.58

Found: C 15.88, H 2.51, N 0.13, Au 69.22

1-Dodecylthiol Stabilised Silver Nanoparticles (100)

An aqueous solution (30ml) of AgNO₃ (0.31g, 1.80mmol) was rapidly stirred with a CH₂Cl₂ solution (50ml) of the phase transfer reagent Aliquat[®]336 (3.31g, 8.20mmol) for 1 hour. The organic layer was collected and 1-dodecylthiol (0.47g, 2.34mmol) was added and the solution stirred at 4°C for 30 minutes. An aqueous solution (50ml) of NaBH₄ (0.78g, 20.6mmol) was prepared and added dropwise to the stirred solution over 5 minutes. Initially the solution turned yellow before turning dark brown and this was stirred for 2 hours maintaining the temperature below 10°C. The organic layer was isolated and washed with H₂O (3x100ml) and then concentrated (~5ml) under reduced pressure. MeOH (200ml) was added and the mixture stored at -18°C for 18 hours. The brown solid was filtered off, washed with MeOH and dried *in vacuo*. (0.13g)

Elemental Analysis for Ag.(C₁₂H₂₅SH):

Expected: C 46.45, H 8.45, Ag 34.77

Found: C 43.19, H 7.82, Ag 32.10

Sodium *N,N'*-Diethyldithiocarbamate Stabilised Silver Nanoparticles (101)

An aqueous solution (30ml) of AgNO₃ (0.10g, 0.60mmol) was rapidly stirred with a CH₂Cl₂ solution (50ml) of the phase transfer reagent Aliquat[®]336 (1.11g, 2.80mmol) for 1 hour. The

organic layer was collected and sodium *N,N'*-diethyldithiocarbamate (0.18g, 0.78mmol) was added and the resulting white precipitate stirred at 4°C for 30 minutes. An aqueous solution (50ml) of NaBH₄ (0.26g, 6.9mmol) was prepared and added dropwise over 5 minutes. The dark brown solution was stirred for 2 hours maintaining the temperature below 10°C. The organic layer was isolated and washed with H₂O (3x100ml) and then concentrated (~5ml) under reduced pressure. MeOH (200ml) was added and the mixture stored at -18°C for 18 hours. The brown solid was filtered off, washed with MeOH and dried *in vacuo*. (0.04g) (Upon precipitation or upon standing for a prolonged period of time resulted in the formation of a brown insoluble solid)

¹H NMR (300MHz, CDCl₃) δ_H: 4.01 (4H, q, J=6.9Hz, CH₂), 1.31 (6H, t, J=6.9Hz, CH₃)

Elemental Analysis for Ag_{19.8}(C₅H₁₀NS₂K):

Expected: C 13.54, H 2.27, N 3.16 Ag 57.76

Found: C 13.72, H 1.98, N 2.98 Ag 58.31

Tetra-Potassium {(butylaminodithiocarbamate)methyl Resorcinarene} Cavitand Stabilised Silver Nanoparticles (102)

Prepared in an analogous method to **(101)** using AgNO₃ (7.6mg, 0.045mmol) Aliquat (83mg, 0.20mmol), tetra-potassium {(butylaminodithiocarbamate)methyl resorcinarene} cavitand **(92)** (22.6mg, 0.014mol) and NaBH₄ (20mg, 0.51mmol). The resulting solution had a significantly higher stability than **(101)**.

Syntheses from Chapter Seven:

Ru(II) bis(2,2'-bipyridine)(*N,N'*-diethyldithiocarbamate) hexafluorophosphate (104)

Sodium *N,N'*-diethyldithiocarbamate trihydrate (0.23g, 1.00mmol) was heated under reflux with Ru(bipy)₂Cl₂ (0.50g, 0.96mmol) in EtOH/H₂O (1:1, 100ml) for 18 hours. The solution was evaporated to dryness and the residue dissolved in H₂O. To this NH₄PF₆ (0.20g, 1.16mmol) was added resulting in the precipitation of a purple solid which was collected and washed thoroughly with H₂O and diethyl ether and dried *in vacuo*. (0.62g, 92%)

¹H NMR (500MHz, CDCl₃) δ_H: 9.64 (2H, d, J=6.0Hz, bipyH⁶), 8.35 (2H, d, J=8.0Hz, bipyH³), 8.22 (2H, d, J=8.5Hz, bipyH⁶), 8.00 (2H, t, J=8.0Hz, bipyH⁴), 7.71 (2H, t, J=8.0Hz, bipyH⁵), 7.60 (2H, t, J=7.5Hz, bipyH⁵), 7.53 (2H, d, J=6.0Hz, bipyH³), 7.10 (2H, t, J=7.0Hz, bipyH⁴), 3.74 and 3.63 (2H, 2q, J=6.5Hz, CH₂), 1.19 (6H, t, J=7.0Hz, CH₃)

¹³C NMR (75.48MHz, CDCl₃) δ_C: 211.73 (CS₂), 157.91, 157.77, 153.36, 150.59, 135.53, 134.93, 126.25, 125.63, 123.58, 123.42 (bipyC), 44.05 (CH₂), 12.46 (CH₃)

³¹P NMR (121.52MHz, CDCl₃) δ_P: -143.18 (septet, J=711Hz, PF₆)

¹⁹F NMR (282.46MHz, CDCl₃) δ_F: -73.40 (d, J=712Hz, PF₆)

ESIMS(m/z): 562.29 [M]⁺; (-ve) 145.26 [PF₆]⁻

Elemental Analysis for C₂₅H₂₆N₅S₂RuPF₆:

Expected: C 42.49, H 3.71, N 9.91

Found: C 42.55, H 3.49, N 9.88

Sodium Piperazine-Spaced 1,4-Bis-Dithiocarbamate Salt (105)

Piperazine (1.00g, 11.98mmol) was dissolved in EtOH (50ml) and stirred at room temperature. NaOH (1.00g, 24.96mmol) was dissolved in the minimum amount of H₂O and added to the stirring solution. CS₂ (1.90g, 24.96mmol) was added to the solution and stirred

for 4 hours. The resulting white precipitate was filtered off, washed with EtOH and dried *in vacuo*. (2.85g, 86%)

^1H NMR (300MHz, D_2O) δ_{H} : 4.32 (8H, s, CH_2)

^{13}C NMR (75.48MHz, D_2O) δ_{C} : 209.35 (CS_2), 50.42 (CH_2)

Elemental Analysis for $\text{C}_6\text{H}_8\text{N}_4\text{S}_2\text{Na}_2 \cdot 2\text{H}_2\text{O}$:

Expected: C 22.63, H 3.80, N 8.80

Found: C 22.82, H 4.33, N 8.77

Potassium *p*-Xylene-spaced Bis-Dithiocarbamate Salt (106)

p-Xylene dibutylamine (**33**) (1.50g, 6.05mmol) was dissolved in THF/ H_2O (2:1, 50ml), KOH (0.85g, 15mmol) was added and the resulting solution stirred at room temperature for 10 minutes. CS_2 (1.15g, 15mmol) was added and the yellow solution stirred for a further 2 hours. The solvent was removed under reduced pressure and the residue precipitated from MeOH/ Et_2O yielding a white powder. (2.75g, 95%)

^1H NMR (300MHz, $\text{DMSO}-d_6$) δ_{H} : 7.18 (4H, s, ArH), 5.38 (4H, s, ArCH_2), 3.83 (4H, m, NCH_2), 1.52 (4H, m, CH_2), 1.13 (4H, m, CH_2), 0.78 (6H, t, $J=7.2\text{Hz}$, CH_3)

^{13}C NMR (75.48MHz, CDCl_3) δ_{C} : 214.26 (CS_2), 137.30, 127.07 (ArC), 54.68, 50.95, 28.63, 19.80 (CH_2), 13.90 (CH_3)

Elemental Analysis for $\text{C}_{18}\text{H}_{26}\text{N}_2\text{S}_4\text{K}_2 \cdot 2\frac{1}{2}\text{H}_2\text{O}$:

Expected: C 41.42, H 5.99, N 5.37

Found: C 41.21, H 5.17, N 5.58

Dinuclear Piperazine-spaced Ru(II) Bis(2,2'-bipyridine) Dithiocarbamate Hexafluorophosphate (107)

Sodium piperazine-spaced 1,4-bis-dithiocarbamate salt (**105**) (0.05g, 0.19mmol) and Ru(bipy)₂Cl₂ (0.20g, 0.38mmol) were refluxed under N₂ for 18 hours in EtOH/H₂O (2:1, 50ml). The solvent was then removed under reduced pressure and the residue redissolved in the minimum amount of MeCN. The crude product was purified by column chromatography over Sephadex LH-20 eluted with MeCN/MeOH (95:5 v/v), collecting the second purple band. The solvent was removed under reduced pressure and the residue redissolved in H₂O MeOH (99:1). NH₄PF₆ (0.065g, 0.40mmol) was added to the solution leading to the precipitation of a purple solid which was filtered off and dried *in vacuo*. (0.20g, 81%)

¹H NMR (300MHz, DMSO-d₆) δ_H: 9.50 (4H, d, J=5.1Hz, bipyH⁶), 8.73 (4H, d, J=7.8Hz, bipyH³), 8.63 (4H, d, J=8.1Hz, bipyH⁶), 8.01 (4H, t, J=7.8Hz, bipyH⁴), 7.90 (4H, t, J=7.8Hz, bipyH⁵), 7.83 (4H, t, J=5.7Hz bipyH⁵), 7.65 (4H, d, J=5.4Hz, bipyH³), 7.29 (4H, t, J=6.6Hz, bipyH⁴), 3.98 (8H, m, CH₂)

¹³C NMR (75.48MHz, DMSO-d₆) δ_C: 212.89 (CS₂), 157.78, 157.44, 153.66, 151.05, 136.02, 135.37, 127.11, 126.41, 123.54, 123.40 (bipyC), 44.98 (CH₂)

³¹P NMR (121.52MHz, DMSO-d₆) δ_P: -143.09 (septet, J=711Hz, PF₆)

¹⁹F NMR (282.46MHz, DMSO-d₆) δ_F: -70.52 (d, J=711Hz, PF₆)

ESIMS(m/z): 531.74 [M]²⁺

Elemental Analysis for C₄₆H₄₀N₁₀S₄Ru₂P₂F₁₂·2H₂O:

Expected: C 39.77, H 3.19, N 10.08

Found: C 39.76, H 3.18, N 9.99

Dinuclear *m*-xylene-spaced (R=cyclohexyl) Ru(II) Bis(2,2'-bipyridine) Dithiocarbamate Hexafluorophosphate (108)

Potassium *m*-xylyl-spaced bis-dithiocarbamate salt (R=cyclohexyl) (**24**) (0.05g, 0.095mmol) and Ru(bipy)₂Cl₂ (0.10g, 0.19mmol) were combined in an analogous method as (**107**). Precipitate with NH₄PF₆ (0.035g, 0.21mmol) yielded a purple solid which was dried *in vacuo*. (0.146g, 98%)

¹H NMR (300MHz, CD₃CN) δ_H: 9.69 (2H, m, bipyH⁶), 9.52 (2H, m, bipyH⁶), 8.45 - 8.24 (8H, m, bipyH³ & bipyH^{6'}), 8.02 (6H, m, bipyH⁴ & ArH), 7.83 - 7.66 (12Hm, bipyH^{5'} & bipyH⁵ & bipyH^{3'}), 7.30 - 7.07 (4H, t, J=6.6Hz, bipyH^{4'} & ArH), 4.88 (6H, m, ArCH₂ & CH), 1.85 - 1.48 (8H, m, CH₂), 1.36 - 0.94 (12H, m, CH₂)

¹³C NMR (75.48MHz, CD₃CN) δ_C: 216.94 (CS₂), 159.59, 159.34, 155.78, 155.59, 153.32, 153.04, 139.23, 137.35, 137.27, 136.64, 128.26, 127.64, 127.56, 126.85 (bipyC & ArC), 61.12 (ArCH₂), 50.03 (CH), 31.50, 26.92, 26.43 (CH₂)

³¹P NMR (121.52MHz, DMSO-d₆) δ_P: -143.21 (septet, J=712Hz, PF₆)

¹⁹F NMR (282.46MHz, DMSO-d₆) δ_F: -70.56 (d, J=712Hz, PF₆)

ESIMS(m/z): 638.45 [M]²⁺

Dinuclear *p*-xylene-spaced (R=*n*-butyl) Ru(II) Bis(2,2'-bipyridine) Dithiocarbamate Hexafluorophosphate (109)

Potassium *p*-xylene-spaced bis-dithiocarbamate salt (**106**) (0.25g, 0.52mmol) and Ru(bipy)₂Cl₂ (0.60g, 1.15mmol) were reacted in an analogous method to (**107**). NH₄PF₆ (0.19g, 1.15mmol) was added, effecting precipitation of a purple solid which was filtered off and dried *in vacuo*. (0.72g, 91%)

¹H NMR (500MHz, CD₃CN) δ_H: 9.69 ((0.5)4H, m, bipyH⁶), 9.59 ((0.3)4H, d, J=9.5Hz, bipyH⁶), 9.69 ((0.2)4H, d, J=9.5Hz, bipyH⁶), 8.43 (4H, m, bipyH³), 8.32 (4H, m, bipyH^{6'}),

8.03 (4H, m, bipyH⁴), 7.82 - 7.66 (12H, m, bipyH⁵, H^{5'} & H³), 7.25 and 7.24 (4H, 2s, ArH), 7.16 (4H, m, bipyH^{4'}), 4.96 (4H, m, ArCH₂), 3.85 - 3.55 (4H, m, NCH₂), 1.61 (4H, m, CH₂), 1.29 (4H, m, CH₂), 0.87 (6H, m, CH₃)

¹³C NMR (74.58MHz, CD₃CN) δ_C : 214.62 (CS₂), 157.92, 157.89, 153.88, 153.79, 151.53, 151.46, 151.35, 135.65, 135.63, 135.34, 135.27, 134.97, 134.90, 127.58, 126.53, 126.49, 126.43, 125.95, 125.91, 125.87, 123.14, 122.98 (bipyC & ArC), 51.63, 51.52, 49.39, 49.19, 28.66, 28.61, 19.58 (CH₂), 13.02 (CH₃)

³¹P NMR (121.52MHz, CD₃CN) δ_P : -143.46 (septet, J=707Hz, PF₆)

¹⁹F NMR (282.46MHz, CD₃CN) δ_F : -73.02 (d, J=708Hz, PF₆)

ESIMS(m/z): 613.09 [M]²⁺

Elemental Analysis for C₅₈H₅₈N₁₀S₄Ru₂P₂F₁₂:

Expected: C 45.97, H 3.86, N 9.24

Found: C 45.97, H 4.36, N 9.34

Tetranuclear Ru(II) Bis(2,2'-bipyridine) Dithiocarbamate-functionalised Resorcinarene Cavitand (110)

Tetra-potassium {(butylaminodithiocarbamate)methyl resorcinarene} cavitand (**92**) (0.36g, 0.22mmol) and Ru(bipy)₂Cl₂ (0.56g, 1.08mmol), were combined in EtOH/H₂O (2:1, 100ml) and refluxed under N₂ for 18 hours. The solvent was then removed under reduced pressure and the residue redissolved in the minimum amount of MeCN. The crude product was purified by column chromatography over Sephadex LH-20 eluted with MeCN/MeOH (95:5), collecting the second purple band. (0.64g, 89%)

Characterisation of Crude Product:

¹H NMR (500MHz, CD₃CN) δ_H : 9.64 (8H, m, bipyH⁶), 8.47 - 8.23 (16H, m, bipyH³ & H^{6'}), 8.09 - 7.96 (8H, m, bipyH⁴), 7.83 - 7.64 (24H, m, bipyH⁵ & H^{5'}), 7.48 (8H, m, bipyH^{3'}), 7.19 -

7.09 (12H, m, bipyH⁴⁺ & ArH), 6.26 (4H, m, OCH₂O[H_{outer}]), 5.63 (4H, m, OCH₂O[H_{inner}]), 4.74 (12H, m, ArCH & ArCH₂), 3.41 - 3.28 (8H, m, NCH₂), 1.41 (40H, m(br), CH₂), 1.13 (8H, m, CH₂), 0.95 (12H, m, CH₃), 0.76 (12H, m, CH₃)

ESIMS(m/z): 777.9 [M]⁴⁺, 1048.9 [M+Cl]³⁺, 1590.9 [M+2Cl]²⁺

Unfortunately, addition of NH₄PF₆ (0.15g, 0.88mmol) resulted in the decomposition of the tetranuclear product.

Potassium Aza-15-crown-5-*N*-Dithiocarbamate (111)

Aza-15-crown-5 (0.50g, 2.28mmol) was dissolved in MeCN (100ml) and stirred at room temperature for 30 minutes. KOH (0.15g, 2.74mmol) was dissolved in 1ml of water and added to the solution and allowed to stir for a further 30 minutes. CS₂ (0.20g, 2.74mmol) was then added and the solution stirred for a further 18 hours. After this time the yellow solution was reduced in volume to 50ml and added dropwise to a stirred solution of Et₂O (250ml) yielding a white solid which was filtered off and dried *in vacuo*. (0.47g, 62%)

¹H NMR (300MHz, D₂O) δ_H: 4.13 (4H, t, J=6.0Hz, NCH₂), 3.78 (4H, t, J=6.0Hz, NCH₂CH₂), 3.57 (12H, s, OCH₂)

Elemental Analysis for C₁₁H₂₀NO₄S₂K.H₂O:

Expected: C 37.58, H 6.31, N 3.98

Found: C 37.39, H 6.22, N 4.07

Aza-15-crown-5-functionalised Ru(II) Bis(2,2'-bipyridine) Dithiocarbamate Hexafluorophosphate (112)

Potassium aza-15-crown-5-*N*-dithiocarbamate (111) (0.10g, 0.30mmol) and Ru(bipy)₂Cl₂ (0.16g, 0.30mmol) were dissolved in EtOH/H₂O (100ml, 2:1) and refluxed under N₂ for 48 hours. The solvent was then removed under reduced pressure and the residue dissolved in the

minimum amount of MeCN and was purified by column chromatography over Sephadex LH-20 eluted with MeCN, then with MeCN:MeOH (95:5) collecting the second fraction. The solvent was removed and the red solid dissolved in H₂O. To this solution NH₄PF₆ (0.06g, 0.35mmol) was added resulting in precipitation of a red solid, which was filtered off and dried *in vacuo*. (0.24g, 90%)

¹H NMR (300MHz, CDCl₃) δ_H: 9.54 (2H, d, J=5.7Hz, bipyH⁶), 8.33 (2H, d, J=8.1Hz, bipyH³), 8.20 (2H, d, J=8.1Hz, bipyH⁶), 8.16 (2H, t, J=7.5Hz, bipyH⁴), 7.64 (4H, m, bipyH⁵ & H⁵), 7.58 (2H, t, J=5.1Hz, bipyH³), 7.06 (2H, t, J=6.6Hz, bipyH⁴), 3.97 (4H, t, J=5.7Hz, NCH₂), 3.81 (4H, t, J=5.7Hz, NCH₂CH₂), 3.62 (12H, s, OCH₂)

¹³C NMR (75.43MHz, CDCl₃) δ_C: 214.23 (CS₂), 157.64, 157.44, 153.52, 150.72, 135.33, 134.79, 126.38, 125.65, 122.86, 122.65, (bipyC), 70.82, 70.31, 69.96, 68.11, 52.26 (CH₂)

ESIMS(m/z): 708.09 [M]⁺

Elemental Analysis for C₃₁H₃₆N₅O₄S₂RuPF₆·H₂O:

Expected: C 42.78, H 4.40, N 8.05

Found: C 42.88, H 4.61, N 8.11

Tetraethylene Glycol Ditosylate (113)

p-Toluenesulphonyl chloride (105g, 0.55mol) was dissolved in CH₂Cl₂ (150ml) and added dropwise to a stirred solution of tetraethylene glycol (48.5g, 0.25mol), NaOH (aq, 75g in 75ml of water), CH₂Cl₂ (250ml) and benzyltriethylammonium chloride (2.3g, 0.01mol). The solution was stirred at room temperature for 18 hours. The mixture was poured into H₂O (500ml) and the organic layer separated and washed with H₂O (3x400ml). The organic layer was dried over MgSO₄ and the solvent removed under reduced pressure producing a yellow oil. (118.2g, 94%)

^1H NMR (300MHz, CDCl_3) δ_{H} : 7.79 (4H, d, $J=8.1$ Hz, ArH), 7.33 (4H, d, 8.1 Hz, ArH), 4.15 (4H, m, TsOCH_2), 3.67 (4H, m, OCH_2), 3.56 (8H, s, OCH_2), 2.44 (6H, s, CH_3)

4-Formyl-benzo-15-crown-5 (114)

Water (4ml) was added to NaOH (7.90g, 0.198mol) with stirring, until no more NaOH dissolved. Butan-1-ol (250ml) was added and the mixture purged with N_2 . 3,4-dihydroxybenzaldehyde (13.00g, 94.1mmol) was added forming a yellow suspension and the mixture refluxed for 30 minutes. Tetraethylene glycol ditosylate (**113**) (47.36g, 94.1mmol) dissolved in CH_2Cl_2 (100ml) was added dropwise to the suspension at reflux over a period of 2 hours. Reflux was continued for 14 hours under N_2 . The suspension was cooled to room temperature, filtered and the silvery/yellow residue washed with CH_2Cl_2 (3x50ml). The filtrate was evaporated to yield a brown oil which was redissolved in CH_2Cl_2 (100ml). Celite® (~10g) was added to the stirred solution and diethyl ether (300ml) added. The brown powdery solid was filtered off. The solid was extracted (Soxhlet) with hexane (800ml) for 4 days. The hexane was removed to give a yellow solid that was recrystallised from isopropyl ether to give white crystals, which were filtered and dried *in vacuo*. (4.04g, 14%)

^1H NMR (300MHz, CDCl_3) δ_{H} : 9.83 (1H, s, CHO), 7.43 (1H, dd, $J=8.1\text{Hz}$ $J'=1.8\text{Hz}$, ArH^5), 7.38 (1H, d, $J=1.8\text{Hz}$, ArH^3), 6.93 (1H, d, $J=8.1\text{Hz}$, ArH^6), 4.19 (4H, m, ArOCH_2), 3.92 (4H, m, OCH_2), 3.76 (8H, m, OCH_2)

Elemental Analysis for $\text{C}_{15}\text{H}_{20}\text{O}_6$:

Expected: C 60.77, H 6.88

Found: C 60.74, H 6.90

(3,4-15-Crown-5)-N-hexyl-benzylamine (115)

4-Formyl-benzo-15-crown-5 (0.20g, 0.68mmol) and *n*-hexylamine (0.07g, 0.68mmol) were dissolved in toluene (100ml) and refluxed for 2 hours using Dean-Stark apparatus and the solvent removed to yield an orange oil. This was dissolved in MeOH (100ml), NaBH₄ (1.00g) was added cautiously and the solution stirred for 1 hour. HCl (aq, 1M) was added until pH=1 and then KOH (aq, 1M) until pH=11. The product was extracted into CH₂Cl₂ (3x50ml) and dried over K₂CO₃. Filtration followed by removal of the solvent under reduced pressure yielding a yellow oil which was dried *in vacuo*. (0.24g, 92%)

¹H NMR (300MHz, CDCl₃) δ_{H} : 7.01 (1H, s, ArH²), 6.85 (1H, d, J=6.0Hz, ArH⁶), 6.80 (1H, d, J=6.0Hz, ArH⁵), 4.19 (4H, m, ArOCH₂), 3.92 (4H, m, OCH₂), 3.76 (8H, m, OCH₂), 2.62 (2H, m, NHCH₂), 1.56 (2H, m, NHCH₂CH₂), 1.30 (6H, m, CH₂), 0.89 (3H, t, J=6.9Hz, CH₃)

**Benzo-15-crown-5-functionalised Ru(II) Bis(2,2'-bipyridine) Dithiocarbamate
Hexafluorophosphate (116)**

(3,4-15-Crown-5)-N-hexyl-benzylamine (**115**) (0.18g, 0.47mmol) was dissolved in THF/H₂O (2:1, 50ml), KOH (0.04g, 0.71mmol) was added and the solution stirred for 10 minutes. Addition of CS₂ (0.05g, 0.71mmol) gave a yellow solution, which was stirred for 1 hour. The solvent was then removed under reduced pressure to generate the off-white potassium dithiocarbamate salt.

The salt was combined with Ru(bipy)₂Cl₂ (0.25g, 4.81mmol) in EtOH/H₂O (100ml, 2:1) and the purple solution refluxed for 18 hours under N₂. The solvent was subsequently removed under reduced pressure and the residue dissolved in the minimum amount of MeCN. Purification was achieved by column chromatography over Sephadex LH-20 eluted initially with MeCN, then with MeCN:MeOH (95:5) collecting the second fraction. The solvent was removed and the red solid was dissolved in H₂O. To this solution NH₄PF₆ (0.06g, 0.35mmol)

was added to resulting in precipitation of a red solid, which was filtered off and dried *in vacuo*. (0.36g, 74%)

^1H NMR (300MHz, DMSO- d_6) δ_{H} : 9.56 and 9.51 (2H, 2d, $J=8.1\text{Hz}$, bipyH 6), 8.73 (2H, d, $J=8.1\text{Hz}$, bipyH 3), 8.63 (2H, d, $J=7.8\text{Hz}$, bipyH $^{6'}$), 8.16 (2H, m, bipyH 4), 7.86 (4H, m, bipyH 5 & H 5), 7.68 (2H, m, bipyH 4), 7.29 (2H, m, bipyH $^{4'}$), 6.92 - 6.86 (2H, m, ArH), 6.81 (1H, s, ArH) 4.94 and 4.77 (2H, 2d, $J=15.3\text{Hz}$, ArCH $_2$), 4.12 (4H, ArOCH $_2$), 3.94 (2H, m, NCH $_2$), 3.78 (4H, s, OCH $_2$), 3.63 (8H, s, OCH $_2$), 1.57 (2H, m, NCH $_2$ CH $_2$), 1.14 (6H, s, CH $_2$), 0.75 (3H, t, $J=6.6\text{Hz}$, CH $_3$)

^{13}C NMR (75.43MHz, DMSO- d_6) δ_{C} : 213.08 (CS $_2$), 157.77, 157.44, 157.58, 157.56, 153.48, 153.40, 151.10, 148.48, 148.11, 135.94, 135.29, 128.29, 126.87, 126.39, 123.59, 123.42, 120.46, 113.51, 113.12 (bipyC & ArC), 70.32, 69.45, 68.68, 68.39, 68.25 (OCH $_2$), 51.33, 48.69, 30.77, 26.25, 25.80, 22.06 (CH $_2$), 13.88 (CH $_3$)

ESIMS(m/z): 870.24 $[\text{M}]^+$

Elemental Analysis for C $_{42}$ H $_{50}$ NO $_5$ S $_2$ RuPF $_6$.H $_2$ O:

Expected: C 48.83, H 5.07, N 6.78

Found: C 48.62, H 4.83, N 7.26

***N*-*t*-Butyloxycarbonyl-protected Iminodiacetic Acid (117)**

To a heterogeneous mixture of iminodiacetic acid, (13.34g, 0.10mol) in dioxane (200ml) was added an aqueous solution of NaOH (4%, 200ml). When a homogeneous mixture formed, di-*t*-butyldicarbonate (24.0g, 0.11mol) was added, forming a cloudy suspension which gradually cleared over 2 - 3 hours. The reaction mixture was stirred at room temperature for 72 hours, then washed twice with diethyl ether, acidified by the addition of HCl (10%, 100ml) and extracted with EtOAc (3x150ml). The organic phase was washed with brine (3x100ml), and dried over K $_2$ CO $_3$. Filtration followed by evaporation afforded a colourless oil which was

crystallised from EtOAc/hexane. The product was collected as large colourless crystals.
(25.30g, 93%)

^1H NMR (300MHz, DMSO- d_6) δ_{H} : 12.53 (2H, s(br), CO_2H), 3.89 and 3.85 (4H, 2s, CH_2), 1.33 (9H, s, CH_3)

^{13}C NMR (75.43MHz, CDCl_3) δ_{C} : 170.97, 154.56 (CO), 79.67 ($\text{C}(\text{CH}_3)_3$) 49.78, 49.27 (CH_2), 28.08 (CH_3)

ESIMS(m/z): 272.02 $[\text{M}+\text{K}]^+$

Elemental Analysis for $\text{C}_9\text{H}_{15}\text{NO}_6$:

Expected: C 46.35, H 6.48, N 6.01

Found: C 46.42, H 6.45, N 6.05

***N*-*t*-Butyloxycarbonyl-protected Bis-*n*-butylamide (118)**

N-*t*-Butyloxycarbonyl-protected iminodiacetic acid (**117**) (1.16g, 5.0mmol), EDCI (2.10g, 11.0mmol) and HOBt (1.40g, 11.0mmol) were stirred in DMF (40ml) under N_2 for 1 hour. *n*-Butylamine (0.80g, 11mmol) was added and stirred for 18 hours. The solution was poured onto HCl (aq, 10%, 100ml) and extracted using EtOAc (200ml). The organic layer was washed with HCl (10%, 100ml), KOH (10%, 2x100ml) and dried over K_2CO_3 . Filtration followed by solvent removal afforded a colourless oil, which was dried *in vacuo*. (1.43g, 83%)

^1H NMR (300MHz, CDCl_3) δ_{H} : 8.08 (1H, s(br), NH), 6.82 (1H, s(br), NH), 3.82, 3.79 (4H, 2s, COCH_2), 3.25 (4H, m, NHCH_2), 1.48 (4H, m, NHCH_2CH_2), 1.40 (9H, s, Bu^t), 1.33 (4H, m, CH_2CH_3), 0.90 (3H, t, $J=7.5\text{Hz}$, CH_3)

^{13}C NMR (75.48MHz, CDCl_3) δ_{C} : 169.78 (CONH), 154.90 (OCO), 81.16 ($\text{C}(\text{CH}_3)_3$), 53.98, 53.41(NCH_2), 39.29, 39.17, 31.42, 31.23 (CH_2), 28.00 ($\text{C}(\text{CH}_3)_3$), 20.00 (CH_2), 13.62 (CH_3)

ESIMS(m/z): 344.29 $[M+H]^+$, 367.38 $[M+Na]^+$, 382.26 $[M+K]^+$, 709.53 $[2M+Na]^+$, 725.52 $[2M+K]^+$

Elemental Analysis for $C_{17}H_{33}N_3O_4 \cdot H_2O$:

Expected: C 56.47, H 9.76, N 11.63

Found: C 56.58, H 9.94, N 12.32

***N*-*t*-Butyloxycarbonyl-protected Bis-*n*-hexylamide (119)**

An analogous method to that used in the preparation of (118) was undertaken, using (117) (1.00g, 4.29mmol), EDCI (1.65g, 8.58mmol), HOBT (1.16g, 8.58mmol) and *n*-hexylamine (0.87g, 8.58mmol). (1.70g, 100%)

1H NMR (300MHz, $CDCl_3$) δ_H : 8.09 (1H, m, NH), 7.00 (1H, m, NH), 3.82 and 3.79 (4H, 2s, NCH_2), 3.24 (4H, m, $NHCH_2$), 1.50 (4H, m, $NHCH_2CH_2$), 1.41 (9H, s, Bu^t), 1.33 (12H, m, (CH_2)), 0.86 (6H, t, $J=6.9Hz$, CH_3)

^{13}C NMR (75.48MHz, $CDCl_3$) δ_C : 169.24 (CONH), 154.67 (OCO), 81.31 ($C(CH_3)_3$), 54.26, 53.64 (NCH_2), 39.87, 39.70 ($NHCH_2$), 31.64, 31.60, 29.63, 29.45 (CH_2), 28.29 ($C(CH_3)_3$), 26.81, 26.70, 22.73 (CH_2), 14.23 (CH_3)

ESIMS(m/z): 400.3 $[M+H]^+$, 422.3 $[M+Na]^+$, 821.6 $[2M+Na]^+$

Elemental Analysis for $C_{21}H_{41}N_3O_4 \cdot \frac{1}{4}H_2O$:

Expected: C 62.42, H 10.35, N 10.40

Found: C 62.43, H 10.11, N 10.40

***N*-butyl-2-(butylcarbamoylmethyl-amino)-acetamide (120)**

Boc-protected bis-amide (118) (1.38g, 4.2mmol) was dissolved in CH_2Cl_2 (100ml), TFA (10ml) added and the resulting solution stirred for 18 hours. KOH was carefully added to the solution until pH=10. The organic layer was separated, washed with water (2x100ml) and

dried over K_2CO_3 . The solvent was removed under reduced pressure yielding a white solid, which was dried *in vacuo*. (0.95g, 93%)

1H NMR (300MHz, $CDCl_3$) δ_H : 6.50 (2H, s(br), CONH), 3.25 (8H, m, $NHCH_2$), 1.48 (4H, m, $NHCH_2CH_2$), 1.32 (4H, m, CH_2CH_3), 0.90 (6H, t, $J=7.2Hz$, CH_3)

^{13}C NMR (75.48MHz, $CDCl_3$) δ_C : 170.72 (CO), 52.53, 38.92, 31.60, 20.03 (CH_2), 13.69 (CH_3)

ESIMS(m/z): 244.21 $[M+H]^+$

Elemental Analysis for $C_{12}H_{25}N_3O_2 \cdot \frac{1}{10}CH_2Cl_2$:

Expected: C 58.10, H 10.13, N 16.50

Found: C 58.33, H 10.00, N 16.35

N-hexyl-2-(hexylcarbamoylmethyl-amino)-acetamide (**121**)

An analogous method to the preparation of (**120**) was undertaken using Boc-protected bis-amide (**119**) (1.40g, 3.50mmol). (1.03g, 98%)

1H NMR (300MHz, $CDCl_3$) δ_H : 6.49 (2H, s(br), CONH), 3.25 (8H, m, $NHCH_2$), 1.51 (4H, m, $NHCH_2CH_2$), 1.32 (12H, m, CH_2), 0.89 (6H, t, $J=6.6Hz$, CH_3)

^{13}C NMR (75.48MHz, $CDCl_3$) δ_C : 170.22 (CO), 52.72, 39.44, 31.62, 29.78, 26.79, 22.75 (CH_2), 14.25 (CH_3)

ESIMS(m/z): 300.3 $[M+H]^+$, 322.3 $[M+Na]^+$, 338.2 $[M+K]^+$, 599.5 $[2M+H]^+$, 821.5 $[2M+Na]^+$, 637.5 $[2M+K]^+$

Elemental Analysis for $C_{16}H_{33}N_3O_2 \cdot \frac{3}{4}CH_2Cl_2$:

Expected: C 55.49, H 9.13, N 11.60

Found: C 55.81, H 9.13, N 11.50

Potassium Dithiocarbamate-Functionalised Bis-Amide (R = *n*-butyl) (122)

(**120**) (0.95g, 3.9mmol) and KOH (0.22g, 3.9mmol) were dissolved in THF:H₂O (2:1, 100ml) and stirred at room temperature for 30 minutes. CS₂ (0.30g, 3.9mmol) was added and the yellow solution stirred for a further 2 hours. After this time the solvent was removed under reduced pressure and dried *in vacuo* affording an off-white solid. (1.17g, 84%)

¹H NMR (300MHz, DMSO-d₆) δ_H: 8.19 (2H, s(br), NH), 4.32 (4H, m, COCH₂), 3.47 (4H, m, NHCH₂), 1.53 (4H, m, NHCH₂CH₂), 1.36 (4H, m, CH₂CH₃), 0.91 (6H, t, J=7.2Hz, CH₃)

¹³C NMR (75.48MHz, DMSO-d₆) δ_C: 217.37 (CS₂), 169.46 (CO), 59.58, 31.16, 30.66, 19.51 (CH₂), 13.69 (CH₃)

Potassium Dithiocarbamate-Functionalised Bis-Amide (R = *n*-hexyl) (123)

Synthesised by an analogous method to that of (**122**) using (**121**) (0.66g, 2.2mmol) yielding an off-white solid. (0.72g, 79%)

¹H NMR (300MHz, DMSO-d₆) δ_H: 8.37 (2H, t, J=6.0Hz, NH), 4.55 (4H, s, NCH₂), 3.01 (4H, q, J=6.9Hz, NHCH₂), 1.36 (4H, m, NHCH₂CH₂), 1.22 (16H, m, CH₂), 0.83 (6H, t, J=6.9Hz, CH₃)

¹³C NMR (75.48MHz, DMSO-d₆) δ_C: 217.42 (CS₂), 169.56 (CO), 58.80, 50.59, 31.08, 29.04, 26.11, 22.11 (CH₂), 13.98 (CH₃)

Bis-amide-functionalised (R = *n*-butyl) Ru(II) bis(2,2'-bipyridine) Dithiocarbamate Complex Hexafluorophosphate Salt - Receptor (124)

Potassium dithiocarbamate-functionalised bis-amide (R = *n*-butyl) (**122**) (0.25g, 0.68mmol) and Ru(bipy)₂Cl₂ (0.35g, 0.68mmol) were combined in EtOH/H₂O (2:1, 50ml) and refluxed under N₂ for 18 hours. The solvent was then removed under reduced pressure and the residue redissolved in the minimum amount of MeCN. The crude product was purified by column

chromatography over Sephadex LH-20 eluted with MeCN/MeOH (95:5), collecting the second purple band. The solvent was removed and the residue redissolved in H₂O/MeOH (99:1). NH₄PF₆ (0.08g, 0.86mmol) was added, effecting precipitation of a purple solid which was collected and dried *in vacuo*. (0.33g, 54%)

¹H NMR (300MHz, CDCl₃) δ_H: 9.49 (2H, d, J=5.1Hz, bipyH⁶), 8.27 (2H, d, J=8.1Hz, bipyH³), 8.16 (2H, d, J=8.1Hz, bipyH^{6'}), 7.93 (2H, dt, J=7.8Hz, J'=1.5Hz, bipyH⁴), 7.86 (2H, t(br), J=5.7Hz, NH), 7.67 (2H, dt, J=7.5Hz, J'=1.5Hz, bipyH^{5'}), 7.59 (4H, m, bipyH⁵ & H^{3'}), 7.05 (2H, t, J=6.6Hz, bipyH^{4'}), 4.29 (4H, m, COCH₂), 3.14 (4H, m, NHCH₂), 1.37 (4H, m, NHCH₂CH₂), 1.23 (4H, m, CH₂CH₃), 0.78 (6H, t, J=6.9Hz, CH₃)

¹³C NMR (75.48MHz, CDCl₃) δ: 218.00 (CS₂), 167.22 (CO), 158.03, 157.63, 154.43, 151.92, 151.13, 135.67, 135.03, 126.62, 125.93, 122.88 (bipyC), 56.28 (NCH₂), 39.74, 31.43, 29.14, 26.48, 22.51 (CH₂), 14.02 (CH₃)

³¹P NMR (121.52MHz, CDCl₃) δ_P: -143.18 (septet, J=713Hz, PF₆)

¹⁹F NMR (282.46MHz, CDCl₃) δ_F: -74.41 (d, J=712Hz, PF₆)

ESIMS(m/z): 732.1 [M]⁺

Elemental Analysis for C₃₃H₄₀N₇O₂S₂RuPF₆·H₂O:

Expected: C 44.29, H 4.73, N 10.96

Found: C 44.54, H 5.12, N 10.79

Bis-amide-functionalised (R = *n*-hexyl) Ru(II) bis(2,2'-bipyridine) Dithiocarbamate Complex Hexafluorophosphate Salt - Receptor (125)

Potassium dithiocarbamate-functionalised bis-amide (R = *n*-hexyl) (**123**) (0.25g, 0.60mmol) was heated under reflux with Ru(bipy)₂Cl₂ (0.31g, 0.60mmol) in EtOH/H₂O (1:1, 100ml) for 18 hours. The solution was evaporated to dryness and the residue dissolved in H₂O. To this NH₄PF₆ (0.15g, 0.92mmol) was added resulting in the precipitation of a purple solid which

was collected and washed thoroughly with H₂O and diethyl ether and dried *in vacuo*. (0.37g, 66%)

¹H NMR (300MHz, CDCl₃) δ_H: 9.48 (2H, d, J=5.7Hz, bipyH⁶), 8.27 (2H, d, J=8.1Hz, bipyH³), 8.16 (2H, d, J=8.1Hz, bipyH^{6'}), 7.93 (2H, dt, J=7.8Hz, J'=1.5Hz, bipyH⁴), 7.85 (2H, t, J=5.4Hz, NH), 7.67 (2H, dt, J=7.5Hz, J'=1.5Hz, bipyH^{5'}), 7.58 (4H, m, bipyH⁵ & H^{3'}), 7.05 (2H, t, J=7.2Hz, bipyH^{4'}), 4.28 (4H, m, COCH₂), 3.13 (4H, m, NHCH₂), 1.39 (4H, m, NHCH₂CH₂), 1.37 (12H, m, CH₂), 0.77 (6H, t, J=6.9Hz, CH₃)

¹³C NMR (75.48MHz, CDCl₃) δ_C: 218.55 (CS₂), 167.23 (CO), 158.02, 157.64, 154.43, 151.12, 135.67, 135.03, 126.60, 125.91, 122.87, 122.80 (bipyC), 56.28, 39.74, 31.43, 29.14, 26.48, 22.51 (CH₂), 14.02 (CH₃)

³¹P NMR (121.52MHz, CDCl₃) δ_P: -143.18 (septet, J=714Hz, PF₆)

¹⁹F NMR (282.46MHz, CDCl₃) δ_F: -72.81 (d, J=712Hz, PF₆)

ESIMS(m/z): 788.19 [M]⁺

Elemental Analysis for C₃₇H₄₈N₇O₂S₂RuPF₆:

Expected: C 47.63, H 5.19, N 10.51

Found: C 47.64, H 5.28, N 10.41

Bis-amide-functionalised (R = *n*-hexyl) Ru(II) bis(2,2'-bipyridine) Dithiocarbamate Complex Chloride Salt - Receptor (126)

An Amberlite IRA-400 column was saturated with aqueous NaCl. The column was then washed with H₂O (100ml), MeCN (100ml), Et₂O (100ml) and MeCN(100ml). Hexafluorophosphate salt (**125**) (0.050g, 0.054mmol) was dissolved in MeCN (5ml) and passed through the column collecting the purple band. The solvent was evaporated yielding a red solid. (0.040g, 91%)

^1H NMR (500MHz, CDCl_3) δ_{H} : 9.61 (2H, d, $J=6.0\text{Hz}$, bipy H^6), 9.12 (2H, t, $J=5.5\text{Hz}$, NH), 8.27 (2H, d, $J=8.0\text{Hz}$, bipy H^3), 8.18 (2H, d, $J=8.0\text{Hz}$, bipy H^6), 7.95 (2H, td, $J=7.5\text{Hz}$, $J'=1.5\text{Hz}$, bipy H^4), 7.71 (2H, td, $J=7.5\text{Hz}$, $J'=1.5\text{Hz}$, bipy $\text{H}^{5'}$), 7.63 (4H, m, bipy H^5 & $\text{H}^{3'}$), 7.07 (2H, t, $J=6.5\text{Hz}$, bipy $\text{H}^{4'}$), 4.45 (4H, s, COCH_2), 3.13 (4H, m, NHCH_2), 1.42 (4H, m, CH_2), 1.22 - 1.16 (12H, m, CH_2), 0.76 (6H, t, $J=7.0\text{Hz}$, CH_3)

^{13}C NMR (75.48MHz, CDCl_3) δ_{C} : 216.95 (CS_2), 166.95 (CO), 157.84, 157.47, 153.92, 151.02, 136.09, 135.43, 126.79, 126.43, 123.57, 123.46 (bipyC), 55.07, 30.97, 28.92, 25.91, 22.07 (CH_2), 13.89 (CH_3)

ESIMS(m/z): 788.19 $[\text{M}]^+$

Elemental Analysis for $\text{C}_{37}\text{H}_{48}\text{N}_7\text{O}_2\text{S}_2\text{RuCl}\cdot 2\text{H}_2\text{O}$:

Expected: C 51.70, H 6.10, N 11.41

Found: C 51.69, H 5.92, N 11.54

Isophthaloyl Bis-*n*-hexyl-amide (127)

Isophthaloyl chloride (2.05g, 10.10mmol) and NEt_3 (2.15g, 21.40mmol) were dissolved in CH_2Cl_2 (100ml, dry). *n*-Hexylamine (2.15g, 21.40mmol) was slowly added to the solution, which was stirred for 18 hours. The solvent was removed under reduced pressure, the residue dissolved in CH_2Cl_2 (50ml) and washed with H_2O (3x100ml). The organic layer was dried over K_2CO_3 and filtered. Dropwise addition of Et_2O afforded a white solid which was collected and dried *in vacuo*. (1.82g, 54%)

^1H NMR (500MHz, CDCl_3) δ_{H} : 8.14 (1H, s, ArH^2), 7.86 (2H, d, $J=8.0\text{Hz}$, $\text{ArH}^{4/6}$), 7.43 (1H, t, $J=8.0\text{Hz}$, ArH^5), 6.48 (2H, s(br), NH), 3.36 (4H, m, NHCH_2), 1.52 (4H, m, NHNC_2CH_2), 1.32 - 1.21 (12H, m, CH_2), 0.81 (6H, t, $J=7.0\text{Hz}$, CH_3)

^{13}C NMR (75.48MHz, CDCl_3) δ_{C} : 166.66 (CO), 134.95, 129.73, 128.84, 125.11 (ArC), 40.23, 31.45, 29.51, 26.63, 22.52 (CH_2), 13.99 (CH_3)

ESIMS(m/z): 333.39 [M+H]⁺, 374.43 [M+K]⁺, 665.69 [2M+H]⁺

Elemental Analysis for C₂₀H₃₂N₂O₂:

Expected: C 72.31, H 9.70, N 8.23

Found: C 72.25, H 8.87, N 8.87

Ru(II) Bis(2,2'-bipyridine) *O*-Ethylxanthate Hexafluorophosphate (128)

Potassium *O*-ethylxanthate (0.10g, 0.62mmol) and Ru(bipy)₂Cl₂ (0.25g, 0.48mmol) were refluxed for 18 hours in EtOH/H₂O (2:1, 50ml). The solvent was then removed under reduced pressure and the residue dissolved in H₂O (50ml). Addition of NH₄PF₆ (0.082g, 0.50mmol) resulted in the precipitation of a purple solid which was collected, washed with H₂O (3x50ml), Et₂O (3x50ml) and dried in vacuo. (0.29g, 89%)

¹H NMR (300MHz, CDCl₃) δ_H: 9.30 (2H, d, J=7.2Hz, bipyH⁶), 8.37 (2H, d, J=8.1Hz, bipyH³), 8.26 (2H, d, J=8.4Hz, bipyH^{6'}), 8.01 (2H, t, J=8.1Hz, bipyH⁴), 7.73 (2H, t, J=7.5Hz, bipyH^{5'}), 7.61 (4H, m, bipyH⁵ & H^{3'}), 7.13 (2H, t, J=6.6Hz, bipyH^{4'}), 4.59 (2H, m, CH₂), 1.42 (3H, t, J=6.9Hz, CH₃)

¹³C NMR (75.48MHz, CDCl₃) δ_C: 231.21 (CS₂), 157.88, 157.66, 154.09, 151.18, 136.22, 135.78, 126.87, 126.28, 123.29, 123.19 (bipyC), 67.99 (CH₂), 13.78 (CH₃)

³¹P NMR (121.52MHz, CDCl₃) δ_P: -143.18 (septet, J=712Hz, PF₆)

¹⁹F NMR (282.46MHz, CDCl₃) δ_F: -73.38 (d, J=712Hz, PF₆)

ESIMS(m/z): 535.02 [M]⁺

Elemental Analysis for C₂₃H₂₁N₄OS₂RuPF₆:

Expected: C 40.65, H 3.11, N 8.24

Found: C 40.79, H 3.36, N 8.25

Potassium *p*-Xylene-spaced Bis-Xanthate (129)

1,4-Benzenedimethanol (1.00g, 7.24mmol) was dissolved in THF/H₂O (2:1, 100ml) and KOH (1.02g, 17.80mmol) was added and the solution stirred at room temperature for 10 minutes. CS₂ (1.38g, 17.80mmol) was added and the solution stirred for a further 18 hours. The solvent was then removed under reduced pressure and the resulting solid suspended in MeCN (100ml) and stirred for 30 minutes. The off-white solid was collected and dried *in vacuo*. (1.20g, 50%)

¹H NMR (300MHz, D₂O) δ_H: 7.29 (4H, s, ArH), 5.26 (4H, s, CH₂)

Elemental Analysis for C₁₀H₈O₂S₄K₂·2H₂O:

Expected: C 29.83, H 3.00

Found: C 29.79, H 2.78

***N*-Butyl-3-hydroxy-acetamide (130)**

Methyl glycolate (2.00g, 22.2mmol) was refluxed with *n*-butylamine (20ml) in 1,4-dioxane (20ml) for 18 hours under N₂. The reaction mixture was evaporated to dryness giving an oily residue. The crude product was dissolved in hexane and cooled to -18°C, resulting in the formation of white crystals which were collected and washed with hexane (cold) and dried *in vacuo*. The crystals melted at room temperature to give a colourless oil. (2.68g, 92%)

¹H NMR (300MHz, CDCl₃) δ_H: 6.84 (1H, s(br), NH), 3.99 (2H, s, CH₂OH), 3.24 (2H, q, J=7.2Hz, CONHCH₂), 1.47 (2H, m, NHCH₂CH₂), 1.31 (2H, m, CH₂CH₃), 0.88 (3H, t, J=6.9Hz, CH₃)

¹³C NMR (75.48MHz, CDCl₃) δ_C: 172.59 (CO), 61.71, 38.55, 31.34, 19.87 (CH₂), 13.58 (CH₃)

ESIMS(m/z): 132.14 [M+H]⁺

Elemental Analysis for C₆H₁₃NO₂:

Expected: C 54.94, H 9.99, N 10.62

Found: C 54.58, H 10.07, N 10.42

Potassium Amide-functionalised Xanthate Ligand (131)

N-Butyl-3-hydroxy-acetamide (**130**) (0.61g, 4.65mmol) was dissolved in THF:H₂O (2:1, 100ml) and KOH (0.26g, 4.65mmol) was added and stirred until dissolved. CS₂ (0.35g, 4.65mmol) was then added and the yellow solution was stirred at room temperature for 18 hours. The solvent was then removed under reduced pressure and the resulting yellow solid was dried *in vacuo*. (0.92g, 81%)

¹H NMR (300MHz, DMSO-d₆) δ_H: 7.74 (1H, s(br), NH), 3.75 (2H, s, COCH₂), 3.06 (2H, q, J=5.7Hz, NHCH₂), 1.38 (2H, m, NHCH₂CH₂), 1.23 (2H, m, CH₂CH₃), 0.85 (3H, t, J=7.2Hz, CH₃)

¹³C NMR (75.48MHz, DMSO-d₆) δ_C: 215.66 (CS₂), 171.62 (CO), 61.37, 37.63, 31.36, 19.53 (CH₂), 13.71 (CH₃)

General Preparation of Mixed-Metal Dithiocarbamate Complexes (132) – (136)

One equivalent of bis-dithiocarbamate salt was dissolved in EtOH/H₂O (2:1) and refluxed under N₂ with one equivalent of Ru(bipy)₂Cl₂ for 18 hours. 1.5 equivalents of either Cu(OAc)₂, Ni(OAc)₂, KAuCl₄ or 1.0 equivalent of CoCl₃ were then added and the solution stirred for a further 18 hours. After this time, the purple solution was filtered and analysed by electrospray mass spectrometry.

(132)

Sodium piperazine-spaced 1,4-bis-dithiocarbamate salt (**105**) (0.05g, 0.21mmol), Ru(bipy)₂Cl₂ (106mg, 0.21mmol) and Cu(OAc)₂ (61mg, 0.30mmol) were combined as described above.

ESIMS(m/z): 682.25 [M]²⁺

(133)

Potassium *p*-xylene-spaced bis-dithiocarbamate salt **(106)** (50mg, 0.11mmol), Ru(bipy)₂Cl₂ (55mg, 0.11mmol) and Cu(OAc)₂ (36mg, 0.17mmol) were combined via the method described above.

ESIMS(m/z): 843.8 [M]²⁺

(134)

Potassium *p*-xylene-spaced bis-dithiocarbamate salt **(106)** (50mg, 0.11mmol), Ru(bipy)₂Cl₂ (55mg, 0.11mmol) and Ni(OAc)₂ (45mg, 0.17mmol) were combined via the method described above.

ESIMS(m/z): 841.56 [M]²⁺

(135)

Potassium *p*-xylene-spaced bis-dithiocarbamate salt **(106)** (50mg, 0.11mmol), Ru(bipy)₂Cl₂ (55mg, 0.11mmol) and KAuCl₄ (68mg, 0.17mmol) were combined via the method described above.

ESIMS(m/z): 607.1 [M]³⁺

(136)

Potassium *p*-xylene-spaced bis-dithiocarbamate salt **(106)** (50mg, 0.11mmol), Ru(bipy)₂Cl₂ (55mg, 0.11mmol) and CoCl₃ (26mg, 0.11mmol) were combined via the method described above.

ESIMS(m/z): 831.17 [M]³⁺

Appendices

Appendix One: Determination of Stability Constants

¹H NMR Spectroscopy

In all cases, tetra-*n*-butylammonium salts were used for titration experiments. These salts were stored in a desiccator under vacuum containing self-indicating silica

¹H NMR titrations were performed by the addition of a tetra-*n*-butylammonium salt of a given anion (0.5M) to a solution of the host (1×10^{-2} M). Spectra were recorded after the addition of 0.0, 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.4, 1.6, 1.8, 2.0, 2.2, 2.6, 3.0, 4.0, 5.0, 7.0 and 10.0 equivalents of the guest. (In the case of the titration between **(126)** and **(127)**, the last two points were not recorded due to solubility constraints.) The resulting data was analysed by the computer program EQNMR.

UV-vis Spectroscopy

UV-vis spectroscopy titrations were performed on a Perkin Lambda 6 spectrophotometer. In a typical titration, aliquots of guest (3×10^{-3} M) were added to 3mL of the host (1×10^{-5} M). Thirty aliquots were added such that 0.0, 0.2,...3.0, 3.5, 4.0,...10.0 equivalents of guest were present in solution. The resulting data was analysed by the computer program Specfit[©].

Appendix Two: Electrochemistry Procedure

Electrochemical studies were undertaken on a Princeton Applied Research potentiostat/galvanostat model 673 using a glassy carbon working electrode and an Ag/AgNO₃ reference electrode ($0.33\text{V} \pm 10\text{mV}$ vs SCE). Electrochemical solutions were degassed with either argon or nitrogen and maintained under a positive pressure for the duration of the experiment. Kermet diamond sprays (6μm, 1μm and 0.25μm) were used to polish the working electrode.

In general, cyclic voltammograms were recorded at a scan rate of 100mVs^{-1} and square wave voltammograms recorded at a scan frequency of 5Hz.

Appendix Three: EPR Experimental Procedures

EPR spectra of solutions of paramagnetic Cu(II) complexes were measured in dry CH_2Cl_2 at 293K and recorded with a Bruker ESP300E instrument (X-band). Parameters used were: modulation frequency, 100kHz; modulation amplitude, 2.0G; microwave power, 20mW; microwave frequency, 9.74 GHz.

Low temperature glassy spectra at 10K and in $\text{CD}_2\text{Cl}_2/\text{toluene-d}_8$, were measured with a Bruker ESP300E instrument (X-band) at Cardiff. Parameters used were: modulation frequency, 12.5kHz; modulation amplitude, 2.0G; microwave power, 0.02mW; microwave frequency, 9.47 GHz.

For the ENDOR spectra the latter spectrometer was fitted with a Bruker ESP360 DICE ENDOR unit and an ENI A-300 RF amplifier operating at a modulation frequency of 12.5kHz in a Bruker EN801 ENDOR cavity.

Appendix Four: Transmission Electron Microscopy Experimental Procedures

Transmission Electron Microscopy (TEM) was carried out at Johnson Matthey Technology Centre. Samples were dispersed in dichloromethane and dried on a TEM grid (Cu). The samples were examined in the Tecnai F20 Transmission Electron Microscope. A voltage of 200 kV, a C_2 aperture of 30 and 50 μm were used and the instrument was used in Bright Field (BF) and STEM (HAADF) modes

Appendix Five: Gold and Silver Nanoparticles

Nanoparticles are assumed to be spherical in shape, formed from the hexagonal packing of metal atoms. Sizes of the metallic core of the particles could be determined via TEM pictures. Particle sizes were measured from 120 nm x 120 nm micrographs. These sizes were categorised to the nearest nanometre and a median and standard deviation was calculated from this frequency distribution.

Formulae used for calculations:

$$\text{Volume of a sphere} = \frac{4}{3}\pi r^3$$

$$\text{Surface Area of a Sphere} = 4\pi r^2$$

$$\text{Covalent Radii: Au (1.34 \text{ \AA}), Ag (1.34 \text{ \AA}), S (1.04 \text{ \AA})^1$$

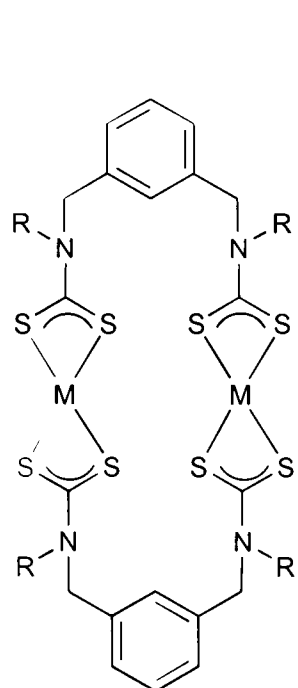
Surface area of a typical dithiocarbamate ligand (13 Å²)

The stabilising ligand is assumed to be adsorbed onto the metal core forming a monolayer protecting the metal core. The ratio of ligand:metal was calculated via elemental analysis (carbon, hydrogen, nitrogen and (where possible) the metal). The analysis of this ratio enabled an estimate of the “best fit” of ligand’s ratio.

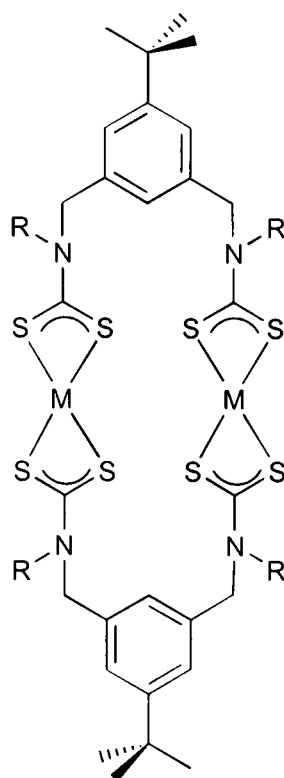
In addition, where the radius of a nanoparticle could be calculated via TEM, an approximate number of metal atoms could be calculated. If the ratio of metal:ligand was also known, an approximate “molecular mass” could be stated.

¹ J. D. Lee, *Concise Inorganic Chemistry* 5th Edition, Chapman & Hall, London, 1996.

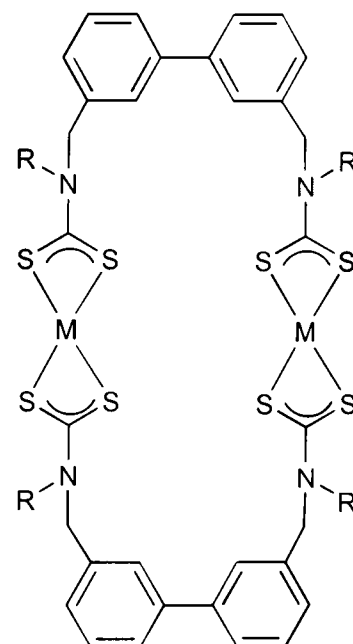
Appendix Six: Dithiocarbamate-Based Complexes from Chapter Two



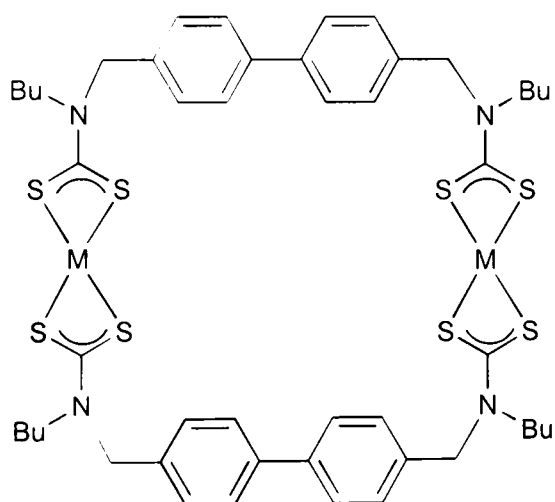
(7-M): R=Bu; M= Cu, Ni
(8-M): R=cyclohexyl;
M=Cu, Ni, Pd, Pt, Pb



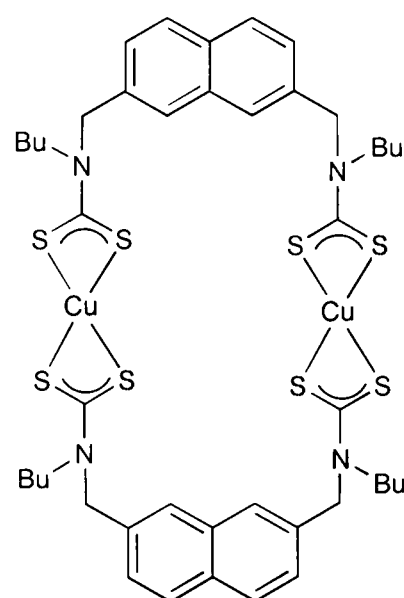
(10-M): R=Bu; M= Cu, Ni, Pd, Pt
(11-M): R=cyclohexyl;
M= Cu, Ni, Pd, Pt



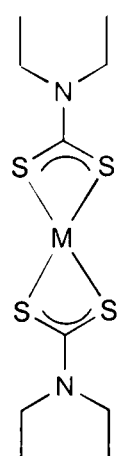
(14-M): R=Bu; M= Cu, Ni, Pd, Pt
(15-M): R=cyclohexyl;
M= Cu, Ni, Pd, Pt



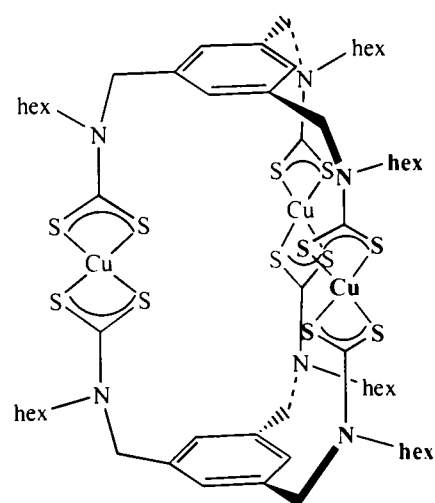
(15-M): M= Cu, Ni, Pd



(18-Cu)

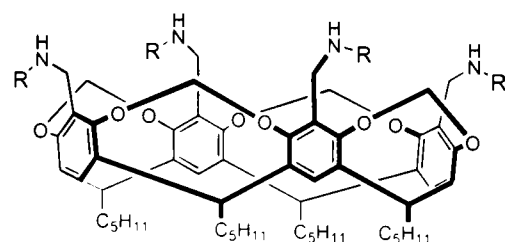


M = Cu (20)
M = Ni (21)
M = Pd (22)
M = Pt (23)

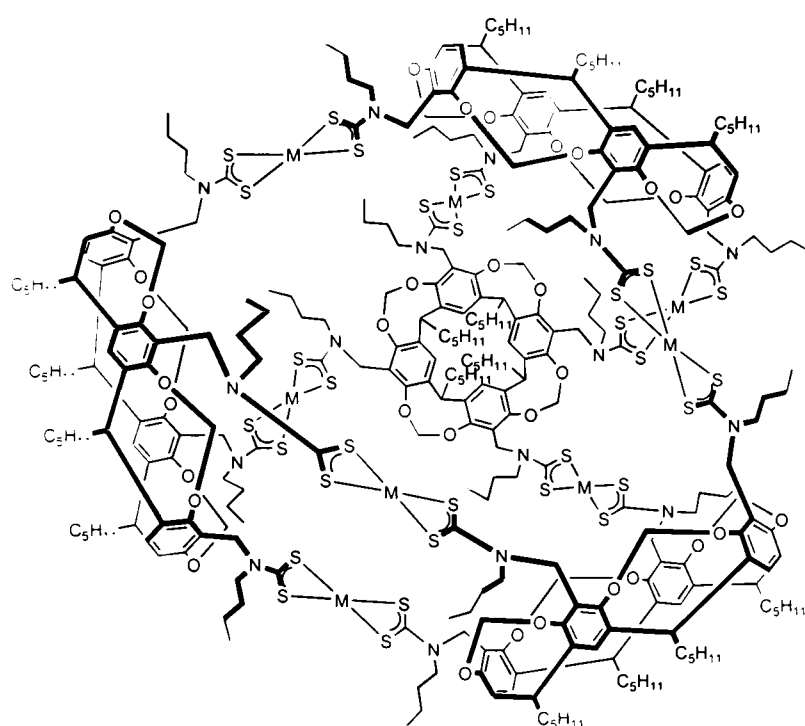


(38)

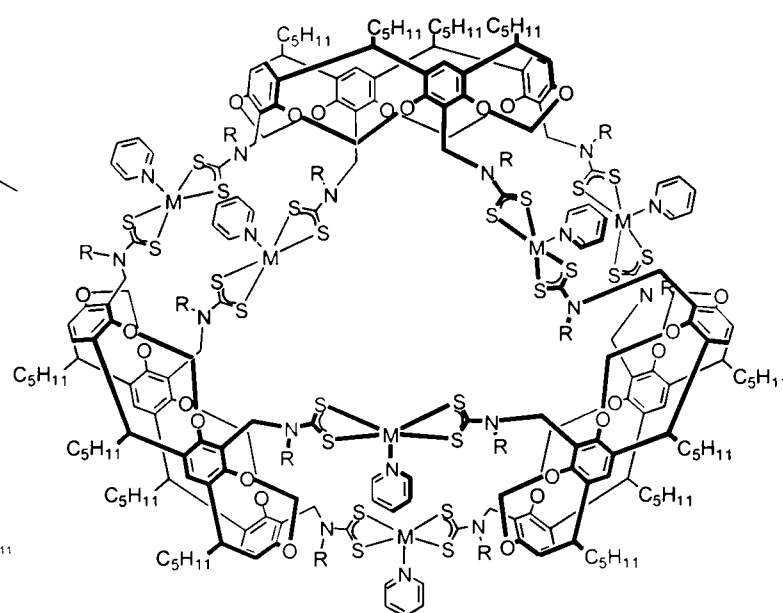
Selected Compounds from Chapter Three



- (43) R = *n*-butyl
 (44) R = *n*-hexyl
 (45) R = cyclohexyl
 (46) R = benzyl

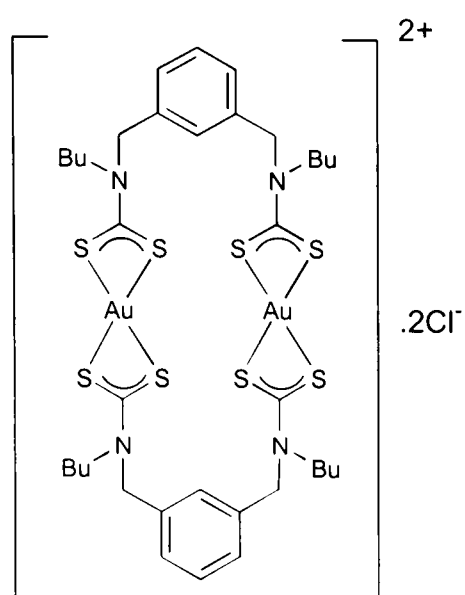


- (47) M = Cu
 (50) M = Ni
 (51) M = Pd

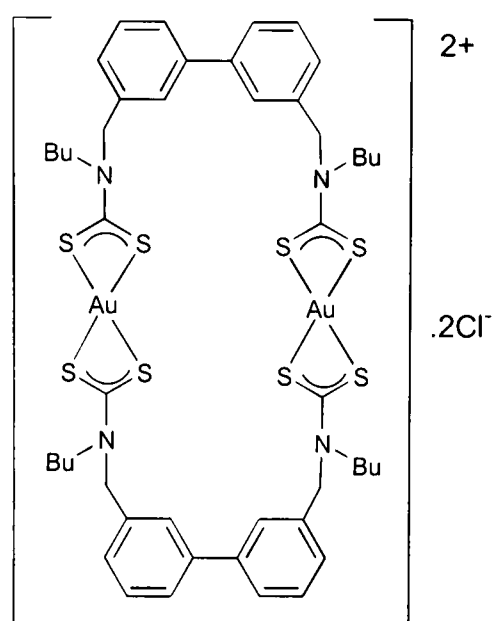


- (48) M = Zn, R = *n*-hexyl
 (49) M = Cd, R = *n*-hexyl

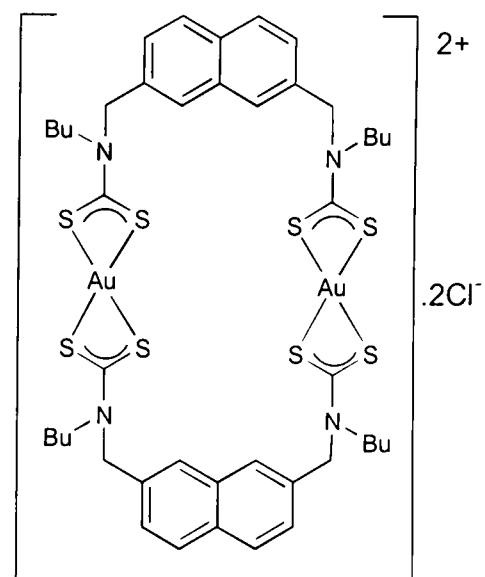
Selected Compounds from Chapters Four and Five



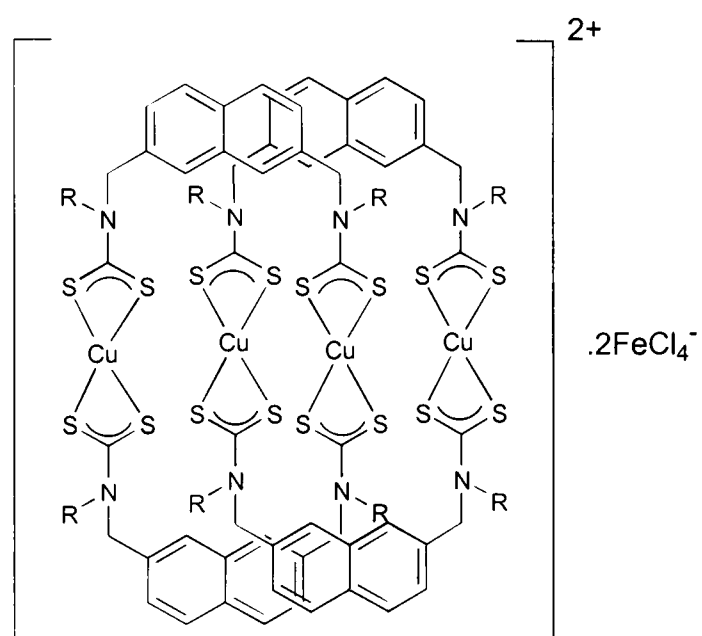
(55)



(56)

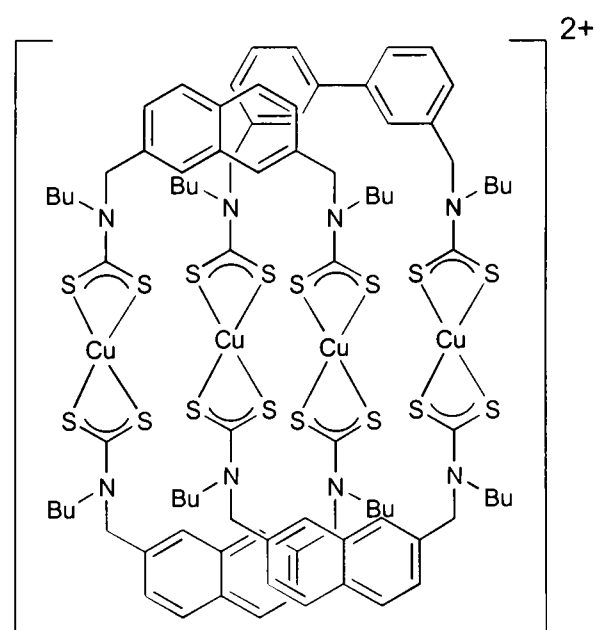


(57)

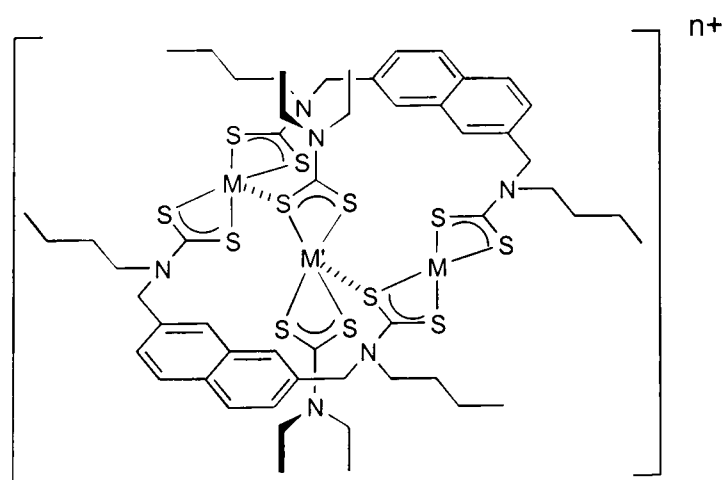


R = *n*-butyl (78)

R = *n*-hexyl (79)

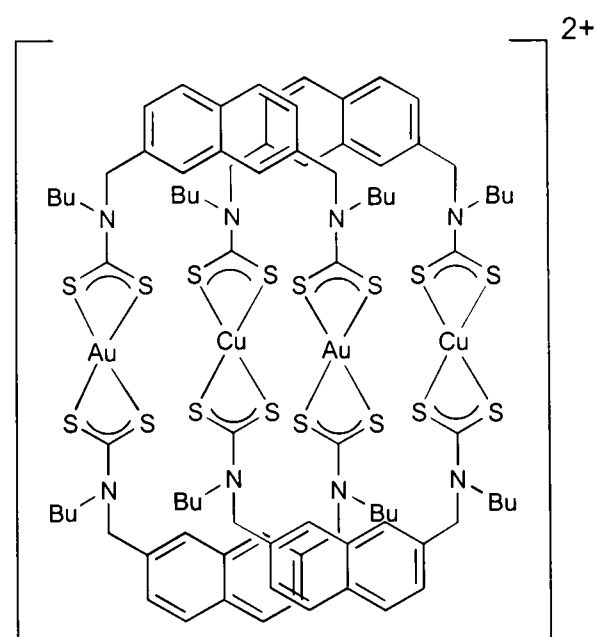


(80)



M = Au, M' = Cu, *n* = 2 (81)

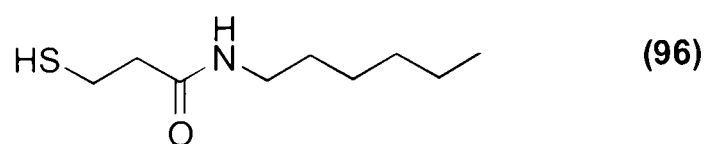
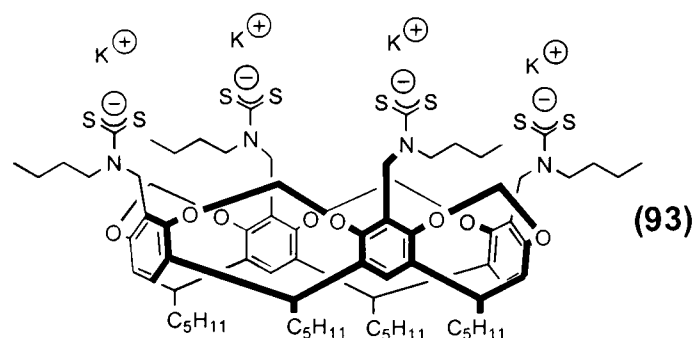
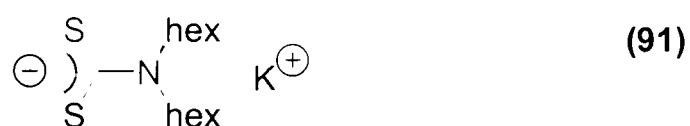
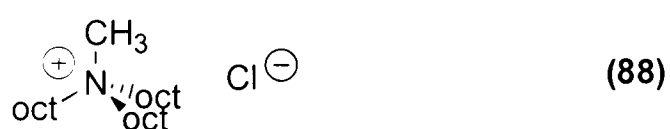
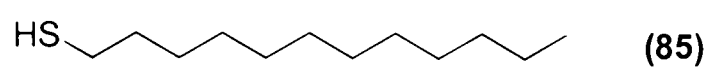
M = Cu, M' = Au, *n* = 1 (82)



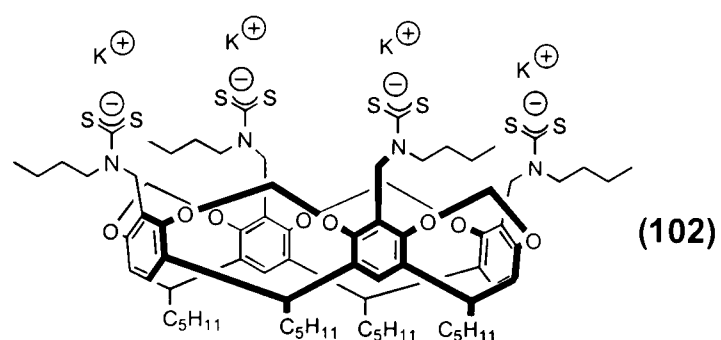
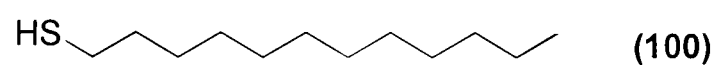
(84)

Selected Compounds from Chapter Six

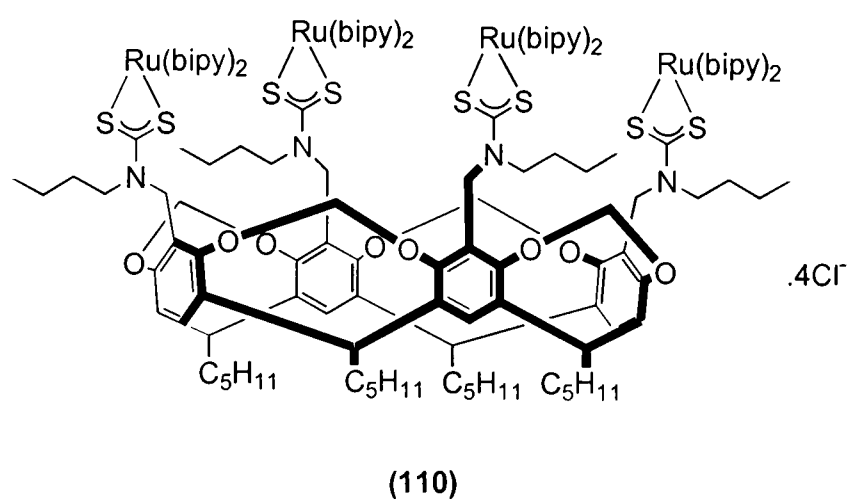
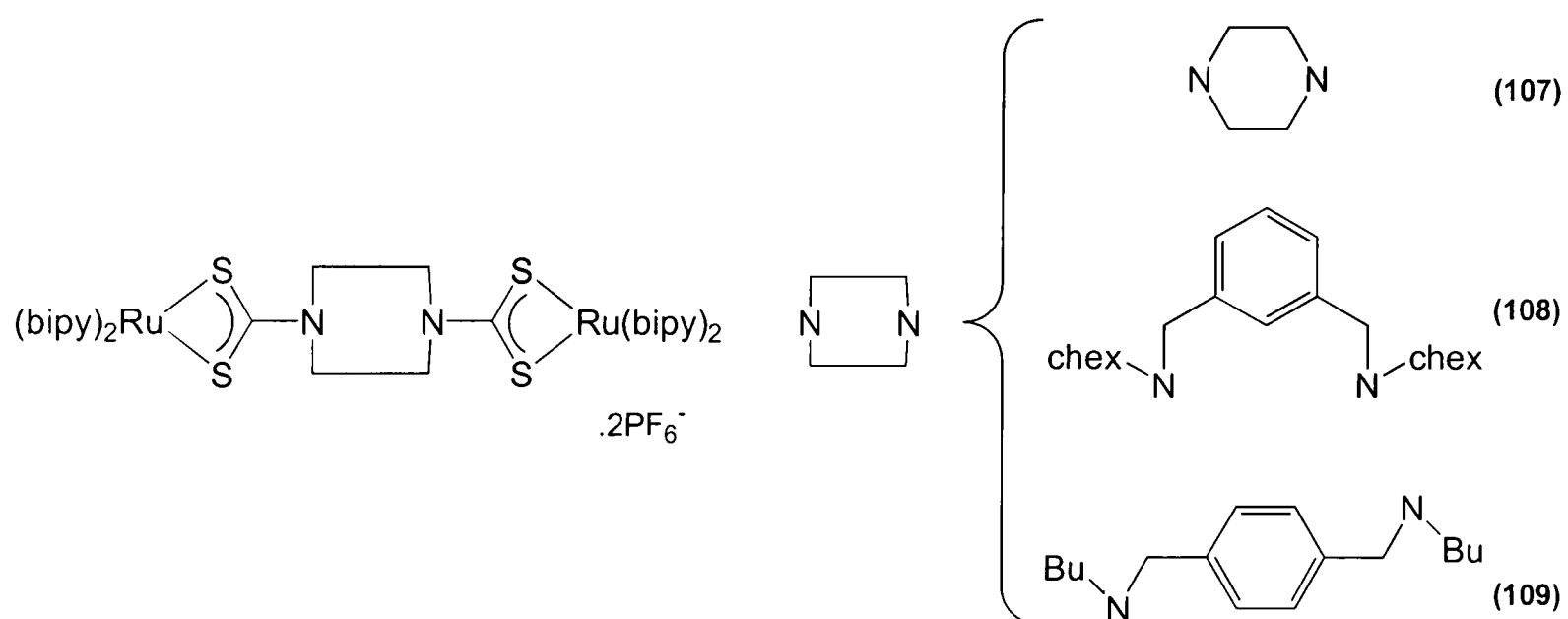
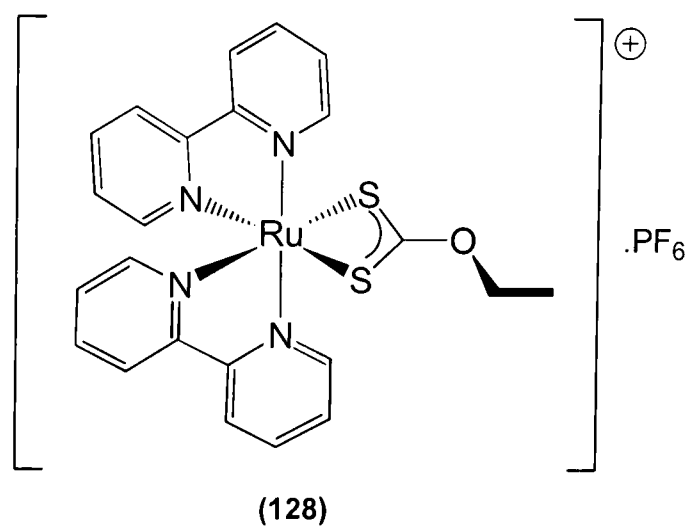
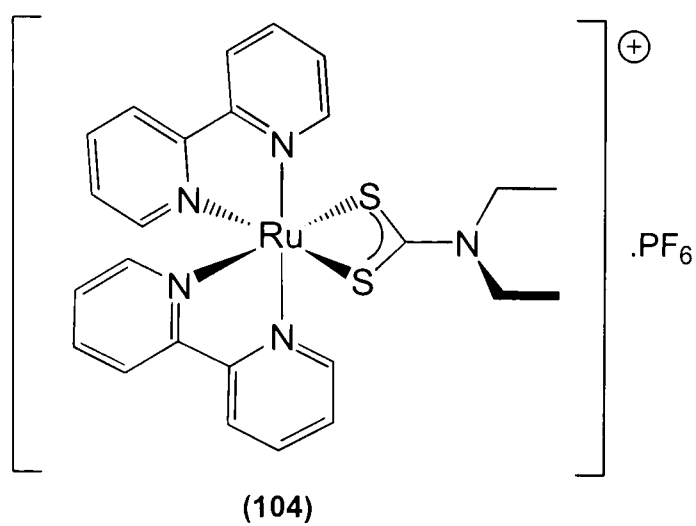
Gold Nanoparticles Stabilised by:



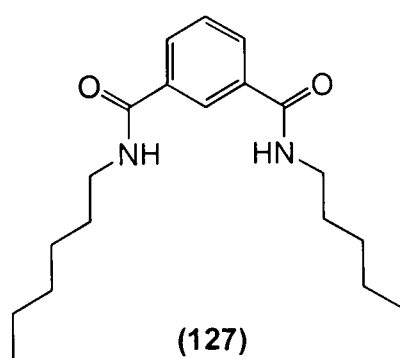
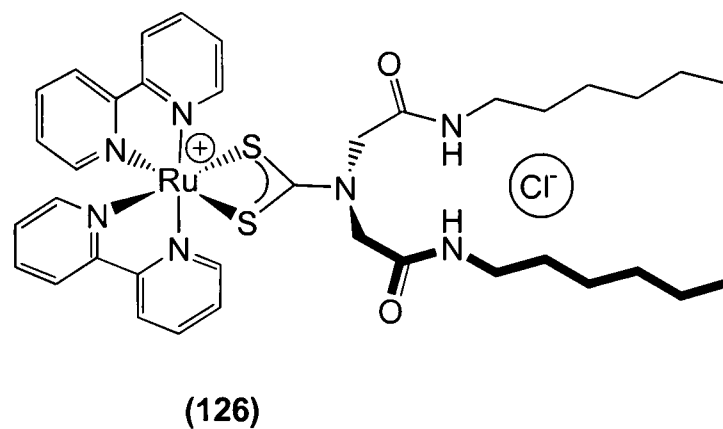
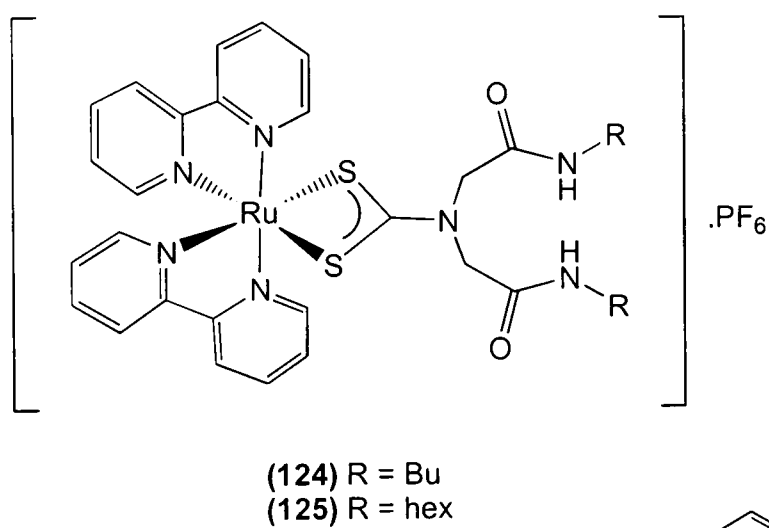
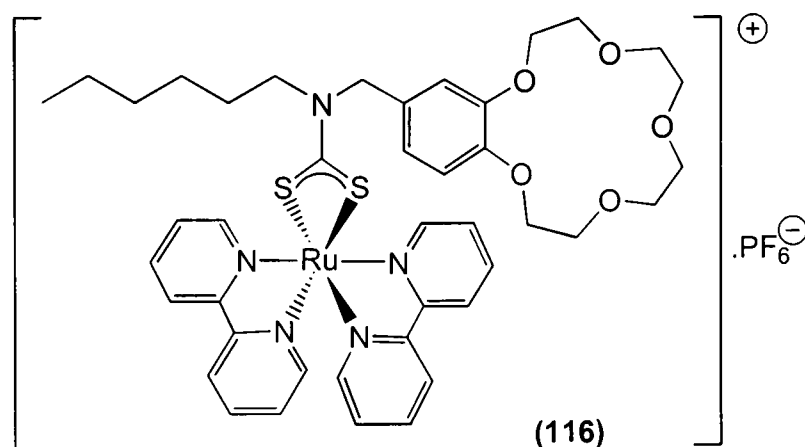
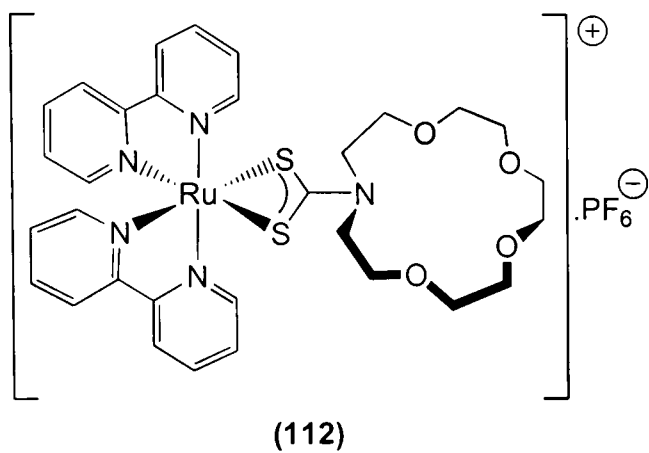
Silver Nanoparticles Stabilised by:



Selected Compounds from Chapter Seven



Selected Compounds from Chapter Seven continued



Appendix Seven: X-Ray Crystallographic Data

X-ray crystal structures were determined by Professor M. G. B. Drew^{*} (University of Reading), Dr. A. R. Cowley[#] and Dr. R. L. Paul[†] (University of Oxford).

Data was obtained using MoK α radiation on an Enraf-Nonius Kappa CCD diffractometer, in Oxford. In general, crystals were mounted on a glass fibre and cooled rapidly to 150K in a stream of cold N₂ using an Oxford Cryosystems CRYOSTREAM unit. Intensity data was processed using the DENZO-SMN² package. Structures were solved by direct methods using the SIR92³ program. Full-matrix least-squares refinement was carried out using the CRYSTALS⁴ program suite.

Data recorded in Reading was obtained by using MoK α radiation and the MAR research Image Plate System. Data analysis was performed with the XDS program⁵. The structures were solved by direct methods using the Shelx86 program⁶. Empirical absorption corrections were applied using the DIFABS program⁷. Structures were refined on F^2 to convergence using Shelxl⁸.

² Z. Otwinowski, W. Minor, *Processing of X-ray Diffraction Data Collected in Oscillation Mode, Methods Enzymol.*, 1997, **276**, Eds C. W. Carter and R. M. Sweet, Academic Press.

³ A. Altomare, G. Cascarano, G. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori, M. Camalli, *J. Appl. Cryst.* 1994, **27**, 435.

⁴ D. J. Watkin, C. K. Prout, J. R. Carruthers, P. W. Betteridge, R. I. Cooper, CRYSTALS issue 11, Chemical Crystallography Laboratory, Oxford, UK, 2001.

⁵ W. Kabsch, *J. Appl. Cryst.*, 1988 **21**, 916.

⁶ Shelx86, G. M. Sheldrick, *Acta Cryst.*, 1990, **A46**, 467.

⁷ DIFABS, N. Walker, D. Stuart, *Acta Cryst.*, 1983, **A39**, 158.

⁸ Shelxl, G. M. Sheldrick, 1993, program for crystal structure refinement. University of Gottingen.

(7-Cu)[‡]

Chemical formula	C ₃₆ H ₅₂ N ₄ S ₈ Cu ₂
Formula weight	924.46
Temperature (K)	150
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	<i>P</i> -1
a (Å)	10.2238(2)
b (Å)	10.4348(3)
c (Å)	11.6194(3)
α (°)	110.925(1)
β (°)	76.7970(14)
γ (°)	73.8324(14)
Cell volume (Å ³)	1156.86(6)
Z	1
Calculated density (Mg/m ³)	1.44
Absorption coefficient (mm ⁻¹)	1.419
F ₀₀₀	496.330
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)	0.75,0.75
θ range for data collection (°)	5.0 ≤ θ ≤ 27.0
Index ranges	-13 ≤ h ≤ 13, -13 ≤ k ≤ 13, -14 ≤ l ≤ 15
Reflections measured	8498
Unique reflections	4846
R _{int}	0.054
Observed reflections (I > 3σ(I))	2863
Refinement method	Full-matrix least-squares on <i>F</i>
Parameters refined	226
Weighting scheme	Chebychev 3-term polynomial
Goodness of fit	1.023
R	0.034
wR	0.041
Residual electron density (min,max) (eÅ ⁻³)	-0.42, 0.34

(8-Cu)*

Empirical formula	C ₅₂ H ₅₄ N ₄ OS ₁₂ Cu ₂ Cl ₂
Formula weight	1333.70
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	monoclinic, C2/c
Unit cell dimensions	a = 12.577(17) Å, b = 16.28(3) Å, c = 15.60(3) Å, β = 107.077(10) °
Volume	3052(8) Å ³
Z, Calculated density	2, 1.451 Mg/m ³
Absorption coefficient	1.079 mm ⁻¹
F(000)	1372
Crystal Size	0.36 x 0.29 x 0.21 mm
θ range for data collection	1.37 to 26.12 °
Index ranges	-15 ≤ h ≤ 15, -19 ≤ k ≤ 19, -19 ≤ l ≤ 19
Reflections collected / unique	9744 / 3124 [R(int) = 0.0975]
Absorption correction	DIFABS
Max. and min. transmission	1.000 and 0.478
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	3124 / 0 / 155
Goodness of fit on F ²	1.051
Final R indices [I>2σ(I)]	R1 = 0.0806, wR2 = 0.1637
R indices (all data)	R1 = 0.1488, wR2 = 0.1881
Extinction coefficient	0.0011(3)
Largest diff. peak and hole	0.488 and -0.442 e.Å ⁻³

(8-Ni)*

Empirical formula	C ₄₆ H ₆₈ N ₄ OS ₈ Ni ₂
Formula weight	1259.30
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	monoclinic, <i>C2/c</i>
Unit cell dimensions	a = 12.461(17) Å, b = 16.51(2) Å, c = 16.05(2) Å, β = 104.276(10)°
Volume	3200(8) Å ³
Z, Calculated density	2, 1.307 Mg/m ³
Absorption coefficient	1.079 mm ⁻¹
F(000)	1320
θ range for data collection	1.31 to 25.78 °
Index ranges	-15 ≤ h ≤ 11, -18 ≤ k ≤ 18, -19 ≤ l ≤ 19
Reflections collected / unique	8504 / 2984 [R(int) = 0.0597]
Absorption correction	DIFABS
Max. and min. transmission	1.000 and 0.345
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data / restraints / parameters	2984 / 0 / 164
Goodness-of-fit on <i>F</i> ²	1.217
Final R indices [I > 2σ(I)]	R1 = 0.0827, wR2 = 0.1779
R indices (all data)	R1 = 0.0827, wR2 = 0.1779
Largest diff. peak and hole	0.459 and -0.579 e.Å ⁻³

(8-Pd)*

Empirical formula	C ₄₄ H ₆₄ N ₄ O ₂ S ₈ Pd ₂
Formula weight	1150.28
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	monoclinic, C2/c
Unit cell dimensions	a = 12.580(17) Å, b = 16.17(3) Å, c = 15.893(17) Å, β = 107.734(10)°
Volume	5945(7) Å ³
Z, Calculated density	2, 1.240 Mg/m ³
Absorption coefficient	0.887 mm ⁻¹
F(000)	1184
θ range for data collection	2.28 to 26.13°
Index ranges	0 ≤ h ≤ 15, -19 ≤ k ≤ 19, -19 ≤ l ≤ 18
Reflections collected / unique	4319 / 2745 [R(int) = 0.1380]
Absorption correction	DIFABS
Max. and min. transmission	1.000 and 0.413
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	2745 / 12 / 138
Goodness of fit on F ²	0.846
Final R indices [I>2σ(I)]	R1 = 0.0845, wR2 = 0.2017
R indices (all data)	R1 = 0.2838, wR2 = 0.2398
Largest diff. peak and hole	0.799 and -0.424 e.Å ⁻³

(10-Cu)*

Empirical formula	C ₄₆ H ₇₂ Cu ₂ N ₄ O ₂ S ₈
Formula weight	1096.64
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	monoclinic, <i>P21/n</i>
Unit cell dimensions	a = 9.907(14) Å, b = 26.19(4) Å, c = 23.15(3) Å, β = 98.227(10) °
Volume	5945(13) Å ³
Z, Calculated density	4, 1.225 Mg/m ³
Absorption coefficient	1.032 mm ⁻¹
F(000)	2312
Theta range for data collection	2.28 to 26.13 deg
Index ranges	0 ≤ h ≤ 11, -32 ≤ k ≤ 32, -28 ≤ l ≤ 27
Reflections collected / unique	14793 / 8722 [R(int) = 0.2233]
Data / restraints / parameters	8722 / 0 / 311
Goodness-of-fit on <i>F</i> ²	0.744
Final R indices [I>2σ(I)]	R1 = 0.1377, wR2 = 0.2984
R indices (all data)	R1 = 0.4386, wR2 = 0.3745
Largest diff. peak and hole	0.525 and -0.506 e.Å ⁻³

(10-Pd)^{#/‡}

Chemical formula	C ₄₅ H ₇₀ Cl ₂ N ₄ Pd ₂ S ₈
Formula weight	1207.26
Temperature (K)	150
Radiation type	Mo K α
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> (Å)	9.8852(1)
<i>b</i> (Å)	25.7912(3)
<i>c</i> (Å)	22.5224(3)
α (°)	90
β (°)	98.5309(5)
γ (°)	90
Cell volume (Å ³)	5678.6
<i>Z</i>	4
Calculated density (Mg/m ³)	1.412
Absorption coefficient (mm ⁻¹)	1.055
<i>F</i> ₀₀₀	2483.381
Crystal size (mm)	0.2 x 0.06 x 0.06
Description of crystal	Yellow plate
Absorption correction	Semi-empirical from equivalent reflections
Transmission coefficients (min,max)	0.83, 0.94
θ range for data collection (°)	5.13 $\leq \theta \leq$ 27.42
Index ranges	-12 $\leq h \leq$ 12, -33 $\leq k \leq$ 33, -29 $\leq l \leq$ 29
Reflections measured	25728
Unique reflections	12913
<i>R</i> _{int}	0.050
Observed reflections (<i>I</i> > 3 σ (<i>I</i>))	6368
Refinement method	Full-matrix least-squares on <i>F</i>
Parameters refined	554
Weighting scheme	Chebyshev 3-term polynomial
Goodness of fit	1.0202
<i>R</i>	0.0514
w <i>R</i>	0.0596
Residual electron density (min,max) (eÅ ⁻³)	-1.36, 1.64

(11-Ni) Green^{#/‡}

Chemical formula	C ₅₀ H ₈₀ Cl ₁₂ N ₄ Ni ₂ S ₈
Formula weight	1608.62
Temperature (K)	150
Radiation type	Mo K α
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> (Å)	9.6790(2)
<i>b</i> (Å)	20.1967(4)
<i>c</i> (Å)	18.6957(3)
α (°)	90
β (°)	97.7277(9)
γ (°)	90
Cell volume (Å ³)	3621.5
Z	2
Calculated density (Mg/m ³)	1.475
Absorption coefficient (mm ⁻¹)	1.232
<i>F</i> ₀₀₀	1670.175
Crystal size (mm)	0.2 x 0.06 x 0.06
Description of crystal	Brown-green plate
Absorption correction	Semi-empirical from equivalent reflections
Transmission coefficients (min,max)	0.78, 0.93
θ range for data collection (°)	5.12 ≤ θ ≤ 25.34
Index ranges	-11 ≤ <i>h</i> ≤ 11, -23 ≤ <i>k</i> ≤ 24, -22 ≤ <i>l</i> ≤ 22
Reflections measured	11585
Unique reflections	6540
<i>R</i> _{int}	0.050
Observed reflections (<i>I</i> > 3 σ (<i>I</i>))	3795
Refinement method	Full-matrix least-squares on <i>F</i>
Parameters refined	370
Weighting scheme	Chebychev 3-term polynomial
Goodness of fit	0.9701
<i>R</i>	0.0477
WR	0.0540
Residual electron density (min,max) (eÅ ⁻³)	-0.19, 0.21

(11-Ni) Brown*

Empirical formula	C ₄₄ H ₆₈ N ₄ S ₈ Ni ₂
Formula weight	1026.92
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Triclinic, <i>P</i> -1
Unit cell dimensions	a = 10.277(12) Å, b = 10.113(12) Å, c = 13.774(16) Å, α = 80.754(10)° β = 78.319(10)° γ = 73.825(10)°
Volume	1338(3) Å ³
Z, Calculated density	1, 1.274 Mg/m ³
Absorption coefficient	1.048 mm ⁻¹
F(000)	544
θ range for data collection	2.46 to 22.42 °
Index ranges	0 ≤ h ≤ 10, -9 ≤ k ≤ 10, -14 ≤ l ≤ 14
Reflections collected / unique	2361 / 2361 [R(int) = 0.0000]
Absorption correction	DIFABS
Max. and min. transmission	1.000 and 0.421
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2361 / 20 / 145
Goodness of fit on F^2	0.929
Final R indices [I>2σ(I)]	R1 = 0.0916, wR2 = 0.2513
R indices (all data)	R1 = 0.1462, wR2 = 0.2877
Extinction coefficient	0.002(4)
Largest diff. peak and hole	0.409 and -0.369 e.Å ⁻³

(13-Cu)*

Empirical formula	C ₂₄ H ₃₀ N ₂ S ₄ Cu ₂
Formula weight	601.82
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Orthorhombic, <i>Pbcn</i>
Unit cell dimensions	a = 14.966(17) Å, b = 19.82(2) Å, c = 17.48(2) Å
Volume	5185(10) Å ³
Z, Calculated density	8, 1.542 mg/m ³
Absorption coefficient	1.978 mm ⁻¹
F(000)	2480
θ range for data collection	1.71 to 26.16 °
Index ranges	0 ≤ h ≤ 18, 0 ≤ k ≤ 24, 0 ≤ l ≤ 19
Reflections collected / unique	4239 / 4239 [R(int) = 0.0000]
Completeness to 2 θ = 26.16	76.2%
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4239 / 0 / 291
Goodness of fit on F^2	1.088
Final R indices [I > 2 σ (I)]	R1 = 0.0660, wR2 = 0.1600
R indices (all data)	R1 = 0.1191, wR2 = 0.1792
Largest diff. peak and hole	0.664 and -0.548 e.Å ⁻³

(18-Cu)[‡]

Chemical formula	C ₄₅ H ₅₈ N ₄ S ₈ Cl ₂ Cu ₂
Formula weight	924.46
Temperature (K)	150
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	<i>P</i> -1
a (Å)	11.5001(2)
b (Å)	11.6296(3)
c (Å)	12.2003(3)
α (°)	101.251(1)
β (°)	109.2882(11)
γ (°)	114.6315(9)
Cell volume (Å ³)	1290.37(6)
Z	1
Calculated density (Mg/m ³)	1.50
Absorption coefficient (mm ⁻¹)	1.289
F ₀₀₀	633.913
Crystal size (mm)	0.04 x 0.06 x 0.20
Description of crystal	Brown block
Absorption correction	Semi-empirical from equivalent reflections
Transmission coefficients (min,max)	0.93,0.95
θ range for data collection (°)	5.0 ≤ θ ≤ 27.0
Index ranges	-14 ≤ h ≤ 13, -15 ≤ k ≤ 15, -15 ≤ l ≤ 15
Reflections measured	9874
Unique reflections	5847
R _{int}	0.050
Observed reflections (I > 3σ(I))	3379
Refinement method	Full-matrix least-squares on <i>F</i>
Parameters refined	274
Weighting scheme	Chebyshev 3-term polynomial
Goodness of fit	1.014
R	0.058
wR	0.069
Residual electron density (min,max) (eÅ ⁻³)	-1.40, 0.74

(27)[#]

Chemical formula	C ₂₅ H ₃₄ N ₂ O ₂
Formula weight	394.56
Temperature (K)	150
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> (Å)	9.1709(2)
<i>b</i> (Å)	21.8970(4)
<i>c</i> (Å)	11.4973(2)
α (°)	90
β (°)	91.8372(7)
γ (°)	90
Cell volume (Å ³)	2307.6
<i>Z</i>	4
Calculated density (Mg/m ³)	1.136
Absorption coefficient (mm ⁻¹)	0.072
<i>F</i> ₀₀₀	856.161
Crystal size (mm)	0.08 x 0.35 x 0.40
Description of crystal	Colourless plate
Absorption correction	Semi-empirical from equivalent reflections
Transmission coefficients (min,max)	0.98, 0.99
θ range for data collection (°)	5.0 ≤ θ ≤ 27.5
Index ranges	-11 ≤ <i>h</i> ≤ 11, 0 ≤ <i>k</i> ≤ 28, 0 ≤ <i>l</i> ≤ 14
Reflections measured	25884
Unique reflections	5366
<i>R</i> _{int}	0.050
Observed reflections (<i>I</i> > 3 σ (<i>I</i>))	3236
Refinement method	Full-matrix least-squares on <i>F</i>
Parameters refined	270
Weighting scheme	Chebyshev 3-term polynomial
Goodness of fit	1.0597
<i>R</i>	0.0406
w <i>R</i>	0.0412
Residual electron density (min,max) (eÅ ⁻³)	-0.19, 0.21

(55)[#]

Empirical formula	C ₂₆ H ₅₂ N ₇ OS ₈ Au ₂ Cl ₃
Formula weight	1219.53
Temperature (K)	150
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	$P \bar{1}$
a (Å)	10.7156(2)
b (Å)	13.7966(2)
c (Å)	16.6194(3)
α (°)	92.5254(7)
β (°)	107.1455(7)
γ (°)	106.7462(7)
Cell volume (Å ³)	2225.8
Z	2
Calculated density (Mg/m ³)	1.820
Absorption coefficient (mm ⁻¹)	7.167
F_{000}	1196.294
Crystal size (mm)	0.06 x 0.10 x 0.12
Description of crystal	Pale-orange fragment
Absorption correction	Semi-empirical from equivalent reflections
Transmission coefficients (min,max)	0.49, 0.65
θ range for data collection (°)	$5.0 \leq \theta \leq 27.5$
Index ranges	$-14 \leq h \leq 13, -18 \leq k \leq 18, 0 \leq l \leq 21$
Reflections measured	25310
Unique reflections	9613
R_{int}	0.042
Observed reflections ($I > 3\sigma(I)$)	7992
Refinement method	Full-matrix least-squares on F
Parameters refined	636
Weighting scheme	Chebychev 3-term polynomial
Goodness of fit	1.0844
R	0.0307
wR	0.0319
Residual electron density (min,max) (eÅ ⁻³)	-1.56, 1.17

(60)[#]

Empirical formula	C ₃₄ H ₄₀ N ₂ S ₄ AuB
Formula weight	812.73
Temperature (K)	150
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	<i>C</i> 2/ <i>c</i>
<i>a</i> (Å)	45.1004(6)
<i>b</i> (Å)	9.0417(1)
<i>c</i> (Å)	18.5407(3)
α (°)	90
β (°)	94.6094(9)
γ (°)	90
Cell volume (Å ³)	7536.2
<i>Z</i>	8
Calculated density (Mg/m ³)	1.433
Absorption coefficient (mm ⁻¹)	4.150
<i>F</i> ₀₀₀	3230.813
Crystal size (mm)	0.10 x 0.24 x 0.30
Description of crystal	Pale-brown tablet
Absorption correction	Semi-empirical from equivalent reflections
Transmission coefficients (min,max)	0.37, 0.66
θ range for data collection (°)	5.0 ≤ θ ≤ 27.5
Index ranges	-58 ≤ <i>h</i> ≤ 58, 0 ≤ <i>k</i> ≤ 11, 0 ≤ <i>l</i> ≤ 24
Reflections measured	30058
Unique reflections	9123
<i>R</i> _{int}	0.057
Observed reflections (<i>I</i> > 3σ(<i>I</i>))	6169
Refinement method	Full-matrix least-squares on <i>F</i>
Parameters refined	542
Weighting scheme	Chebyshev 3-term polynomial
Goodness of fit	1.0048
<i>R</i>	0.0373
w <i>R</i>	0.0424
Residual electron density (min,max) (eÅ ⁻³)	-0.96, 2.49

(61)[#]

Chemical formula	C ₁₀ H ₂₀ N ₂ S ₄ AuPF ₆
Formula weight	638.45
Temperature (K)	150
Wavelength (Å)	0.71073
Crystal system	Orthorhombic
Space group	<i>P</i> 2 ₁ 2 ₁ 2 ₁
<i>a</i> (Å)	8.7437(2)
<i>b</i> (Å)	12.1893(4)
<i>c</i> (Å)	18.2936(5)
α (°)	90
β (°)	90
γ (°)	90
Cell volume (Å ³)	1949.72(9)
<i>Z</i>	4
Calculated density (Mg/m ³)	2.175
Absorption coefficient (mm ⁻¹)	8.107
<i>F</i> ₀₀₀	1216.134
Crystal size (mm)	0.06 x 0.08 x 0.12
Description of crystal	Yellow block
Absorption correction	Semi-empirical from equivalent reflections
Transmission coefficients (min,max)	0.38, 0.61
θ range for data collection (°)	$5.0 \leq \theta \leq 27.5$
Index ranges	$-11 \leq h \leq 11, 0 \leq k \leq 15, 0 \leq l \leq 23$
Reflections measured	11827
Unique reflections	4420
<i>R</i> _{int}	0.054
Observed reflections (<i>I</i> > 3 σ (<i>I</i>))	3353
Refinement method	Full-matrix least-squares on <i>F</i>
Parameters refined	218
Weighting scheme	Chebychev 3-term polynomial
Goodness of fit	1.0841
<i>R</i>	0.0348
w <i>R</i>	0.0325
Residual electron density (min,max) (eÅ ⁻³)	-1.73, 1.53

(62)[#]

Empirical formula	C ₁₀ H ₂₀ N ₂ S ₄ AuCuCl ₂
Formula weight	627.094
Temperature (K)	150
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	<i>C</i> 2/ <i>c</i>
<i>a</i> (Å)	13.4136(4)
<i>b</i> (Å)	14.4071(5)
<i>c</i> (Å)	9.9945(3)
α (°)	90
β (°)	92.6986(16)
γ (°)	90
Cell volume (Å ³)	1929.3
<i>Z</i>	4
Calculated density (Mg/m ³)	2.162
Absorption coefficient (mm ⁻¹)	9.398
<i>F</i> ₀₀₀	1193.719
Crystal size (mm)	0.08 x 0.14 x 0.16
Description of crystal	Black block
Absorption correction	Semi-empirical from equivalent reflections
Transmission coefficients (min,max)	0.27, 0.47
θ range for data collection (°)	5.0 ≤ θ ≤ 27.5
Index ranges	-17 ≤ <i>h</i> ≤ 17, 0 ≤ <i>k</i> ≤ 18, 0 ≤ <i>l</i> ≤ 12
Reflections measured	7390
Unique reflections	2176
<i>R</i> _{int}	0.044
Observed reflections (<i>I</i> > 3σ(<i>I</i>))	1683
Refinement method	Full-matrix least-squares on <i>F</i>
Parameters refined	133
Weighting scheme	Chebychev 3-term polynomial
Goodness of fit	0.9979
<i>R</i>	0.0251
w <i>R</i>	0.0397
Residual electron density (min,max) (eÅ ⁻³)	-1.59, 1.42

(63)[#]

Empirical formula	C ₁₀ H ₂₀ N ₂ S ₄ AuCuCl ₃
Formula weight	663.39
Temperature (K)	150
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	$P\bar{1}$
<i>a</i> (Å)	8.4712(2)
<i>b</i> (Å)	10.8511(2)
<i>c</i> (Å)	11.4864(3)
α (°)	85.2967(10)
β (°)	84.6119(11)
γ (°)	68.0596(9)
Cell volume (Å ³)	973.8
<i>Z</i>	2
Calculated density (Mg/m ³)	2.262
Absorption coefficient (mm ⁻¹)	9.449
<i>F</i> ₀₀₀	631.114
Crystal size (mm)	0.08 x 0.10 x 0.10
Description of crystal	Dark-green fragment
Absorption correction	Semi-empirical from equivalent reflections
Transmission coefficients (min,max)	0.39, 0.47
θ range for data collection (°)	$5.0 \leq \theta \leq 27.5$
Index ranges	$-10 \leq h \leq 11, -13 \leq k \leq 14, 0 \leq l \leq 14$
Reflections measured	12468
Unique reflections	4447
<i>R</i> _{int}	0.035
Observed reflections (<i>I</i> > 3σ(<i>I</i>))	3972
Refinement method	Full-matrix least-squares on <i>F</i>
Parameters refined	191
Weighting scheme	Chebychev 3-term polynomial
Goodness of fit	1.0301
<i>R</i>	0.0233
w <i>R</i>	0.0274
Residual electron density (min,max) (eÅ ⁻³)	-1.21, 0.90

(64)[#]

Chemical formula	C ₂₀ H ₄₀ N ₄ S ₈ Au ₂ Cu ₂ Cl ₆
Formula weight	1326.78
Temperature (K)	150
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	$P \bar{1}$
a (Å)	8.1579(2)
b (Å)	11.0286(4)
c (Å)	11.2891(4)
α (°)	83.2403(14)
β (°)	78.1345(14)
γ (°)	87.3517(14)
Cell volume (Å ³)	986.8
Z	1
Calculated density (Mg/m ³)	2.232
Absorption coefficient (mm ⁻¹)	9.325
F_{000}	631.114
Crystal size (mm)	0.03 x 0.08 x 0.09
Description of crystal	Orange fragment
Absorption correction	Semi-empirical from equivalent reflections
Transmission coefficients (min,max)	0.47, 0.76
θ range for data collection (°)	$5.0 \leq \theta \leq 27.5$
Index ranges	$-10 \leq h \leq 10, -14 \leq k \leq 14, 0 \leq l \leq 14$
Reflections measured	14006
Unique reflections	4433
R_{int}	0.055
Observed reflections ($I > 3\sigma(I)$)	3106
Refinement method	Full-matrix least-squares on F
Parameters refined	193
Weighting scheme	Chebyshev 3-term polynomial
Goodness of fit	1.0520
R	0.0259
wR	0.0297
Residual electron density (min,max) (eÅ ⁻³)	-1.24, 1.00

(65)[#]

Chemical formula	C ₂₀ H ₄₀ N ₄ S ₈ Au ₂ CuCl ₃
Formula weight	1156.88
Temperature (K)	150
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	<i>C</i> 2/ <i>c</i>
<i>a</i> (Å)	17.0700(3)
<i>b</i> (Å)	26.6810(6)
<i>c</i> (Å)	9.2832(2)
α (°)	90
β (°)	120.776(1)
γ (°)	90
Cell volume (Å ³)	3632.6
<i>Z</i>	4
Calculated density (Mg/m ³)	2.115
Absorption coefficient (mm ⁻¹)	9.338
<i>F</i> ₀₀₀	2201.828
Crystal size (mm)	0.10 x 0.10 x 0.10
Description of crystal	Orange-brown fragment
Absorption correction	Semi-empirical from equivalent reflections
Transmission coefficients (min,max)	0.39, 0.39
θ range for data collection (°)	5.0 ≤ θ ≤ 27.5
Index ranges	-22 ≤ <i>h</i> ≤ 19, 0 ≤ <i>k</i> ≤ 34, 0 ≤ <i>l</i> ≤ 12
Reflections measured	20370
Unique reflections	4236
<i>R</i> _{int}	0.033
Observed reflections (<i>I</i> > 3σ(<i>I</i>))	2871
Refinement method	Full-matrix least-squares on <i>F</i>
Parameters refined	178
Weighting scheme	Chebyshev 3-term polynomial
Goodness of fit	1.0573
<i>R</i>	0.0205
w <i>R</i>	0.0213
Residual electron density (min,max) (eÅ ⁻³)	-1.00, 0.53

(66)[#]

Empirical formula	C ₅ H ₁₀ NS ₂ AuCl ₂
Formula weight	416.14
Temperature (K)	150
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> (Å)	17.2243(3)
<i>b</i> (Å)	7.0350(1)
<i>c</i> (Å)	17.2262(3)
α (°)	90
β (°)	97.7197(6)
γ (°)	90
Cell volume (Å ³)	2068.4
<i>Z</i>	8
Calculated density (Mg/m ³)	2.672
Absorption coefficient (mm ⁻¹)	15.085
<i>F</i> ₀₀₀	1519.916
Crystal size (mm)	0.09 x 0.12 x 0.24
Description of crystal	Yellow block (but see comment above)
Absorption correction	Semi-empirical from equivalent reflections
Transmission coefficients (min,max)	0.16, 0.26
θ range for data collection (°)	5.0 ≤ θ ≤ 27.5
Index ranges	0 ≤ <i>h</i> ≤ 22, 0 ≤ <i>k</i> ≤ 9, -22 ≤ <i>l</i> ≤ 22
Reflections measured	22708
Unique reflections	4676
<i>R</i> _{int}	0.037
Observed reflections (<i>I</i> > 3σ(<i>I</i>))	4426
Refinement method	Full-matrix least-squares on <i>F</i>
Parameters refined	200
Weighting scheme	Chebychev 3-term polynomial
Goodness of fit	0.8911
<i>R</i>	0.0249
w <i>R</i>	0.0299
Residual electron density (min,max) (eÅ ⁻³)	-1.50, 0.738

(67)[#]

Chemical formula	C ₄₂ H ₈₆ Au ₄ Cl ₁₂ N ₈ Ni ₂ OS ₁₆
Formula weight	2546.89
Temperature (K)	150
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	$P \bar{1}$
a (Å)	11.5468(1)
b (Å)	15.7930(1)
c (Å)	23.8335(3)
α (°)	90.3377(4)
β (°)	92.6061(4)
γ (°)	104.0860(4)
Cell volume (Å ³)	4210.6
Z	2
Calculated density (Mg/m ³)	2.009
Absorption coefficient (mm ⁻¹)	8.193
F_{000}	2451.422
Crystal size (mm)	0.03 x 0.06 x 0.12
Description of crystal	Green fragment
Absorption correction	Semi-empirical from equivalent reflections
Transmission coefficients (min,max)	0.61, 0.78
θ range for data collection (°)	$5.0 \leq \theta \leq 27.5$
Index ranges	$-14 \leq h \leq 14, -20 \leq k \leq 20, 0 \leq l \leq 30$
Reflections measured	77470
Unique reflections	19070
R_{int}	0.048
Observed reflections ($I > 3\sigma(I)$)	14000
Refinement method	Full-matrix least-squares on F
Parameters refined	765
Weighting scheme	Chebyshev 3-term polynomial
Goodness of fit	1.0456
R	0.0419
wR	0.0471
Residual electron density (min,max) (eÅ ⁻³)	-2.13, 1.95

(104)[‡]

Chemical formula	C ₂₅ H ₂₆ N ₅ S ₂ RuPF ₆
Formula weight	706.68
Temperature (K)	150
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	<i>P</i> 2/ <i>n</i>
<i>a</i> (Å)	14.9344(3)
<i>b</i> (Å)	12.0166(3)
<i>c</i> (Å)	17.1984(5)
β (°)	113.305(1)
Cell volume (Å ³)	2834.62(12)
<i>Z</i>	4
Calculated density (Mg/m ³)	1.66
Absorption coefficient (mm ⁻¹)	0.822
<i>F</i> ₀₀₀	1420.241
Crystal size (mm)	0.20 x 0.20 x 0.20
Description of crystal	Red block
Absorption correction	Semi-empirical from equivalent reflections
Transmission coefficients (min,max)	0.85, 0.85
θ range for data collection (°)	5.0 ≤ θ ≤ 27.0
Index ranges	-19 ≤ <i>h</i> ≤ 19, -15 ≤ <i>k</i> ≤ 13, -22 ≤ <i>l</i> ≤ 22
Reflections measured	9895
Unique reflections	6414
<i>R</i> _{int}	0.030
Observed reflections (<i>I</i> > 3σ(<i>I</i>))	4430
Refinement method	Full-matrix least-squares on <i>F</i>
Parameters refined	361
Weighting scheme	Chebychev 3-term polynomial
Goodness of fit	1.029
<i>R</i>	0.028
w <i>R</i>	0.033
Residual electron density (min,max) (eÅ ⁻³)	-0.78, 0.030

(117)[‡]

Chemical formula	C ₉ H ₁₅ NO ₆
Formula weight	233.22
Temperature (K)	150
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	<i>P</i> 21/ <i>n</i>
<i>a</i> (Å)	10.8051(3)
<i>b</i> (Å)	9.3006(2)
<i>c</i> (Å)	12.3245(4)
β (°)	110.925(1)
Cell volume (Å ³)	1156.86(6)
<i>Z</i>	4
Calculated density (Mg/m ³)	1.34
Absorption coefficient (mm ⁻¹)	0.113
<i>F</i> ₀₀₀	496.330
Crystal size (mm)	0.20 x 0.20 x 0.20
Description of crystal	Colourless block
Absorption correction	Semi-empirical from equivalent reflections
Transmission coefficients (min,max)	0.98, 0.98
θ range for data collection (°)	5.0 ≤ θ ≤ 27.0
Index ranges	-13 ≤ <i>h</i> ≤ 14, -12 ≤ <i>k</i> ≤ 9, -15 ≤ <i>l</i> ≤ 15
Reflections measured	4855
Unique reflections	2616
<i>R</i> _{int}	0.036
Observed reflections (<i>I</i> > 3σ(<i>I</i>))	1710
Refinement method	Full-matrix least-squares on <i>F</i>
Parameters refined	146
Weighting scheme	Chebyshev 3-term polynomial
Goodness of fit	1.026
<i>R</i>	0.059
w <i>R</i>	0.074
Residual electron density (min,max) (eÅ ⁻³)	-0.46, 1.07

(124)[‡]

Chemical Formula	C ₆₆ H ₈₂ N ₁₄ O ₄ S ₄ Ru ₂ .SO ₄ .H ₂ O
Formula weight	2187.90
Temperature (K)	150
Radiation type	Mo K α
Wavelength (Å)	0.710730
Crystal system	Monoclinic
Space group	<i>C</i> 2/ <i>c</i>
<i>a</i> (Å)	30.8237(4)
<i>b</i> (Å)	9.5096(1)
<i>c</i> (Å)	31.4146(4)
α (°)	90
β (°)	90
γ (°)	116.3669(6)
Cell volume (Å ³)	8250.3
Z	8
Calculated density (Mg/m ³)	1.09
Absorption coefficient (mm ⁻¹)	0.526
F ₀₀₀	3648.275
Crystal size (mm)	0.04 x 0.16 x 0.24
Description of crystal	Red crystal
Absorption correction	Semi-Empirical from equivalent Reflections
Transmission coefficients (min,max)	0.92, 0.98
θ range for data collection (°)	$5 \leq \theta \leq 27$
Index ranges	$-39 \leq h \leq 39$, $-11 \leq k \leq 12$, $-40 \leq l \leq 40$
Reflections measured	16466
Unique reflections	9064
R _{int}	0.0002
Observed reflections ($I > 3 \sigma(I)$)	5812
Refinement method	Full-matrix least-squares on <i>F</i>
Parameters refined	508
Weighting scheme	Chebyshev polynomial with 3 parameters
Goodness of fit	1.054
R	0.050
wR	0.057
Residual electron density (min, max) (eÅ ⁻³)	-0.96, 0.94

