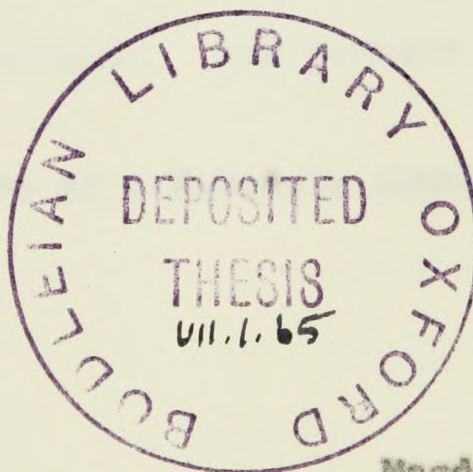


EXPERIMENTS WITH POLIDENTATE LIGANDS

by

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ABSTRACT

This thesis describes the preparation of a number of polydentate ligands having nitrogen, or nitrogen and phosphorus as the donor atoms. Complexes of these ligands with several transition metals were studied and their preparations and properties are described. Deductions of the stereochemistry of the resulting complex ions are made where possible.

The attempted preparation of the ligand 1:2 dipentyl ethylene diamine is described and the preparations of 1,2 diphenyl ethylene diamine (*m*-stien) and the para-para' isopropyl derivative (*p*-stien) are discussed. The following ligands were prepared with both phosphorus and nitrogen donor atoms: tris(*o*-dimethylaminophenyl)phosphine, PTN; bis(*o*-dimethylaminophenyl)phenyl phosphine, PDN; and *o*-dimethylaminophenyl diphenyl phosphine, PN.

They were synthesised by the action of a suitable chlorophenyl phosphine on the ortho-lithio derivative of dimethyl aniline.

m-stien complexes of copper II were prepared and studied. The general formula was $[m\text{-stien}_2\text{CuX}_2]\text{nH}_2\text{O}$, (where $\text{X}=\text{Cl}$, $n=1$; $\text{X}=\text{Br}$, $n=1, 0$; $\text{X}=\text{I}$, $n=0$; $\text{X}=\text{SCN}$, $n=1$; $\text{X}=\text{NO}_3$, $n=0$; $\text{X}=\text{ClO}_4$, $n=0$; $\text{X}=\frac{1}{2}\text{SO}_4$, $n=1$; $\text{X}=\text{acetate}$, $n=1$; $\text{X}=\text{oxalate}$, $n=1$). The compounds varied between violet and green in colour and were almost all insoluble in nitromethane.

Magnetic and spectral studies of the m-stien copper complexes showed them to be tetragonal with four nitrogen atoms in a square plane. The ligand field of water in $m\text{-stien}_2\text{CuBr}_2\cdot\text{H}_2\text{O}$ causes it to be violet whilst the anhydrous material, with a weaker ligand field, is green. Where deductions could be made, the infra-red spectra confirm that there is some interaction between the metal and anionic ligands.

Some m-stien complexes of palladium II were prepared. The general formula was $m\text{-stien}_2\text{PdX}_2$ (where $\text{X}=\text{Cl}$, Br , SCN , NO_3). These compounds were less well characterised than the copper ones. Physical studies on these compounds showed them to be essentially square planar; they were not sufficiently soluble in non-donor solvents to make further studies possible, and so tri- and tetradentate ligands of this type were not prepared.

The compounds $[p\text{-stien}_2\text{NiX}_2]\text{nH}_2\text{O}$ were then studied (where $\text{X}=\text{Cl}$, $n=4, 0$; $\text{X}=\text{I}$, $n=2, 0$). In the chloride complex, removal of the water of hydration changes the yellow colour

to green and changes the magnetic moment from 0 to 2.68 BM. This behaviour is similar to that of the Lifschitz complexes of nickel with *m*-stien. However, it is unusual to observe the formation of a paramagnetic species on dehydration.

The spectral and magnetic evidence of structure in these compounds is compared with some parallel cases, and it is deduced that the yellow compound is essentially square planar whilst the green compound is a mixture of 'octahedral' and square planar stereochemistries.

Compounds of the type *p*-stien₂PdX₂·2H₂O were also prepared (where X=Cl, Br, NO₃). These white compounds were similar to the *m*-stien analogues and the para-isopropyl groups on the ligand seemed to confer no special advantages over *m*-stien with palladium. Thus neither system was suitable for the study of complexes of tri- or tetradentate ligands of this type. The mixed phosphorus-nitrogen ligands were, therefore, prepared and their complexes studied.

The platinum and palladium complexes of PTN, PDN and PN were isolated. They were of the formula [LMX₂] (where L=PTN, PDN, PN; M=Pt, Pd; and X=Cl, Br, I). These compounds were more soluble than the stien derivatives in non-donor solvents and were extensively studied. Magnetic, spectral and NMR. evidence showed that the compounds were all *cis*-square planar, the metal being bound to two halide ions,

one phosphorus and one nitrogen atom. It is of great interest that although PTN is formally analogous to the ligand tris(diphenylarsinophenyl)-arsine, QAS, it does not form the trigonal bipyramidal complexes well known for the latter ligand with palladium and platinum. Instead the more familiar square planar stereochemistry is retained in the d^8 ions. It is possible that a considerable amount of π -bonding is required to stabilise the five-coordinate ion.

Compounds of the three ligands with nickel were prepared. They had the formula $[LMX_2]$ (where $L=PTN, PDN, PN$, $X=Cl, Br, I$; and $L=PTN$, $X=SCN$). These complexes were less soluble than the palladium and platinum ones and were paramagnetic. The spectral and magnetic evidence suggests that, in these compounds too, the organic ligand is bound to the metal by one nitrogen and one phosphorus atom in each case. The evidence is not conclusive but does strongly suggest that the nickel is in an essentially tetrahedral environment, though tetragonally distorted. Differences in the spectra are then attributed to interactions, either steric or electronic, between the metal and the 'free' nitrogen atoms in PDN and PTN.

The cobalt compounds of the formula $[LCoX_2]$ (where $L=PTN, PDN, PN$ and $X=Cl, Br$) were prepared. In this case the iodide complexes could not be isolated. These compounds

had quartet ground states and ultraviolet spectra suggested that these compounds were probably tetrahedral. Interactions with the 'free' nitrogen atoms explained small differences in both the spectra and the magnetic moments.

Finally some complexes of copper I were prepared, of the formula $[LCuX]$ (where $L=PTN, PDN$; $X=Cl, Br, I$ and $L=PN, X=Cl$) and $[L_2CuX]$ (where $L=PN, X=Br, I$). No firm deductions could be made on the available evidence of the stereochemistries of these compounds, although the infra-red spectra suggest that all the ligands may be bound only through phosphorus.

Thus the work in the present thesis suggests that, with the metals studied, the mixed phosphorus-nitrogen ligands owe much of their coordinating ability to the phosphorus atom with its π -bonding potential. The ligand PTN does not form the five-coordinate analogues of QAS despite its chelating ability and rigid stereochemistry.

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PART ONE

THESE ARE THE FIRST OF THE SEVEN PARTS OF THE REPORT. THE REPORT IS A SUMMARY OF THE INFORMATION OBTAINED FROM THE INTERVIEW OF THE SUBJECT. THE INFORMATION IS PRESENTED IN A SUMMARY FORM, AND IS NOT A DETAILED ACCOUNT OF THE INTERVIEW. THE INFORMATION IS PRESENTED IN A SUMMARY FORM, AND IS NOT A DETAILED ACCOUNT OF THE INTERVIEW.

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CHAPTER I

INTRODUCTION

The study of metal ammine complexes has been a fruitful field for many years. For example Magnus' green salt $[\text{Pt}(\text{NH}_3)_4][\text{PtCl}_4]$ was discovered in 1828. More recently comparative study of complexes formed using different Group Vb donor atoms has yielded many interesting results.

Compounds of the type R_3X containing elements nitrogen, phosphorus, arsenic and antimony in their trivalent states have all been employed as ligands, where R is an aryl or alkyl group. An investigation of the adducts formed by the compounds $(\text{CH}_3)_3\text{X}$ with trimethyl gallium (1), trimethyl aluminium (2) and with boron trifluoride and trimethyl borane (3) gives a measure of the relative σ bonding strength of

these donor atoms. This is the only bonding mechanism available in these cases and the order of stability is always



However, a comparison of the stability of the complexes formed by transition metal ions with ligands using these donor atoms shows that the relative stabilities depend strongly on the nature and oxidation state of the acceptor metal.

In 1954 the differences in relative stabilities were rationalised by Ahrlund (4) and Larsson and they divided the acceptor metals into two classes. Class (a) in which the order of affinity for group Vb donors is $N \gg P > As > Sb > Bi$ and for the halogens is $F \gg Cl > Br > I$ and Class (b) where the order is $N \ll P > As > Sb > Bi$ and similarly $F \ll Cl > Br > I$.

The main group of class (b) metals lies in groups VIII and Ib of the periodic table, although VIa, VIIa and IIb metals show some (b) character. The extent of the (b) character varies with oxidation state of the metal, increasing with low oxidation state within a transition series. However, outside the series with full d orbitals, (b) character increases with increasing oxidation state as the amount of screening from the outer s and p electrons decreases.

Class (b) character may be explained in terms of the availability of electrons from metal d orbitals of the correct symmetry and energy for back-donation into empty π -orbitals on the ligands. Such back-donation cannot occur with nitrogen as the donor atom since nitrogen contains no suitable acceptor orbitals. However, phosphorus and arsenic have empty 3d and 4d orbitals, respectively, of the right energy and symmetry to form strong π -acceptor bonds. Similar arguments clearly apply to the halogen series.

The variation in the properties of a complex with a changing donor atom was discussed by Tsuchida (5) who constructed a spectrochemical series for ligand molecules. Van Vleck (6), Owen (7) and Orgel (8) interpreted this empirical series in terms of a variation of the splitting of the d electron energy levels, Δ , as a function of the ligand field. Then taking account of both electrostatic and covalent bonding we may write

$$\Delta = +(\text{electrostatic effect}) + \sigma(L \rightarrow M) - \pi(L \rightarrow M) + \pi(M \rightarrow L).$$

where $\sigma(L \rightarrow M)$ represents the dative σ -bond etc. The term $\pi(M \rightarrow L)$ arises from the back donation of electrons into empty d orbitals on the ligand as discussed above. This lessens the build-up of negative charge on the metal ion and enhances the stability. Clearly a term $\pi(L \rightarrow M)$ will have the reverse effect.

A change in the group R attached to the Group Vb donor atom can have a marked effect on both σ -donor and π -acceptor properties of the ligand molecule. In the case of nitrogen the strongest σ bonds are formed by primary aliphatic amines and the behaviour follows the order for ease of protonation. Thus tertiary amines are weak bases, triphenylamine is only protonated in a concentrated acid solution, and they are the weakest donor atoms.

Both alkyl and aryl phosphines and arsines form strong bonds with transition metal ions but here the σ bonding may be enhanced by π bonding. When R is an alkyl group the inductive effect will increase the availability of electrons in the sp^3 hybridised orbital forming the donor bond and a strong σ bond will be formed. On the other hand, if R is an aryl group the σ donor power of the molecule will be reduced. Here, however, a marked effect on the π acceptor orbitals is to be expected. Direct competition will occur between electrons of the delocalised benzene ring system overlapping empty d orbitals on, say, phosphorus and a similar overlap with the suitable d orbitals from the metal atom.

The effect of the nature of R on the properties of R_3P have been investigated for complexes of divalent nickel(9).

Trialkyl and dialkylaryl phosphines formed complexes $[(R_3P)_2NiX_2]$ which were diamagnetic and square planar.

Triaryl phosphines gave tetrahedral complexes with two unpaired electrons whilst diarylalkyl phosphines gave compounds in both stereochemical forms.

The d orbital splittings for square planar and tetrahedral complexes are:-

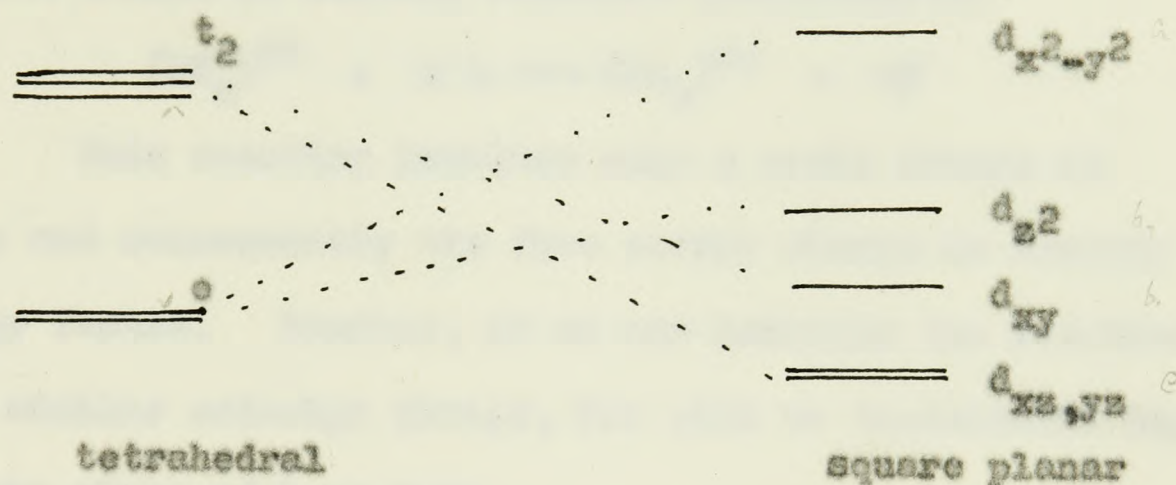


Figure 1.1

Clearly for nickel II, with eight d electrons, the square planar configuration will be preferred unless the ligand has a relatively weak field.

A low value for the " $t_2 - e$ " splitting will occur when both σ and π bonding are at a minimum, and thus the evidence supports the previous discussion on the relative effects of aryl and alkyl groups on bond strength. One further effect, not considered, is the possibility of steric hindrance between bulky aryl groups in square planar configuration which causes the molecule to distort into a tetragonal form. This possible effect is more difficult to assess.

The stability of a complex in which tertiary amines are the donating species may be enhanced if a polydentate rather than monodentate ligand is used. This is due to the chelate effect.

A monodentate ligand will form a complex with a metal ion (which is usually solvated previously):-



This reaction involves only a small change in entropy and consequently the free energy change is largely an enthalpy factor. However, if we now consider the reaction with a similar enthalpy change, but with an 'n-dentate' ligand L' in the place of L we have

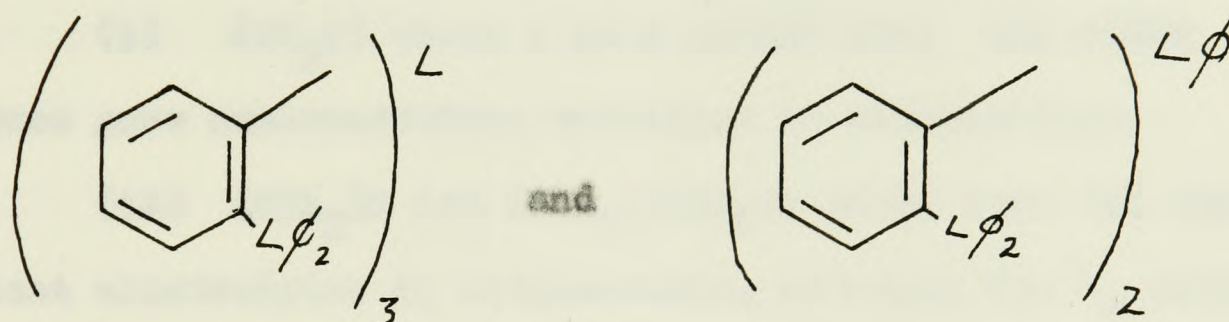


Here the number of particles increases as the reaction proceeds and the large increase in entropy will lead to a greater free energy change and thus enhanced thermodynamic stability of a complex.

The kinetic stability will also be greater. A donor atom which dissociates from the metal is linked to another attached atom, and so will be held in such a position to favour recombination. A monodentate ligand, in similar circumstances, is able to travel away from the sphere of influence of the metal ion immediately.

Complexes of transition metals with polydentate ligands containing group Vb donors have been studied by many workers. In this laboratory particular interest has been taken in the use of ligands having stringent stereochemical requirements in order to observe the effects of changes in the stereochemistry upon the properties of the complex.

To this end polydentate ligands of the type:-



have been prepared where L = As in QAS and TAS, referring to the quadri- and tridentate ligands respectively and L = P in the phosphorus analogues QP and TP, (10,11).

Provided that all the donor atoms are attached, the steric requirements of the quadridentate ligands preclude the square planar stereochemistry which is energetically favoured for d^8 metal ions. The metal is forced to adopt trigonal bipyramidal five coordination, the fifth position being filled by a suitable monodentate ligand such as a halide ion.

Distortion of the ligand bond angles will, however, permit octahedral coordination. The five coordinate species were described in the d^8 system by Brewster and Savage (12) and

Hartley (13). An X-ray crystallographic determination confirmed the trigonal bipyramid structure for $[\text{PtQASl}](\text{BPh}_4)$. The five coordinate complexes of the d^8 ions described by Nyholm (14,a,b) and Livingstone (15,a,b) are also of interest. These investigations considered complexes of the divalent metals with bidentate arsenic and arsenic-sulphur chelating ligands (L). Three types of complex were formed:-

(i) $[\text{MX}_2\text{L}]$ where X is a halide ion; all these complexes gave non-conducting solutions in nitrobenzene.

(ii) $[\text{MXL}_2]\text{X}$ and $[\text{MXL}_2](\text{ClO}_4)$, which were all univalent electrolytes in nitrobenzene, although low λ_H values suggested equilibria with six-coordinate species or alternatively $[\text{MXL}_2]^+\text{X}^- \rightleftharpoons [\text{MX}_2\text{L}] + \text{L}$. In aqueous solution the complexes tended to dissociate to 1:2 electrolytes as $[\text{ML}_2]^{+2}$ species.

(iii) $[\text{ML}_2](\text{ClO}_4)_2$ which were 1:2 electrolytes.

The factors which influence a d^8 metal ion and lead it to adopt four or five coordination may be considered. One more σ bond is formed by the attachment of the fifth ligand. However, there is an attendant increase in the energy of d_{z^2} , d_{xz} and d_{yz} orbitals due to electrostatic repulsion between electrons in these orbitals and those from the ligand approaching along the z-axis.

When π bonding is considered we have two further opposing effects.

Metal to ligand π -donation will withdraw charge from the d_{xz} and d_{yz} orbitals upon the formation of the π bond and so the repulsion effect on the fifth ligand will be reduced. On the other hand, four-coordination may be stabilised with respect to five-coordination by the following mechanism. The metal forms four planar bonds by dsp^2 hybridisation. This leaves the p_z orbital which is capable of forming hybrids with d_{xz} , d_{yz} orbitals to give strongly directional π bonding p-d hybrid orbitals with greatly increased overlap (fig. 1.2).

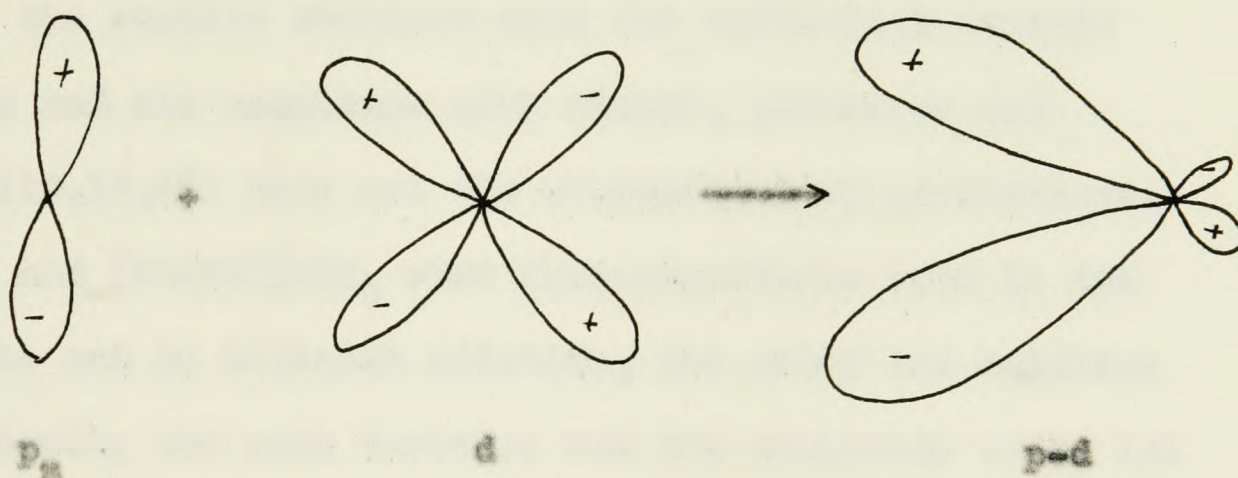


Figure 1.2

This will lead to stronger π bonding than pure d-d interaction. The dsp^3 hybridisation required for five-coordination does not leave a p_z orbital available for such hybridisation.

The stability of five-coordinate species is found to be in the order $Ni > Pd \geq Pt$. This is to be expected since the s-p separations in platinum and palladium are larger than

that of nickel (16). Consequently the heavier metals prefer the dsp^2 scheme with one less high energy p orbital. Further, the possible distortion of the d-electron charge cloud from spherical symmetry is always much greater in the second and third transition series than in the first series and so the ligand field splitting and stabilisation of electrons in d_{z^2} non-bonding orbital for square planar configuration is much greater. In general the ligand field splitting increases by ca. 1:1.45 in moving from the first to the second transition series (17).

The results obtained with the tridentate arsenic ligand TAS and its complexes with nickel, palladium and platinum (10,12,18) bear out the stereochemical predictions. $[TASPtI]I$ and $[TASPtI]ClO_4$ were four-coordinate both in the solid state and in methanol solution, the solid and solution spectra showing the same features and the compounds being 1:1 electrolytes in nitrobenzene. However, the palladium analogue $[TASPdI_2]$ is five-coordinate in the solid state and in benzene solution. In methanol its spectrum is equivalent to that of $[TASPdI]ClO_4$ and it is thus four-coordinate. It has a low conductivity in nitrobenzene due to an equilibrium $[TASPdI_2] \rightleftharpoons [TASPdI]^+ + I^-$. The nickel compounds show infra-red spectral evidence of a fifth bond even in a perchlorate complex.

Comparison with the corresponding TP complexes shows that, as expected, the phosphorus donor gave complexes with a greater tendency to four-coordination. The greater electronegativity of phosphorus leads to stronger π acceptor properties and thus supports the above hypothesis that p-d hybridisation may occur in this case. This increases the tendency to four-coordination.

The case of nitrogen as a donor atom raises many interesting points. This atom has no π acceptor orbitals but it has a greater electronegativity than phosphorus. Thus if the four-coordination is favoured by π bonding one might expect that the nitrogen analogue would yield five-coordinate species the series being $N > P < As$. On the other hand, if the effect is an electrostatic polarisation effect then the four-coordinate species will be favoured in the series $N > P \gg As$.

Several polydentate nitrogen ligands and their complexes with platinum and palladium were studied during the Part II thesis (19). Many complexes of this type have also been described in the literature. The salts $[Mtrien][MCl_4]$, (where trien is the quadridentate triethylene tetramine, fig. 1.3) are known and redissolve in presence of excess ligand to give pale yellow aqueous solutions.



trien

Figure 1.3

Jonassen and Cull (20) carried out spectrophotometric studies on the platinous ions in aqueous solution and found the species similar to $[\text{M}(\text{en})_2]^{+2}$, where en = ethylene diamine. Neither platinum nor palladium complexes of trien could be isolated as pure crystalline substances (19). They were prepared by refluxing the bis-dimethyl sulphide metal dihalide in anhydrous solvent with trien and were cream or white powders and very hygroscopic. They contrasted with the $[\text{M}(\text{en})_2]\text{X}_2$ complexes prepared by Plowman (21).

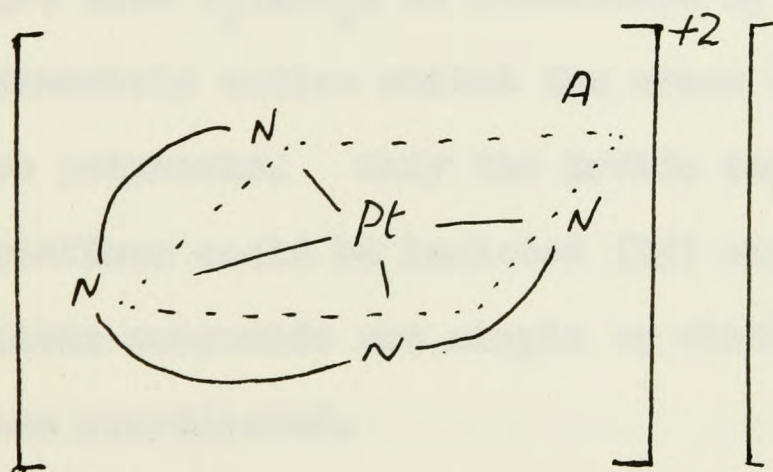
 $[\text{Pt trien}]^{+2}$

Figure 1.4

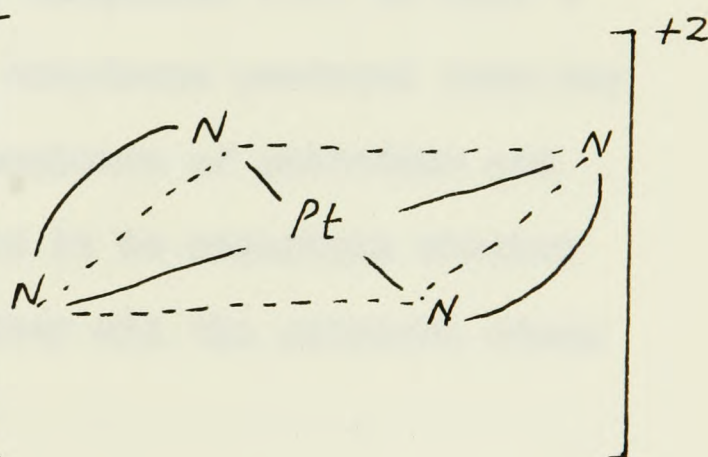
 $[\text{Pt}(\text{en})_2]^{+2}$

Figure 1.5

It is possible that the H-C-C-N distances are slightly too short to yield right-angled H - Pt - N bond angles and thus the whole molecule is strained in the trien complex (fig. 1.4) but not in the bis-ethylene diamine complex (fig. 1.5). Aquation could then occur as attack would be easy at A.

An alternative possibility is that the hygroscopic substance is polymeric with H-C-C-N bridging groups.

Complexes of the ligand tris(β -aminoethyl)amine, tren, with palladium and platinum have also been reported (22, 23). This ligand cannot form square planar complexes and Mann and Pope suggested that it would form tetrahedral complexes. However, the intra-molecular distances involved are too small for this stereochemistry. Two forms of the platinum iodide complex are known. The white crystalline $[\text{Pt tren I}_2] \cdot 2\text{H}_2\text{O}$ is considered by Jørgensen (24) to have a monomeric cation whilst the cream anhydrous powdered form may be polymeric. Only the iodide complexes of palladium and platinum could be isolated (19) and it is uncertain whether these compounds are simple or whether all the nitrogen atoms are coordinated.

Seeking a comparison with the TAS and TP complexes described above, some complexes of diethylene triamine, dien, were prepared and studied (19). The complexes $[\text{Pd dien X}]X$, where X is a halide ion, were all found to be 1:1 electrolytes

in aqueous solution although the high value for the dichloride suggests a possibility of a reaction



In solution in such a very strongly donating solvent as water it is not surprising that no evidence for five-coordination is observed. A weakly bound ionic ligand on the z-axis would gain in energy by hydration whilst its perturbation could be replaced by that of dipolar water molecule.

The ultra-violet spectra of the complexes in aqueous solution showed typical ligand field shifts from the chloride to the iodide complex. Noteworthy, however, was the difference between solid and solution spectra in each case. The solid spectra had an additional peak at 24,000-28,000cm.⁻¹, lower than any feature observed in the solution spectra. This was interpreted as evidence of interactions in the solid consistent with a higher coordination number in this phase.

Full studies of the above complexes had been limited by the insolubility of the compounds in non-coordinating solvents. One of the aims in the present work was to devise a ligand of similar type which would form complexes with better solubility properties.

Bidentate nitrogen ligands were chosen for the first experiments, being the simplest compounds to synthesise. The ligands meso-stilbene diamine, m-stien, and the para isopropyl

derivative, p-stien, were synthesised. Although they did not meet the requirements exactly, several compounds of these ligands have been prepared during the current study and their properties discussed. The background to this research with complexes of copper II and nickel II will now be considered.

For many years compounds of these metals with this type of ligand have been known. One very interesting part of the study of this type of complex has been the magnetic behaviour, particularly in the case of nickel II. Compounds of nickel II may be classified as either "low-spin" complexes, which are diamagnetic, or "high spin" complexes which are paramagnetic. The latter have magnetic moments corresponding to two unpaired electrons. Providing that there is no significant orbital contribution the value of μ_{eff} is approximately 2.8 Bohr magnetons.

Bivalent nickel has eight d electrons and in the free ion, with all d levels degenerate, we may state from Hund's rules that there will be two unpaired electrons.

Removal of the degeneracy in an octahedral field (fig. 1.6) will not change the magnetic moment as the doubly degenerate e_g level will contain the two unpaired electrons. Distortion of the field along the z-axis, however, will have the effect of removing such a degeneracy. The e_g energy levels may be described as $d_{x^2-y^2}(b_{1g})$ and $d_{z^2}(a_{1g})$.

Elongation of the bonds on the z-axis (tetragonal distortion) is accompanied by shortening of those in the plane; the energy of the $d_{x^2-y^2}$ orbital is increased and that of d_{z^2} lowered. Finally in the square planar configuration this distortion is complete. The complex will remain paramagnetic until Δ' is larger than the energy required to pair two electrons.

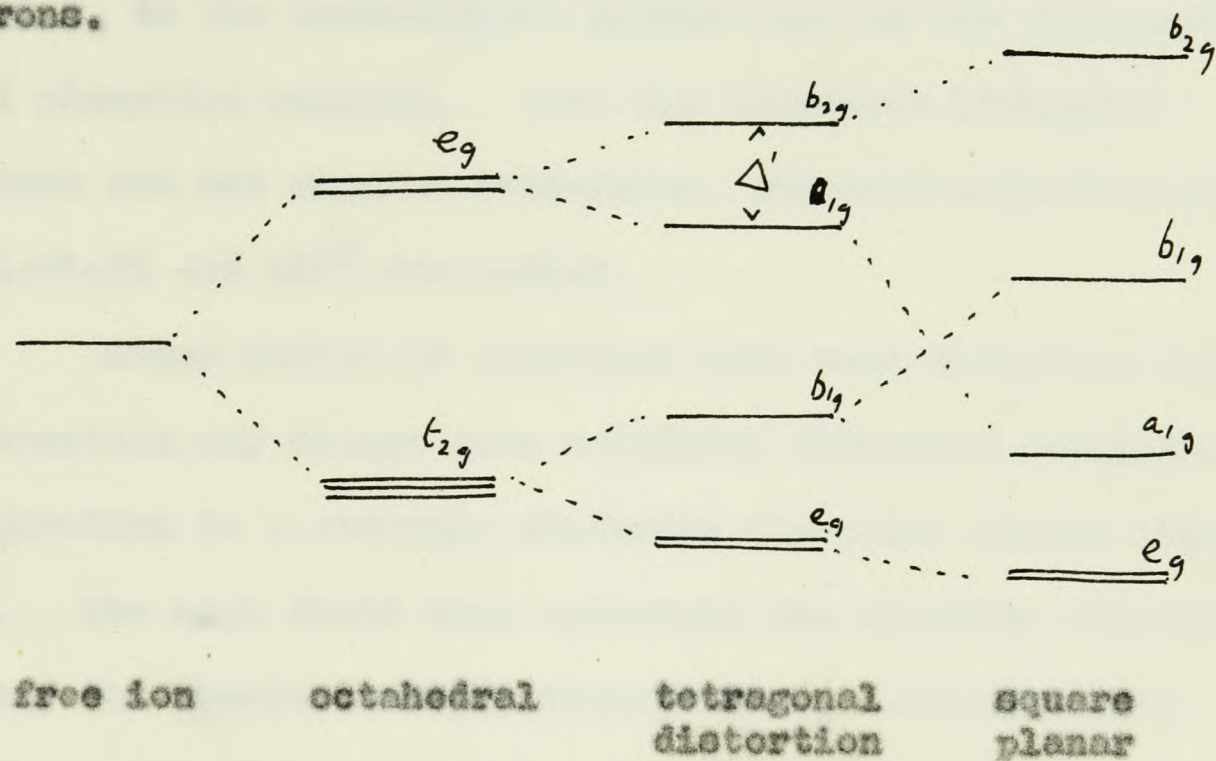


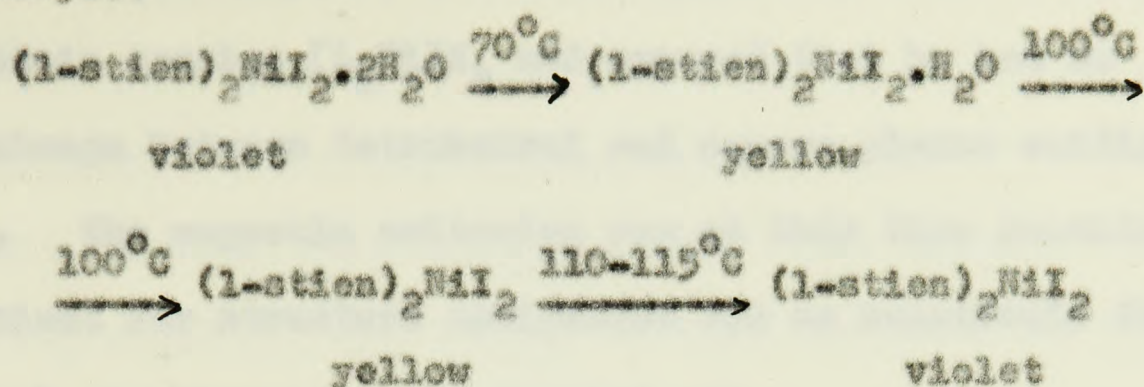
Figure 1.6

In a tetrahedral environment nickel would again be paramagnetic as the upper level is triply degenerate (t_2). Thus on magnetic criteria alone we may choose between a square planar or strong tetragonally distorted complex of nickel II which is diamagnetic and an octahedral or tetrahedral complex which will be paramagnetic.

quite small changes in environment may cause a change from tetrahedral to square planar complexes. The work of Coussemaeker and Venanzi (25,26) on trisubstituted phosphine nickel II complexes has shown that the structures of the bis-phosphine nickel halides change from tetrahedral with triphenyl phosphine, through the tetragonal complexes of n-butyl diphenyl phosphine, to the trans-square planar form of the di-n-butyl phenyl phosphine complex. Even the triphenyl phosphine complexes are not regular tetrahedra, the bond angles are 131° for Cl-Ni-Cl and 108° for P-Ni-P.

Other series of complexes have been described where the structure may change from a slightly distorted octahedral configuration to a strongly distorted one under higher ligand field. The high field then outweighs the electron repulsion term and the complex becomes diamagnetic. Lifschitz and co-workers (27,28,29) and also Hein (30,31) have described complexes of nickel with some C substituted ethylene diamines $(H_2NCHRCRHNH_2)_2 \cdot L$. The complexes have the general formula $L_2NiX_2 \cdot H_2O$ and the coordination numbers and stereochemical arrangements seem to depend in no obvious way on the diamine, anion, hydration or conditions of formation.

For example:



where (1-stien) is laevo-stilbene diamine, $R = \text{C}_6\text{H}_5$.

D. M. L. Goodgame (32) has surveyed the very large number of diamine nickel complexes described in the literature. The compounds fall into two main groups; blue or violet and usually paramagnetic compounds and yellow or orange diamagnetic ones. Glaser and Pfeiffer (33) postulated that the blue bis-ethylene diamine nickel diperchlorate dihydrate had the water molecules coordinated to the nickel ion to form octahedral complexes. These water molecules were lost on heating and the molecule degraded to the yellow, square planar diamagnetic form.

Lifschitz investigated many bis-diamine nickel complexes. He also observed that in some cases both anhydrous and hydrated forms of the complex were yellow and diamagnetic whilst in others anhydrous and hydrated complexes of the same stoichiometry possessed different colours and magnetic properties. Lifschitz measured the electrolytic conductance of five of his compounds in alcohol, showed them

to be 1:2 electrolytes; he deduced that they were four-coordinate species $[L_2Ni]X_2$ and assumed that he had an interchange between tetrahedral and square planar configurations. The magnetic criterion was at this time considered sufficient for structure assignment and so relatively few physical measurements were carried out.

Goodgame (32) investigated a series of N and C substituted ethylene diamine complexes of nickel and compared the physical properties of the series.

These complexes had the general formula $[L_2NiX_2].nH_2O$. Frequently hydrates were of a different colour and magnetism to the anhydrous compound; thus the compound $[Ni(a-dien)_2Br_2]$, where a-dien is N,N diethyl ethylene diamine is orange and diamagnetic whilst the dihydrate is blue and paramagnetic.

Goodgame measured the electrolytic conductances of his complexes in nitrobenzene and found that all blue complexes were non-electrolytes; so also were the yellow forms of $[Ni(m-stien)_2(CCl_3CO_2)_2]$ and $[Ni(m-stien)_2(CHCl_2CO_2)_2]$. In all of these compounds the anion must be firmly attached, presumably on the z-axis. The majority of the yellow and orange bis-diamine dihalide and nitrate complexes were intermediate electrolytes in nitrobenzene. In these cases partial solvolysis must occur.

Complexes of divalent cobalt are also of interest.

The d^7 ion may form tetrahedral or octahedral species the latter having either high or low spin. Thus

$[(dipy)_3Co](ClO_4)_2$ has a $\mu_{eff.}$ of 4.86 (34) whilst

$*[(das)_3Co](ClO_4)_2$ has a $\mu_{eff.}$ of 1.92 (35), (where $dipy$ is 2,2'-dipyridyl and das is *o*-phenylene bis-dimethyl arsine).

Hartley (18) found that cobalt (II) halides, $CoX_2 \cdot 6H_2O$ reacted with QP on refluxing in ethanol to give complexes $[CoXQP]X$, the five-coordinate species. The corresponding QAS complexes were not formed in ethanol, the QAS was presumably unable to displace the ligands with oxygen donor atoms. Mawby (36) prepared QAS complexes of Co II in the absence of oxygen donors; from QAS and the bis-triphenyl phosphine cobalt dihalide. The only compounds that he isolated were, however, the complex species described as $[CoXQAS]_2[CoX_4]$. However, the conductivities of these species in nitrobenzene were low for the 1:2 electrolytes suggested. Also the conductivity increased when methyl iodide was added due to the quaternarisation reaction.



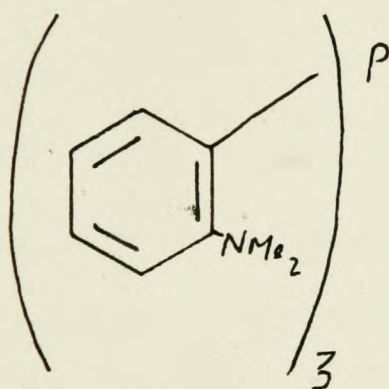
Either the metal-arsenic bonds were severed in such a reaction or possibly the ligand did not have all the arsenic atoms coordinated.

The QP complexes of Hartley had magnetic moments in the range 1.82-1.92 B.M. and so contain one unpaired electron. The QAS complexes have a moment, when corrected for the value of the $[\text{CoX}_4]^{-2}$ ion, of 3.4-2.8 B.M. This is low for three unpaired electrons, possibly these complexes come on the borderline of high and low spin.

Monovalent copper complexes have also been extensively studied. Monophosphines form compounds of the empirical formula $[\text{R}_3\text{P.MI}]$ (37). A tetrameric structure has been ascribed to this, the four copper atoms lying at the apices of a tetrahedron with coordination number of four. Burrows and Sandford (38) reported some copper I complexes, prepared from a monoarsine and either copper I or copper II halide. No cupric complex was isolated.

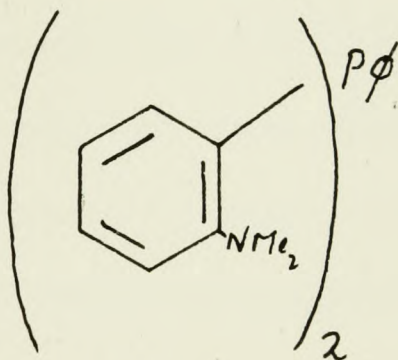
Chelating ligands yielded monomeric complexes. Thus *o*-phenylene bis-dimethyl arsine, das, gave compounds $[\text{Cu}(\text{das})_2]\text{X}$ and $[\text{Cu}(\text{das})_2][\text{CuCl}_2]$ (39). The copper II analogues could not be isolated. Mann et al. prepared complexes of the same type with *o*-diethylphosphinophenyl diethyl arsine (40). QP forms cuprous complexes of the empirical formula $[\text{qPCuX}]$ (41). The methyl iodide quaternization reaction was positive, suggesting that either the P atoms are very weakly bonded to copper or that all of the atoms are not attached initially.

The work described in this thesis consists of the preparation of a series of nitrogen ligands and a study of the complexes of these ligands with some transition metal ions. Part of the work describes some complexes of meso stilbene diamine with divalent copper and complexes of the *pp'* isopropyl derivative with nickel II. The greater part of the work is an investigation of the complexes of the polydentate nitrogen/phosphorus ligands designated PTN, PDN and PN, where PTN is tris(*o*-dimethylaminophenyl)phosphine (fig. 1.7); PDN is bis(*o*-dimethylaminophenyl)phenyl phosphine (fig. 1.8) and PN is *o*-dimethylaminophenyl diphenyl phosphine (fig. 1.9).



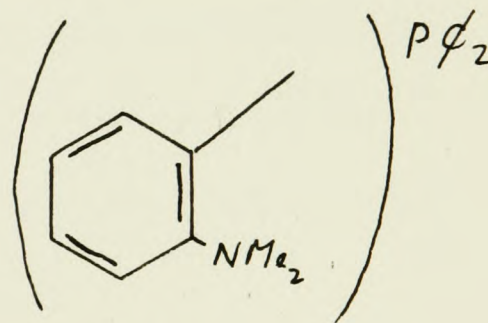
PTN

Figure 1.7



PDN

Figure 1.8



PN

Figure 1.9

The complexes studied were of the ions Ni II, Pd II, Pt II, CuI and Co II.

The mixed donor atom ligands were chosen rather than, say, Q^N , tris(*o*-dimethylaminophenyl)amine, as the tertiary aromatic amine would be expected to have exceedingly weak donor

properties; further such a synthesis would involve nitrogen trichloride as a reagent and finally the positioning of a single π acceptor on the z-axis would give rise to stronger complexes with b class metals without attendant loss of symmetry in a C_{3v} trigonal bipyramid. These ligand systems seemed most suitable for comparing the complexes formed with those of the analogous ligands with heavy group Vb donor atoms.

The general description of the ligands, complexes and discussion of the results obtained is contained in the first part of the thesis. Part two contains the experimental details of preparations, analytical methods and results together with the details of the physical measurements.

CHAPTER II

SYNTHESIS OF THE LIGANDS

Studies of the complexes of the ligands diethylene triamine, triethylene tetramine and tris(β -amino-ethyl)amine described in the Part II thesis (19) had been limited by the insolubility of such ionic species in non-polar solvents. Attempts were, therefore, made to prepare analogues of these ligands which would improve the solubility properties of the complexes. Bidentate ligands were used as these were the simplest to prepare and were adequate to discover whether the complexes exhibited the required properties.

A. Attempted synthesis of 1,2 dipentyl ethylene diamine.

The synthetic route is illustrated diagrammatically in figure 2.1.

The hexanoic acid was esterified by refluxing with a threefold excess of methanol in the presence of concentrated sulphuric acid. The pure redistilled ester was produced in 85% yield.

25.

Attempted Preparation of $\text{C}_5\text{H}_{11}\text{CH}(\text{NH}_2)\text{CH}(\text{NH}_2)\text{C}_5\text{H}_{11}$

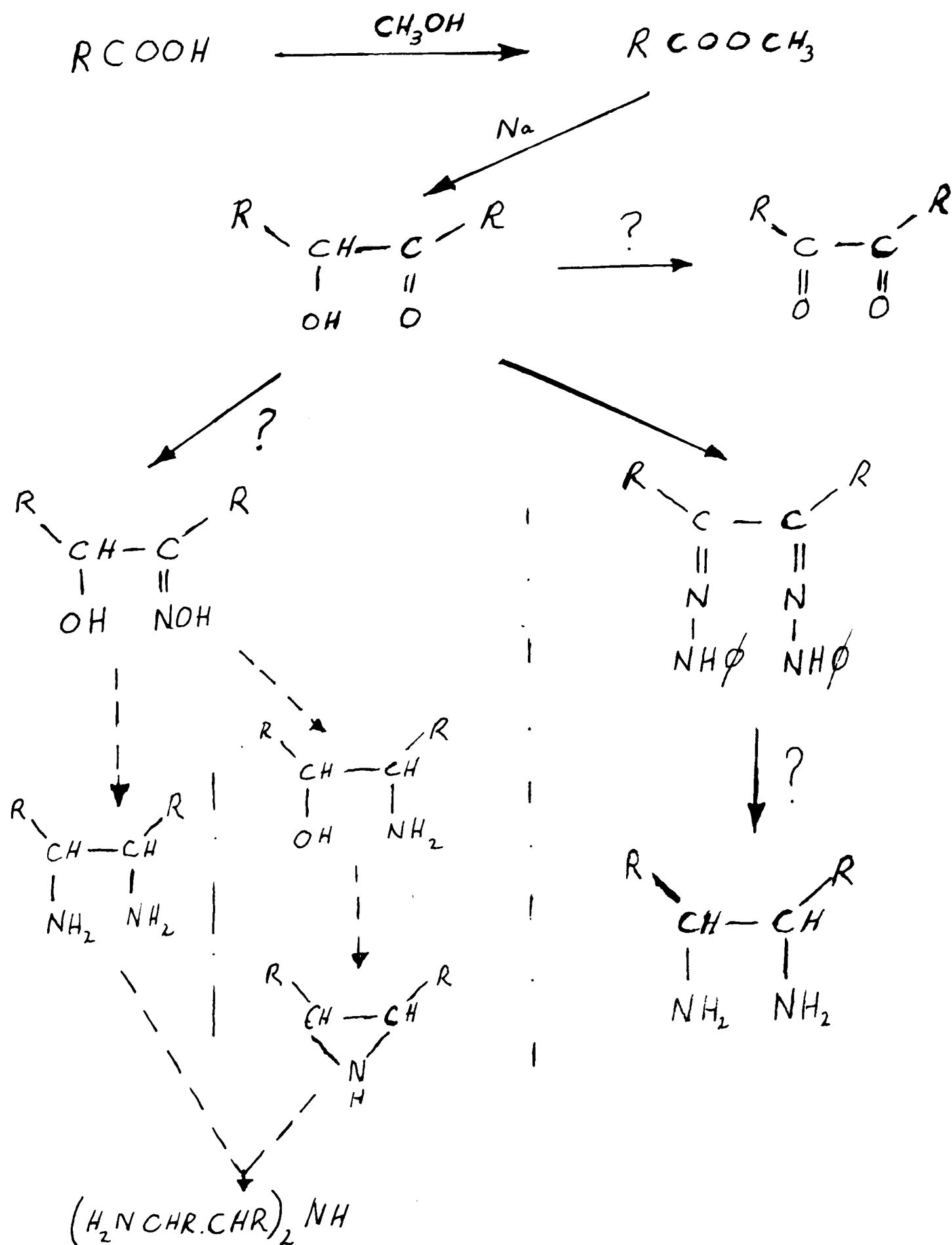


FIGURE 2.1

The ester was used in a coupling reaction to produce the basic C_{12} chain required, with activated carbon atoms at C_6 and C_7 . An acyloin condensation was employed (42-4) and was performed with molten sodium suspended in dry xylene. The method and concentration described in the literature led to severe problems in the stirring of the reaction mixture as the reaction proceeded. The mixture must be intimate as the heat of reaction is employed to keep the temperature in the limits of 105-110°C. Local overheating caused by inefficient mixing of the reactants led to reduction of yields and an increase of impurities, such as the α -diketone, which were difficult to remove from the product. As the reaction proceeded the mixture slowly became more viscous and achieved a gel-like consistency. The first attempts at this reaction gave low yields and several designs of stirrer and concentrations were tried to find the optimum conditions. The best stirring system was found to be a twisted Nichrome wire stirrer attached to a glass rod and shaped to sweep the surface of a 5 litre flanged flask. The best dilution of the reactants was found to be 92gm. sodium in 3 litre xylene with the addition of 180ml. methyl hexanoate. The excess sodium was destroyed by the addition of methanol and after cooling, the alkali removed, by extraction with water and washing with acid and sodium bicarbonate. The caproin was

isolated by removal of the xylene by vacuum distillation (Bpt. $58^{\circ}\text{C}/44\text{mm.}$) rather than the steam distillation described and the product fractionated under nitrogen.

The infra-red spectra of the three fractions boiling between $98-112^{\circ}\text{C}$ at $1.8-2\text{mm.}$ all showed both hydroxyl and carbonyl peaks, though the relative intensities varied, increasing in $\text{C}=\text{O}$ as the boiling point rose.

Thus the first fraction contained most of the acyloin together with some α -diketone.

As further purification was not possible, the caproin was used in an attempt to prepare the α -hydroxy-oxime. The usual method (45,46) was employed, an aqueous solution of hydroxylamine hydrochloride and ethanolic solution of the ketone being mixed, and a concentrated aqueous solution of sodium hydroxide added slowly with cooling. The mixture was shaken mechanically for five minutes and then refluxed for a further five minutes. The cooled solution was poured into 10% hydrochloric acid. However, no crystalline oxime was formed by this method. The method was repeated with longer refluxing times but in no case was a crystalline product isolated.

It is possible that the contamination with α -diketone led to a mixture of partially oximated products and the mixed product then failed to crystallise. An attempt was,

therefore, made to oxidise the impure acyloin to the diketone and isolate this as the dioxime.

The method of oxidation used is reported to give 90-100% yields with benzoin. The impure acyloin was placed in a flask fitted with two reflux condensers and was oxidised with ammonium nitrate/cupric acetate in acetic acid (47). The reaction was initiated by warming and stirring to dissolve the constituents and then cooling to moderate the reaction as nitrogen was evolved. Refluxing for two hours and cooling gave no crystalline product. On dilution with water a brown oil separated. As no dioxime was formed on treatment with hydroxylamine hydrochloride the experiment was repeated and the oil fractionated. Infra-red spectra showed no evidence of conversion to the diketone - much starting material and a variety of oxidation products were present.

This reaction was not pursued as a further reaction route was available. The route was the conversion of the caproin to its osazone by the method of Bloink (48). It was found necessary to modify the described method by adding 5% propionic acid to the acetic acid solvent at 0°C, in which system the phenyl hydrazine reacted smoothly with the α -hydroxy-ketone and after one hour a white crystalline precipitate was formed. The osazone was recrystallised from ethanol and the pure product showed the expected infra-red

absorption bands; the C = N stretching frequency is lowered by about 40cm.^{-1} in this conjugated system from that usually found, but there are no carbonyl bands visible. This complex ^{ound} gave good analytical results.

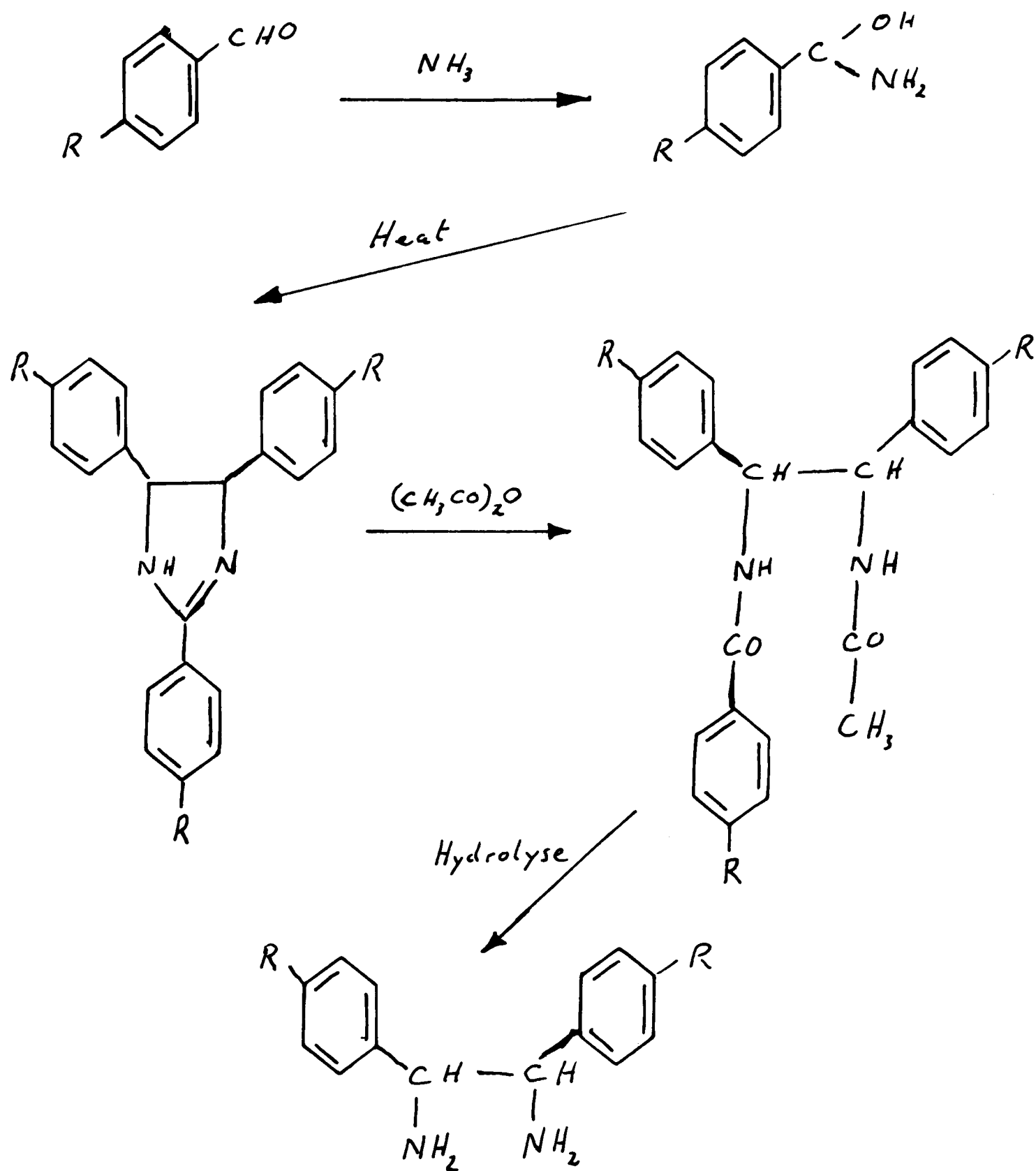
A suitable method of reduction of this compound to the diamine was sought. Several reduction techniques were applied. Reduction with aluminium amalgam gave a tarry substance, from which no diamine could be isolated, under a variety of reaction temperatures. Reduction with hydrogen on 'new' platinum, the method of H. C. Brown and G. A. Brown (49), was then attempted. Fresh platinum was deposited on carbon by reduction of sodium chloroplatinite with sodium borohydride in absolute ethanol. Hydrogen was then produced by slowly adding the borohydride solution to the acidified reaction mixture. The oily product was extracted with ether from a basic medium and fractionated. However, the infra-red spectra of the fractions showed N = N peaks still in evidence in the first fraction. The second fraction was certainly reduced but still contained phenyl groups and was presumably partially reduced polymeric material. Further, neither fraction gave typical ethylene diamine type complexes with a nickel chloride solution and thus the desired reduction was not accomplished. The synthesis was, therefore, abandoned and other possible routes to suitable diamine and polyamine ligands were investigated.

B. Meso-stilbene diamine.

The synthesis of this ligand is essentially that of Mills and Quibell (50) and is shown diagrammatically in figure 2.2.

Hydrobenzamide was prepared in 90% yield on shaking benzaldehyde and ammonia as described by Francis (51). This was converted to 2,4,5-triphenyl, 2-imidazoline by controlled heating, the method of Bertagnini (52). The preparation of benzoyl acetyl stilbene diamine was accomplished by refluxing the crude product with acetic anhydride. A modification of the quoted conditions involved refluxing for three hours and then pouring into 10% hydrochloric acid whilst still hot. After about one minute the fine white product precipitated and thus it was unnecessary to heat for the customary two hours on a water bath. Boiling out twice with ethanol served to purify this product and a yield of 40-50% was achieved.

The last stage, hydrolysis of the substituted amine to meso-stilbene diamine was the most difficult. Hydrolysis was achieved with 50% sulphuric acid and the benzoic acid steam-distilled from the reaction mixture. Using a 50% mixture the distillation took about twelve hours, by which time considerable decomposition of the diamine had occurred. Increase in the acid strength reduced the time required but increased the rate of oxidation of the amine. Optimum



$R = \text{H}$ in *m*-stien ; $R = \text{C}_3\text{H}_7$ in *P*-stien

FIGURE 2.2

conditions were found to be 550ml. acid to 500ml. water. It was found to be essential to cool the mixture thoroughly when neutralising the acid mixture with .880 ammonia, careful stirring in a 5 litre beaker full of ice sufficed. The average yield of the last stage was 17%, the overall yield being 7.7% of pure meso-stilbene diamine.

The complexes of this ligand are discussed in the next chapter; they did not have the required solubility properties in non-polar solvents and so tridentate and tetradentate derivatives of this ligand were not prepared. Instead a substituted stilbene diamine was prepared with the aim of providing a more suitable ligand for the study of the complexes.

C. P,p'-isopropyl meso-stilbene diamine, p-stien.

This ligand was prepared using the method described above for the unsubstituted stilbene diamine. Para-isopropyl benzaldehyde (technical) was redistilled but its reaction with ammonia did not give a solid product. Shaking with .880 ammonia for seven days only yielded a milky semi-solid glue and a supernatant aqueous layer. This was converted to the substituted amarin by heat, as before, and the ring was opened by acetylation under the same conditions. The overall yield of the benzoyl acetyl derivative was 30%.

The hydrolysis of this to yield the diamine was carried out with 59% sulphuric acid, steam-distilling the benzoic acid as before, but the yields in this stage were very low due to oxidation and decomposition of the amine. The yield was 3.5% of pure p,p'-isopropyl meso-stilbene diamine reprecipitated from aqueous solution with sodium hydroxide.

The yield was improved at this stage by two slight modifications. Firstly the sulphuric acid/water mixture used was 520ml. acid to 500ml. water, minimizing charring and oxidation. Secondly the aqueous extraction of the product led to further decomposition and it was found to be preferable to extract with ethanol and to precipitate the product with dilute aqueous alkali. The yield in the hydrolysis stage was then 10% giving an overall yield of 3%. The infra-red spectrum and analysis confirmed that this was the required product.

Complexes of this ligand were studied but were found to have unusual solvation effects and it was decided to prepare the three ligands below as a comparison with the phosphorus and arsenic analogues QP and QAS to observe the effects produced by changing the group V donor atom.

- D. Tris(o-dimethylaminophenyl)phosphine, PTN; bis-(o-dimethylaminophenyl)phenyl phosphine PDN, and o-dimethylaminophenyl diphenyl phosphine, PH.

The synthetic route used in the preparation of these ligands is shown diagrammatically in figure 2.3.

Stage I : The o-bromaniline was methylated with a threefold excess of dimethyl sulphate by the method of Gilman (53) and the product was fractionated under argon at 12mm. The infra-red spectra of the product fractions showed that all contained secondary amine and the higher boiling ones primary amine groupings. Thus the methylation was incomplete. Repeated fractionation using long columns did not serve to separate the primary and secondary components, whose boiling points were very similar. The boiling points are recorded as 107-8°C/14mm. for the tertiary amine and 117°C/14mm. for the secondary amine. Recourse was, therefore, made to chemical separation of the mixture.

The Hinsburg separation technique was first attempted using p-tolyl sulphonyl chloride. This was shaken in alkaline solution with the amine and the residual (tertiary) amine extracted from ethereal solution with aqueous acid, liberated and fractionated. Infra-red examination of the fractions showed that the product still contained some secondary amine, though the N - H stretching frequency peak was considerably reduced in intensity.

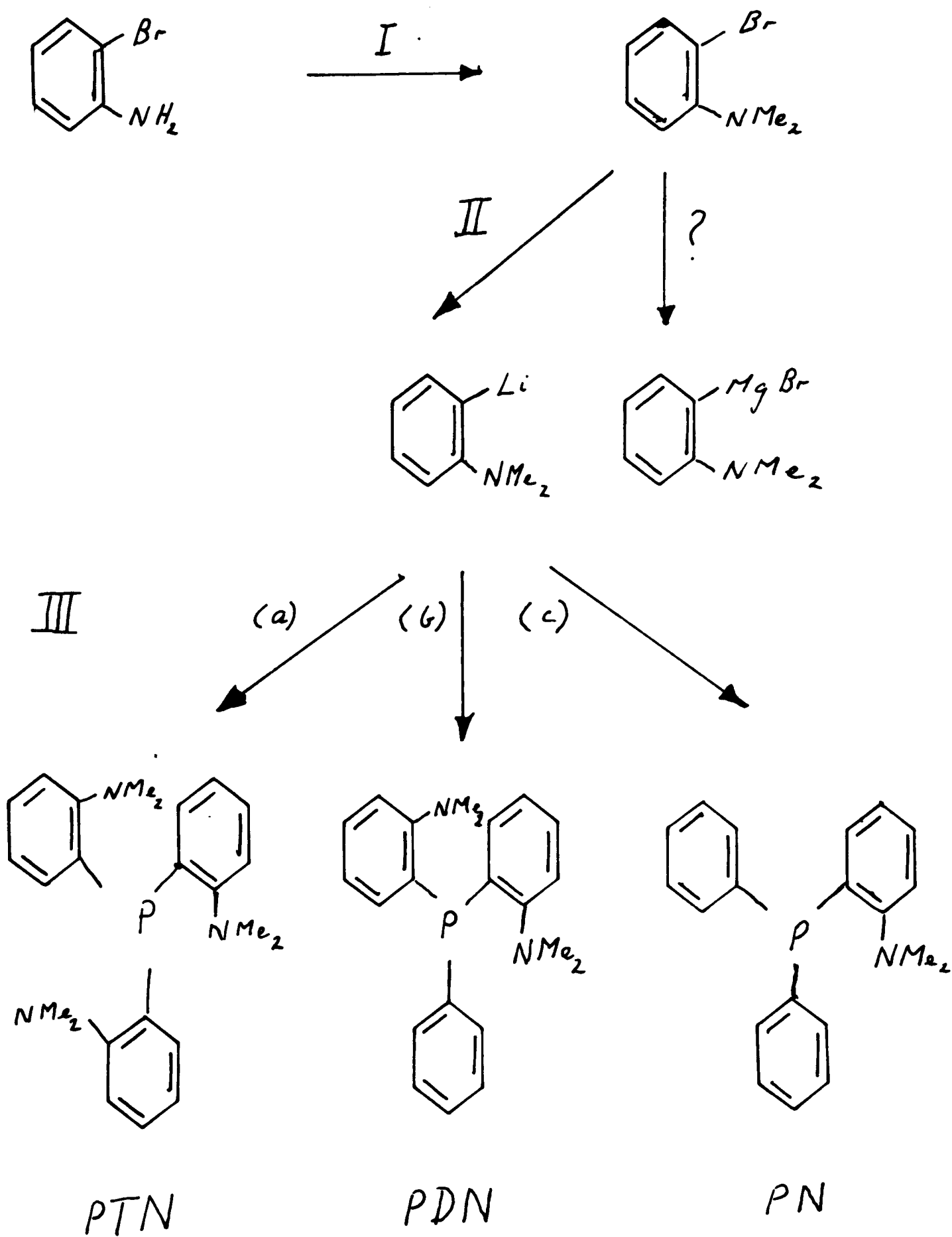


FIGURE 2.3

It was most important to remove all the activated hydrogen atoms from the product before attempting Stage II and so a second purification method, of Auwers (54) was used.

The impure amine was refluxed with excess acetic anhydride in order to acetylate all the unwanted primary and secondary amines. The product was separated and extracted with acid, neutralised and extracted with ether. This product showed no N - H peak in its infra-red spectrum but did contain a strong band at 1670cm.^{-1} assigned to C = O. The product was, therefore, carefully fractionated under reduced pressure and under argon and the final product then had the spectrum expected for o-bromodimethyl aniline and was used in the next stage.

Stage II : Several authors (55-7) have prepared the Grignard reagents of compounds similar to o-bromodimethyl aniline and so this method was first attempted. It was found to be very difficult to initiate the Grignard reaction with o-bromodimethyl aniline, despite meticulous drying of apparatus, reactants and solvent. Neither an iodine crystal nor a few drops of liquid bromine were successful; 1,2 dibromethane or methyl iodide being required.

In one instance the magnesium soon became coated with a sticky deposit but on other occasions the reaction proceeded smoothly, with cooling in an ice-bath. The reaction

product (presumably the Grignard reagent) was then reacted in situ with the calculated quantity of phosphorus trichloride. This was added very slowly over several hours to the Grignard reagent in a dilute solution in dry ether. Even so, cooling in an acetone/ CO_2 bath was required to keep the temperature at -10°C . The product was hydrolysed with ammonium chloride in the usual manner and the basic constituents of the product extracted with ether. Although the infra-red spectrum showed evidence of the type of product expected, it was very complex and the required phosphine could not be isolated from this mixture by fractionation or chemical separation.

The Grignard method having failed, the alternative route via the lithio derivative was now attempted. Again this route has been followed by several authors (18,56,58) with similar compounds.

All apparatus was very carefully dried and a solution of n-butyl lithium in ether prepared as described in the experimental section. Hartley (18) had used coils of lithium wire to prevent the fusing of the lithium during this reaction but this had the disadvantage that considerable surface oxidation of the lithium occurred during the preparation of the coils. A preferable method was found to be the hammering of the lumps of metal into a thin sheet, this being cut into thin strips with scissors. Also the reaction was

carried out under argon and at lower temperatures than suggested by Hartley, the yield being improved by these modifications.

Stage III : (a) The o-bromodimethyl aniline was lithiated and the calculated quantity of phosphorus trichloride in dilute ethereal solution was slowly added. Hydrolysis, and extraction gave an off-white product which when recrystallised from ethanol proved to be tris(o-dimethylaminophenyl)phosphine, PTN. This being confirmed by the infra-red spectrum and by analysis.

The yield in the last stage was 30% and the overall yield 21%.

(b) The same general method as that above was used to prepare the tridentate ligand bis(o-dimethylaminophenyl) phenyl phosphine, PDN. The calculated quantity of phenyldichlorophosphine was added instead of PCl_3 in dilute ethereal solution at the last stage.

The first preparation of PDN yielded a brown oil which was difficult to purify. Fractionation removed dimethylaniline and other impurities at 1.3mm. under argon but left a tarry oil. The infra-red spectrum had the expected features and so purification was attempted. Extraction with ethanol yielded no solid precipitate, and dry HCl gas produced a sticky impure product.

The addition of an ethanolic solution of this to an excess of nickel bromide in ethanol did form a powdered precipitate of a complex which had similar properties to the PTN analogue. This was then warmed with an aqueous solution of disodium ethylene diamine tetra-acetic acid and an oil was liberated, the nickel going into solution. This oil was extracted and on removal of ether crystallised to a white solid, which was recrystallised from 80% aqueous ethanol. The second preparation of PDN gave a better yield and did not require such elaborate purification. The phenyl dichlorophosphine had been redistilled for this preparation. The yield of PDN was 45% giving an overall yield of 32%.

(c) Again, the same method was employed in the synthesis of *o*-dimethylaminophenyl diphenyl phosphine, PN. In the last stage, diphenyl chlorophosphine was added to the lithioderivative at -40°C very slowly. The reaction proceeded smoothly and the solid product was recrystallised from ethanol in good yield. The overall yield of PN was 39%.

E. Attempted preparation of tris(*o*-aminophenyl)phosphine.

This ligand would show modification of the infra-red N - H stretching frequencies on the formation of a coordinate link and this would provide valuable evidence as to the number of nitrogen atoms coordinated in a complex.

The route was as above except that three equivalents of butyl lithium were required to both lithiate the ortho-bromine atom and react with the labile hydrogen atoms. POl_3 was then added and the product hydrolysed to regenerate the primary amino grouping as well as to liberate the phosphine. However, no product could be isolated the various fractions showing evidence of degradation and polymerisation reactions.

CHAPTER III

COMPLEXES OF M-STIEN AND P-STIEN

A. Copper II complexes of m-stien

The bis-diamine cupric complexes were prepared by the general method of addition of 1 mole of the cupric salt in water to a solution of two mole of m-stien in the minimum of boiling water (27). The aqueous solutions were deep blue. The di-iodide, sulphate and dithiocyanate separated immediately from the hot solution as powdered materials. The nitrate, perchlorate and oxalate separated on standing for a short period whilst the chloride, bromide and acetate required concentration of the solution in a vacuum desiccator over concentrated sulphuric acid. $[m\text{-stien}_2\text{CuBr}_2]$ crystallised initially as a violet compound from aqueous solution. However, on standing over concentrated sulphuric acid for a week these violet crystals could be converted into a green form and recrystallised from anhydrous methanol in this form.

The method employed for recrystallisation of the complexes varied. The very insoluble substances were

soxhlet-extracted with water for purification as no solvent for recrystallisation could be found. The other substances were recrystallised from methanol or aqueous ethanol.

The complexes prepared, together with their colours, decomposition points and conductivities in nitromethane are listed in Table 3.1. Analyses of the compounds confirmed the formulae quoted in the table and further evidence of hydration was given in appropriate cases by the infra-red spectra discussed below. Analysis for copper caused some difficulties but these are discussed in the analytical section. The infra-red spectra in the sodium chloride region showed the typical bands for meso-stilbene diamine with some noteworthy modifications.

A metal amine complex of the type $M-NH_3$ will be represented by a model of the type MX_3 . Six vibrations will be expected for this model; antisymmetric and symmetric N-H stretching, NH_3 asymmetric and symmetric deformations; NH_3 rocking and M-N stretching. For the point group C_{3v} all will be infra-red active. The N-H stretching frequencies are in general lower than those in the free ligand molecule. Several factors may be responsible for this frequency shift and this has been discussed by Nakamoto (59). One is the effect of coordination; in the series

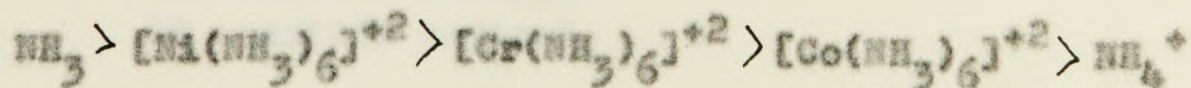


TABLE 3.1

Physical Properties of m-stien Complexes

<u>Formula</u>	<u>Colour</u>	<u>Decomposition Point °C</u>	<u>Molar Cond. in Nitromethane at 22°C (mhos)</u>
<u>COPPER (II)</u>			
[m-stien ₂ CuCl ₂].H ₂ O	violet/blue	231.5	1
[m-stien ₂ CuBr ₂].H ₂ O	violet	233	1
[m-stien ₂ CuBr ₂]	green	-	1
[m-stien ₂ CuI ₂]	green	212.3	1
[m-stien ₂ Cu(SCN) ₂].H ₂ O	blue	161.5	88.6; 19.9*
[m-stien ₂ Cu(NO ₃) ₂]	deep lilac	215 d.	1
[m-stien ₂ Cu(ClO ₄) ₂]	pink/lilac	246.5 d.	91.4; 24.6*
[m-stien ₂ Cu(SO ₄) ₂].H ₂ O	pale lilac	260.5	1
[m-stien ₂ Cu(AC) ₂].H ₂ O	lilac	197	1
[m-stien ₂ Cu(OX) ₂].H ₂ O	lilac/pink	210 d.	1
[p-stien ₂ CuCl ₂].H ₂ O	violet	121 d.	1
<u>PALLADIUM (II)</u>			
[m-stien ₂ PdCl ₂]	white	249-51 d.	1
[m-stien ₂ PdBr ₂]	white	248-50 d.	1
[m-stien ₂ Pd(SCN) ₂]	white	210 d.	1
[m-stien ₂ Pd(NO ₃) ₂]	white	271-3 d.	1

* values measured in nitrobenzene at 22°C

1 compound insoluble in warm nitromethane

d compound decomposed

AC acetate radical

OX oxalate radical

10⁻³ M

the stretching frequency decreases in the order shown. The stability order for these compounds is $\text{Co(II)} > \text{Cr(III)} > \text{Ni(II)}$. Then the N-H bond strength (and frequency) decreases as the M-N bond strength increases in the order given. Hydrogen bonding must also lower the N-H stretching frequency as it weakens the N-H bond.

The primary amine complexes of transition metals have the point group C_s and from this symmetry the following modes arise in approximate decreasing energy:- NH_2 asymmetric and symmetric stretching modes approximately the same as those in the previous case; NH_2 tilt, NH_2 bend and NH_2 rock which must be assigned by inspection where possible and an M-N stretch. Frequencies of M-R stretch, tilt and wag will also occur but are not assigned.

The complexity of such N-H stretching regions in the infra-red spectra in compounds $\text{trans}[L \text{RNH}_2 \cdot \text{PtCl}_2]$ have been discussed by Duncanson and Venanzi (60). The differences between spectra with different alkyl groups R attached to the primary amine may be interpreted in terms of restricted rotation of the amine about the M-N bond. Potential barriers to rotation may arise through several causes, firstly steric repulsion between R and chlorine atoms, secondly intermolecular hydrogen bonding and thirdly interaction between N-hydrogen atoms and non-bonding d electrons in the metal.

Intermolecular hydrogen bonding may occur either through a water molecule or through an anion such as a halide and differences are observed in the N-H frequencies of hydrated and anhydrous cupric compounds.

In the rather complex system here considered the strong N-H stretching frequencies are clearly defined. The frequencies listed in Table 3.2, correspond to peaks which appear in the complex spectrum but not in that of the free ligand. The range below $1,000\text{cm.}^{-1}$ has not been studied due to the profusion of aromatic bands and indistinct bending modes. Figures 3.1-4 show the N-H stretching region for the m-stien complexes.

With bis-diamine complexes two asymmetric and two symmetric N-H stretching frequencies would be expected, although these may be accidentally degenerate. The free ligand and the complexes with large anions show two bands which may be assigned to such degenerate modes. It is interesting to note that these bands split in the cases of the dibromide and di-iodide. Presumably a resolution of the degeneracy occurs, due possibly to a change in the local environment in the crystal. Further, in some spectra a strong band at less than $3,100\text{cm.}^{-1}$ is observed in addition to two N-H bands. This is possibly an aromatic C-H stretching band which has 'borrowed' intensity from the close approach of the

TABLE 3.2

Infra-red absorption frequencies of m-stien cupric complexes
4,000-1,000cm.⁻¹

Only changes compared with the ligand are listed.

m-stien	3350m	3280m	3085w	3032w
	3065w	1590s	1490s	
[m-stien ₂ CuCl ₂].H ₂ O	3265m	3245m	3170m	3090s
	1580w	1560w	1490w	
[m-stien ₂ CuBr ₂].H ₂ O	3450m	3380s	3190s	3110m
	1565s	1490w		
[m-stien ₂ CuBr] ₂	3330m	3315m	3275s	3220s
	3210s	3132s	1600w	1570s
	1490w	1035s	1620s	
[m-stien ₂ CuI ₂].H ₂ O	3318w	3275m	3220-3210-3170s	
	3095s	1570s	1490w	
[m-stien ₂ CuI ₂]	3320m	3295m	3215s	3200s
	3115m	1570s	1490w	
[m-stien ₂ Cu(SCN) ₂].H ₂ O	3330-3315m		3290m	3215s
	3125m	<u>2108-2070s</u>	same as iodide	
^{Cu} [m-stien ₂ (ClO ₄) ₂]	3330s	3270s	3155w	1570s
	1490w	<u>1088vs</u>		
^{Cu} [m-stien ₂ (NO ₃) ₂]	3315s	3240s	3120m	same as
		bromide, hydrate	<u>1490-1450vs</u>	
^{Cu} [m-stien ₂ (SO ₄)].H ₂ O	3375 broad		3320m	3300m
	3220m	3095m	same as bromide, hydrate	
	<u>1160m</u>	<u>1110m</u>	<u>1090-1050vs</u>	
	<u>1030sh</u>	<u>1000s</u>		
^{Cu} [m-stien(AC) ₂].H ₂ O	3240 broad		3135m	<u>1600s</u>
	<u>1570-1550-1500m</u>		<u>1340m</u>	
^{Cu} [m-stien(ox) ₂].H ₂ O	3305m	3200 broad		<u>1600m</u>
	<u>1550s</u>	<u>1500s</u>	<u>1300s</u>	

vs, very strong; s, strong; m, medium; w, weak; sh, shoulder
 vw, very weak intensities; Underlined are bonds due to the anion

47.

$m\text{-stien}_2\text{CuCl}_2 \cdot \text{H}_2\text{O}$

3600

3400

3200

3000

% TRANSMITTANCE

$m\text{-stien}$

$m\text{-stien}_2\text{CuBr}_2$

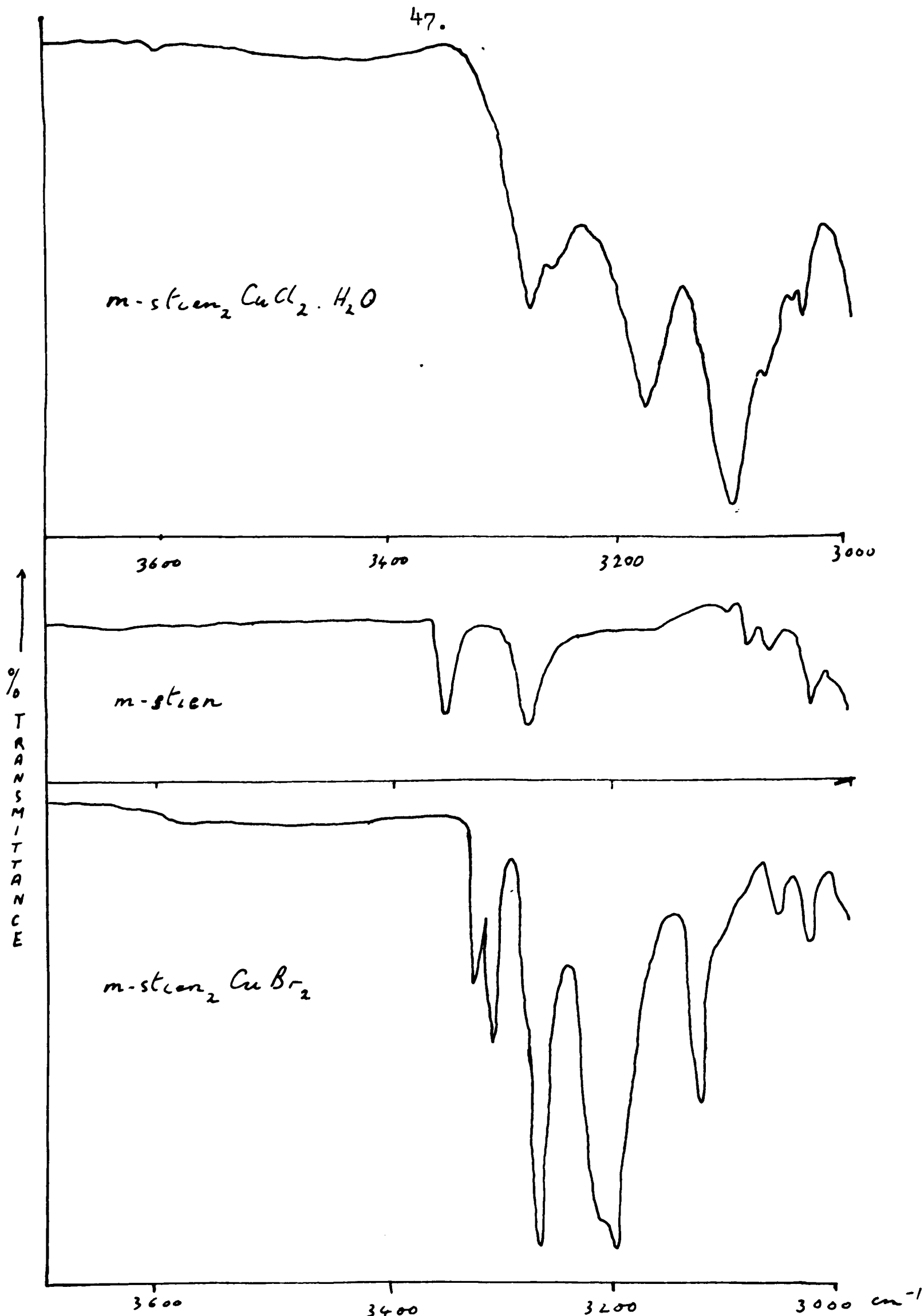
3600

3400

3200

3000 cm^{-1}

FIGURE 3.1



48.



3600

3400

3200

3000

?

% TRANSMITTANCE



3600

3400

3200

3000 cm^{-1}

FIGURE 3.2

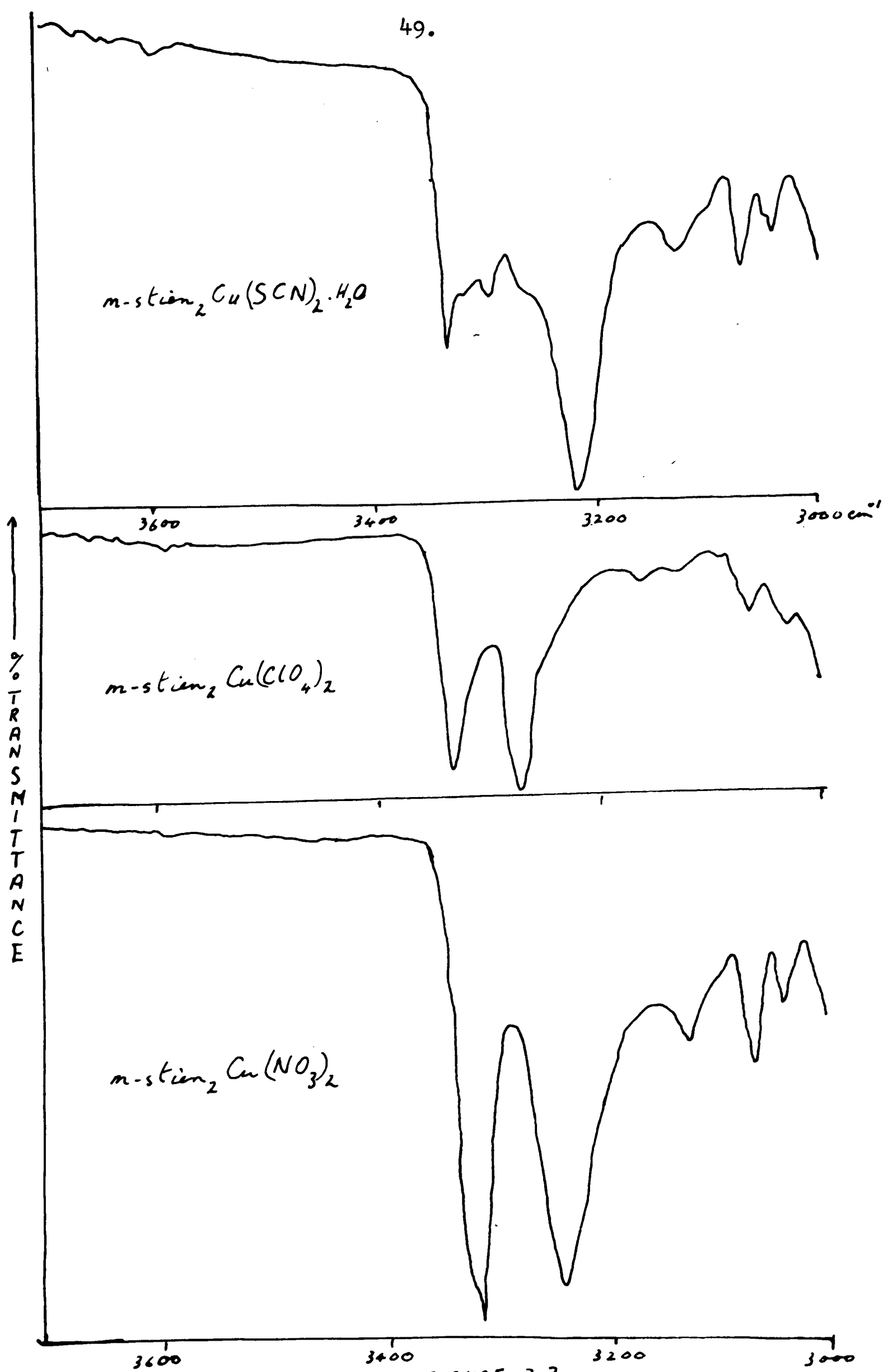


FIGURE 3.3

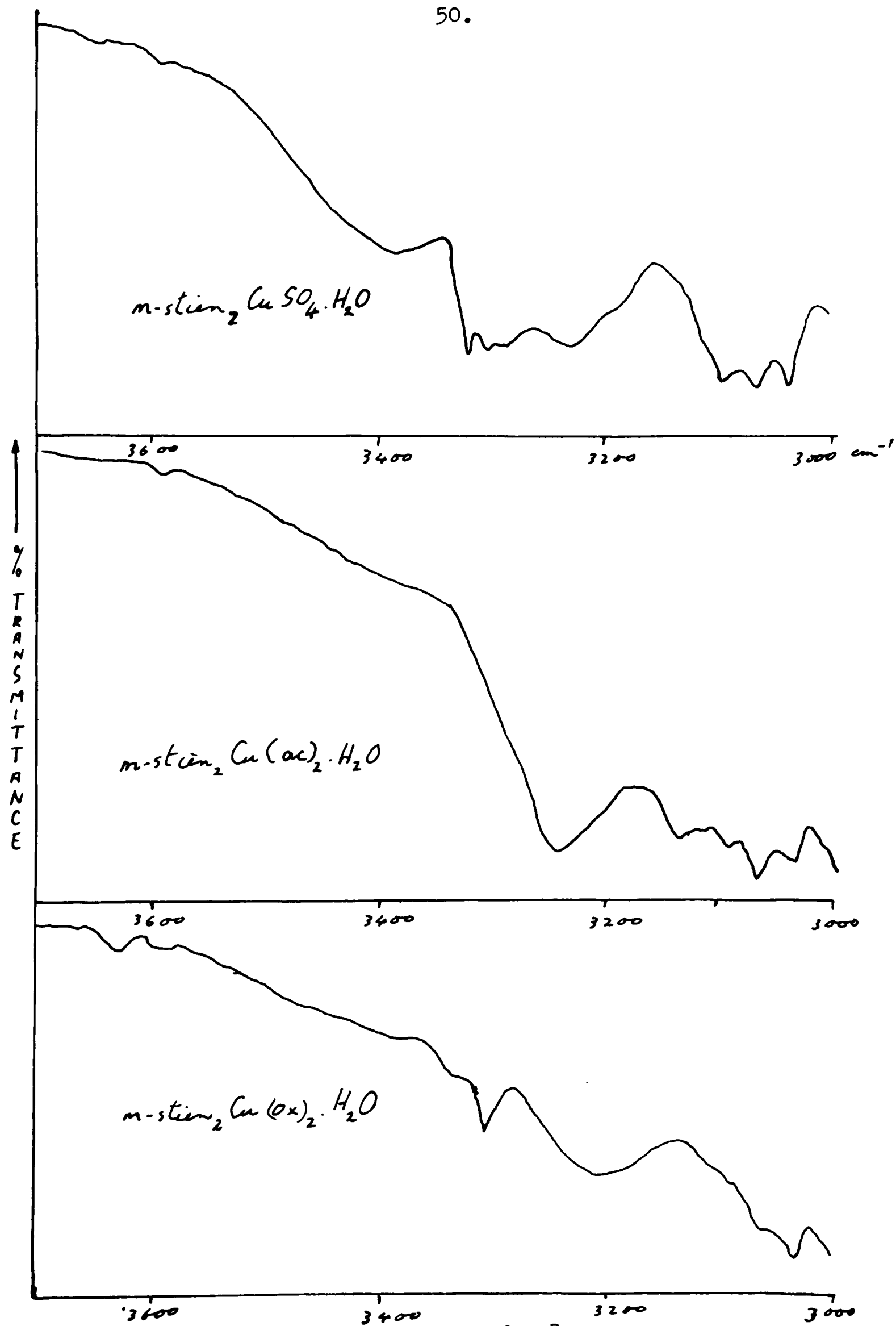


FIGURE 3.4

symmetric N-H stretch. This assignment is supported since the band only occurs with the N-H bands of lowest energies.

The other modes of vibration of metal amine complexes have not been assigned in the $[\alpha\text{-stien}_2\text{CuX}_2]$ complexes. They occur in regions with many bands and cannot be unequivocally selected as they are rather weak. Powell and Sheppard (61) studied some $[\text{M}(\text{en})_2]\text{Cl}_2$ and $[\text{M}(\text{en})_3]\text{Cl}_3$ complexes, where en = ethylene diamine. They found two types of spectra designated A and B.

Type A was exemplified by Co III, Cr III, Ru III octahedral and Pt II and Pd II square planar complexes and were more complex than the type B exemplified by Ni II octahedral and Cu II square planar complexes. These authors suggested a distinction with respect to cis or gauche conformation of the ethylene diamine molecules. In a later paper (62) this theory is refuted as an X-ray determination ~~and~~ showed that both types of spectra could arise from gauche conformation, no explanation is given for the differences observed. The N-H stretching frequencies of the divalent ions studied ~~by Powell and Sheppard~~ are listed in Table 3.2.

In the region $4,000\text{--}3,000\text{cm.}^{-1}$ the symmetric and asymmetric stretching frequencies for water also occur ($3,550\text{--}3,200\text{cm.}^{-1}$, ref. 63). These bands are sharp in coordinated water but in the case of lattice water extremely

broad bands may be observed stretching over as much as $3,500-1,700\text{cm.}^{-1}$ (64). In the cupric complexes studied, the water bands were in general indistinct.

As well as bands due to the ligand, at lower energies, the infra-red spectra showed the characteristic bands of the anions in the complexes (Table 3.2). The symmetry of many anions is altered by coordination. The change in point group will cause splitting of some of the previous degeneracies and alteration of the selection rules. Thus infra-red spectra may be used to estimate the amount of coordination in such ions. This has been discussed by many authors and here we shall consider one case, that of the sulphate radical.

The free sulphate ion belongs to the symmetry point group T_d and, of the four fundamentals, only $\nu_3(1,105\text{cm.}^{-1})$ and $\nu_4(611\text{cm.}^{-1})$ (59) are infra-red active. If the ion is coordinated to a metal, the symmetry is lowered and splitting of degenerate modes occurs. The change of symmetry is different for uni- and bidentate complexes as shown (fig. 3.5)

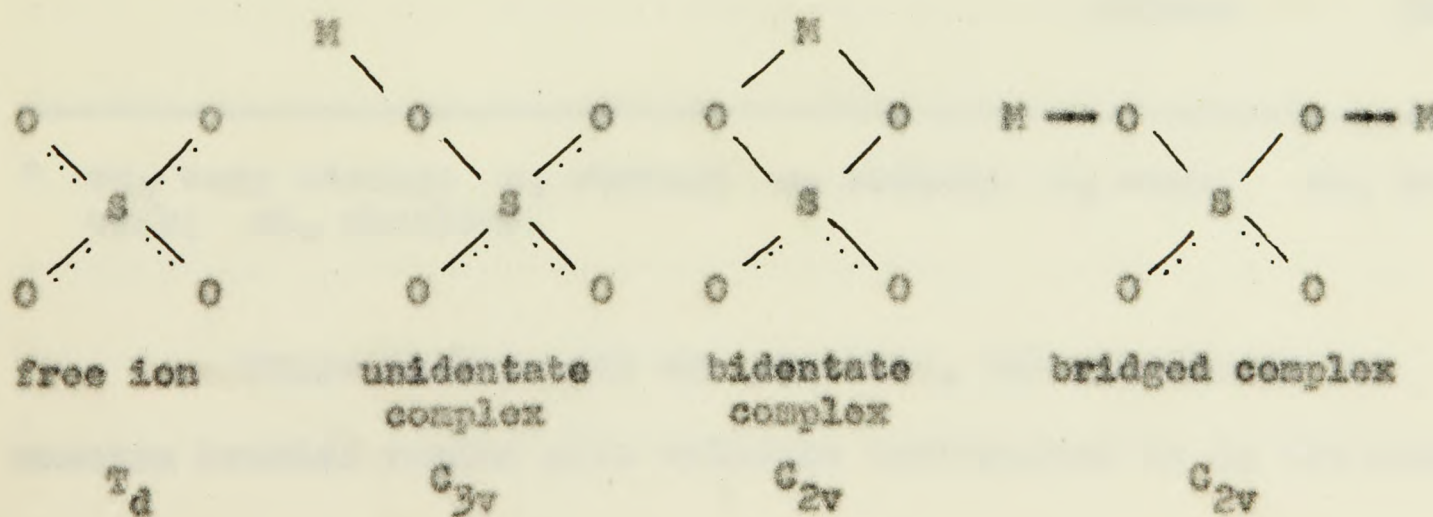
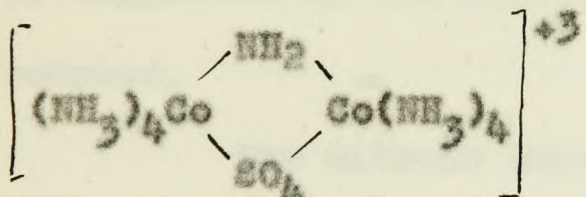


Figure 3.5

Table 3.3 shows the frequencies observed by Nakamoto et al. for typical sulphate complexes. The appearance of ν_1 in $[\text{Co}(\text{NH}_3)_6]_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$ may be attributed to a solid state perturbation as the T_d symmetry seems to hold.

TABLE 3.3

<u>Compound</u>	<u>Symmetry</u>	ν_1	ν_2	ν_3	ν_4
$[\text{SO}_4]^{-2}$ ion	T_d	-	-	1104vs*	613s
$[\text{Co}(\text{NH}_3)_6]_2[\text{SO}_4]_3 \cdot 5\text{H}_2\text{O}$	T_d	973vw	-	1130-1140vs	617s
$[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Br}$	C_{3v}	970m	438m	(1032-1044s 1117-1143s)	645s 604s
	C_{2v}	995m	462m	(1050;1060s 1170s 1105s)	641s 610s 571m
$[\text{m-stien}_2\text{Cu}]\text{SO}_4 \cdot \text{H}_2\text{O}$	-	1000w	468w	1160m 1110m 1090-1050vs 1030sh	 642m 606s 562m

* vs, very strong; s, strong; m, medium; w, weak; vw, very weak; sh, shoulder.

Where assignments are possible, the spectra in the caesium bromide region give valuable information as to the nature

of bonding. The metal-anion stretching frequencies often appear in this region and so interpretation of interactions in the solid state are facilitated. In the *m*-stien cupric complexes this information was of great value. Table 3.3 includes the observed frequencies for [*m*-stien₂Cu]SO₄ and shows the frequencies expected for a bidentate sulphate ligand. We may interpret this as having the sulphate radicals stacked in the crystal along the *m*-axis of the copper. Each sulphate radical will then serve as a bidentate ligand to two neighbouring copper ions.

The chloride complex shows a strong band at 35 μ which may be assigned to the Cu-Cl stretch. This assignment is supported by the lack of such a band in the di-iodide complex.

The nitrate complex shows four new bands in the CsBr region at 38 μ ,*m*; 32.8 μ ,*s*; 27.6 μ ,*m*; 22.1 μ ,*m*. No other work has studied nitrate complexes in this region and these bands are not assigned. The broad band at 38 μ is probably due to water. As discussed below the nitrate is probably essentially ionic in the complex. The anhydrous bromide complex shows a broad absorption at 36.5 μ which may be ascribed to the Cu-Br stretching frequency. This band is not observed in the violet hydrated bromide. The thiocyanate shows a band at 21.7 μ (447cm.⁻¹) which may be assigned to the NCS

deformation mode. The CsBr spectra, therefore, suggest that interactions between anion and metal often occur in the π -stien complexes.

The perchlorate complex gives a single very strong absorption at $1,058\text{cm.}^{-1}$ which is consistent with an ionic model. Coordinate bonding in perchlorate ions has been observed and is discussed by Hathaway and Underhill (66). The $1,080\text{cm.}^{-1}$ band is split in such instances. The ionic assignment is supported by the observation of a single band at 16.3μ in the CsBr region. The quoted value for an ionic perchlorate is 16.4μ and it is split by covalent bonding.

The nitrate complex show two anion bands, one very strong broad band at $1,490-1,450\text{cm.}^{-1}$ (ν_3) and the out-of-plane bending mode ν_2 appears at 820cm.^{-1} . This ion would seem to be 'free' in the lattice. Both acetate and oxalate acid radicals give ^{complex} spectra in the region $1,600-1,300\text{cm.}^{-1}$ and these peaks have not been assigned. The thiocyanate complex shows two peaks in the $\text{C}\equiv\text{N}$ stretching region at $2,108$ and $2,070\text{cm.}^{-1}$, both very strong absorptions. Tramer (67) discusses changes in thiocyanate spectra due to coordination of the SCN^{-1} ion. He lists a series of compounds where the ion is either S or N bonded and deduces the sequence listed in Table 3.4

The two bands observed in the null spectrum suggest that the SCN^{-} ion interacts with the copper, probably along

TABLE 3.4

	<u>C≡N stretch</u> $\checkmark_1$	<u>C-S stretch</u> $\checkmark_3$	<u>N≡C-S deform.</u> $\checkmark_2$
SCN ⁻ free ion	2055	749	475
M - SCN	2105-2125	729-694	-
M - NCS	2085-2095	809-839	-

the z-axis and linking neighbouring copper atoms with both N and S atoms participating in the bonding. Alternatively, the two bands may be due to symmetric and asymmetric modes of vibration for the C-N bound to copper by nitrogen in two SCN⁻ radicals. The mean of the two bands falls at $2,088\text{cm.}^{-1}$ - the value quoted for SCN-M by Tramer.

The cupric compounds, other than thiocyanate and perchlorate, were found to be insoluble in nitromethane and nitrobenzene and so their conductivities could not be measured in non-coordinating solvents. Both the thiocyanate and perchlorate had conductivities of the order $1:1 < \lambda < 2:1$ _m electrolytes in nitromethane. The molar conductance of a complex may be related to the number of ions present in the solution at low concentrations; such a relationship is due to similar sizes and mobilities of the complex ions and thus can only be approximate. Table 3.5 lists typical conductances of complexes in 0.001 M solution in some ionizing solvents.

TABLE 3.5

<u>Number of ions</u>	0	1	2
λ nitrobenzene	0-2	20-25	40-50
nitromethane	0-10	65-75	100-140
methyl cyanide	0-10	170-180	230-250
water	0-10	120	240

The ideal solvent would have a high dielectric constant and yet no coordinating ability. The solvents listed in Table 3.5 increase in coordinating power from nitrobenzene to water. Then a true non-electrolyte of the $[L_4MX_2]$ may react with a coordinating solvent to give the species $[L_4MXS]^+$ and $[L_4MS_2]^{+2}$, where S is a molecule of solvent. This is particularly serious with complexes of nickel II and copper II with two anions on the z-axis, as these are quite labile.

The z-stien cupric perchlorate and thiocyanate gave values of molar conductance in nitrobenzene of 24.6 and 19.9 respectively. These are of the order of magnitude for a 1:1 electrolyte and thus correspondingly lower than the values in nitromethane. Clearly these compounds, which are formulated as 1:2 electrolytes, have substantial interactions with the

TABLE 3.6

Magnetic Susceptibilities of m-stien Complexes

<u>Formula</u>	χ_m uncorr. (cgs units) ($\times 10^6$)	Diamagn. Corr. (cgs units) ($\times 10^6$)	χ_m corr. (cgs units) ($\times 10^6$)	$\mu_{\text{eff.}}$ B.M.	$T^\circ K$
COPPER (II)					
[m-stien ₂ CuCl ₂].H ₂ O	1051 (1054/5amp.)	359	1412	1.83	295.5
[m-stien ₂ CuBr ₂].H ₂ O	1480 (1520/5amp.)	379	1879	2.11	295.7
[m-stien ₂ CuBr ₂]	1766	367	2133	2.26	296
[m-stien ₂ CuI ₂]	1236	387	1623	1.97	296
[m-stien ₂ Cu(SCN) ₂].H ₂ O	1020	377	1397	1.83	296.5
[m-stien ₂ Cu(NO ₃) ₂]	1048	346	1394	1.83	297
[m-stien ₂ Cu(ClO ₄) ₂]	1050	374	1424	1.85	296
[m-stien ₂ Cu(AC) ₂].H ₂ O	1119 (1239/5amp.)	379	1488	1.89	297
[m-stien ₂ Cu(SO ₄) ₂].H ₂ O	1026	368	1394	1.83	296
[m-stien ₂ Cu(OX) ₂].H ₂ O	548	338	896	1.47	297
[p-stien ₂ CuCl ₂].H ₂ O	926.3	499	1425	1.85	296

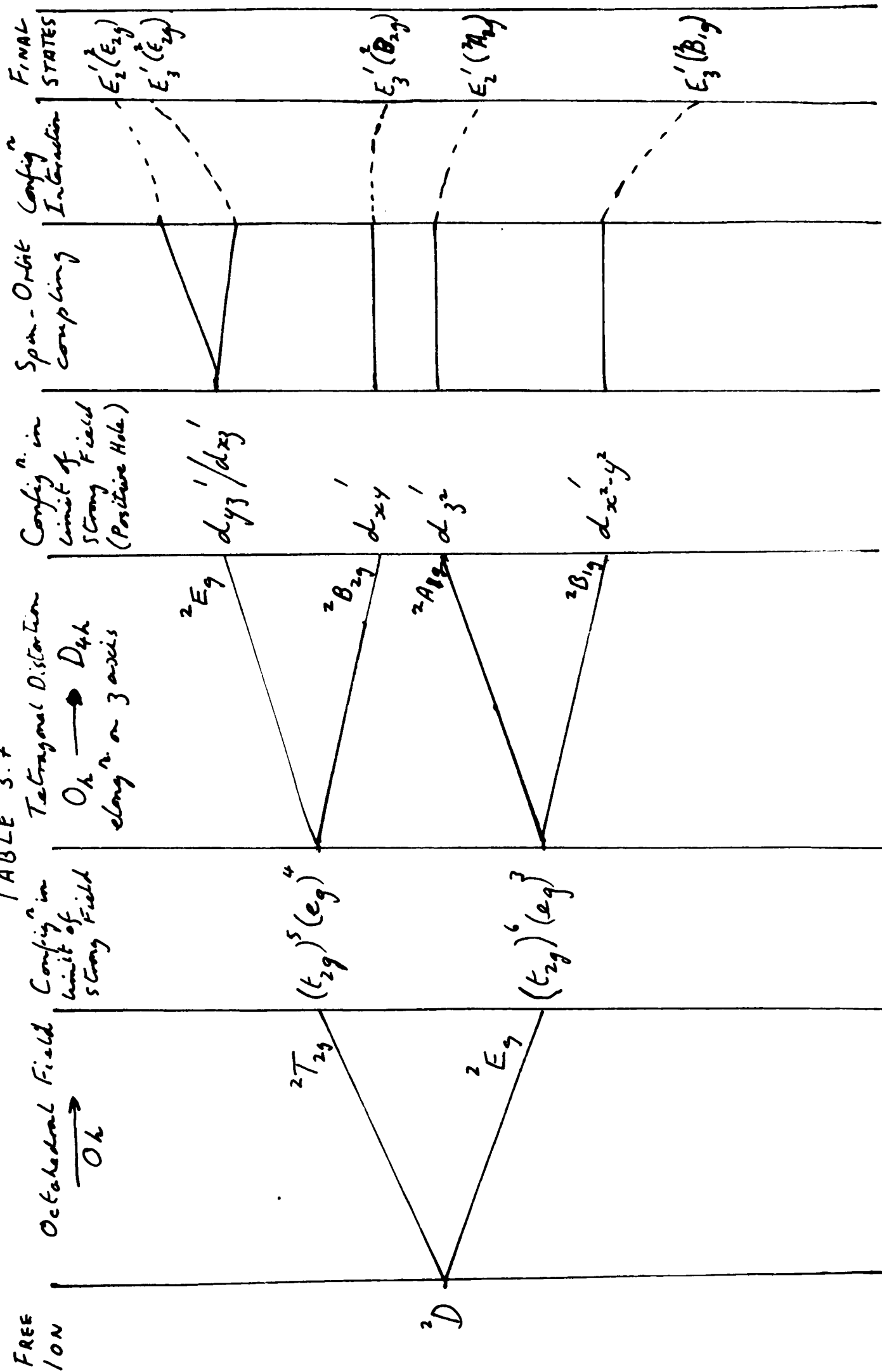
All palladium complexes are diamagnetic

 χ_m ca. $\pm 100 \times 10^{-6}$

cupric ion in these solvents, though such interaction may well be largely an electrostatic ion pair attraction.

The magnetic moments of the complexes were measured on a Faraday balance and the effective magnetic moments of the cupric ions were calculated. These values are listed in Table 3.6. The calculated "spin-only" moment for copper II is $\mu_{\text{eff.}} = \sqrt{4S(S+1)} = 1.73$ Bohr Magnetons (where $S = 1/2$). The moments of the cupric ions are thus somewhat greater than the spin-only value. This would be expected for an octahedral or tetragonal configuration; copper II gives rise to a 2D spectroscopic state which is split in an octahedral field into triply and doubly degenerate levels with a splitting of $10,000-20,000\text{cm.}^{-1}$. The lower lying E_g state cannot give rise to an orbital contribution to the magnetic moment. However, Cu II has a large spin-orbit coupling constant ($A = 852\text{cm.}^{-1}$) and thus considerable interaction occurs between T_{2g} and E_g levels. Table 3.7 correlates the energies of the states with the constraints applied to the system. A tetragonal distortion is inevitable in copper II (Jahn-Teller theorem) and in the case now considered we have non-equivalence of ligands and thus a strongly tetragonal field. The diagram shows that the spin-orbit coupling splits the upper E_g level and mixing of the resultant states may then occur to give rise to an appreciable orbital contribution. Values of $\mu_{\text{eff.}}$ from

TABLE 3.7



1.8-2.0 B.M. are frequently observed. Figgis and Harris (68) list a series of results for square planar complexes supporting this theory, though in one case they find a moment less than the spin only value of 1.73 B.M. There is no obvious explanation of this from the theory. The case of copper acetate is well-known where the value of $\mu_{\text{eff.}}$ is lower than the spin-only value. The explanation here is that of a co-operative effect; either a δ -bond is formed or a "super-correlation" occurs through the bridging acetate groups in the dimeric molecule. The m-stien oxalate complex has a low moment (1.47). However, this may be due to inaccuracy of measurement, as the diamagnetic part of the susceptibility almost exactly equalled the paramagnetic part in this substance (4 bracket) and so only a very small resultant deflection was observed on the Faraday balance. The other complexes have the moments expected for copper II complexes with tetragonal crystal fields.

The ultraviolet absorption and solid reflectance spectra of the complexes were measured. Table 3.8 lists the wavelengths and extinction co-efficients of the features in the spectra. Figures 3.6-8 are correlation tables showing the effects of the ionic ligands and hydration on the spectra whilst figures 3.9-14 reproduce the observed spectra, the extinction co-efficients being plotted on a log. scale.

TABLE 3.8

Solution and Solid Spectra of m-stien Complexes

<u>Formula</u>	<u>Solution in methanol</u>		<u>Solid</u>	
	$\lambda_{\text{max.}} (\text{cm.}^{-1})$	$\epsilon_{\text{max.}}$	$\lambda_{\text{max.}}$	μ
[m-stien ₂ CuCl ₂].H ₂ O	37,600	5,880		
	36,800	5,440		
	35,500	sh		
	30,500	sh	33,200	1.38
	26,000	sh		
	22,400	sh		
	17,650	160	18,500	1.35
[m-stien ₂ CuBr ₂].H ₂ O	37,700	5,830		
	37,000	5,160		
	35,600	sh	32,100	1.29
	26,600	sh		
	17,700	164	18,500	1.25
[m-stien ₂ CuBr ₂]	37,600	6,410		
	37,000	5,910	23,500	sh
	ca. 27,000	sh	15,000	sh
	14,800	172	13,400	.983
[m-stien ₂ CuI ₂]	37,600	5,990*		
	36,800	5,310		
	35,500	sh	ca. 25,000	1.62
	17,850	183	22,600	sh
	13,700	sh	13,400	1.56

cont.

<u>Formula</u>	<u>Solution in methanol</u>		<u>Solid</u>	
	<u>$\lambda_{\text{max.}} (\text{cm.}^{-1})$</u>	<u>$\epsilon_{\text{max.}}$</u>	<u>$\lambda_{\text{max.}}$</u>	<u>'D'</u>
$[\text{m-stien}_2\text{Cu}(\text{SCH})_2] \cdot \text{H}_2\text{O}$	37,600	5,710		
	36,600	8,060		
	35,000	sh		
	ca. 30,000	sh	29,800	sh
	ca. 27,000	sh		
	17,200	203	12,800	.822
$[\text{m-stien}_2\text{Cu}(\text{NO}_3)_2]$	37,600	5,460		
	36,800	4,970		
	35,600	sh		
	29,800	sh		
	25,800	sh		
	18,400	140	18,800	1.4
	ca. 15,800	sh	17,400	sh
$[\text{m-stien}_2\text{Cu}(\text{ClO}_4)_2]$	37,800	5,570		
	36,800	4,920	36,500	sh
	35,600	sh	34,000	sh
	29,800	sh	31,000	sh
	26,400	sh		
	18,400	147	19,400	.725
	14,000	sh	ca. 16,000	sh
$[\text{m-stien}_2\text{Cu}(\text{AC})_2] \cdot \text{H}_2\text{O}$	37,800	6,870		
	37,000	6,300		
	ca. 35,500	sh	31,000	sh
	17,600	128	17,600	1.2
	14,000	sh	16,000	sh

cont.

<u>Formula</u>	<u>Solution in methanol</u>		<u>Solid</u>	
	<u>$\lambda_{\text{max.}}$ (cm.⁻¹)</u>	<u>$\epsilon_{\text{max.}}$</u>	<u>$\lambda_{\text{max.}}$</u>	<u>'D'</u>
[m-stien ₂ Cu(ox) ₂].H ₂ O	37,700	4,320		
	37,000	sh		
	34,400	sh	31,100	sh
	29,800	sh	18,800	sh
	16,800	131	17,400	sh
	15,600	sh	16,100	1.34
	14,000	sh	14,500	sh
[p-stien ₂ CuCl ₂].H ₂ O	37,900	sh [‡]		
	ca. 34,800	sh		
	18,000	145	17,600	.66
	13,900	sh	14,000	sh
[m-stien ₂ PdCl ₂]	38,100	sh	38,500	sh
	37,300	sh		
	36,500	sh		
	35,000	sh	ca. 35,000	sh
[m-stien ₂ Pd(SCN) ₂]	Not measured		ca. 36,000	1.45
			33,000	sh
			29,000	sh
[m-stien ₂ Pd(NO ₃) ₂]	Not measured		ca. 38,500	1.32
			34,300	.99
			28,000	sh

* solution was violet, although the complex was green

‡ both methanol and carbon tetrachloride

The spectra are characterised by a broad diffuse peak of low extinction coefficient, (less than 200), extending over some $10,000\text{cm.}^{-1}$. This peak is not generally symmetric and probably corresponds to more than one absorption band, each being broad. Such broad band envelopes, rather than sharp line spectra, are characteristic of d-d transitions in transition metal complexes. Such transitions are "Laporte-forbidden" but become "allowed" due to vibronic coupling in the complex. The force constants and equilibrium distances are different in the ground and excited states and so mixing of the states can occur; asymmetric vibrations permit otherwise forbidden electronic transitions and thus broad weak d-d transitions arise.

From Table 3.7 we see that the expected transitions in a field of symmetry D_{4h} will be ${}^2B_{1g} \longrightarrow {}^2A_{1g}$; ${}^2B_{1g} \longrightarrow {}^2B_{2g}$; ${}^2B_{1g} \longrightarrow {}^2E_g$ in descending order of energy. This order is the inverse of that given by Belford et al. (69) as they list the energy levels of tetragonal copper II as $B_{2g} > A_{1g} > B_{1g} > E_g$. This would seem to be false as we may discuss the levels in terms of "positive-hole" formalism for a d^9 system. The labelling of the orbitals in a tetragonal field in terms of the position of the positive hole is included in Table 3.7. Clearly a positron will be most stabilised in positions of maximum negative charge and we thus

U/V SOLUTION SPECTRA

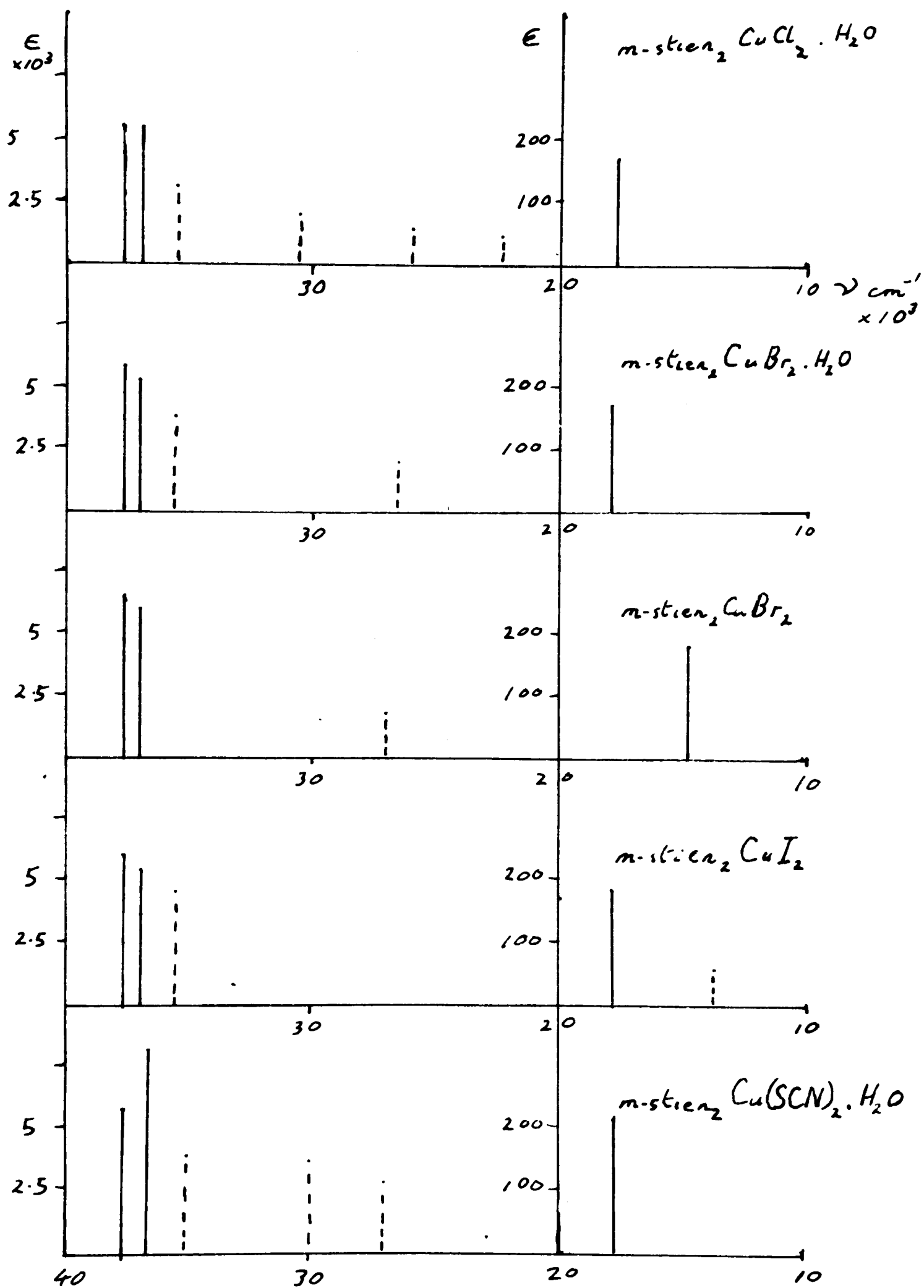


FIGURE 3.6

U/V SOLUTION SPECTRA

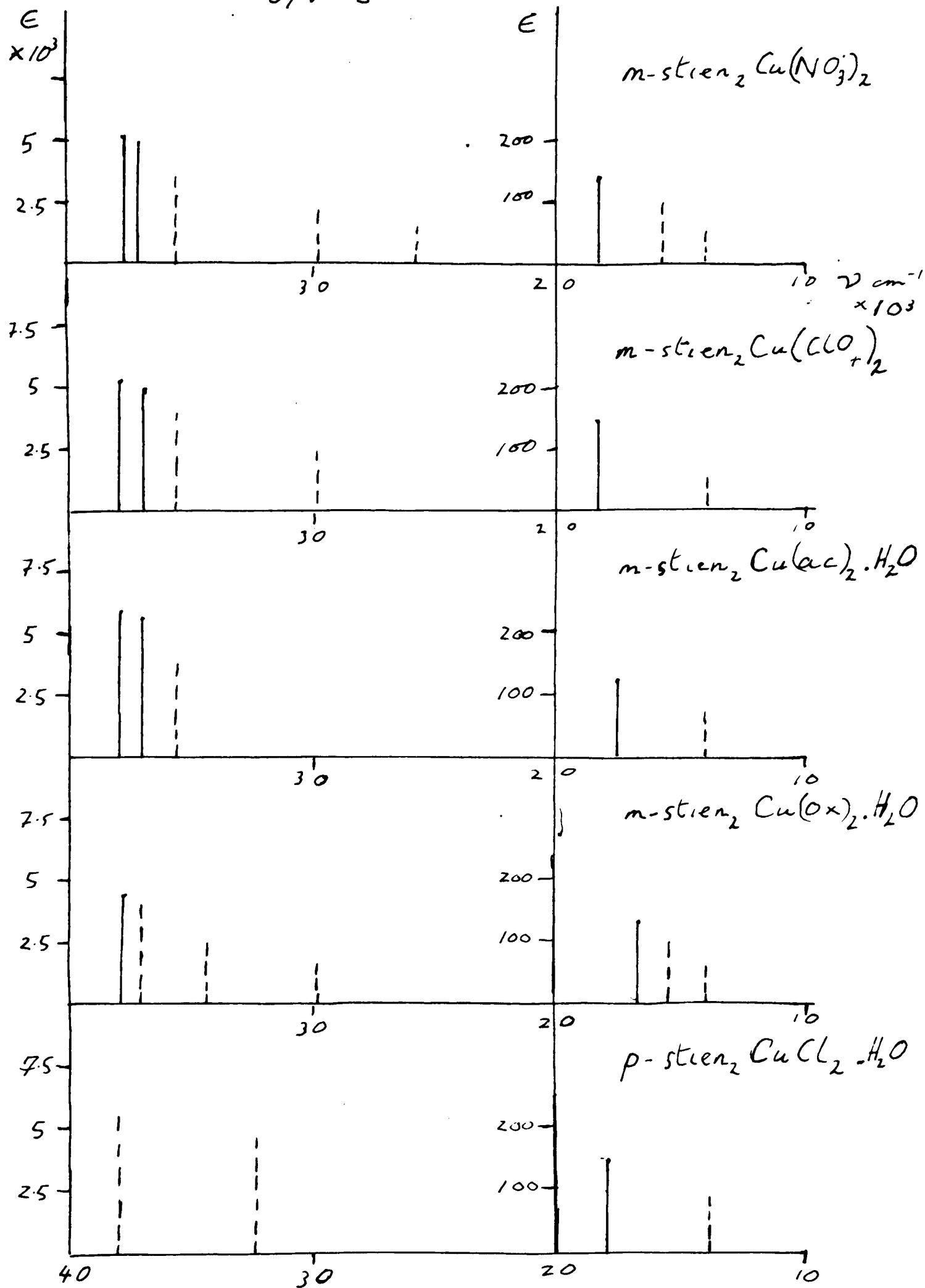


FIGURE 3.7

U/V SOLID REFLECTANCE SPECTRA.

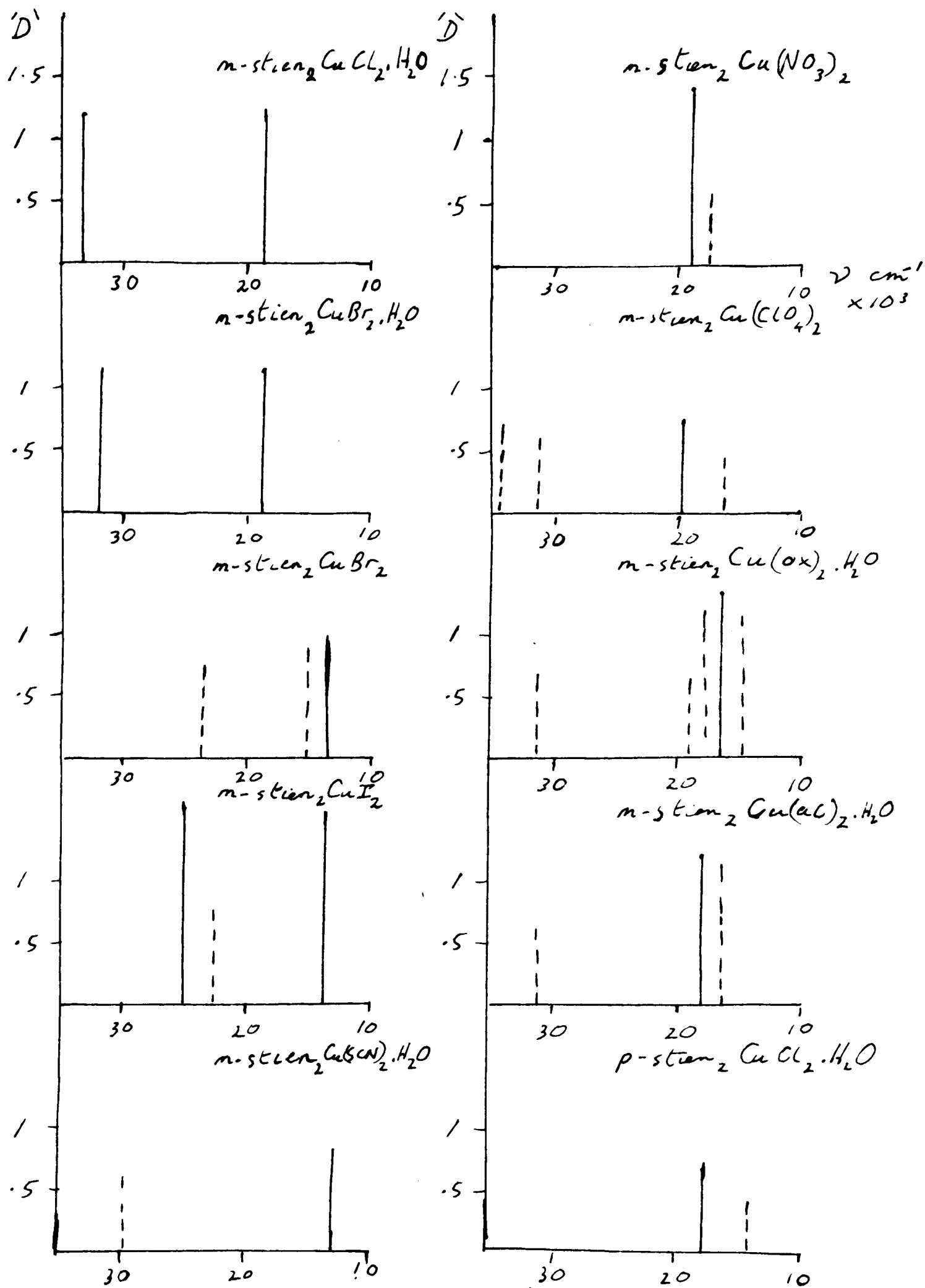


FIGURE 3.8

U/V SOLUTION SPECTRA

CH_3OH { $m\text{-stien}_2\text{CuCl}_2\cdot\text{H}_2\text{O}$ —
 $m\text{-stien}_2\text{CuBr}_2\cdot\text{H}_2\text{O}$ --
 CCl_4 $m\text{-stien}_2\text{CuBr}_2$ -.-

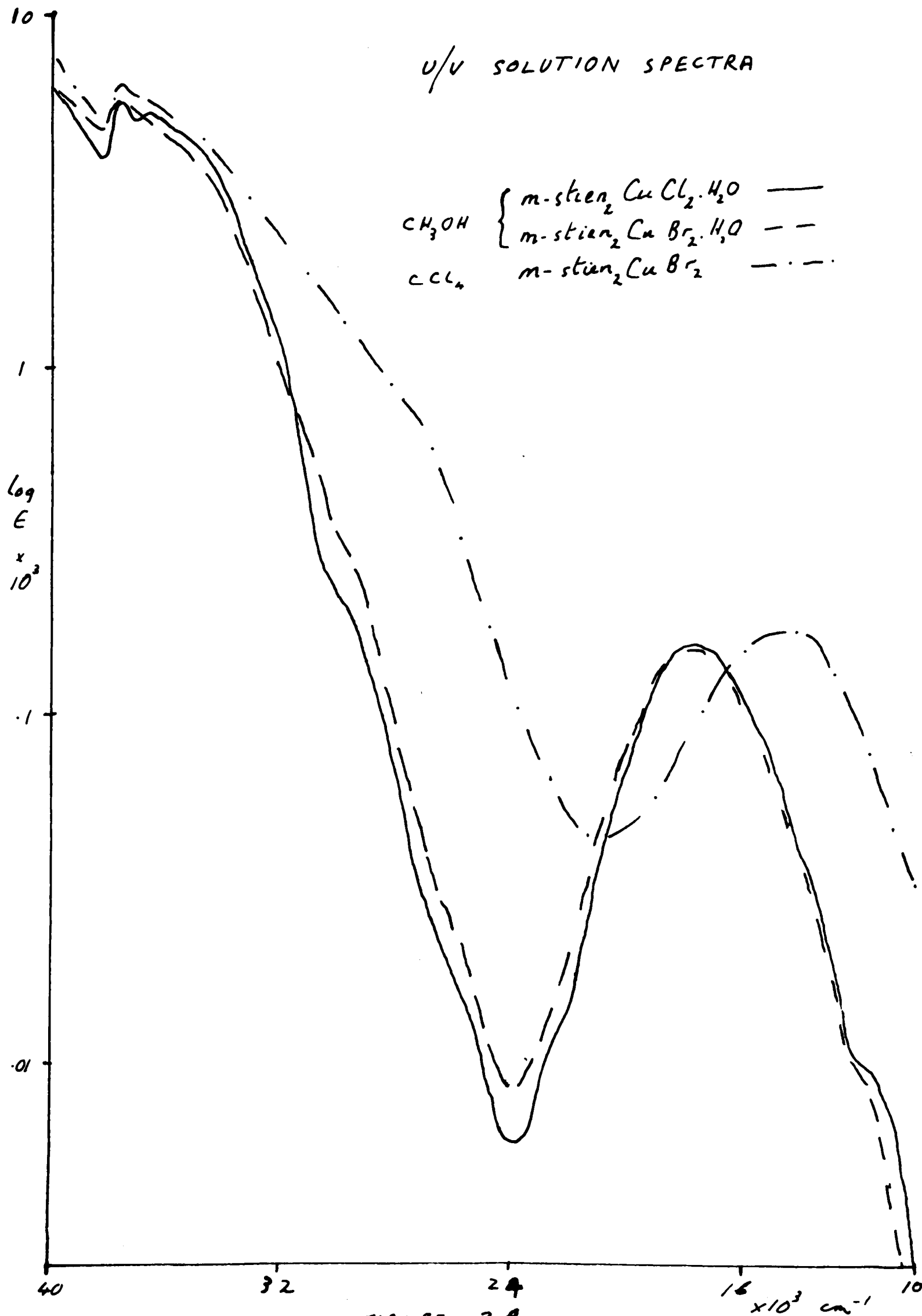


FIGURE 3.9

U/V SOLUTION SPECTRA

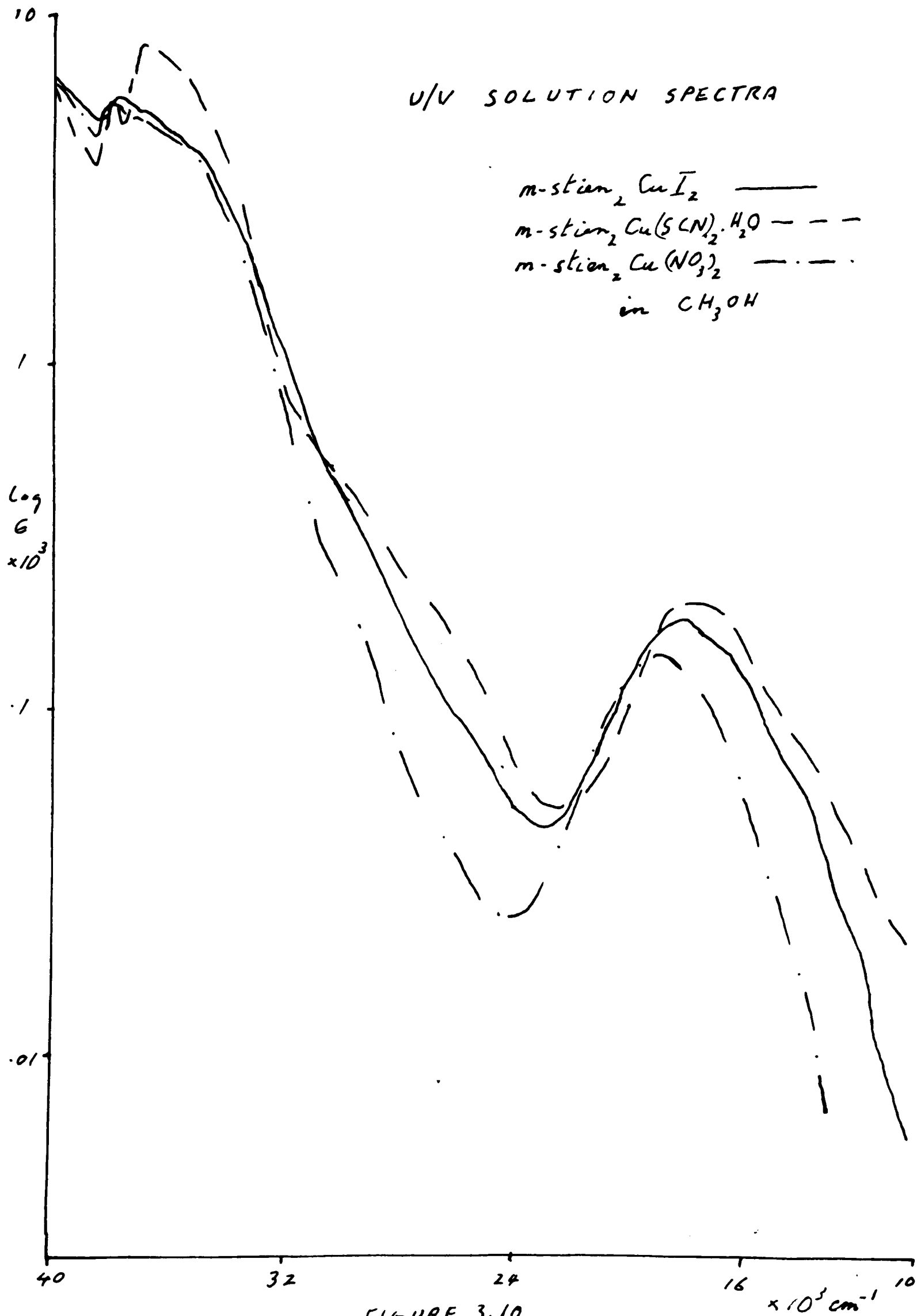


FIGURE 3.10

U/V SOLUTION SPECTRA

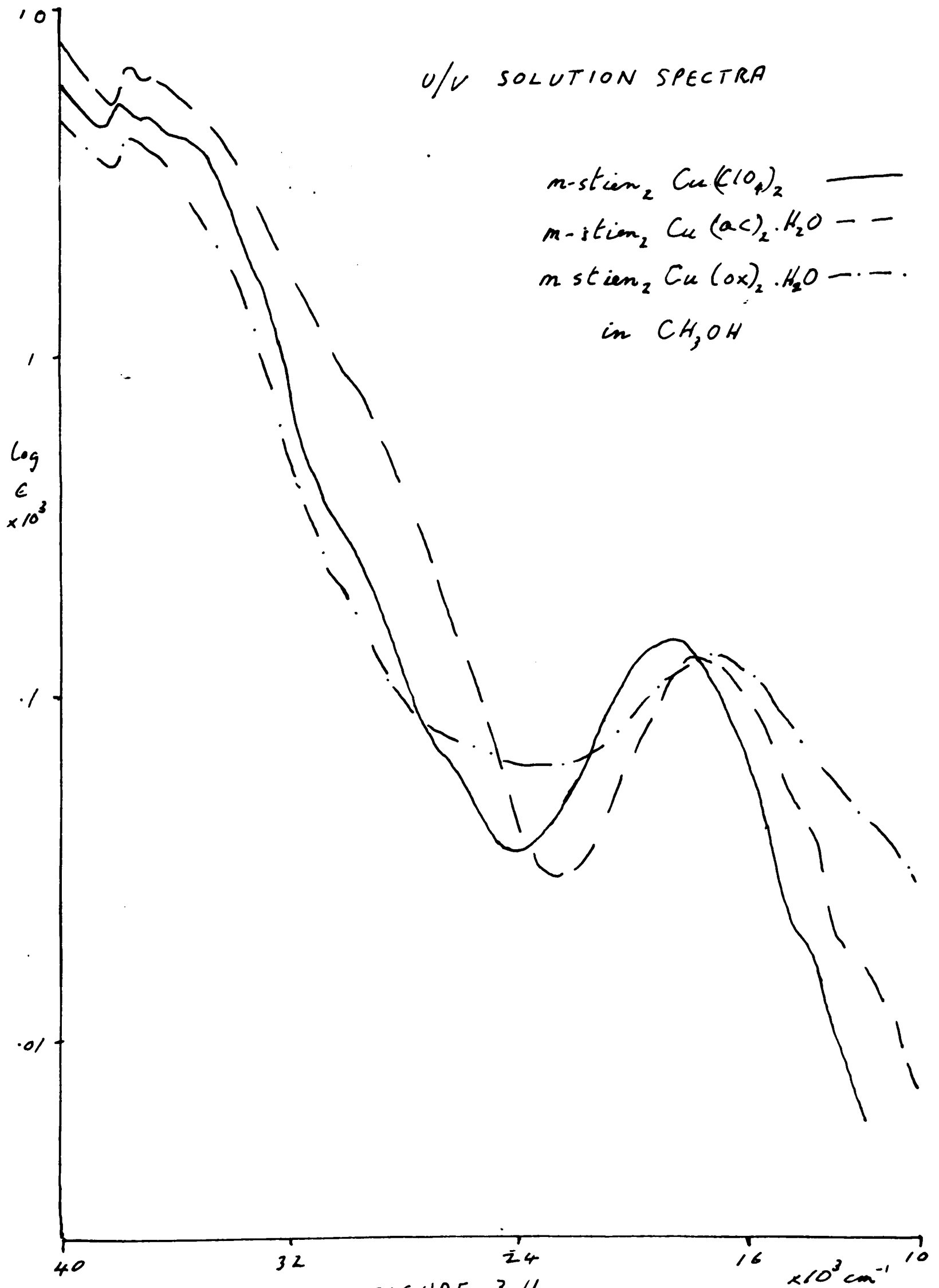


FIGURE 3.11

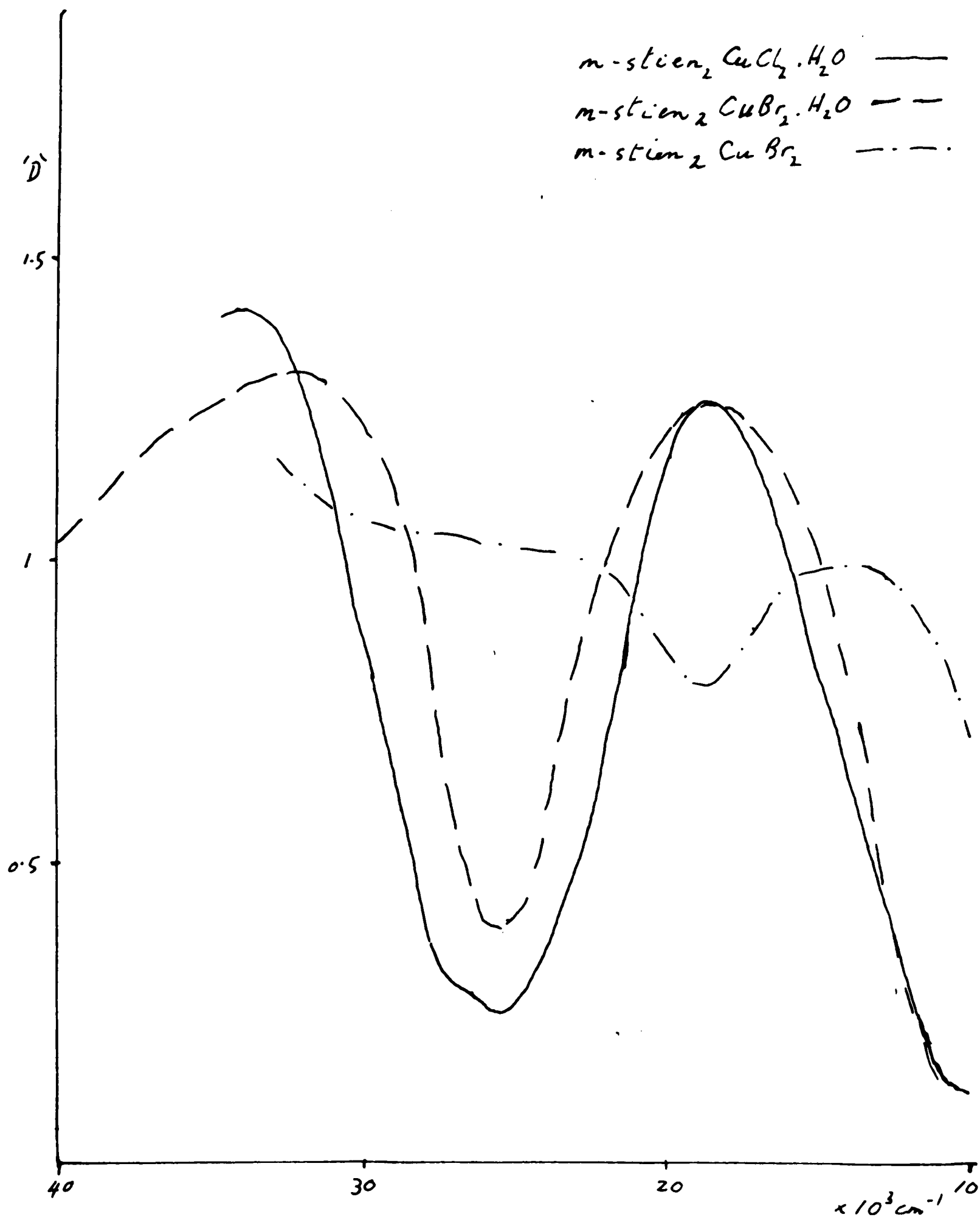
U/V SOLID REFLECTANCE
SPECTRA

FIGURE 3.12

U/V SOLID REFLECTANCE SPECTRA.

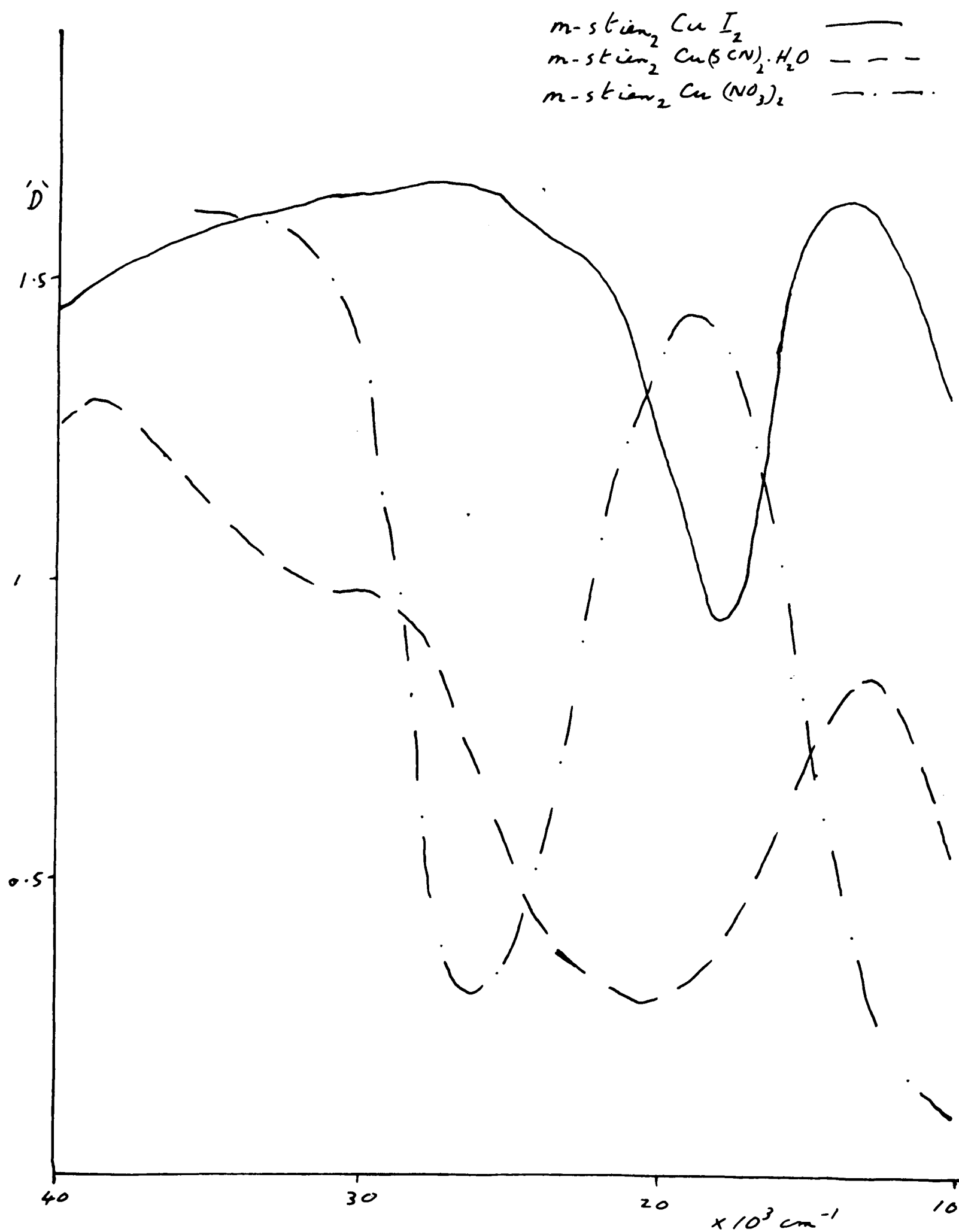


FIGURE 3.13

U/V SOLID REFLECTANCE SPECTRA

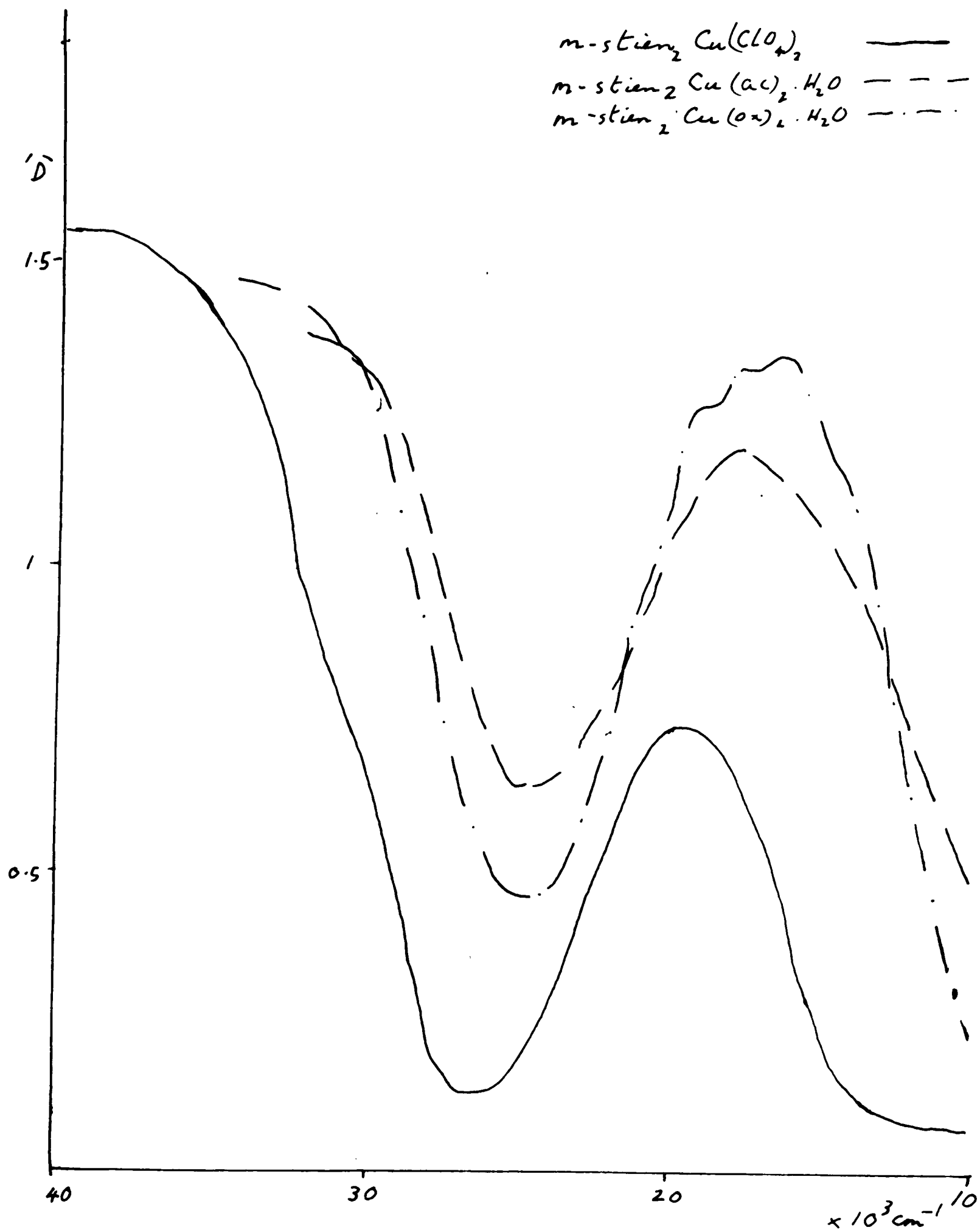


FIGURE 3.14

assign the orbitals arising from the E_g state as $(d_{x^2-y^2})^+$ being lower in energy than $(d_{z^2})^+$ when the distortion corresponds to an elongation of the z-axis. Similarly we would expect the $(d_{xz})^+$ and $(d_{yz})^+$ orbitals to have identical energies higher than that of $(d_{xy})^+$ in this symmetry. The order of energy levels is thus the same as that for the d^1 case but with a change of sign. This assignment then places the E_g state as having the highest energy. This state is split by spin-orbit coupling, as discussed earlier, but this will have negligible effect here, causing only a slight further broadening of the band.

In practice absorption spectra of tetragonal copper II ions are much more simple than suggested by the above discussion. The m-stien complexes were studied in methanol solutions. In this medium the predominant coordination sphere will presumably be $[m\text{-stien}_2\text{Cu}(\text{CH}_3\text{OH})_2]^{+2}$, the two methanol groups lying on the z-axis in trans-positions. Were this a complete description, we should expect that all the spectra would be identical with respect to the ligand field bands. As may be seen from the correlation diagrams (figures 3.6,7) this is approximately the case although there are some interesting differences. The anhydrous dibromide gave a green solution in methanol with a peak at $14,800\text{cm}^{-1}$ compared with the usual value of $18,500\text{cm}^{-1}$ for the hydrated bromide and chloride.

This latter value is slightly higher than that quoted for the bis-ethylene diamine cupric ion of $18,200\text{cm.}^{-1}$ (70) and thus suggests that the bonding in the stilbene diamine complex is a little stronger, giving rise to a greater ligand field splitting. In the anhydrous bromide there must be considerable residual interaction between bromide ion and copper - the smaller ligand field of bromide would then account for the lower energy of the absorption peak in this case. There is no obvious explanation of why this should be true only in the case of the bromide.

The green iodide complex dissolves to give a violet solution in methanol with a peak at $17,800\text{cm.}^{-1}$. In this case, however, there is evidence of a shoulder at lower energy. Belford et al. (67) discuss the spectra of copper bis-acetylacetonate and in several solvents resolve them into three bands by Gaussian analysis. This compound has less "blue tail-off" than the α -stien complexes because the charge transfer bands occur at much higher energy. Even in this case Belford et al. admit that such broad spectral features make such analysis of limited value. The solvents used ranged from chloroform to pyridine and piperidine, but in none of these is the spectrum resolved into three bands, although the chloroform spectrum is very asymmetric, suggesting two peaks. Unfortunately the insolubility of the α -stien complexes in non-donor

solvents precluded a wider range of study of this type. It is concluded that in methanol solution three ligand field bands occur superimposed upon each other to give a single broad peak (ϵ_{max} . approximately 150).

The position of the band is the same in hydrated chloride and bromide and in iodide, nitrate, perchlorate and thiocyanate, but is considerably shifted to lower energies in acetate, oxalate and the anhydrous bromide. The spectrum of $[\text{p-stien}_2\text{CuCl}_2]\cdot\text{H}_2\text{O}$ shows a band at $18,000\text{cm}^{-1}$ and it is thus similar to the m-stien complexes discussed above. The preparation of spectrum of this complex was used as a confirmation of the preparation of the ligand p-stien. Where not obscured by a charge-transfer band, the spectra often show a weak shoulder at approximately $28,000\text{cm}^{-1}$. This has no obvious explanation as it cannot arise from a d-d transition in this system. It may arise from some singlet-triplet absorption in the aromatic system although this explanation is not entirely convincing.

The solid reflectance spectra of the m-stien cupric complexes do not present such a clear picture as the solution spectra. Assignment is not possible in general in the solid state as packing in the crystal lattice can give rise to distortions of the symmetry around the cupric ion. Without accurate X-ray evidence one cannot state categorically what

factors are influencing the energy levels of the metal ion.

The hydrated compounds ^egenerally show bands in the same region as in the solution spectra and it is reasonable to assume that the environment of the copper atom may be as shown below (figure 3.15):

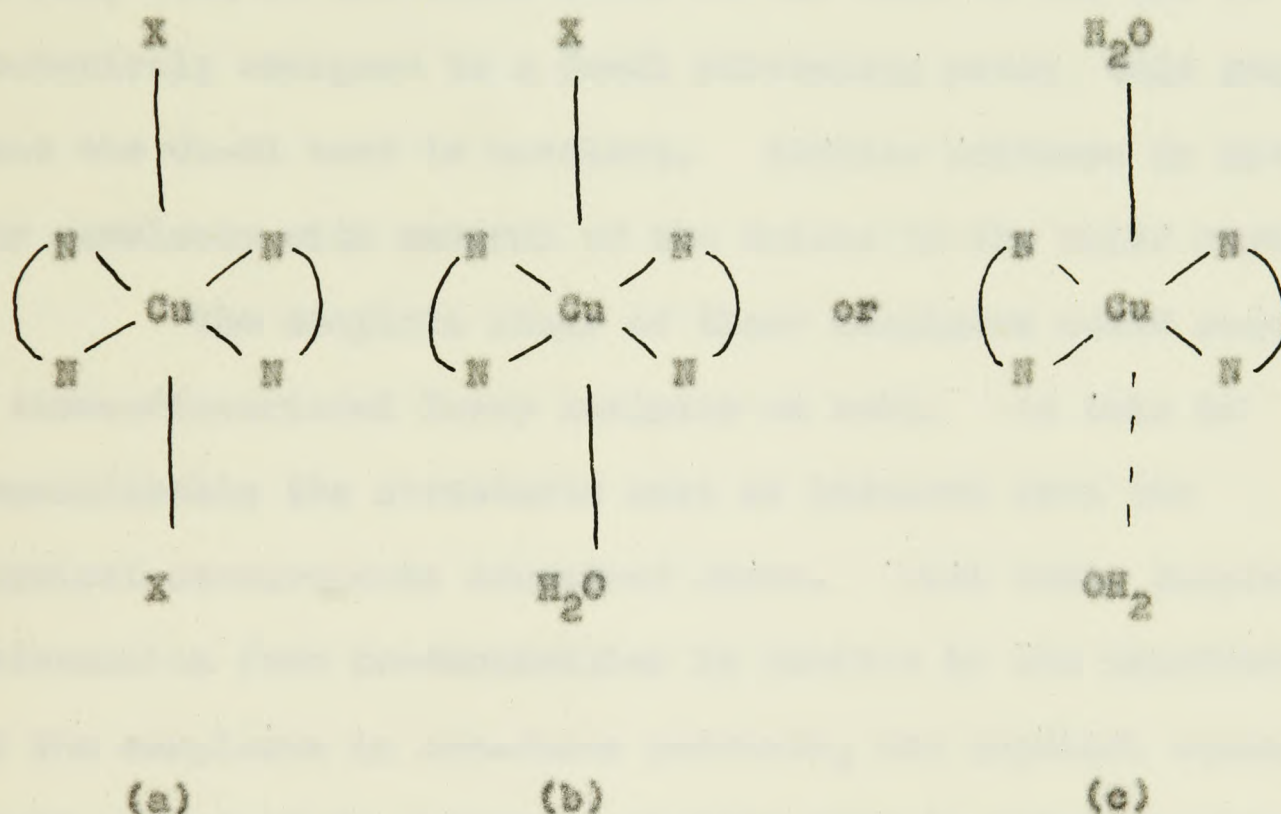


Figure 3.15

Deviations from this value of ca. $18,000\text{cm.}^{-1}$ for the main band may be caused by pressures in the crystal increasing or decreasing the ligand perturbations on the z-axis. Also the anions themselves may interact to modify the splitting, although the degeneracy is not lifted by changes on the z-axis.

In both (b) and (c) the centre of inversion is lost in the complex ion and so the g and u subscripts no longer have meaning. This has the effect of increasing the intensity of a possible transition.

The spectrum of the chloride complex in the CsBr region (discussed earlier), lends weight to formulations such as 3.15 (a), in the solid state as the band at ca. 35μ is tentatively assigned to a Cu-Cl stretching mode; this requires that the Cu-Cl bond is covalent. Similar evidence is cited for covalency with several of the anions in the solid state.

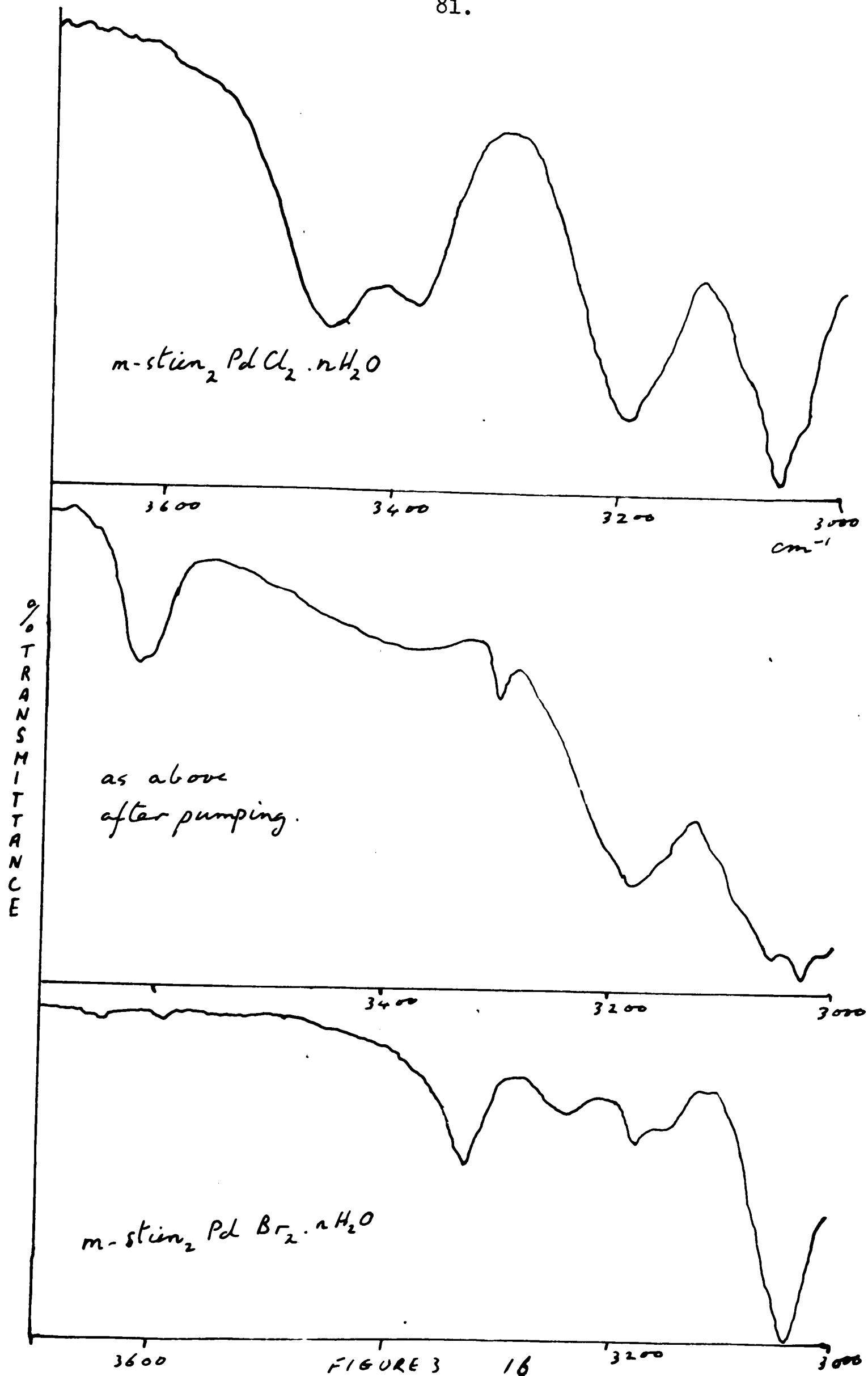
The complete study of these complexes would require a three-dimensional X-ray analysis on each. As this is impracticable the structures must be inferred from the physical measurements described above. With these complexes information from conductivities is limited by the insolubility of the complexes in non-donor solvents, the physical measurements performed do, however, confirm that in these complexes copper II has a tetragonal environment with two diamine molecules in square planar arrangement, and at a greater distance on the z-axis, two weaker ligand groups. Of course, differences of the metal environment between the solution and solid states may arise. Uniformity of behaviour with different acid radicals is not necessarily to be expected and the exact configurations cannot be unambiguously stated.

The complexes have the magnetic moments expected for one unpaired electron in $3d^9$ and show a single broad U/V absorption band with a ligand field of the same order of magnitude as that of ethylene diamine.

B. π -stien complexes of Palladium

The bis-stilbene diamine palladium complexes were prepared by the general method of refluxing 2 mole of ligand with one mole of the palladous salt in ethanol for four to six hours. The hot ethanolic solution was filtered from a small amount of palladium black, and on cooling a cream or white powder separated. This was recrystallised from ethanol, again as an amorphous white powder. The complexes prepared, together with their decomposition points, are listed in Table 3.1 (p.43). Several unsuccessful attempts were made to isolate an iodide complex but none was obtained.

Analyses of the complexes gave most unsatisfactory results for palladium. Examination of the infra-red spectra showed strong hydroxyl bands, as illustrated in figures 3.16 and 3.17. These may be attributed to either water or ethanol of crystallisation. The compounds were dried thoroughly by pumping them at 10^{-4} mm/60°C for a week. The infra-red spectra still indicated the presence of hydroxyl groups. When the



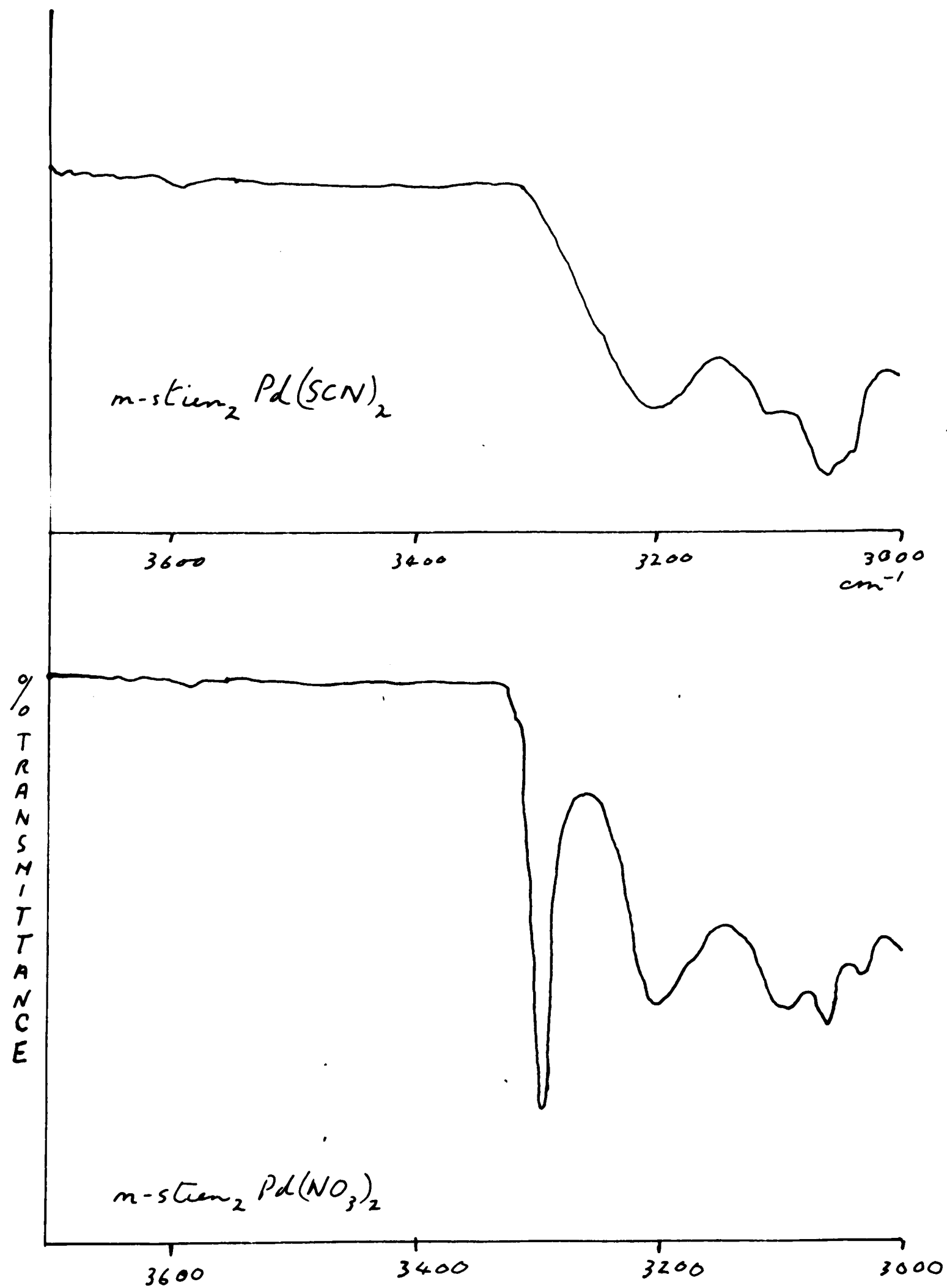


FIGURE 3.17

palladium content was redetermined it was found to have increased markedly, although it had not achieved the calculated percentage for the anhydrous compound. Repeated pumping did not yield this value except in the case of the dithiocyanate. The infra-red spectrum of this complex shows no sign of the hydroxyl bands so noticeable in the other complexes. These complexes were, therefore, not as well characterized as the preceding ones. Nevertheless, some physical investigations were carried out to check further the suitability of this ligand for stereochemical investigation.

As well as the hydroxyl bands already described, the infra-red spectra of the compounds showed complex bands in the N-H stretching region and these, too, are shown in figures 3.16, 17. At lower energies the thiocyanate and nitrate complexes show typical bands due to the anions. Of the SCN^- bands only the $\text{C}\equiv\text{N}$ stretching frequency was observed, at $2,040, 2,060\text{cm.}^{-1}$. The band splitting was thus smaller than in the cupric complexes - corresponding to a smaller interaction with the metal in this case. The nitrate shows its usual very strong absorption at $1,390, 1,370, 1,335\text{cm.}^{-1}$ (ν_3). It would appear that neither of these ions is strongly bound to the metal in the complex. Table 3.9 lists the main frequencies of the absorption peaks in these complexes which are not equivalent to those of the free ligand, over the range $4,000-1,000\text{cm.}^{-1}$.

TABLE 3.9

Infra-red absorption frequencies of m-stien Palladium II complexes.4,000-1,000cm.⁻¹

Only changes compared with the ligand are shown.

m-stien	3350m	3280m	3085w	3065w
	3032w	1590w	1490s	
[m-stien ₂ PdCl ₂].nH ₂ O	3455-3380s		3190s	3060-3030m
	1625w	1570m	1490w	1050m
[m-stien ₂ PdCl ₂] (pumped)	3620m	3300w	3780m	3060-3030w
	1570s	1300-1250w		
[m-stien ₂ PdBr ₂]	3325s	3230w	3170-50w	3035s
	1585s	1490w	1084/5	1054s
	1025s			
[m-stien ₂ Pd(SCN) ₂]	3200m	3100w	3050m	<u>2060vs</u>
	<u>2040m</u>	1570s		
[m-stien ₂ Pd(NO ₃) ₂]	3297s	3200s	3100m	3065-3035w
	1620-1580-1540m		1490w	
	<u>1390-1570-1335vs</u>			

 m, medium; w, weak; s, strong; vs, very strong

All the π -stien palladium complexes were insoluble in nitromethane and nitrobenzene and so no information was available, from conductivity measurements, of the coordination number in these solvents.

The magnetic susceptibilities of these complexes were all of the order of $\pm 50 \times 10^{-6}$ cgs. units. This would be expected for a square planar d^8 complex and the values are comparable with those found by Belova (71) for some Pd II diamine complexes:

$$[\text{Pd}(\text{NH}_3)_4]\text{Cl}_2 \cdot \text{H}_2\text{O} \quad \chi_{\text{Mcorr.}} = +19 \times 10^{-6};$$

$$[\text{Pd}(\text{NH}_3)_4]\text{Cl}_2 \quad \chi_{\text{Mcorr.}} = +26 \times 10^{-6};$$

$$[\text{Pd}(\text{en})_2]\text{Cl}_2 \quad \chi_{\text{Mcorr.}} = +20 \times 10^{-6} \text{ cgs. units.}$$

The ligand field splitting in the second transition series is large enough to ensure that the low-spin square planar configuration for d^8 is preferred to a high-spin tetragonal or even octahedral configuration.

The complexes are white, suggesting a strong ligand field and this is borne out by the ultraviolet absorption spectra. They are rather featureless and were not all measured. The ligand field bands are of high energy and so are lost in the edge of the much stronger charge-transfer bands. The solid reflectance spectra are reproduced in figure 3.18. Jørgensen (24) lists the absorption bands for

U/V SOLID REFLECTANCE
SPECTRA

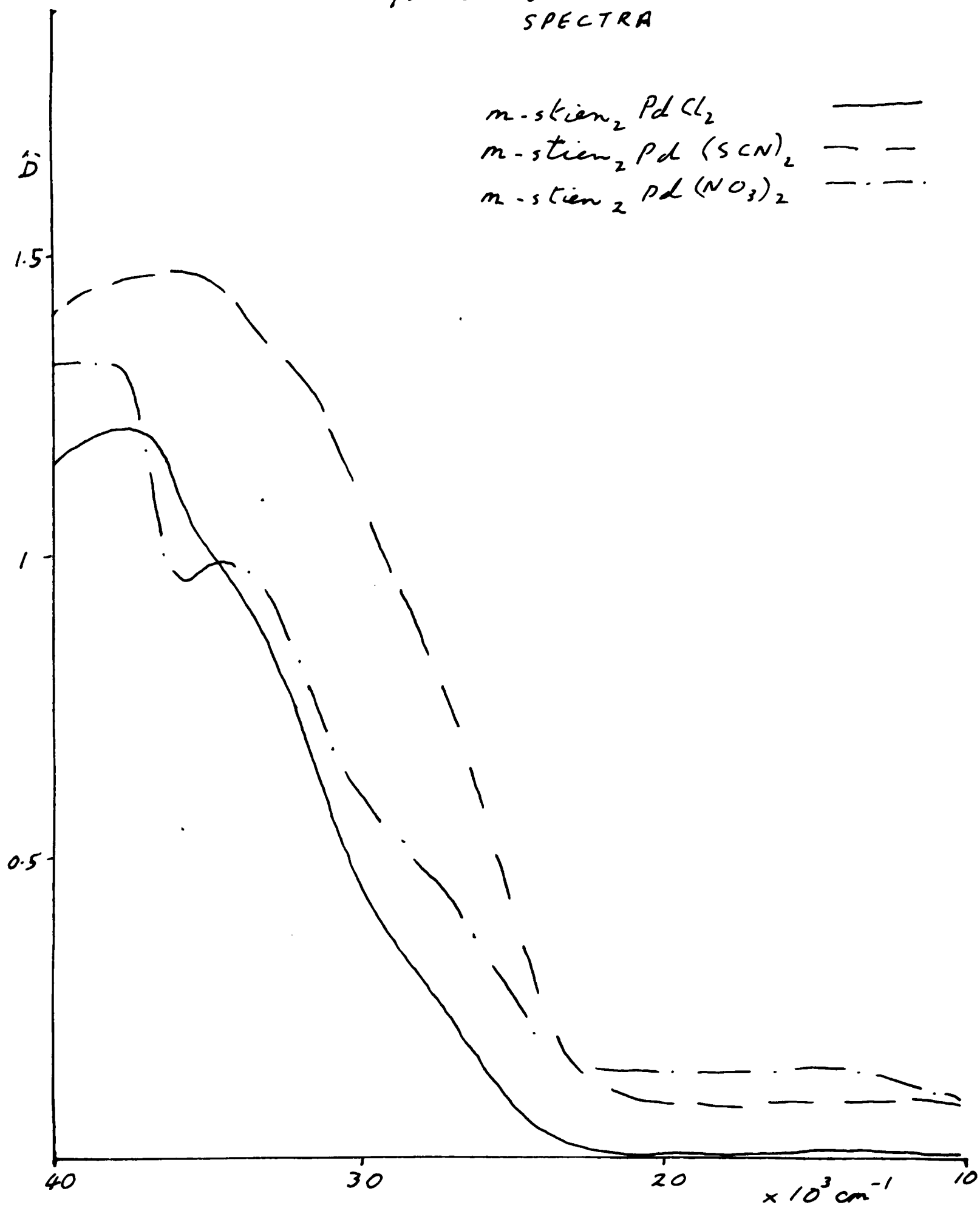


FIGURE 3.18

$[\text{Pd}(\text{en})_2]^{+2}$ and $[\text{Pd}(\text{NH}_3)_4]^{+2}$ as: $29,400\text{cm.}^{-1}$, shoulder (triplet); $34,800\text{cm.}^{-1}$ (singlet), and $27,200\text{cm.}^{-1}$, shoulder (triplet), $33,800\text{cm.}^{-1}$ (singlet), respectively. The m-stien complexes show a shoulder at approximately $35,000\text{cm.}^{-1}$ which presumably corresponds to Jørgensen's singlet transition but the inclusion of benzene rings in the molecule swamps the ligand field spectrum in this region. The features in the spectra are listed in Table 3.6 (p.62). The m-stien palladium complexes were thus square planar bis-diamine complexes with indeterminate solvation. They are of the type represented by $[\text{Pd}(\text{en})_2]^{+2} \cdot x_2$.

The difficulties of characterisation, insolubility in non-donor solvents and lack of resolution of the ultraviolet absorption spectra made these complexes far from ideal for the purpose of this work. Therefore, ligand with isopropyl groups in the para-positions on the benzene rings, p-stien, was prepared and some complexes of this ligand were investigated.

C. Nickel II complexes of p-stien.

The bis-diamine nickel II complexes were prepared by the general method of adding one mole of the nickel salt in hot ethanol to two mole of the ligand in ethanol. The solution

was filtered and on standing yellow crystalline precipitates slowly separated in good yield. The complexes were recrystallised from ethanol. The products, together with their decomposition points and conductivities, are listed in Table 3.10; analyses of the compounds confirmed the formulae given. Both the chloride and the iodide changed in appearance after being pumped at 10^{-4} mm./60°C for several days. The chloride changed from large bright-yellow crystals to a green microcrystalline complex. The iodide also became microcrystalline but this complex remained yellow. Analysis of these substances confirmed that the complexes were now anhydrous. This behaviour is comparable with that of the Lifschitz complexes of *n*-stien considered in the Introduction, and discussion of the points raised by these complexes will be deferred until the physical properties have been described.

The infra-red spectra of the compounds are listed in table 3.11 and show the usual complex series of bands in the region 4,000-3,000cm.⁻¹ reproduced in figures 3.19,20.

The broad band at 3,450-3,500cm.⁻¹ corresponds to lattice water. The green chloride has a very diffuse spectrum in this region, suggesting that it may have more than one type of interaction in the solid phase. The possible structure of this compound is discussed later. The 'anhydrous' iodide still shows the presence of water, though

TABLE 3.10

Physical Properties of p-stien Complexes

<u>Formula</u>	<u>Colour</u>	<u>Decomposition Point °C</u>	<u>Molar Cond. in Nitrobenzene at 20°C (mhos)</u>
<u>NICKEL II</u>			
$[p\text{-stien}_2\text{NiCl}_2] \cdot 4\text{H}_2\text{O}$	chrome yellow	197	13
$[p\text{-stien}_2\text{NiCl}_2]$	green	-	8
$[p\text{-stien}_2\text{NiI}_2] \cdot 2\text{H}_2\text{O}$	deep yellow	251.5	6.6
$[p\text{-stien}_2\text{NiI}_2]$	yellow	-	8
<u>PALLADIUM II</u>			
$[p\text{-stien}_2\text{PdCl}_2] \cdot 2\text{H}_2\text{O}$	white	224-25	1
$[p\text{-stien}_2\text{PdCl}_2]$	white	-	1
$[p\text{-stien}_2\text{PdBr}_2] \cdot 2\text{H}_2\text{O}$	white	260	1
$[p\text{-stien}_2\text{Pd}(\text{NO}_3)_2] \cdot 2\text{H}_2\text{O}$	white	262	1

TABLE 3.11

Infra-red absorption frequencies of p-stien complexes4,000-1,000cm.⁻¹

Only changes compared with the ligand are shown.

p-stien	3355m	3270s-3180m	3090w	3058w
	3020w	1600s	1605m	
p-stien ₂ NiCl ₂ ·4H ₂ O	3440m broad	3200m	3070m	
	1600m broad	1160w	1060m	
p-stien ₂ NiCl ₂	3500-3000 broad	3350w	3220w	3150w
	1585m	1160w		
p-stien ₂ NiI ₂ ·2H ₂ O	3500s broad	3180s	3090s	1580m
	1160w	1060m		
p-stien ₂ NiI ₂	3410w broad	3160s	3060s	1585m
	1160m	1065m		
p-stien ₂ PdCl ₂ ·2H ₂ O	3430m broad	3200m	3070m	1060m

The pumped palladium compound gave the same spectrum as the unpumped material.

m, medium; s, strong; w, weak

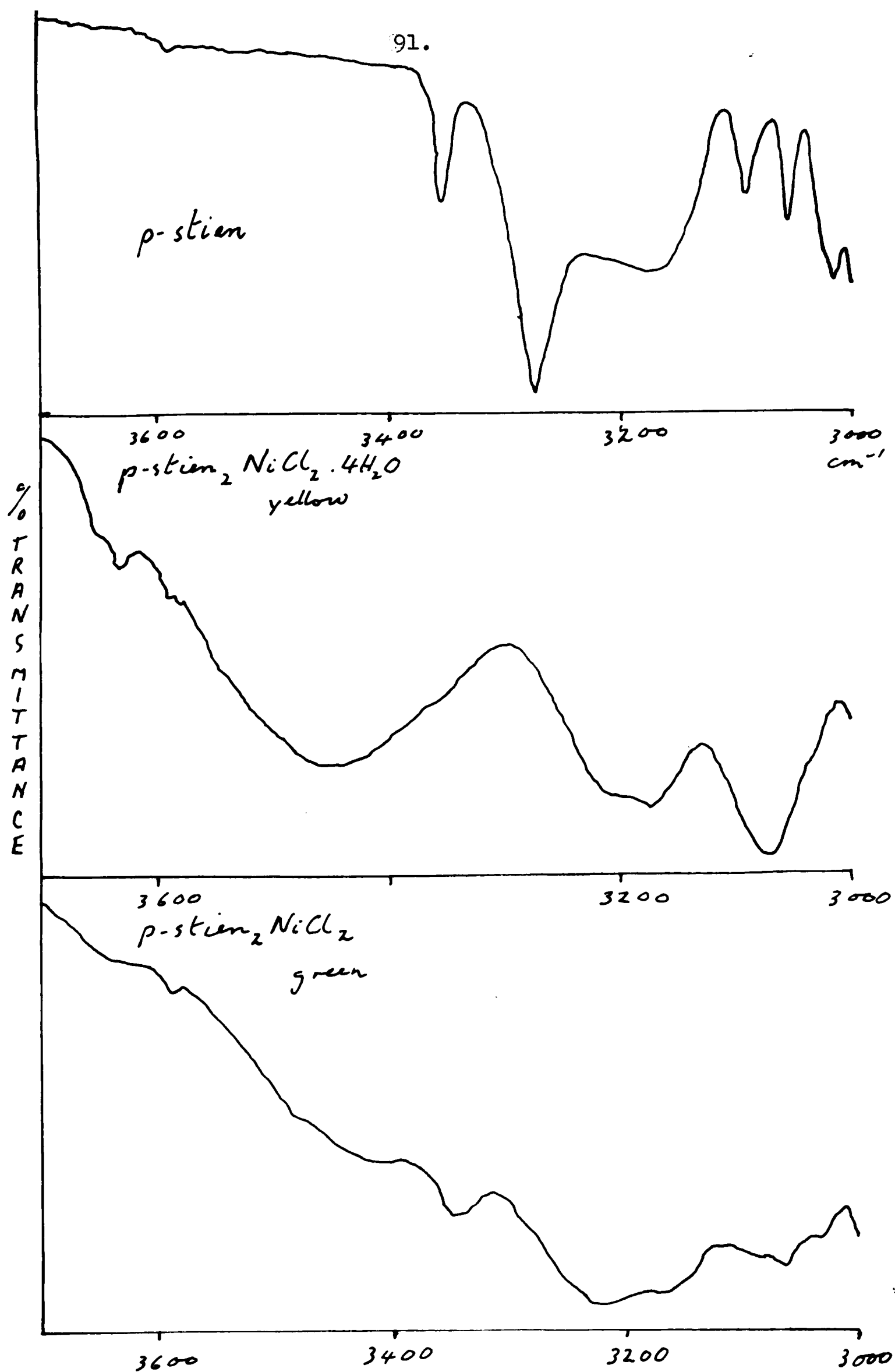


FIGURE 3. 19

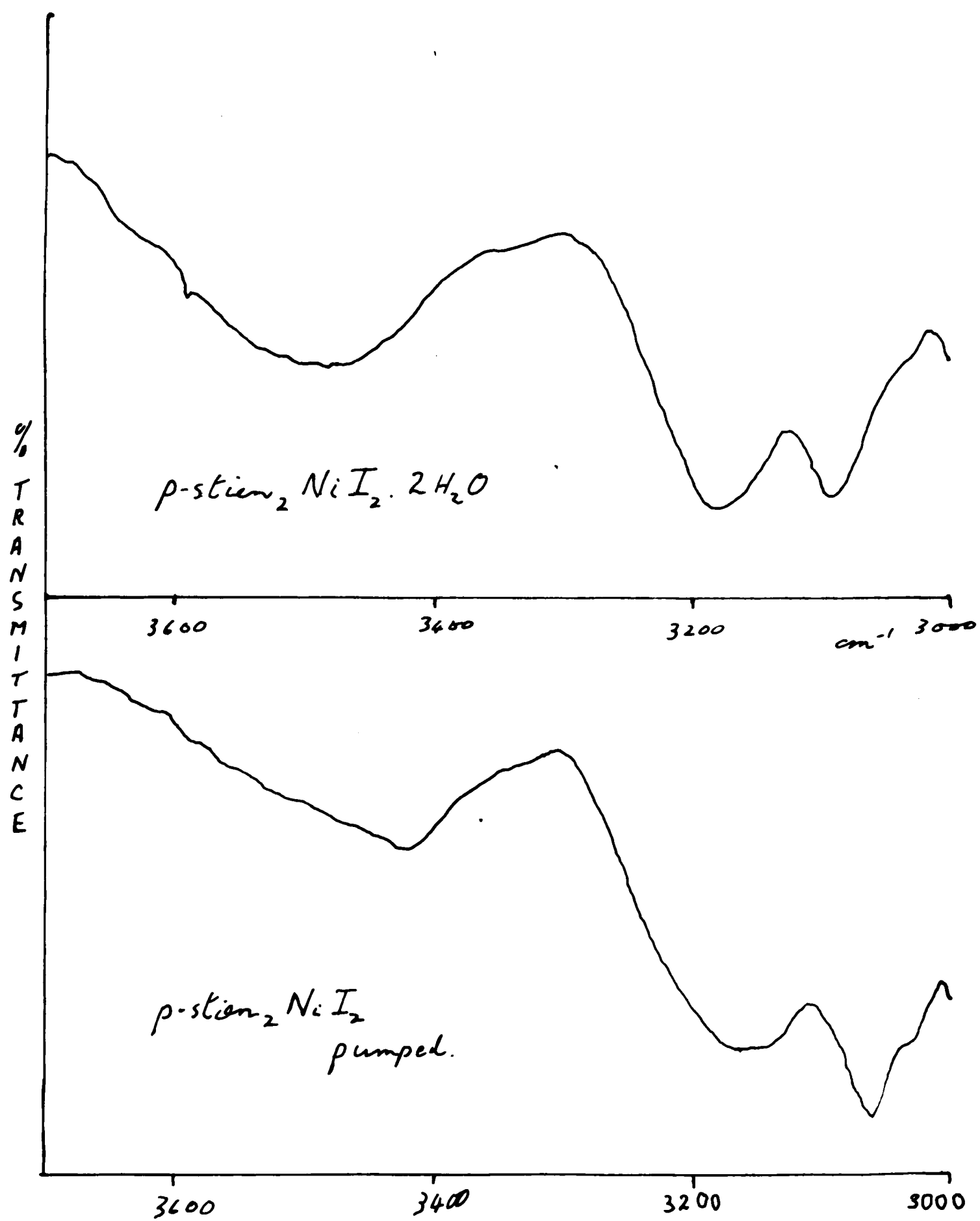


FIGURE 3.20

reduced in intensity, which may have been absorbed during mulling. The sample for analysis was pumped and then dried over $\text{c.H}_2\text{SO}_4$ for a week.

The complexes were soluble in nitrobenzene and so the molar conductivities were measured in this solvent (Table 3.10). All are seen to be intermediate electrolytes with conductivities less than 1:1 electrolytes. The hydrated chloride is considerably more conducting than the other compounds in this solvent. The CsBr spectrum of the anhydrous chloride complex shows no evidence of a Ni-Cl stretching frequency, however, and so interaction must be principally electrostatic in origin to account for the low conductivity.

The magnetic measurements of the complexes are of great interest and are listed in Table 3.12. Both the hydrated and anhydrous iodides and the yellow chloride are diamagnetic, the value of the corrected magnetic susceptibility being 0, within the limits of experimental error. $[\text{p-stien}_2\text{NiCl}_2] \cdot 4\text{H}_2\text{O}$ was pumped at 10^{-1} mm./ 50°C for four hours in the Faraday balance and the magnetic moment of the resulting anhydrous substance was redetermined. A value of 2.68 B.M. was obtained and this value was not altered by further pumping. The loss of weight of the sample corresponded to the loss of four water molecules from the formula weight above.

TABLE 3.12

Magnetic Properties of p-stien Complexes

<u>Formula</u>	χ_m uncorr. (cgs units) ($\times 10^6$)	Diamagn. Corr. (cgs units) ($\times 10^6$)	χ_m corr. (cgs units) ($\times 10^6$)	$\mu_{\text{eff.}}$ B.M.	$T^\circ K$
<u>NICKEL II</u>					
$[p\text{-stien}_2\text{NiCl}_2] \cdot 4\text{H}_2\text{O}$	-518.6	538	+ 19	0	297.5
$[p\text{-stien}_2\text{NiCl}_2]$	2514	490	3004	2.68	296
$[p\text{-stien}_2\text{NiI}_2] \cdot 2\text{H}_2\text{O}$	-522.3	520	-2.3	0	296
$[p\text{-stien}_2\text{NiI}_2]$	diamagnetic		-2.3	0	296

PALLADIUM II

All complexes diamagnetic
 χ_m corrected $\pm 50 \times 10^{-6}$

TABLE 3.13

Solution and Solid Spectra of p-stien Complexes

<u>Formula</u>	<u>Solution in methanol</u>		<u>Solid</u>	
	<u>$\lambda_{\text{max.}}(\text{cm}^{-1})$</u>	<u>$\epsilon_{\text{max.}}$</u>	<u>$\lambda_{\text{max.}}$</u>	<u>'D'</u>
[p-stien ₂ NiCl ₂].4H ₂ O	39,200	35,500	ca. 37,600	1.29
	38,200	35,100	30,000	sh(w)
	37,400	sh(m)	22,900	.61
	24,000	sh(s)	14,500	.15
	22,400	665		
[p-stien ₂ NiCl ₂]	38,000	24,500*	36,400	1.5
	ca. 36,600	sh(s)	26,000	sh(s)
	ca. 35,200	sh(w)	22,700	.89
	25,200	sh(s)	18,400	.445
	22,400	374	ca. 10,000	.42
	16,400	129		
	12,600	sh(w)		
	9,900	85.7		
	9,000	sh(m)		
	7,800	sh(m)		
[p-stien ₂ NiI ₂].2H ₂ O	39,200	48,900	ca. 31,500	sh(s)
	38,200	47,500	ca. 24,200	sh(w)
	37,400	sh(m)	22,300	.835
	22,400	877	15,300	.06(vw)
[p-stien ₂ NiI ₂]	identical to dihydrate		ca. 36,400	sh(s)
			ca. 32,200	sh(s)
			22,600	.575
			ca. 16,000	sh(w)

cont.

<u>Formula</u>	<u>Solution in methanol</u>		<u>Solid</u>	
	$\lambda_{\text{max.}}(\text{cm}^{-1})$	$\epsilon_{\text{max.}}$	$\lambda_{\text{max.}}$	'D'
[p-stien ₂ PdCl ₂].2H ₂ O			37,000	1.3
			34,800	sh(s)
[p-stien ₂ PdCl ₂] (pumped)	The solution spectra showed only the shoulders already observed in the solid reflectance spectra.		27,700	sh(w)
			37,700	1.2
			34,000	sh(s)
			28,000	sh(w)
p-stien ₂ PdBr ₂			37,000	1.4
			34,800	sh(s)
			30,500	sh(w)
	as above			
p-stien ₂ Pd(NO ₃) ₂			37,700	sh(s)
			34,800	sh(s)
			30,000	sh(w)

* solution in carbon tetrachloride

m medium

s strong

w weak

wv very weak

The ultraviolet and visible absorption spectra of the complexes were studied and the features of the spectra are listed in Table 3.13. Figure 3.21 is a correlation table of the features of the solid and solution spectra. Figures 3.22-24 reproduce the actual spectra, extinction coefficients being plotted on a log. scale.

The spectra are all virtually identical in methanol solution. Both the yellow and green forms of the chloride dissolve to give yellow solutions with a single intense broad peak at $22,500\text{cm}^{-1}$. The peak is not completely symmetric and has a definite high energy shoulder suggesting that it is a composite feature of two or more absorption bands. The equivalence of these spectra suggest that the species in this solution is $[\text{p-stien}_2\text{Ni}(\text{CH}_3\text{OH})_2]^{+2}$. The iodide complex was insoluble in carbon tetrachloride but both forms of the chloride dissolved to give green solutions in this solvent. The yellow hydrate required heating to dissolve it in CCl_4 but the green compound was readily soluble. This may be a function of the lattice energy of the two forms but it is possible that the heat helped to 'loosen' firmly bound water molecules on the z-axis of the hydrated complex.

A comparison of the spectra of the two species, green in CCl_4 and yellow in CH_3OH , is given in figure 3.23. It may be seen that the green form shows evidence of the peak

U/V SOLUTION & SOLID SPECTRA

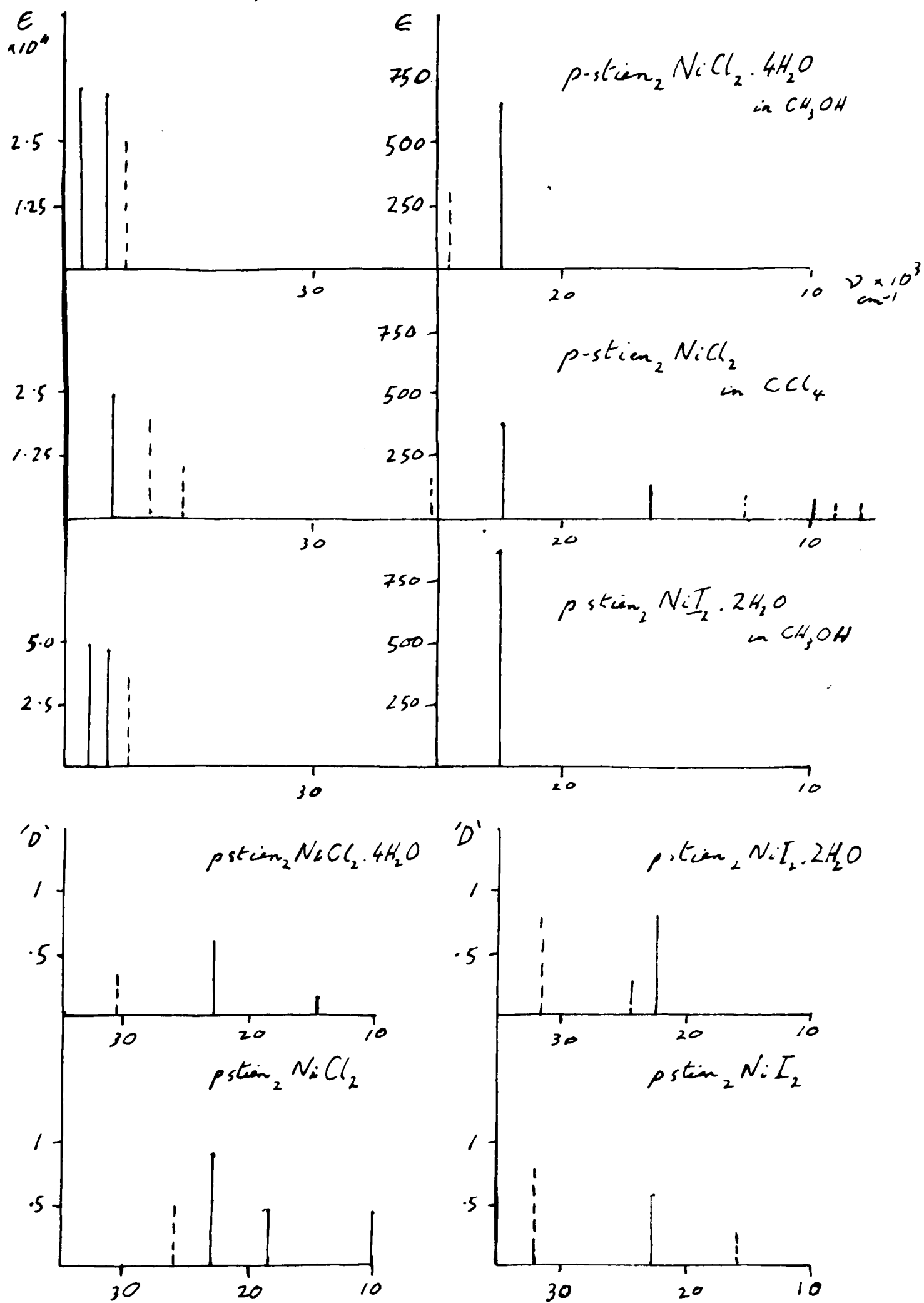


FIGURE 3.2

1/V SOLUTION SPECTRA

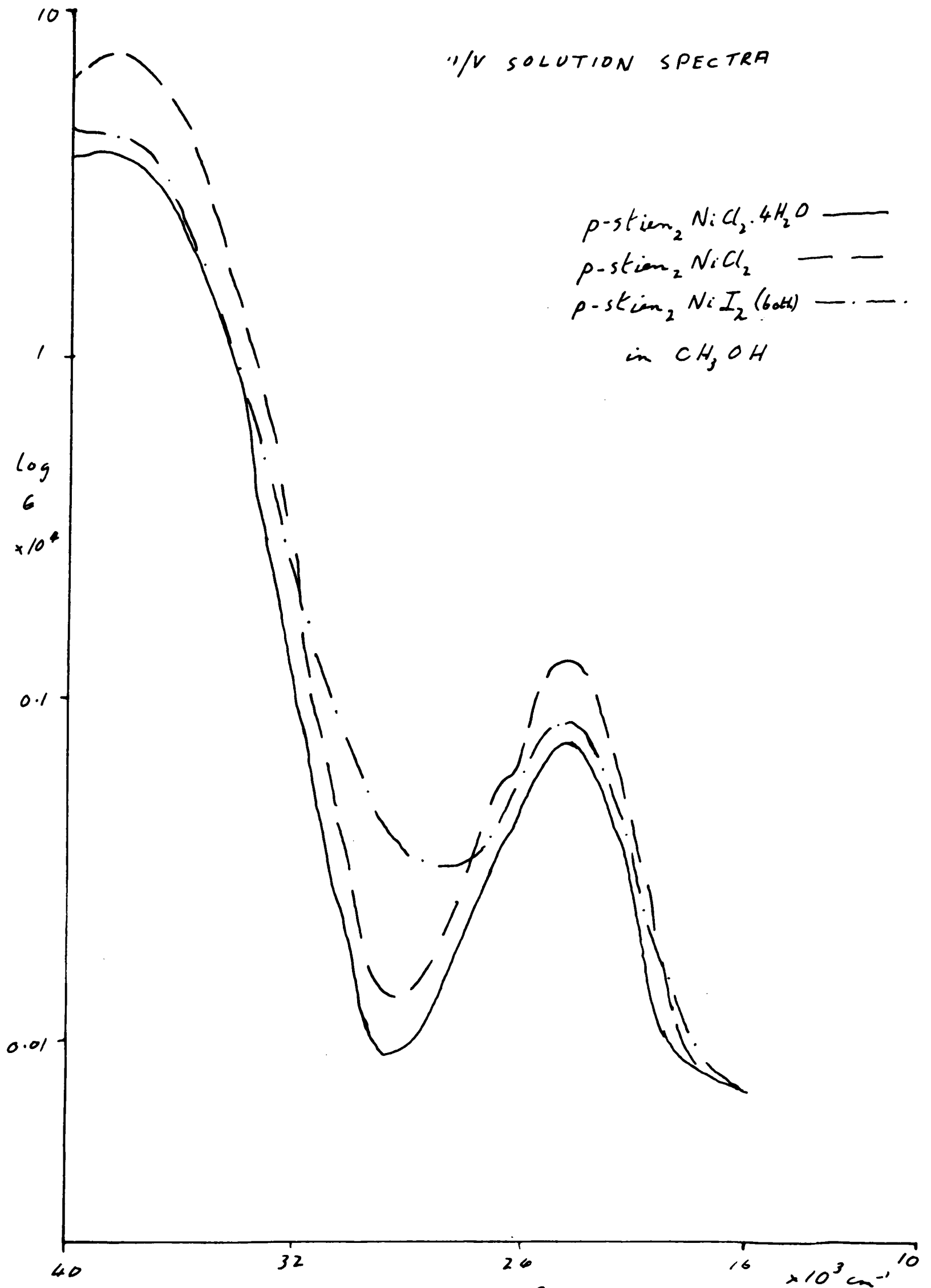


FIGURE 3.22

U/V SOLUTION SPECTRA

$p\text{-stien}_2 \text{NiCl}_2$

$.4\text{H}_2\text{O}$ yellow in CH_3OH ———

anhyd. green in CCl_4 - - - -

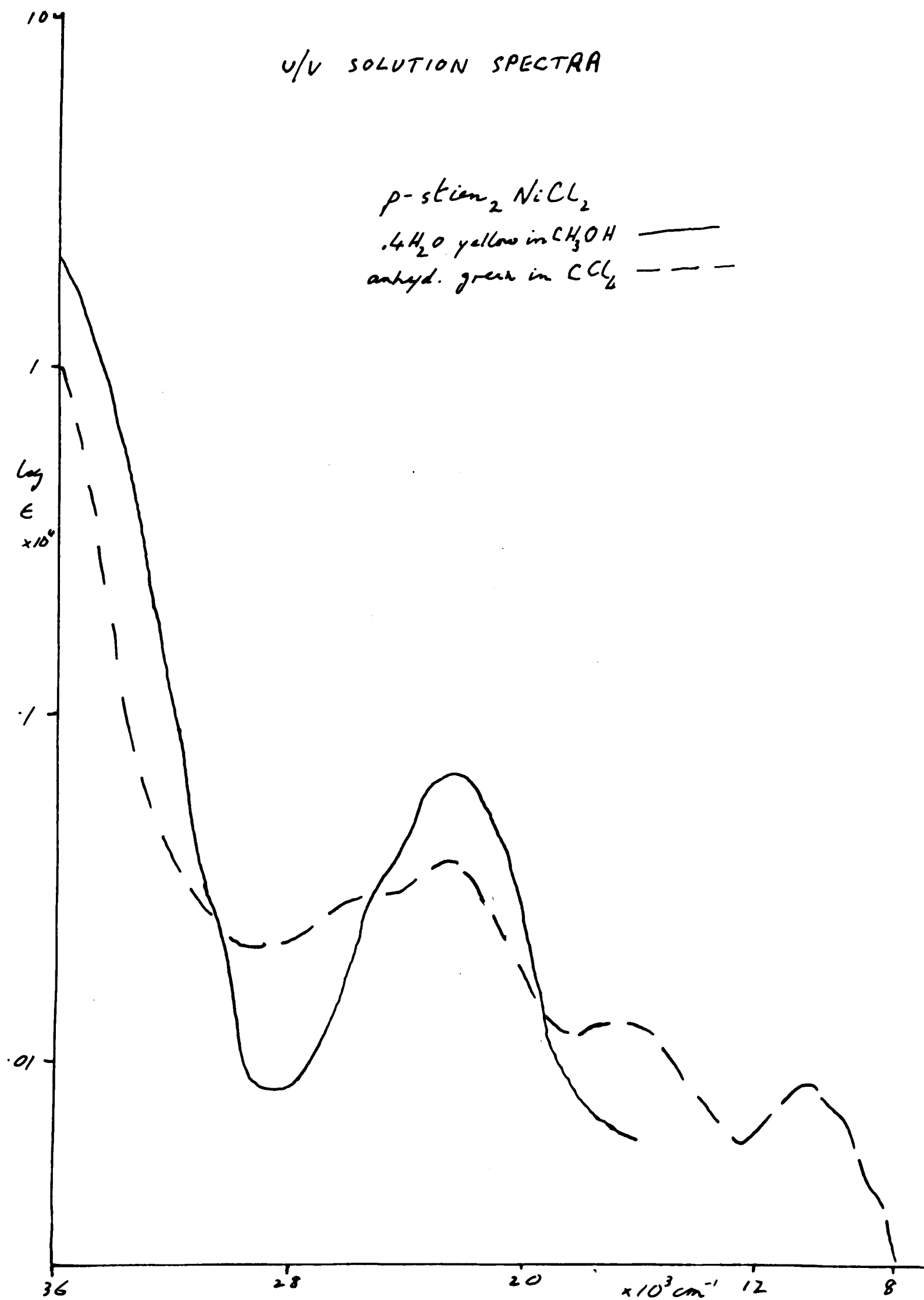


FIGURE 3. 23

U/V SOLID REFLECTANCE
SPECTRA.

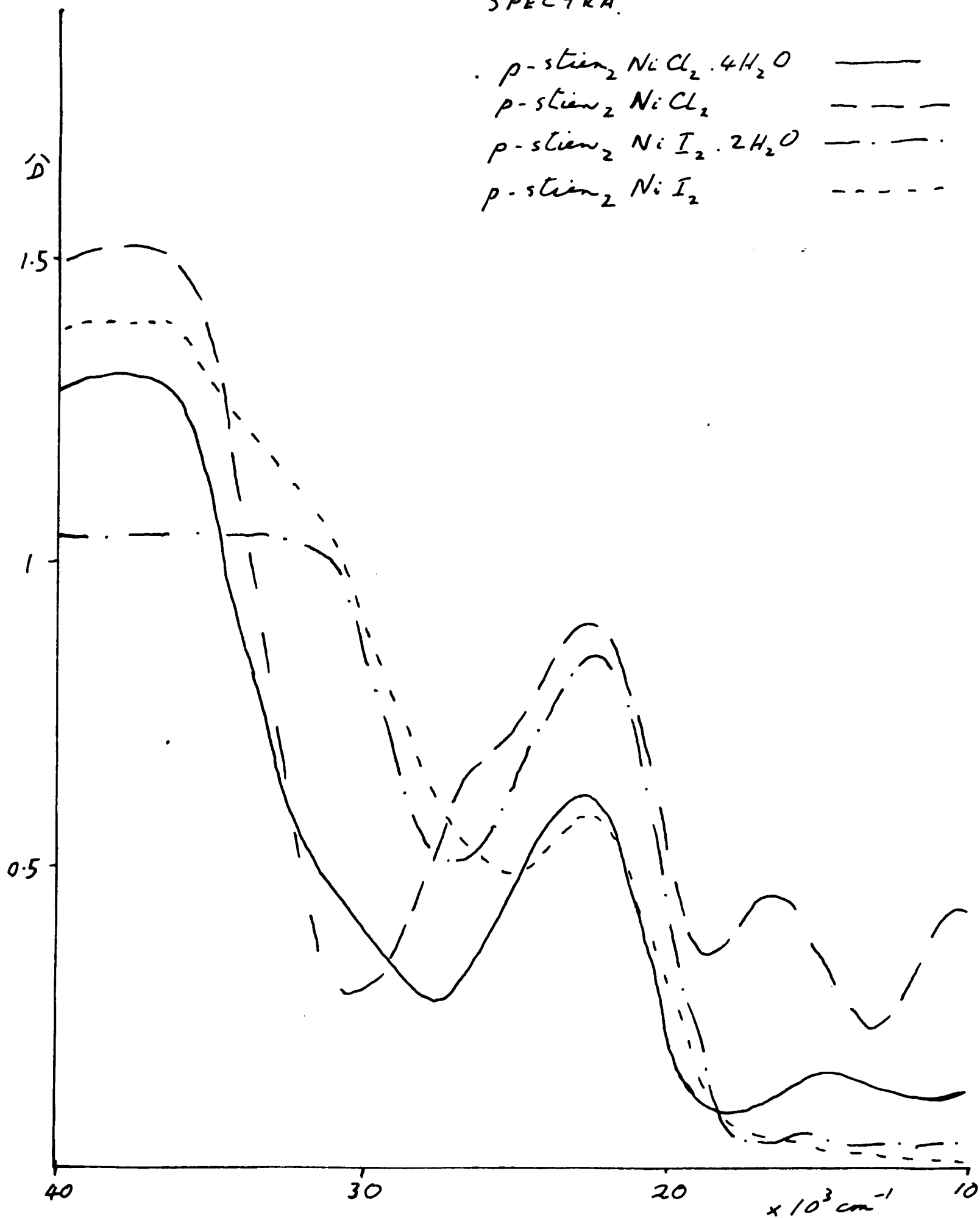


FIGURE 3.24

at $22,500\text{cm.}^{-1}$ as well as many additional features. Similar behaviour is observed in the solid reflectance spectra, although an additional, weak, band at $14,500\text{cm.}^{-1}$ is observed for the yellow hydrate. The similarity of solid and solution spectra suggest that the factors influencing the energy levels of the metal ion are practically the same in each case.

Recently there has been much discussion regarding the molecular structures of the $[\text{m-stien}_2\text{Ni}]^{+2}$ complexes of Lifschitz described briefly in the Introduction. These complexes should be analogous to the p-stien complexes here considered. The m-stien complexes frequently contain solvent of crystallisation and may exist in ⁶⁶blue paramagnetic (μ approximately 3.1 B.M.) or yellow diamagnetic forms. Weakly paramagnetic forms $\mu < 2.83$ B.M. are also described.

Furlani (72) compared the absorption spectra of the blue and yellow m-stien nickel complexes with the term systems calculated with the aid of Hartmann's theory of electrostatic complexes. Various possible symmetries (O_h , T_d , D_{4h} , D_{2h} , D_{2d} and C_{2v}) were considered. Figure 3.25 is a correlation table (after Furlani) showing some observed and calculated absorption maxima. In the blue complexes agreement between calculated and observed spectra is obtained on the basis of a distorted octahedral configuration with two ligand groups on an elongated z-axis. For the yellow diamagnetic isomer,

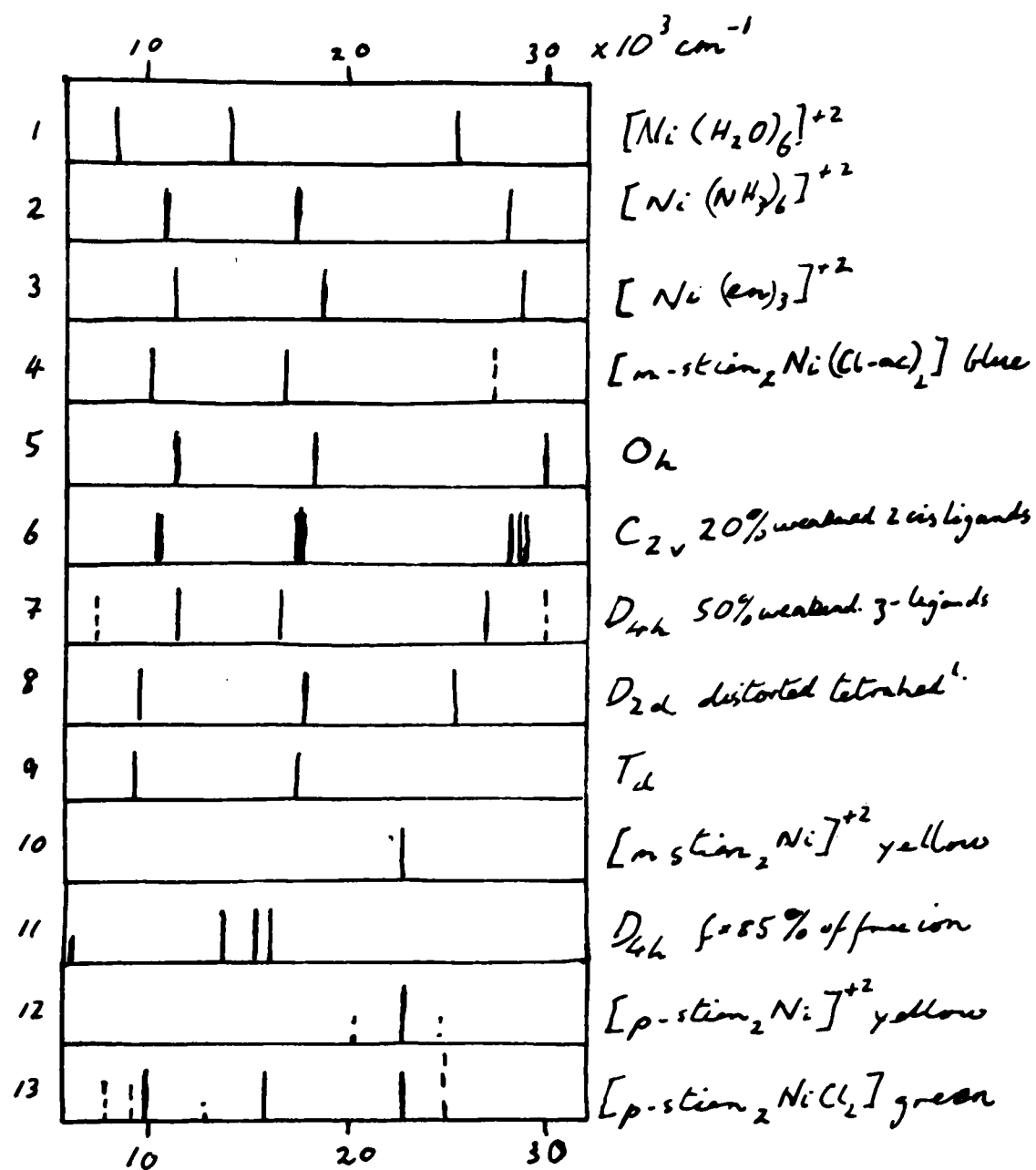


FIGURE 3.25

three bands in close proximity are expected, in substantial agreement with the one large band observed in both *m*-stien and *p*-stien complexes. The quantitative agreement of the frequency values is less satisfactory. It can be improved if some covalent bonding between the central ion and ligand groups is assumed. Furlani shows that D_{4h} symmetry is the only one compatible with the anomalous magnetism of the nickel complex. Calculations indicate that even a small axial component of the ligand field can strongly destabilize the lowest singlet state and thus restore paramagnetic character to the complex. A diagonal distortion in the plane (D_{2h}) leaves the term system for D_{4h} substantially unaltered.

The splitting of the energy levels in a field of D_{4h} symmetry has also been discussed by Maki (73, a,b) and Lichr and Ballhausen (74). The latter give the simplified energy level diagram (figure 3.26) for the splitting of the energy levels in strongly tetragonal nickel II complexes.

The transition from paramagnetic to diamagnetic character depends on the strength of the axial perturbation. The spectral assignments involve singlet-triplet transitions, an alternative assignment is described later. - The transitions expected for the *p*-stien Ni complexes are marked on the diagram.

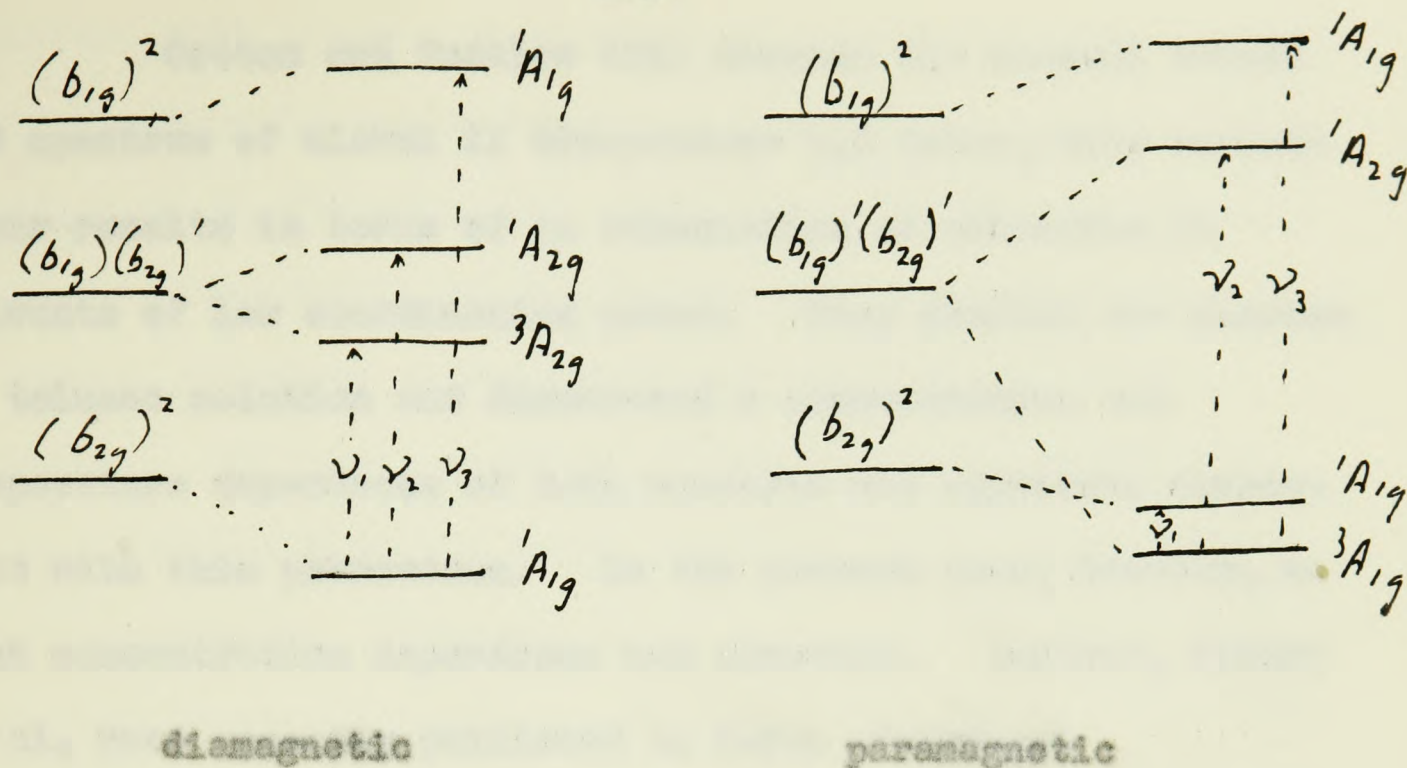


Figure 3.26

It seems surprising, at first, that in the p-stien complexes the hydrate is the diamagnetic species whilst the anhydrous compound is paramagnetic. The ligand field of water is stronger than that of a halide ion and so stronger axial perturbation would be expected in the hydrated molecule. This latter behaviour is frequently shown in the Lifschitz complexes. However, the hydrated chloride contains four water molecules and so the crystal packing of this species may be rather poor. Removal of the water will cause a collapse of the expanded structure and a corresponding increase in the perturbation caused by the axial ligands - in this case chloride ions.

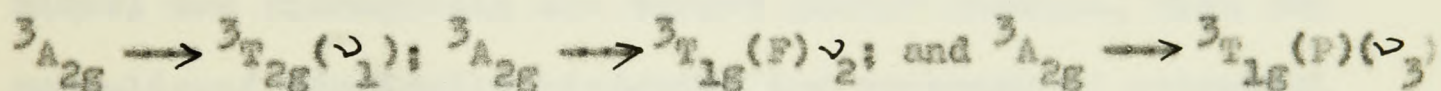
The anomalous magnetic moment and the "mixed" form of the spectrum of the green compound call for further comment.

Cotton and Fackler (75) discuss the unusual moment and spectrum of nickel II bis-pentane 1.5 dione, they explain their results in terms of an association of molecules in solvents of low coordinating power. They studied the complex in toluene solution and discovered a concentration and temperature dependence of both spectrum and magnetism consistent with this phenomenon. In the present case, however, no such concentration dependence was observed. Further, Nyburg et al. have recently published an X-ray structural determination of $[m\text{-stien}_2\text{Ni}(\text{CHCl}_2\text{COO})_2]$ and also discuss the spectra and magnetic moment of this compound. They studied two forms of this complex. The blue compound had the formula $[m\text{-stien}_2\text{NiX}_2] \cdot 4\text{H}_2\text{O}$ and contained octahedrally coordinated nickel, whilst the yellow or yellow-green complex had the formula $3.[m\text{-stien}_2\text{NiX}_2] \cdot 20\text{C}_2\text{H}_5\text{OH} \cdot 2\text{H}_2\text{O}$. These crystals contained both octahedral six-coordinate nickel and planar four-coordinate nickel, the crystal cell containing two molecules of the former and one of the latter type. These authors interpret their spectral and magnetic results in the light of this evidence. They observe a magnetic moment of 2.58 B.M. for this yellow complex. The magnetic moment for octahedral nickel II is ca. 3.16 B.M. and their value may be indicative of the mixed octahedral and planar environments. The absorption spectra give further support,

[*m*-stien₂NiCl₂] has a single peak at 22,500cm.⁻¹ $\epsilon_{\text{max.}} = 66$, whereas Nyburg's yellow complex has a peak at 22,600cm.⁻¹ $\epsilon_{\text{max.}} = 24$ in 95% ethanol. This may be taken as a measure of the concentration of the diamagnetic species in the solution and gives an answer of one third of the complex species. The X-ray analysis of the blue dichloroacetate complex showed that the axial positions were occupied by water molecules. However, in aqueous solution dissociation occurred leaving a yellow planar complex. The authors conclude that in solution the axial positions are sterically hindered, preventing the close approach of anions or solvent molecules. This argument is supported by the observation that, whilst the *meso*-diamine gives these yellow solutions, the racemic diamine gives blue aqueous solutions.

The *p*-stien complex here considered is again that of the *meso* form of the diamine and corresponds closely with the *m*-stien case. The moment for the green form of this complex is 2.68 and it may thus have a similar crystal structure to the yellow-green *m*-stien dichloroacetate. Certainly the UV absorption spectrum of this complex in CCl₄ is of a 'mixed' form and suggests that octahedral and planar molecules co-exist in this solvent. This point is clearly illustrated in figure 3.25. The sum of the spectra of the blue *m*-stien nickel dichloroacetate (no.4) and the yellow

dichlorides (no's.10,12) is identical with that of the green p-stien complex. The X-ray structure described above then allows the postulation of a structure similar to that of the 'yellow' dichloroacetate, having a mixture of octahedral and square planar forms. Further confirmation of this structure would require an X-ray determination. Again from figure 3.25 it is seen that the 'octahedral' frequencies correspond quite well with the Furlani's calculations for O_h and D_{4h} . Nyburg (76) has calculated the energy differences of the transitions in the m-stien complex and, having assumed a reduction in the ${}^3F - {}^3P$ separation from that of the free ion, he obtained very good agreement with experiment. For the 'octahedral' species he assigns the spectrum as



This contradicts the assignment given earlier by Ballhausen, who considers the transitions to be spin-forbidden. Of course, the ${}^3A_{2g}(F) \longrightarrow {}^3T_{1g}(P)$ transition is formally a two-electron jump; though in a weak field state mixing will occur. In D_{4h} symmetry the T_g levels will split into E_g and either A_g or B_g levels and thus four spin allowed transitions would be expected from a triplet ^{ou}grand state. The situation is not clear, though as seen in figure 3.25 no.5, the calculated transitions for O_h , assigned as above, are in good agreement with experiment.

The green p-stien complex shows a weak shoulder at 12,600cm.⁻¹. This would seem to be analogous to a weak band described by Nyburg at this frequency. It is assigned to a 'forbidden' ${}^3A_{2g} \longrightarrow {}^1E_g$ transition. Spin-orbit coupling will cause the latter term to mix with ${}^3T_{2g}$ and ${}^3T_{1g}$ and so the intensity of the band is enhanced.

The single absorption band in the diamagnetic complexes may be assigned to a transition from the ${}^1A_{1g}$ ground state in this case to ${}^1A_{2g}(G)$ although agreement between the experimental value and that calculated from a simple crystal field model is poor, as always, with planar nickel II complexes.

In conclusion, the yellow p-stien complexes of nickel are diamagnetic and square planar species, with the meso-ligand sterically hindering the approach of potential ligands on the z-axis. The green form of the chloride may be a mixture of octahedral and planar forms both in the solid and in carbon tetrachloride solution. This contention is supported by the spectrum and magnetic moment and the complex may be analogous to the m-stien dichloroacetate of Nyburg.

D. Palladium II complexes of p-stien

The palladium complexes of p-stien were prepared by the same general method as were the m-stien analogues, the

refluxing of stoichiometric quantities of ligand and salt in ethanolic solution. The compounds were isolated as white powders and were recrystallised from ethanol as such. The compounds prepared, together with their colours, decomposition points and conductivities are listed in Table 3.10 (p.89). The analytical results for these complexes were much better than for the *m*-stien palladium II complexes and correspond closely to a formula $p\text{-stien}_2\text{PdX}_2 \cdot 2\text{H}_2\text{O}$. Pumping of the complexes at 10^{-4} mm./60° gave indeterminate states of hydration for all the complexes. The chloride complex was reanalysed to give values close to those for the anhydrous compound, although the infra-red spectrum of this species was the same as that of the hydrate, showing a broad peak due to water at $3,440\text{cm.}^{-1}$. The infra-red spectra of these complexes were rather indistinct in the N-H stretching region due to the broad water absorption and have not been reproduced here. The nitrate complex showed the usual strong band for an ionic nitrate.

All the complexes except for the chloride dihydrate were insoluble in nitrobenzene. The chloride dissolved in the hot solvent and gave a negligible conductivity. The CaBr spectrum showed no evidence of a Pd-Cl bond and so it is possible that the complex existed as an uncharged ion triplet in nitrobenzene. Alternatively, the chloride ion may still

be attached to palladium, though rather weakly. The electronic repulsions on the z-axis will tend to make this so in a diamagnetic square planar complex. The metal-halide stretch will then fall outside the observable region. Certainly no Pd-Cl stretch has been observed for the axial chloride in $[\text{QASPdCl}]^+$.

The magnetic susceptibilities of the complexes were all $\pm 50 \times 10^{-6}$ cgs. units as expected for square planar d^8 ions.

The ultraviolet absorption spectra of p-stien complexes were again very featureless; they are recorded in Table 3.13(p.95). As with m-stien the ligand field bands were at high energy and consequently obscured by charge transfer bands. The solid reflectance spectra (figure 3.27) show shoulders at $34,500\text{cm.}^{-1}$ and $28,000\text{cm.}^{-1}$, which correspond with the bands discussed previously and assigned by Jørgensen as singlet-singlet and singlet-triplet transitions, respectively. The solution spectra were not all measured as there was not any clarification or modification of spectral features in this state.

Thus the p-stien palladium complexes are fully analogous to the m-stien compounds and the para-isopropyl groups attached to the benzene rings of the ligand do not give any substantial benefits in the study of conductivities in non-polar solvents.

U/V SOLID REFLECTANCE SPECTRA

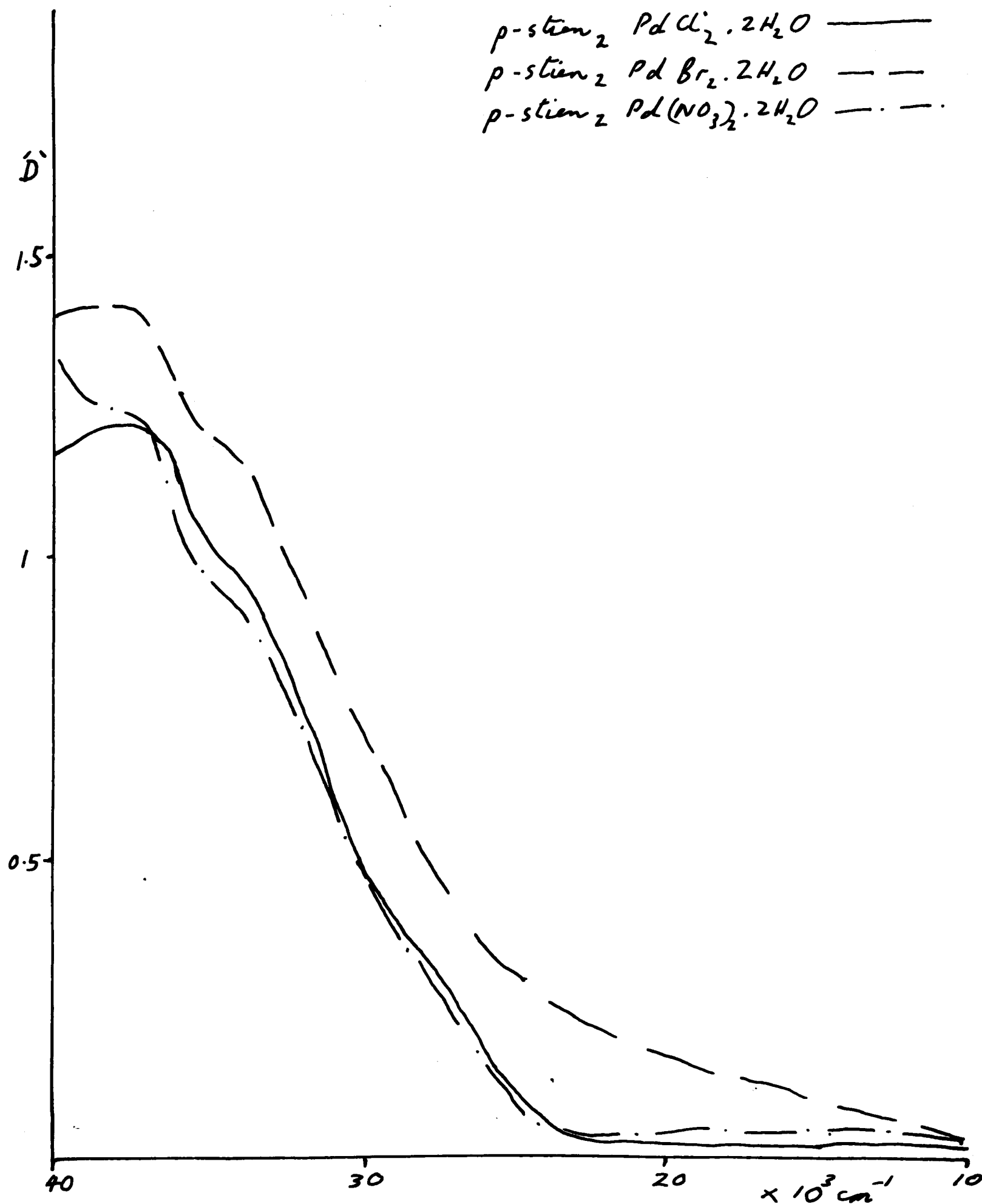


FIGURE 3.27

The synthesis of this bidentate ligand had proceeded in very low yield and so it was decided not to attempt to prepare polydentate ligands of this type, as they would probably not give the required properties to complexes with d^8 metals. Consequently the mixed phosphorus/nitrogen ligands were prepared and complexes of these ligands are described in the next chapter.

CHAPTER IV

THE COMPLEXES OF PTN, PDN, AND PN

The compound PTN, formulated as a quadridentate ligand, was prepared with the aim of comparison with similar arsenic and phosphorus compounds, QAS and QP. A mixed ligand, rather than 'QN' with four nitrogen donor atoms, was prepared since nitrogen at the apex of a pyramidal molecule would be too small to allow the whole to be stable other than in planar configuration. Thus triphenylamine is almost planar with the benzene rings in 'propeller' orientation. Secondly, the synthetic route employed phosphorus trichloride which is much more readily handled than NCl_3 . The nitrogen atoms are necessarily tertiary in the synthesis although they will have lower donor power. However, Mann and Watson (77) have prepared complexes of bidentate tertiary amines and found these to be robust complexes.

PDN and PN, formulated as tri- and bi-dentate ligands, were prepared once doubt had been thrown upon the effective coordination number of PTN in its palladium and

platinum complexes. Compounds of these metals will be first discussed.

A. Complexes of Platinum II and Palladium II.

The chloride complexes were prepared by the general method of mixing one mole of ligand in ethanol with one mole of sodium chloropalladite or platinite in ethanol. The solution was filtered hot and on standing yellow or cream crystals separated. These were washed with water and methanol and recrystallised from butanol or ethanol. The bromide and iodide analogues were prepared by mixing ethanolic solutions of the sodium halide with the chlorometallite solutions and filtering the resultant MBr_4^{-2} or MI_4^{-2} solution into the hot solution of the ligand. In some cases recrystallisation of bromide and iodide complexes from methylene chloride and ethanol did not give analytically pure products. For example, the compound $[PDNPTI_2]$ gave increasingly high values for P and Pt analysis on repeated recrystallisation. Inspection of its infra-red spectrum in the caesium bromide region showed a band at 30μ increasing in intensity which is assigned to a Pt - Cl stretching mode. This exchange was due to methylene chloride and was quenched by adding sodium iodide to the solvent. All the substances

then gave very good analytical results and their formulae, together with colours, decomposition points, and conductivities in nitromethane are listed in Table 4.1.

The infra-red spectra of the complexes confirmed the absence of water. The free ligand had a peak at $2,775\text{cm.}^{-1}$ in PTN, to $2,780\text{cm.}^{-1}$ in PN. This peak has been assigned as a N-CH_3 frequency (78,79). It has been suggested that this is a C-H stretching frequency of the N-CH_3 group; but a more attractive suggestion is that it is a combination of this with the overtone of the symmetric CH_3 deformation mode at $1,430\text{cm.}^{-1}$ to give a Fermi resonance doublet, observed in Raman spectra.

Weekins and Hill (78) list some typical frequencies: dimethyl aniline, $2,807\text{cm.}^{-1}$; o-methyl derivative $2,785\text{cm.}^{-1}$; p-methyl derivative, $2,797\text{cm.}^{-1}$; m-methyl derivative $2,803\text{cm.}^{-1}$; diethyl aniline, no band. The ortho substituted derivative thus corresponds closely with the PN ligands. Figure 4.1 shows the I/R spectra of spectra of two free N-CH_3 compounds and their charged and coordinated derivatives. In each case the band at $2,800\text{cm.}^{-1}$ has disappeared in the derivative.

Braunholtz (79) observed that even in p-nitro dimethyl aniline the band has disappeared, although it is present in the meta derivative. Presumably the charged

TABLE 4.1

Physical Properties of Pt II and Pd II complexes
of PTH, PDN and PN.

<u>Formula</u>	<u>Colour</u>	<u>Melting Point (°C)</u>	<u>Molar Cond. in Nitromethane at 20°C (mhos)</u>
[PTNPtCl ₂]	pale yellow	238 d.	8
[PTNPtBr ₂]	pale yellow	232 d.	8.3
[PTNPtI ₂]	yellow	216 d.	5.6
[PTNPdCl ₂]	yellow	229 d.	5.1
[PTNPdBr ₂]	orange	225 d.	6.8
[PTNPdI ₂]	deep red	219 d.	9.3*
[PDNPtCl ₂]	cream-white	274	0.2
[PDNPtBr ₂]	pale yellow	272.5	3.2
[PDNPtI ₂]	chrome-yellow	263.5	3
[PDNPdCl ₂]	chrome-yellow	274	1
[PDNPdBr ₂]	yellow-orange	263	6
[PDNPdI ₂]	deep red	254.5	8.6
[PNPtCl ₂]	cream-white	295	1.3
[PNPtBr ₂]	pale yellow	285	5
[PNPtI ₂]	chrome-yellow	279	7
[PNPdCl ₂]	chrome-yellow	287-8	0.3
[PNPdBr ₂]	yellow-orange	284-5	2
[PNPdI ₂]	deep red	268	4*

* Conductivity also measured in methyl cyanide

[PTNPdI₂] = 330; [PNPdI₂] = 183.

quinonoid species is responsible for the disappearance. Thus the absence of this band is indicative of coordination in N-CH_3 compounds.

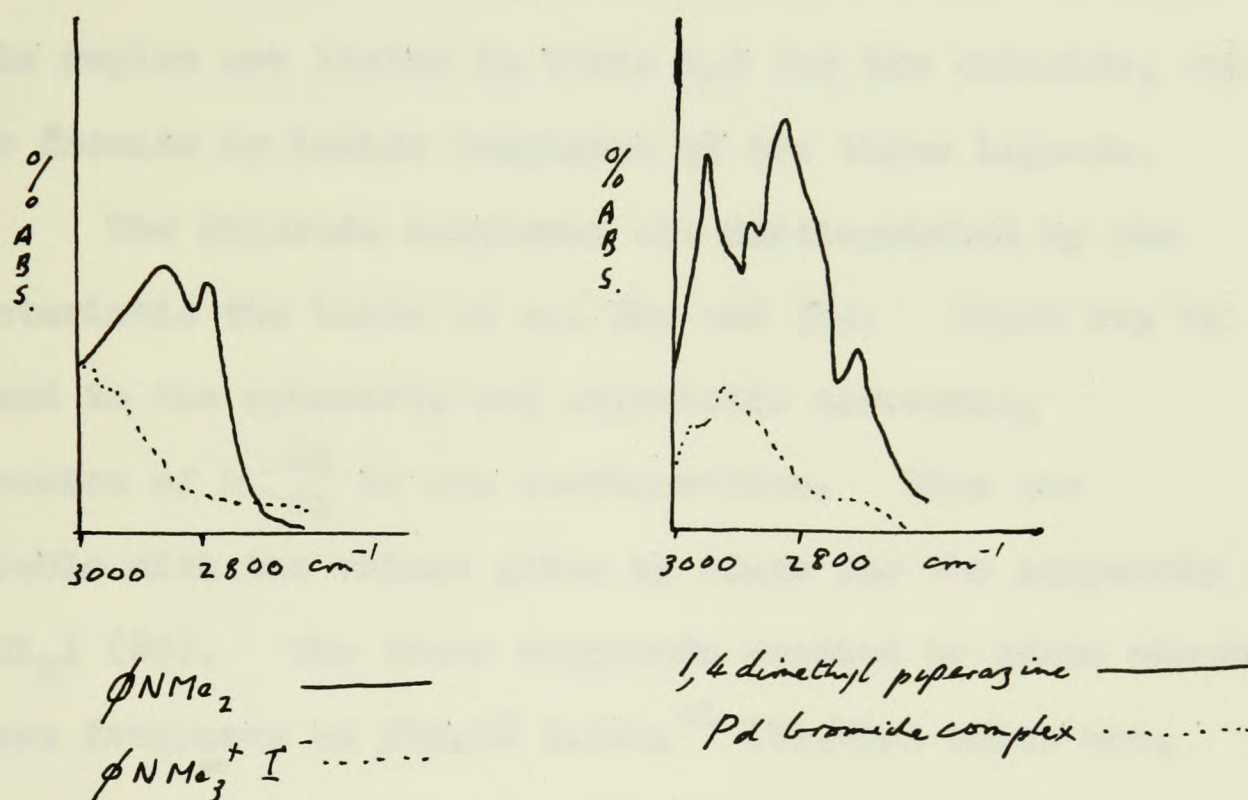


Figure 4.1

The Pd and Pt complexes showed such a band at $2,882\text{cm.}^{-1}$ in the PTN complexes, $2,890$ in PDN complexes; but this band was completely absent in the PN complexes. This observation suggests that all the donor atoms in PTN and PDN are not, in fact, coordinated. In other respects the infrared spectra of the complexes in the sodium chloride region show no features of interest and are not reproduced here. The spectra of complexes of the same ligand are all identical

and show slight changes from the spectra of the free ligands. The main differences between the ligands are the appearance of modes associated with mono-substituted benzene rings.

The spectra in the caesium bromide region are much more interesting. The frequencies of the absorption bands in this region are listed in Table 4.2 for the chloride, and either bromide or iodide complexes of the three ligands.

The chloride complexes are distinguished by the characteristic two bands at ca. 30μ and 35μ . These may be assigned to the symmetric and asymmetric stretching frequencies of $M \begin{smallmatrix} \diagup Cl \\ \diagdown Cl \end{smallmatrix}$ in cis configuration. They are comparable with the values given by Adams for the compounds $[L_2PtCl_2]$ (80). The trans compounds studied by Adams showed only one frequency at $339.5 \pm 3.1 \text{ cm.}^{-1}$ (29.45μ) which was, therefore, insensitive to the ligand. The cis compounds gave a wide range of values very dependent upon the ligand. Thus

for L = pyridine (Pt-Cl) = $343.4(28.6\mu)$ $327.9, \text{vs}$ (30.6μ)

for L = NH_3 = $326.8(30.7\mu)$ $258.8, \text{vs}$ (39.6μ)

for L = $P(C_2H_5)_3$ = $303.2, \text{vs}$ (33μ) $280.8, \text{vs}$ (35.7μ).

The very low value for NH_3 may be due to hydrogen bonding in this case weakening the M-N bond. In the P/N complexes, where P/N represents any of the ligands, we have two non-equivalent groups L and two cis chlorine groups (further

TABLE 4.2

Infra-red Absorption Bands of Pt and Pd Complexesin the range 15-40 μ (715-250cm.⁻¹).

[PNPdCl ₂]	16.3s18-19.3vs	22-22.4s	29 broad vs
	17.5s19.6-20vs	23.5s25w	34 broad vs
[PNPdI ₂]	16.3-16.6m20.2vs	22.2-22.6m	
	18.2-19.4-19.8vs	23.7m	
[PNPtCl ₂]	16.3m17.9vs	21.8s	29.7-30.4sh,vs
	19.1-19.7-20vs	22.8-23.2m	33.6vs36.6s
[PNPtI ₂]	16.3m17.4s18.2s	21.9s	
	19.2-19.6-19.9s	22.8-23.3m	
[PDNPdCl ₂]	16.5m17.6s18.2vs	20.8m22-22.9m	30.3 broad s
	19.1-19.5-19.9vs	23.7s26.4w	35.6 broad vs
[PDNPdI ₂]	identical to chloride below 30 μ		
[PDNPtCl ₂]	16.3m17.4s18.2s	20.7s22.3-22.7m	29.7 broad s
	19-19.3-19.5vs	23.6s26.2w	34.1 broad s
[PDNPtI ₂]	16.8w17.9-18.6m	21.1m22.6-23w	
	19.4-19.7-20s	23.9m26.6w	
[PTNPdCl ₂]	16.3m19-19.6vs	21.2-21.8-22.3s	30.2 broad vs
	17.4-17.8-18.3s	24.2s25.9w	35.6 broad vs
[PTNPdBr ₂]	16.5w17.2-17.6-18.2m20.4w21-21.7m		
	19-19.4-19.6m	23-23.9s26.2w	
[PTNPtCl ₂]	17.4-17.8-18.3s	20.4-21.5broad,s	29.4 broad vs
	16.3m19-19.6vs	22.5m24.2s	35.8 broad vs
[PTNPtI ₂]	same as chloride	21.1m22.6-23w	
	below 20 μ	23.9m26.6w	

vs, very strong; s, strong; m, medium; w, weak

evidence is given for this later) and so we should expect the two Pt-Cl bands to be quite widely separated in energy, as is seen to be the case in Table 4.2. Certainly the infra-red evidence suggests that the two chlorine atoms are in sites equivalent to the cis square planar complexes of Adams and thus suggests that all the N-donor atoms may not be coordinated.

The conductivities of the complexes were measured in nitromethane solution. These ligands gave complexes readily soluble in this solvent. The values of the conductivities are given in Table 4.1. Both the metals, with all three ligands, gave complexes with molar conductances of less than 10. Thus on the criteria discussed earlier (c.f. Table 3.5, p.57) the complexes are essentially non-electrolytes in this solvent, although a little solvolysis may have occurred. These results are particularly significant for the PTN complexes as a trigonal bipyramidal complex of this ligand would be a 1:1 electrolyte, as are the QAS complexes. However, the standard test for uncoordinated donor atoms gave a negative result. This is the addition of methyl iodide to the solution. A 'loose' atom will be methylated and positively charged, whilst an iodide ion is released. The conductivity rises rapidly in such an instance. Certainly the free ligand and dimethyl aniline

are very sensitive to the methyl iodide test. It was the conflicting evidence of this test and the U/V spectra of PTN and PDN discussed later, that was resolved by the preparation of complexes of PN. The methyl iodide test was shown to be quite invalid in this instance. Presumably this is due to a deactivation of the nitrogen atom in the conjugated system of the coordinated molecule, thus in o-dimethylaminophenyl diethyl phosphine only a mono-methiodide is isolated.

The complexes were all diamagnetic, as expected, for d^8 second and third transition series in what is shown to be square planar stereochemistry.

The ultraviolet and visible absorption spectra were measured in both the solid and in solution in non-polar solvents. The data for the complexes of the three ligands with all the metals studied are listed in Tables 4.3-5.

Figures 4.2,3 reproduce the solution spectra of the platinum and palladium complexes, the values of extinction coefficient being plotted on a log. scale. The spectra of the compounds with all three ligands were identical and only one set is reproduced. This evidence clearly indicated that the coordination number of the ligand is the same in each case, and so all the nitrogen atoms in the quadri- and tridentate ligands cannot be coordinated in methylene chloride solution.

TABLE 4.3

Solution and Solid Spectra of PTN Complexes

<u>Formula</u>	<u>Solution*</u>		<u>Solid**</u>	
	$\lambda_{\text{max.}} (\text{cm}^{-1})$	$\epsilon_{\text{max.}}$	$\lambda_{\text{max.}}$	'D'
{ [PTNPtCl ₂]	ca. 43,000	sh		
	ca. 37,500	sh	ca. 32,200	sh
	ca. 30,000	sh	ca. 29,600	sh
{ [PTNPtBr ₂]	42,000	sh	38,600	sh
	37,000	sh	32,500	sh
	ca. 32,600	sh	29,000	sh
{ [PTNPtI ₂]	42,600	sh		
	39,000	sh		
	31,500	sh	31,200	sh
	26,900	2,700	26,700	.838
{ [PTNPdCl ₂]	ca. 36,800	sh [†]		
	ca. 30,000	sh		
	27,600	2,320	26,900	.572
{ [PTNPdBr ₂]	35,200	13,900	30,600	sh
	ca. 29,400	sh	27,200	sh
	26,500	2,640	26,000	.825
{ [PTNPdI ₂]	ca. 40,000	sh		
	ca. 36,000	sh	ca. 37,000	sh
	31,200	12,700	31,300	.865
	25,600	2,730	25,500	.69
	21,800	3,260	21,500	.77

Solution spectrum in CH₃CN

25,200 peak

cont.

<u>Formula</u>	<u>Solution</u>		<u>Solid</u>	
	$\lambda_{\text{max.}} (\text{cm}^{-1})$	$\epsilon_{\text{max.}}$	$\lambda_{\text{max.}}$	'D'
[PTNNiCl ₂]	insoluble		35,500	sh
			32,000	sh
			29,000	.865
			22,300	.36
			19,500	sh
			13,800	.372
			9,800	.32
[PTNNiBr ₂]	37,600	8,500		
	34,000	sh	32,300	sh
	ca. 29,000	sh	27,800	.965
	ca. 25,000	sh	21,700	.315
	ca. 20,300	sh	18,600	sh
	13,100	sh	13,300	.387
	11,700	85		
	8,800	64.5		
[PTNNiI ₂]	37,500	sh		
	34,000	sh		
	29,900	4,100	29,700	1.03
			28,100	sh
			27,200	sh
	24,300	3,050	23,300	1.025
	21,000	sh	21,100	sh
			14,200	sh
	11,200	152	12,900	.317
	ca. 8,000	sh		
[PTNNi(SCN) ₂]	not measured		35,000	sh
			28,000	sh
			20,200	.5
			16,600	sh
			13,500	sh
[PTNCoCl ₂]	ca. 34,000	sh	34,600	sh
	ca. 30,000	sh	30,000	sh
	17,200	202	17,000	.415
	15,400	226		
	14,600	268	14,600	sh(strong)
	10,000	26.6	12,100	.158
	7,400	46		
	6,200	sh		cont.

<u>Formula</u>	<u>Solution</u>		<u>Solid</u>	
	$\lambda_{\text{max.}} (\text{cm.}^{-1})$	$\epsilon_{\text{max.}}$	$\lambda_{\text{max.}}$	'D'
[PTNCoBr ₂]	34,000	sh		
	32,400	sh	33,400	sh
	26,600	sh	29,600	sh
	16,400	230	16,700	.45
	15,000	sh		
	14,600	286	14,200	.28
	9,800	30	12,000	.176
	7,200	56		
	6,000	sh		
[PTNCuCl]	37,400	3,640		
	ca. 34,000	sh	30,200	sh
	ca. 31,000	sh		
	ca. 29,000	sh	29,200	sh
[PTNCuBr]	36,800	sh		
	32,100	sh	ca. 32,000	sh
	30,100	sh	ca. 30,000	sh
[PTNCuI]	37,400	sh		
	33,000	sh	ca. 30,000	sh
	27,000	sh	ca. 26,000	sh

* solution in dichloromethane

** solid reflectance spectra, solid
diluted with KCl to 10% solution.

‡ solution in chloroform

TABLE 4.4

Solution and Solid Spectra of PDN Complexes

<u>Formula</u>	<u>Solution</u>		<u>Solid</u>	
	<u>$\lambda_{\text{max.}} (\text{cm}^{-1})$</u>	<u>$\epsilon_{\text{max.}}$</u>	<u>$\lambda_{\text{max.}}$</u>	<u>'D'</u>
E { [PDNPtCl ₂]	37,500	sh		
	36,600	sh	36,600	sh
	33,500	sh	34,500	sh
	29,000	sh	29,000	sh
[PDNPtBr ₂]	36,800	sh		
	33,000	sh	32,200	sh
	28,100	sh	27,900	sh
[PDNPtI ₂]	38,800	sh		
	31,000	sh	30,300	sh
	26,800	2,122	26,700	.805
B { [PDNPdCl ₂]	37,200	13,200		
	ca. 34,000	sh		
	27,400	1,930	27,400	.955
[PDNPdBr ₂]	35,200	13,000 [†]	35,000	
	29,600	sh		
	26,000	2,460	26,000	.69
[PDNPdI ₂]	38,700	sh		
	36,200	sh		
	31,400	13,100	31,600	1.18
	25,900	sh	26,200	sh
	21,800	3,260	22,000	1.0

† solution in chloroform

cont.

<u>Formula</u>	<u>Solution</u>		<u>Solid</u>	
	$\lambda_{\text{max.}} (\text{cm}^{-1})$	$\epsilon_{\text{max.}}$	$\lambda_{\text{max.}}$	'D'
[PDNNiCl ₂]	36,000	9,350		
	ca. 34,200	sh		
	ca. 30,000	sh	30,000	sh
			22,200	.426
	19,600	140	19,500	sh
	ca. 12,400	sh	13,300	.46
	11,600	52		
	8,800	57		
[PDNNiBr ₂]	ca. 36,700	sh		
	ca. 35,000	sh		
	ca. 32,000	sh	31,800	sh
	ca. 28,000	sh	27,800	sh
			21,300	.391
	19,600	201	19,000	sh
	11,400	83	12,900	.383
	8,800	63		
[PDNNiI ₂]	ca. 37,600	sh		
	ca. 34,400	sh		
	29,800	3,800	30,000	sh
	ca. 24,500	sh		
	ca. 21,000	sh	21,700	.765
			19,100	sh
			14,000	sh
	10,800	165	12,000	.333
[PDNCoCl ₂]	ca. 37,500	sh		
	ca. 35,600	sh		
	ca. 30,000	sh	30,800	sh
			27,300	sh
	17,400	242	17,300	.36
	15,400	225	15,800	.39
	14,500	314		
	9,600	20	11,500	.205
	7,600	55		
	6,000	sh		

cont.

<u>Formula</u>	<u>Solution</u>		<u>Solid</u>	
	<u>$\lambda_{\text{max.}}$ (cm.⁻¹)</u>	<u>$\epsilon_{\text{max.}}$</u>	<u>$\lambda_{\text{max.}}$</u>	<u>'ρ'</u>
[PDNCoBr ₂]	ca. 37,600	sh		
	ca. 33,700	sh		
	ca. 29,600	sh	30,300	sh
	27,000	sh	25,800	sh
	16,600	295	16,400	.68
	15,000	sh	15,000	sh
	14,300	430	14,300	.76
	10,000	29.5	10,700	.31
	7,200	69.5		
	6,200	sh		
[PDNCuCl]	ca. 37,600	sh		
	ca. 33,600	sh	31,200	1.06
	ca. 28,400	sh		
[PDNCuBr]	ca. 38,000	sh		
	ca. 33,600	sh	30,800	.935
	ca. 28,200	sh		
[PDNCuI]	ca. 38,000	sh		
	ca. 33,600	sh	33,000	sh
	ca. 28,000	sh	ca. 30,000	sh

TABLE 4.5

Solution and Solid Spectra of PN Complexes

<u>Formula</u>	<u>Solution</u>		<u>Solid</u>	
	<u>$\lambda_{\text{max.}} (\text{cm}^{-1})$</u>	<u>$\epsilon_{\text{max.}}$</u>	<u>$\lambda_{\text{max.}}$</u>	<u>'D'</u>
[PNPtCl ₂]	37,400	5,400		
	36,700	sh	33,200	sh
	30,800	sh	30,100	.455
[PNPtBr ₂]	37,000	sh		
	36,200	sh		
	32,000	sh	31,900	sh
	ca. 28,600	sh	29,000	sh
	ca. 25,000	sh	25,800	sh
[PNPtI ₂]	37,600	17,800		
	32,300	sh	ca. 32,500	sh
	26,400	2,020	26,500	.97
	ca. 22,600	sh	ca. 23,000	sh
[PNPdCl ₂]	36,200	7,350	ca. 36,000	.9
	28,300	1,220	27,800	.785
[PNPdBr ₂]	34,400	13,900		
	28,200	2,900	28,500 26,000	sh .597
[PNPdI ₂]	31,200	14,100	30,800	1.08
	26,000	2,320	26,000	.905
	21,700	3,090	21,500	.965

Spectrum in CH₃CN

26,000 sh
22,100 peak

cont.

<u>Formula</u>	<u>Solution</u>		<u>Solid</u>	
	$\lambda_{\text{max.}} (\text{cm}^{-1})$	$\epsilon_{\text{max.}}$	$\lambda_{\text{max.}}$	'D'
[PNNiCl ₂]	37,600	8,600		
	36,600	sh	33,000	sh
	30,400	2,450	29,400	sh
	28,000	sh	26,700	.91
			21,400	.48
	19,800	184	18,700	sh
	11,000	80	14,600	sh
	9,200	sh	13,000	.42
[PNNiBr ₂]	37,600	6,600		
	36,900	sh		
	35,400	sh	31,300	.99
	31,800	sh	29,300	sh
	27,200	2,700	26,200	sh
	19,300	205	19,400	.51
			16,100	sh
	15,100	sh	14,800	sh
	10,600	126	11,000	.49
[PNNiI ₂]	38,000	sh		
	36,800	sh		
	33,700	sh		
	29,400	3,670	29,500	sh
	23,900	2,860	23,300	.85
	20,500	2,130	20,500	.79
			16,100	sh
	14,000	sh	13,900	sh
	10,500	224	10,500	.475
[PNCocl ₂]	37,400	sh		
	36,500	sh		
	3,100	sh	29,500	sh
	17,600	345	17,500	.52
	15,700	290	15,700	.51
	14,600	475	14,400	.575
	9,500	sh	11,100	.217
	7,800	62		
	6,800	sh		

cont.

<u>Formula</u>	<u>Solution</u>		<u>Solid</u>	
	<u>$\lambda_{\max.}(\text{cm}^{-1})$</u>	<u>$\epsilon_{\max.}$</u>	<u>$\lambda_{\max.}$</u>	<u>'D'</u>
[PNCuBr ₂]	38,100	sh		
	34,000	sh	31,000	sh
			26,400	sh
	22,000	sh	20,000	sh
	16,600	390	16,700	.64
	15,100	sh	15,400	.65
	14,200	620	14,200	.71
	10,400	25.6	11,000	.285
	7,400	76		
	6,000	sh		
[PNCuCl]	37,000	sh		
	33,500	sh	30,800	.482
			28,000	sh
[PN ₂ CuBr]	37,600	sh	31,300	.69
[PN ₂ CuI]	38,200	sh	31,800	.795

ULTRA VIOLET SOLUTION SPECTRA

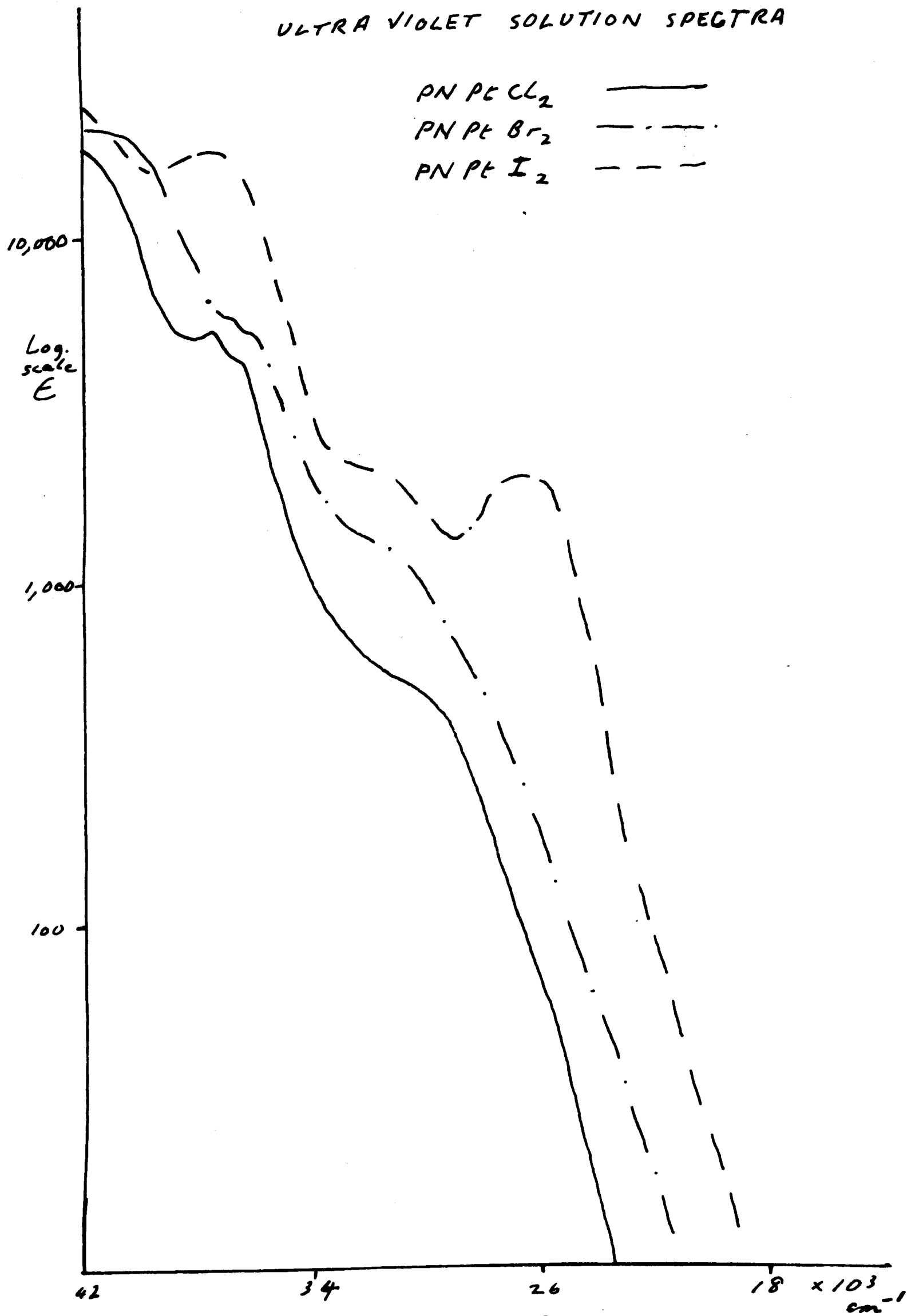


FIGURE 4.2

ULTRA VIOLET SOLUTION SPECTRA.

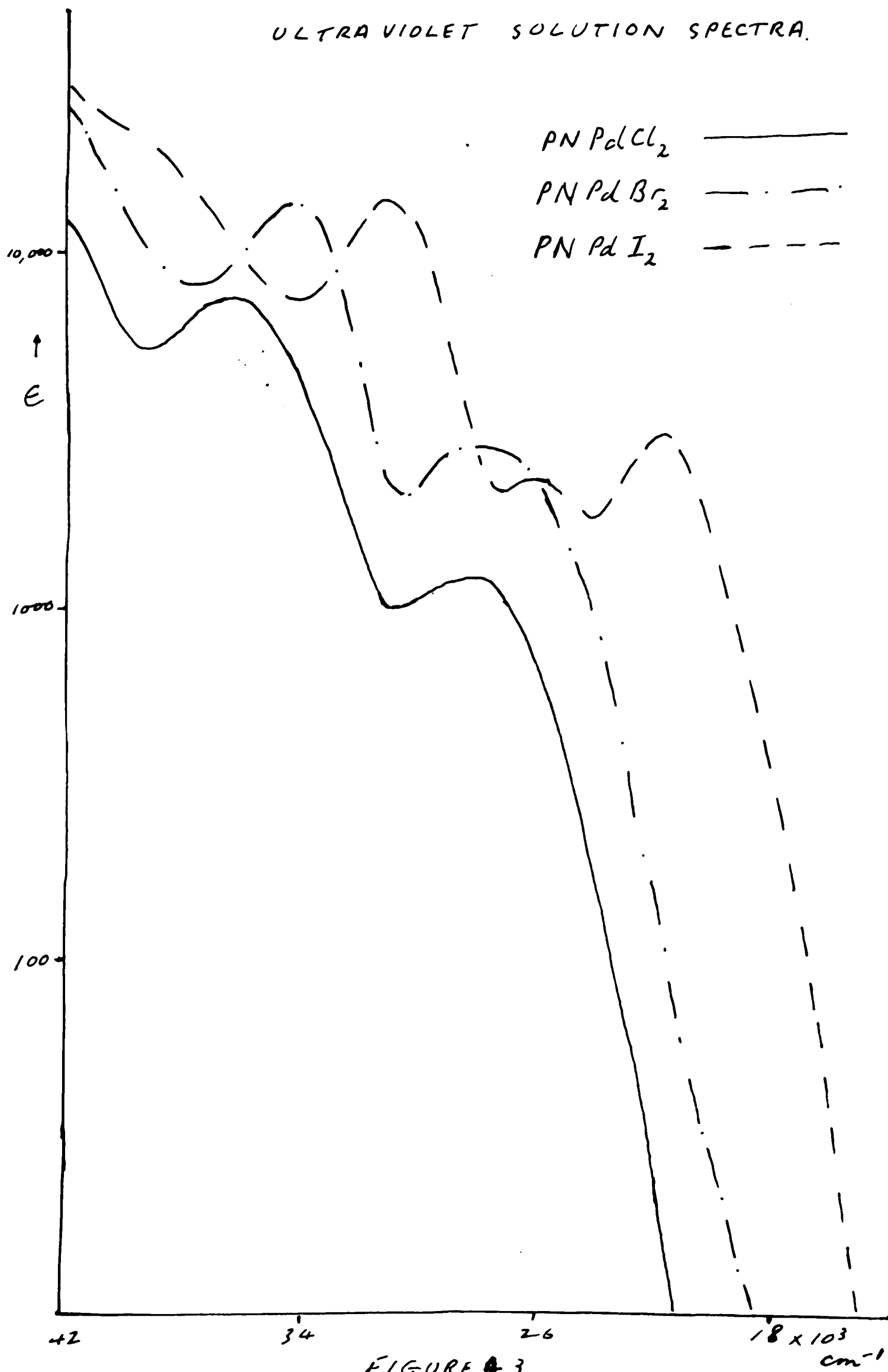


FIGURE 4.3

The solid reflectance spectra and reproduced in figures 4.4-6. All these spectra were measured on the 'diluted' solid. The solid was ground with potassium chloride to give an intimate mixture containing approximately 10% of the complex. The resolution of the spectra was then much greater with lower values of the optical density, though, of course, the relative values of 'D' are meaningless under these conditions. Slight and apparently random variations in the solid spectra can be attributed to differences in the crystal packing in the various compounds. These apart, the solid spectra are fully analogous to the solution spectra. All show regular shifts of the ligand field bands to lower energies from chloride to iodide complexes as would be expected from the usual spectrochemical series.

Figure 4.7 gives a comparison of the spectrum of PBN iodide complexes of Pt, Pd and Ni. Clearly in this series the platinum and palladium spectra have the same features, although shifted in energy. However, the nickel complexes are paramagnetic with a triplet ground state and so will not have the same ligand field bands. Such a change of magnetic behaviour is expected for the average ligand field of nitrogen, phosphine and two halide ions.

The square planar palladium and platinum compounds have the singlet ground state configuration

$^1A_{1g}, (e_g)^4 (a_{1g})^2 (b_{2g})^2$. In a d^8 complex, therefore, all the

SOLID REFLECTANCE SPECTRA

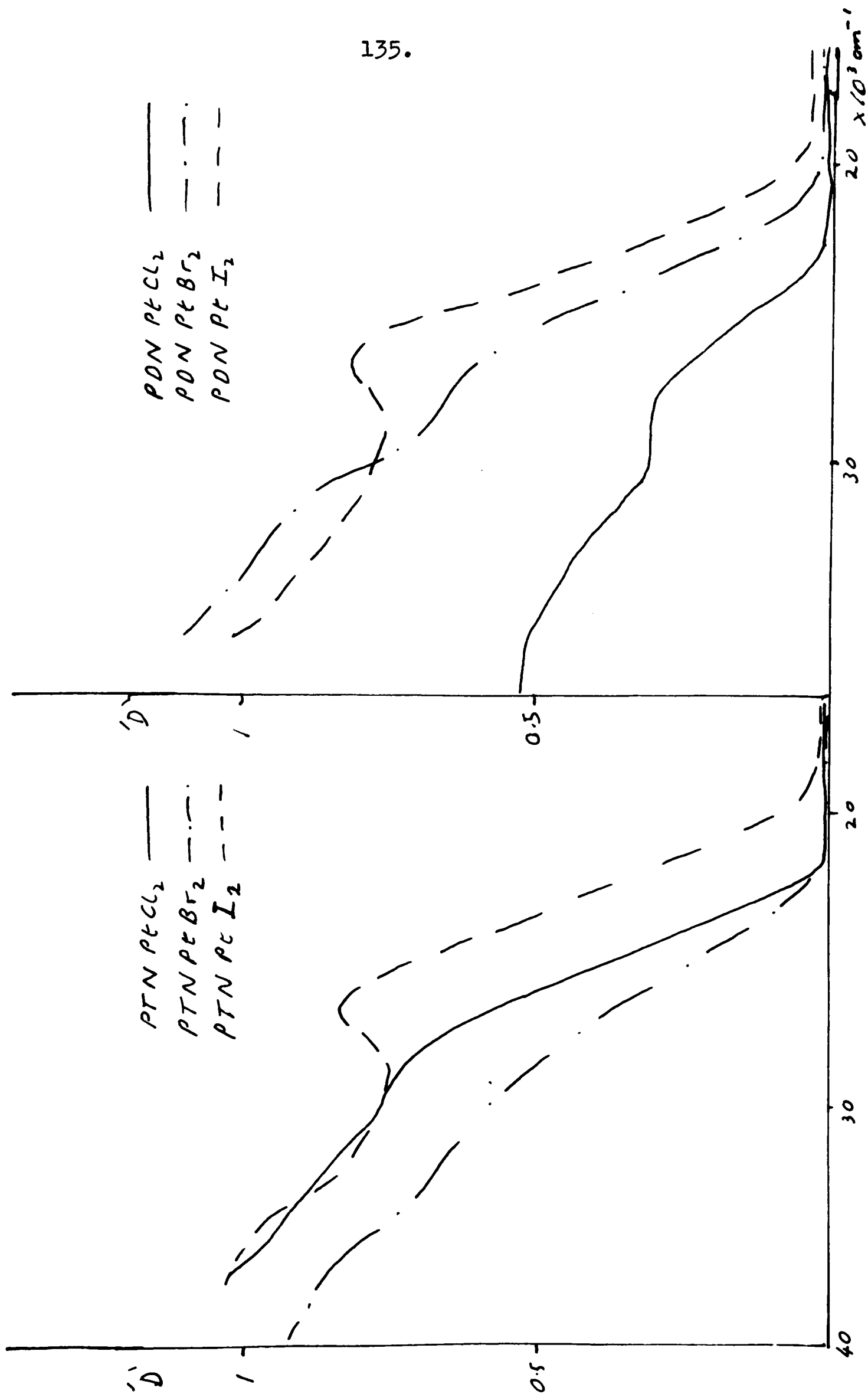


FIGURE 4-4

SOLID REFLECTANCE SPECTRA

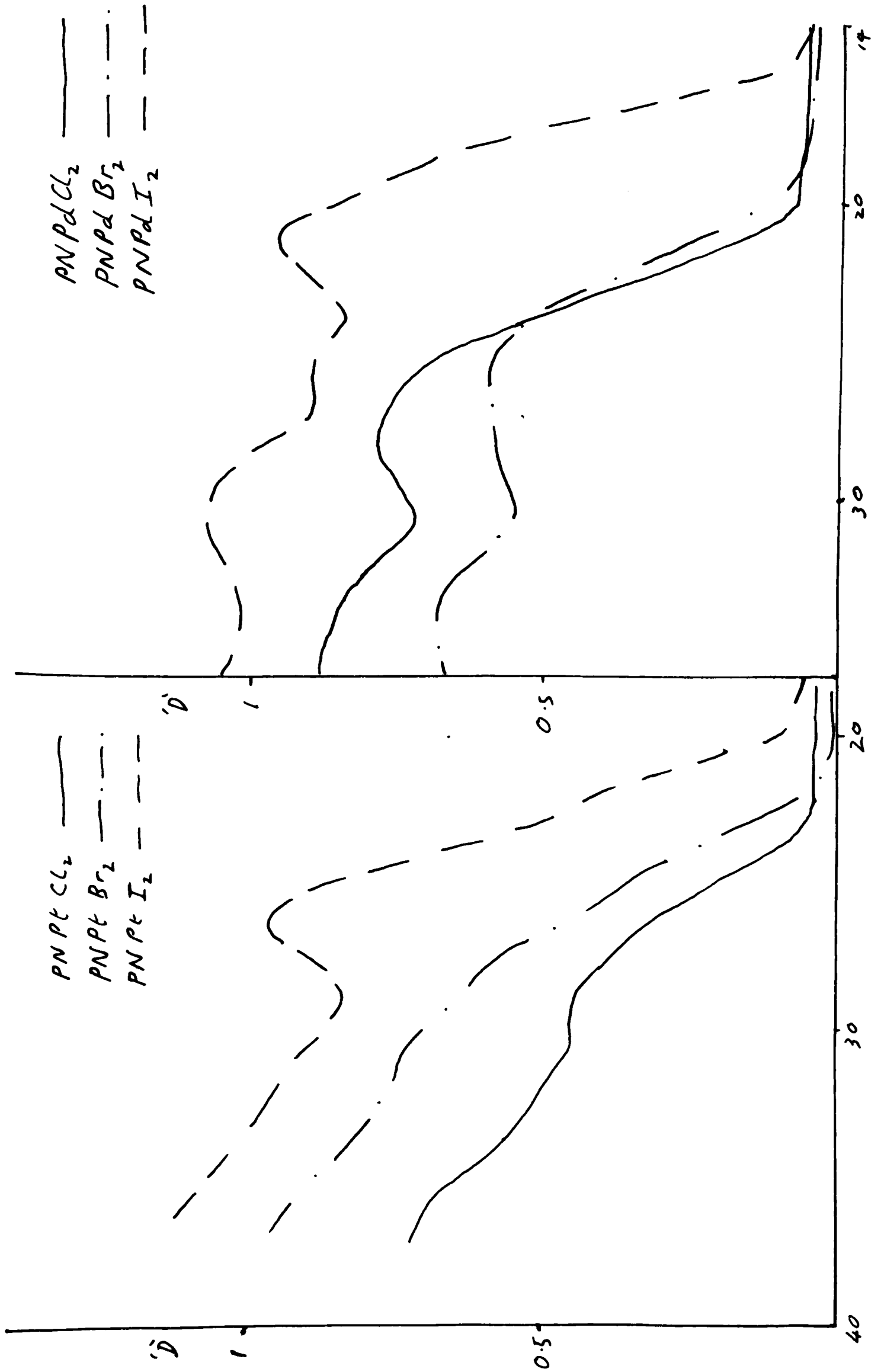


FIGURE 4.5

SOLID REFLECTANCE SPECTRA.

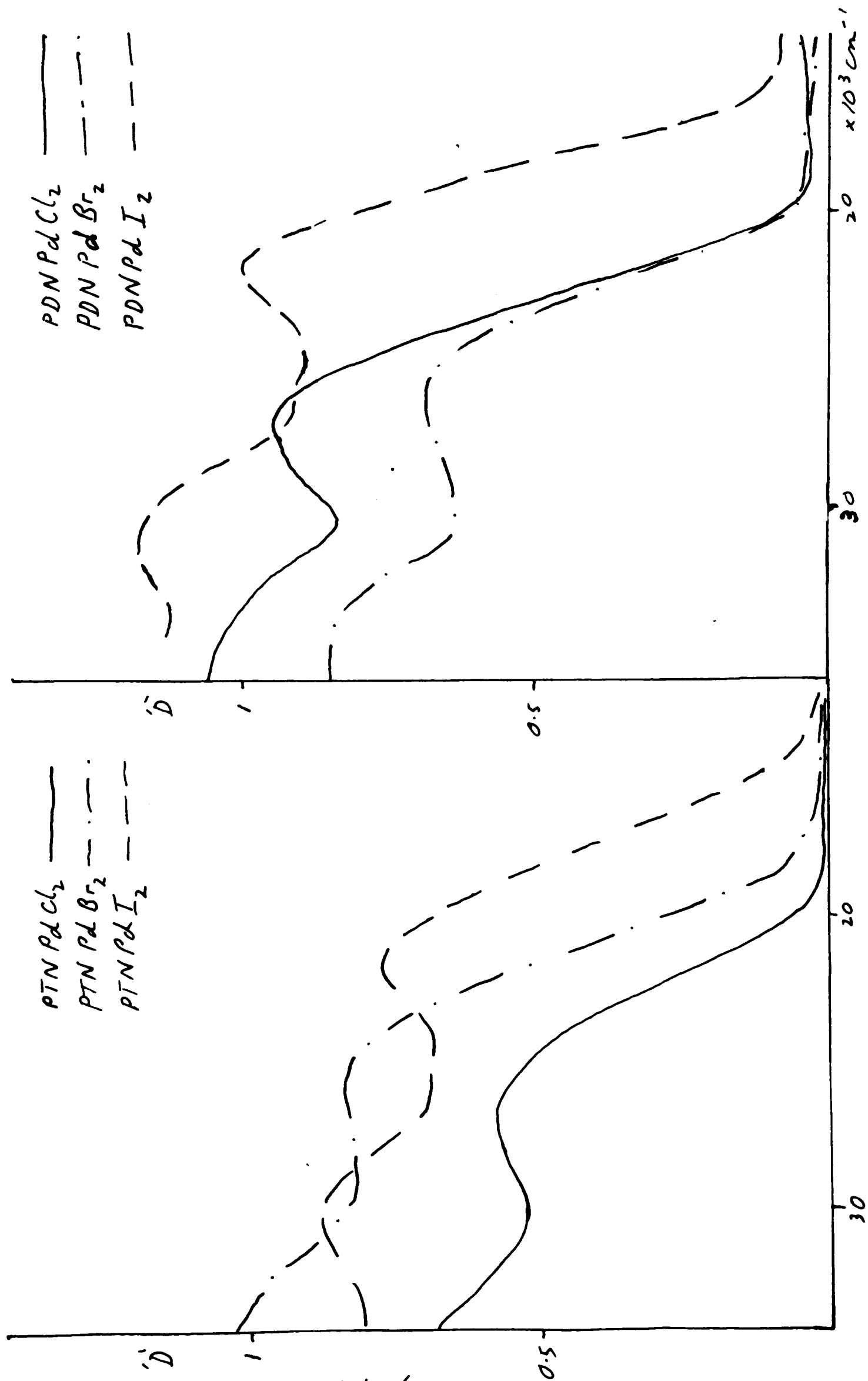


FIGURE 4 6

U/V SOLUTION SPECTRA

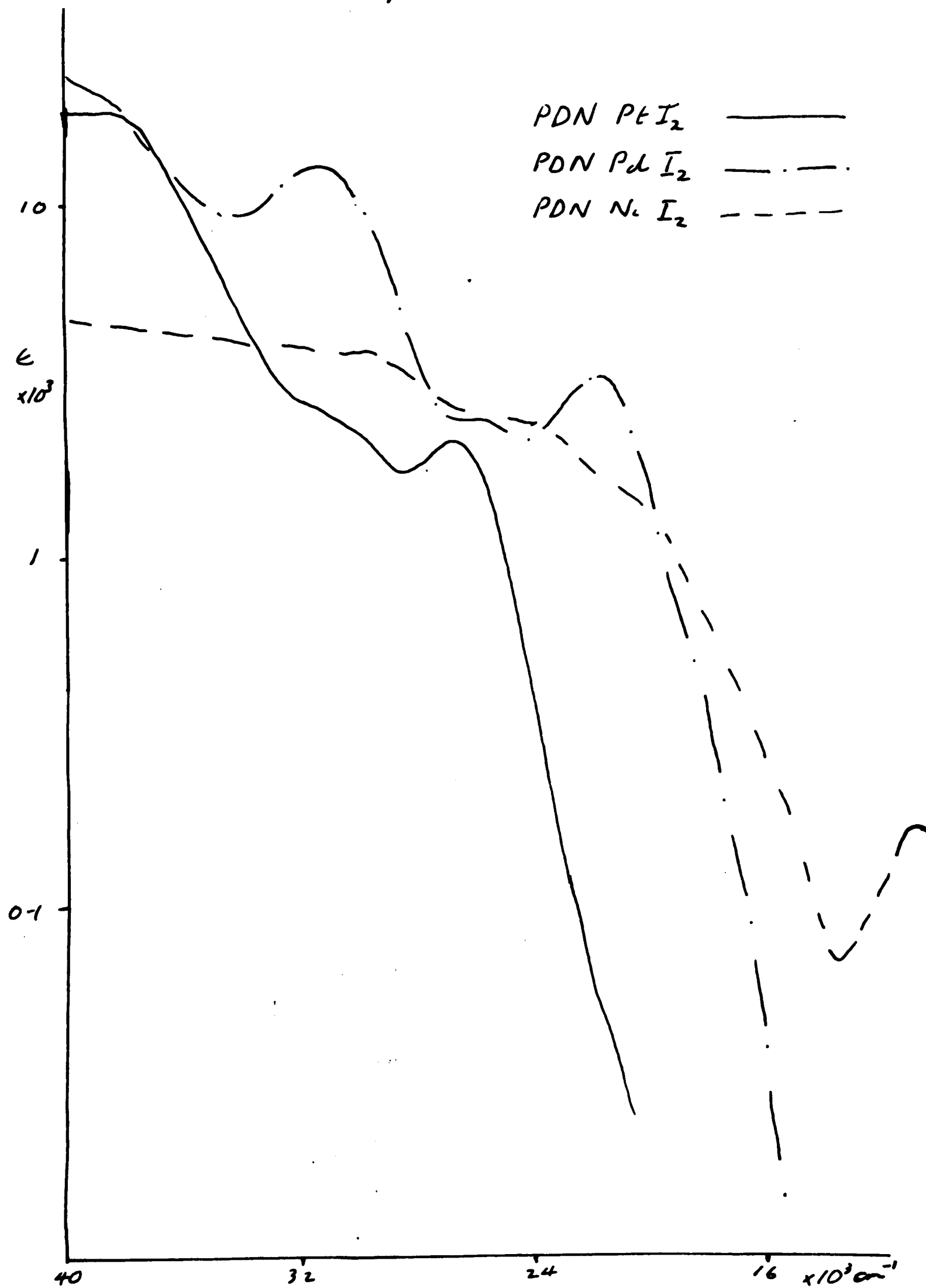


FIGURE 4.7

subshells are full and the transitions may be discussed in terms of the one electron moving from each of the orbitals b_{2g} ; a_{1g} ; e_g to the empty b_{1g} orbital. Both singlet-singlet and singlet-triplet transitions can arise, but the 'forbidden' character of all transitions is weakened in the case here considered. The interpretation of the spectrum is made difficult as in the second and third transition series spin-orbit coupling destroys the usefulness of the spin quantum number (81) and so the extinction coefficient for singlet-triplet approaches that of the singlet-singlet type. Furthermore, the non-symmetric nature of the complexes will lend intensity to the transitions. Thus we should expect three formally 'forbidden' bands in the spectra to occur with moderate intensity.

Three bands are observed in the palladium iodide complexes at $31,200\text{cm.}^{-1}$, $26,000\text{cm.}^{-1}$ and $21,700\text{cm.}^{-1}$, and also a shoulder at ca. $36,000\text{cm.}^{-1}$. However, although the low energy band is almost certainly a d-d band, the iodide complex will have a Pd-I low energy charge transfer band, possibly that at $31,200\text{cm.}^{-1}$ since the extinction coefficient of this band is high ($14,400$). The ratio of ^{the frequencies} ~~intensities~~ of the first band in the platinum and palladium iodide complexes is $26.4:21.7 = 1.22:1$. This agrees well with the general order of increase in ligand field splitting from second to

third transition series of 1.21:1 (81). Chatt, Gamlen and Orgel (82) assigned the spectra of a series of compounds $[\text{Pt}(\text{NH}_3)_n\text{Cl}_{4-n}]^{+(n-2)}$ and related compounds. Of particular interest was the compound $\text{cis}-[(\text{C}_5\text{H}_{11}\text{NH}_2)_2\text{PtCl}_2]$ which is analogous to the present compounds, although singlet-triplet transitions will be more intense in the less symmetric molecule. Their values and assignments are listed in Table 4.6.

TABLE 4.6

	$\lambda_{\text{max.}}$ (cm. ⁻¹)	$\epsilon_{\text{max.}}$	assignment
$[(\text{C}_5\text{H}_{11}\text{NH}_2)_2\text{PtCl}_2]$	24,000	3.2	triplet $d_{xy} \longrightarrow d_{x^2-y^2}$
	27,300	23	triplet $d_{xz,yz} \longrightarrow d_{x^2-y^2}$
	33,100	128	singlet $d_{xy} \longrightarrow d_{x^2-y^2}$
	37,200	68.5	singlet $d_{xz,yz} \longrightarrow d_{x^2-y^2}$

This assignment is supported by the observation of a red shift in polar solvents of the 27,300cm.⁻¹ and 37,200cm.⁻¹ bands. Interaction of the solvent on the z-axis would perturb the d_{xz} , d_{yz} energy levels but would not influence the d_{xy} level and no such shift occurs with the 33,100cm.⁻¹ band.

In the P/N complexes the absorptions due to the benzene rings and charge transfer bands overlay the ligand field bands and so only the lowest energy feature can be clearly distinguished in the platinum iodide complexes.

Final proof of the stereochemistry of the complex ion in the Pt and Pd complexes of the three ligands came from a study of the nuclear magnetic resonance (NMR) spectra of these complexes. The features of the spectra are recorded in Table 4.7. Some of the spectra are recorded in figures 4.8-12. Integrated intensities confirmed the assignment of features.

The NMR spectra are due to Dr. H. Frits of Munich University.

1. PLATINUM COMPLEXES

The NMR spectra of the platinum complexes show unambiguously that in no case is more than one of the nitrogen atoms from each ligand coordinated to the metal. The results are listed in Table 4.7. Whilst in the free ligand the proton resonance signal from the methyl group attached to the nitrogen atoms shows a chemical shift of 154-161cps. with the respect to the tetramethyl silane standard (fig. 4.8), in $[\text{PNPtBr}_2]$ and $[\text{PNPtI}_2]$ the shift

TABLE 4.7

NMR. Spectra of Pd II and Pt II Complexes

Chemical Shifts in cps. at 305°K

<u>Compound</u>	<u>H_{Ar}[*]</u>	<u>H_{coord.}</u>	<u>H_{uncoord.}</u>	<u>J(¹⁹⁵Pt- N-C-N)</u>	<u>Solvent</u>	<u>Concen- tration</u>
PN	435		154		CH ₂ Cl ₂	5%
PDN	422		159		"	15%
PTN	422		160.5		"	sat.

[PdBr ₂ (PN)]						
PNPdBr ₂	459	217			"	sat.
PNPdI ₂	455	218.5			"	10%
PDNPDBr ₂	446	179	179		"	sat.
PDNPDi ₂	444	178	178		"	10%
PTNPDBr ₂	447	167	167		"	10%
PTNPDi ₂	443	168	168		"	sat.
PNPtBr ₂	453	227.5		33.5	"	sat.
PNPtI ₂	460	229.5		34	"	sat.
PDNPTBr ₂	448	230 / 214.5	145.5	32 34	"	sat.
PDNPTi ₂	448	234.5 / 219	143	34 35	"	sat.
PTNPTi ₂	444	226	141	36	"	5%

Chemical Shifts in cps. @ 220°K from tetramethyl silane @ 60^M/cs.

PDNPDBr ₂	446	219.5/204.5	146		CDCl ₃	sat.
PDNPDi ₂	444	220.5/207.5	142		"	sat.

* The results in cps. refer to the centre of the signal group.

H_{Ar} - Aromatic proton signalH_{coord.} - Protons of the coordinated (CH₃)₂ N - groupsH_{uncoord.} - Protons of the free (CH₃)₂ N - groups

143.

NMR SPECTRA

PTN in CDCl_3 intensity
 $\times 2\frac{1}{2}$ PDN in CDCl_3 PN in CDCl_3 I
N
T
E
N
S
I
T
Y

460

440

420

180

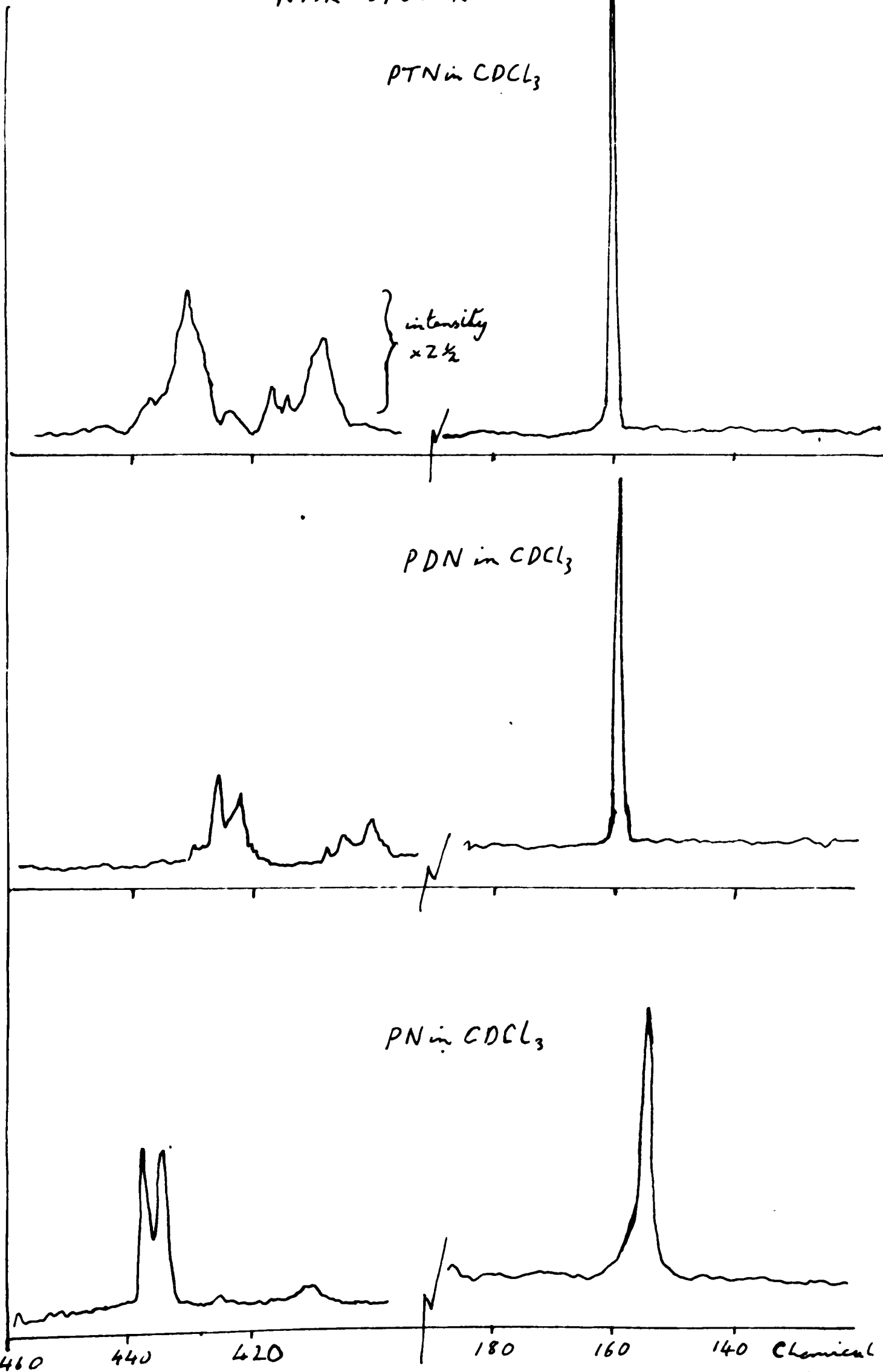
160

140

Chemical

shift cps.

FIGURE 4.8



NMR SPECTRA.

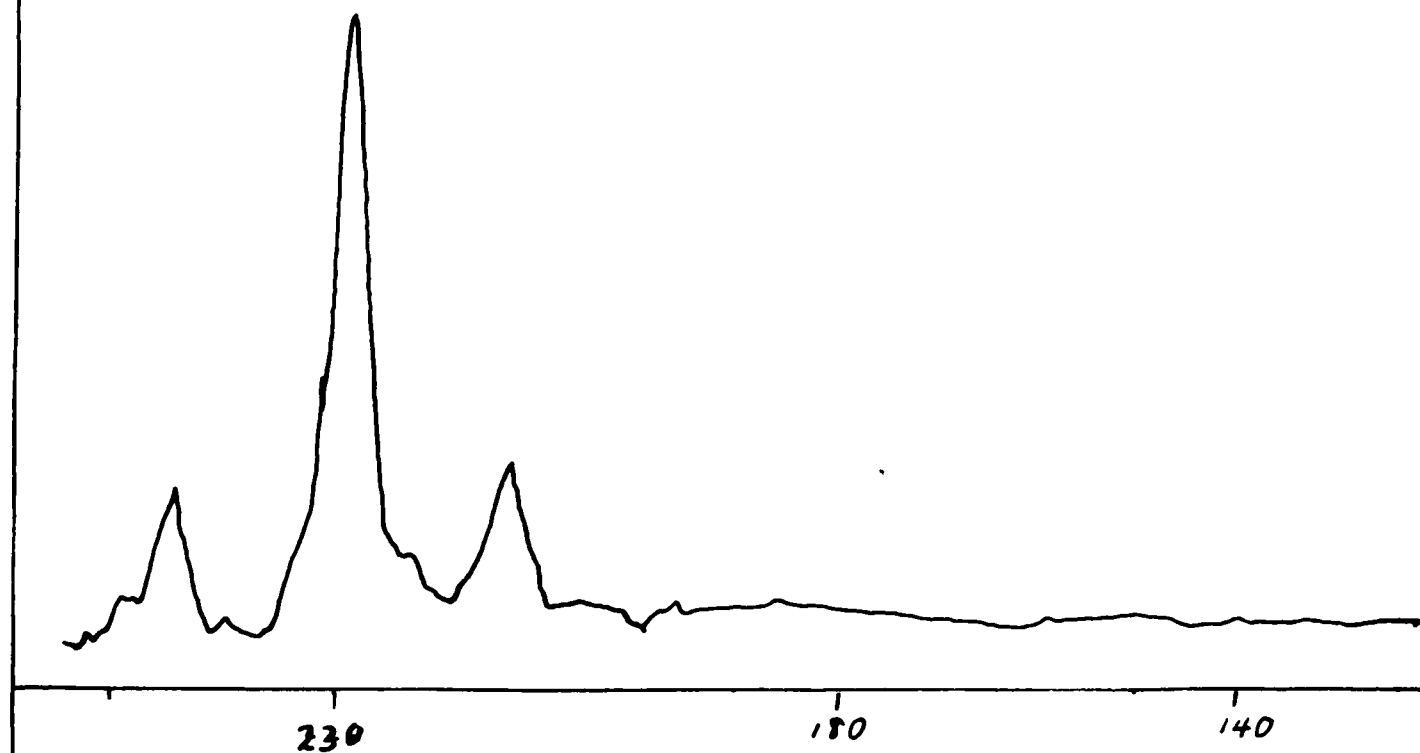
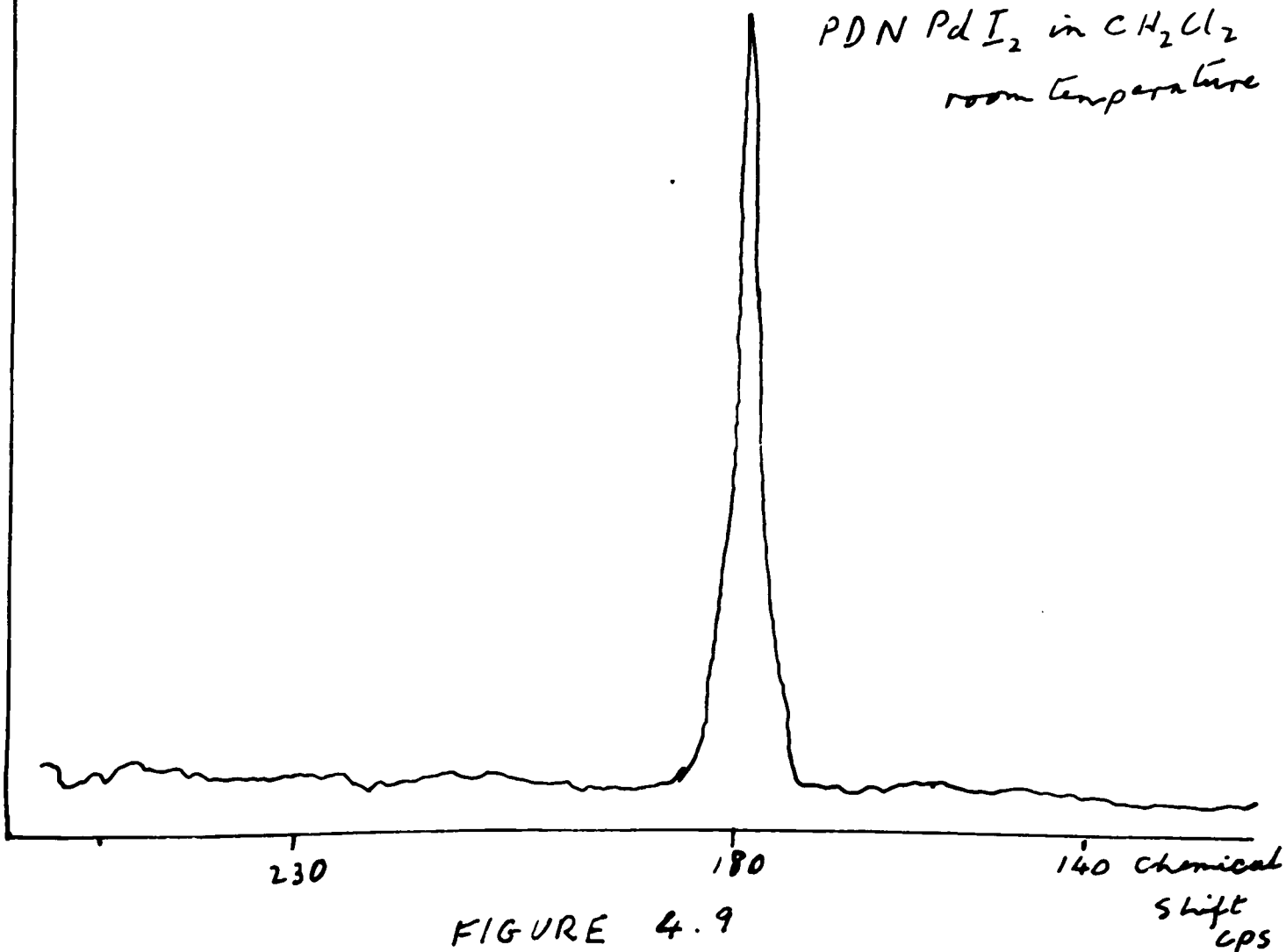
PN Pt I₂ in CDCl₃I
N
T
E
N
S
I
T
YPDN Pd I₂ in CH₂Cl₂
room temperature

FIGURE 4.9

NMR SPECTRA

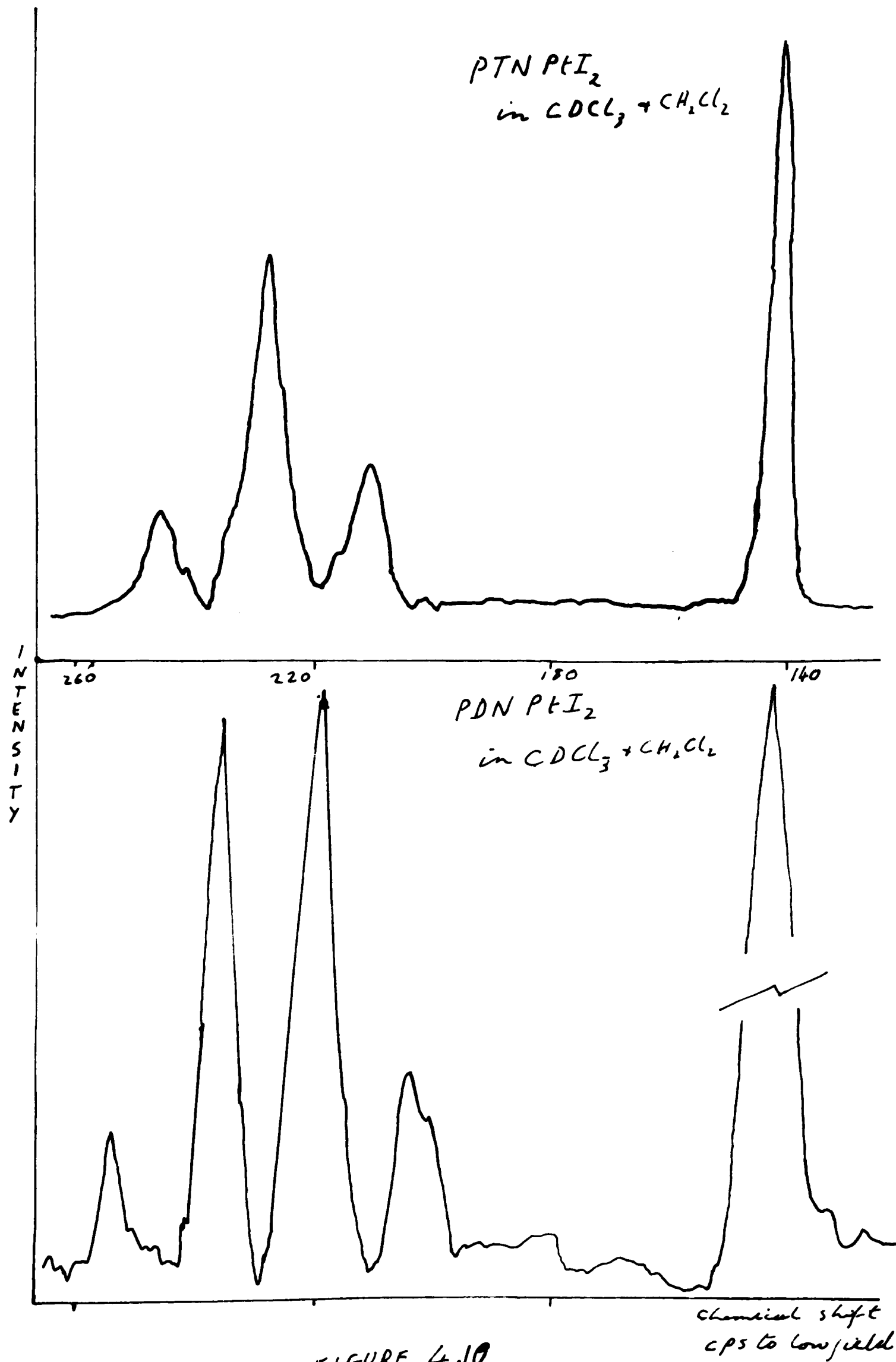


FIGURE 4.10

NMR SPECTRA

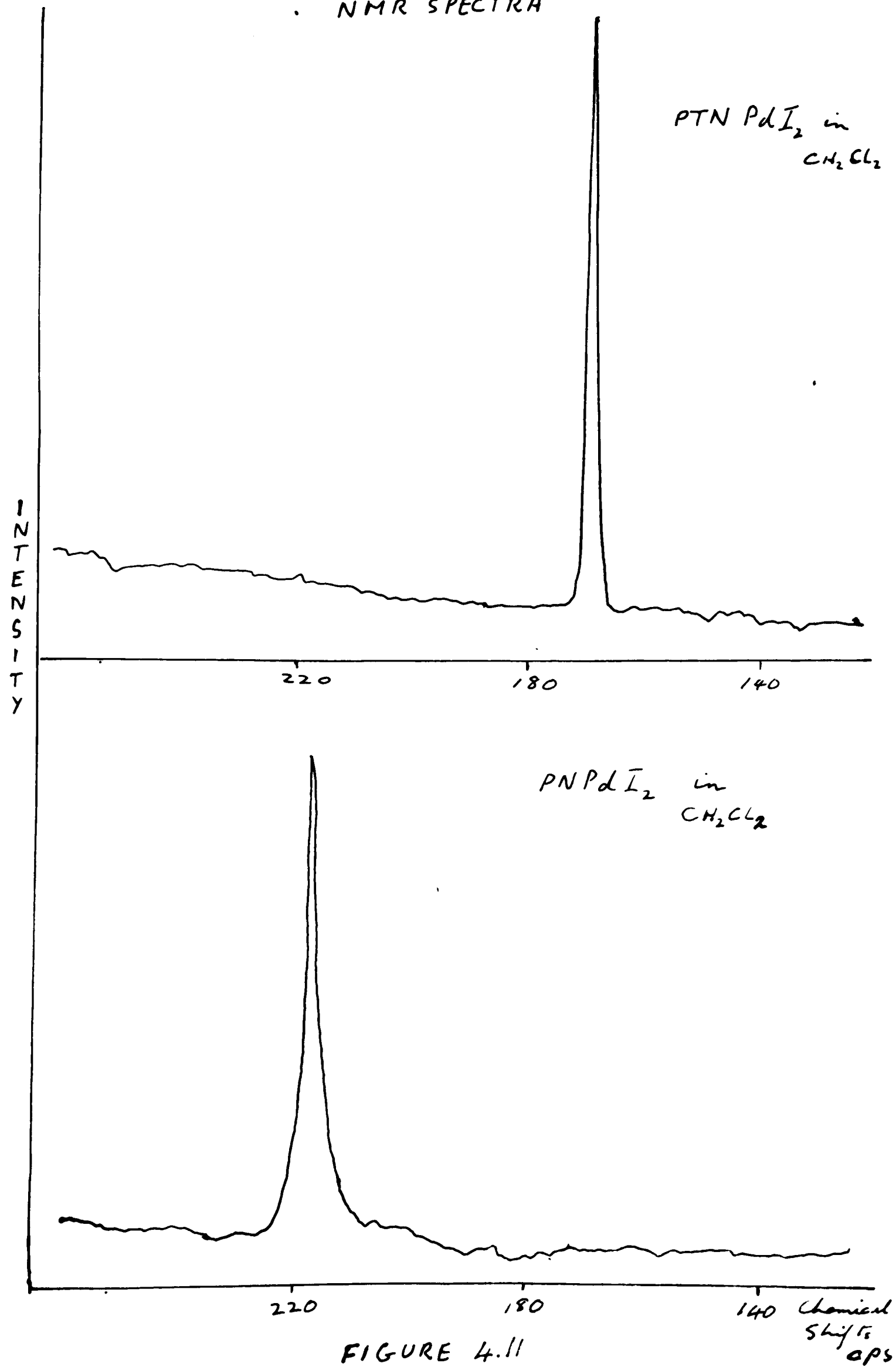


FIGURE 4.11

NMR SPECTRA

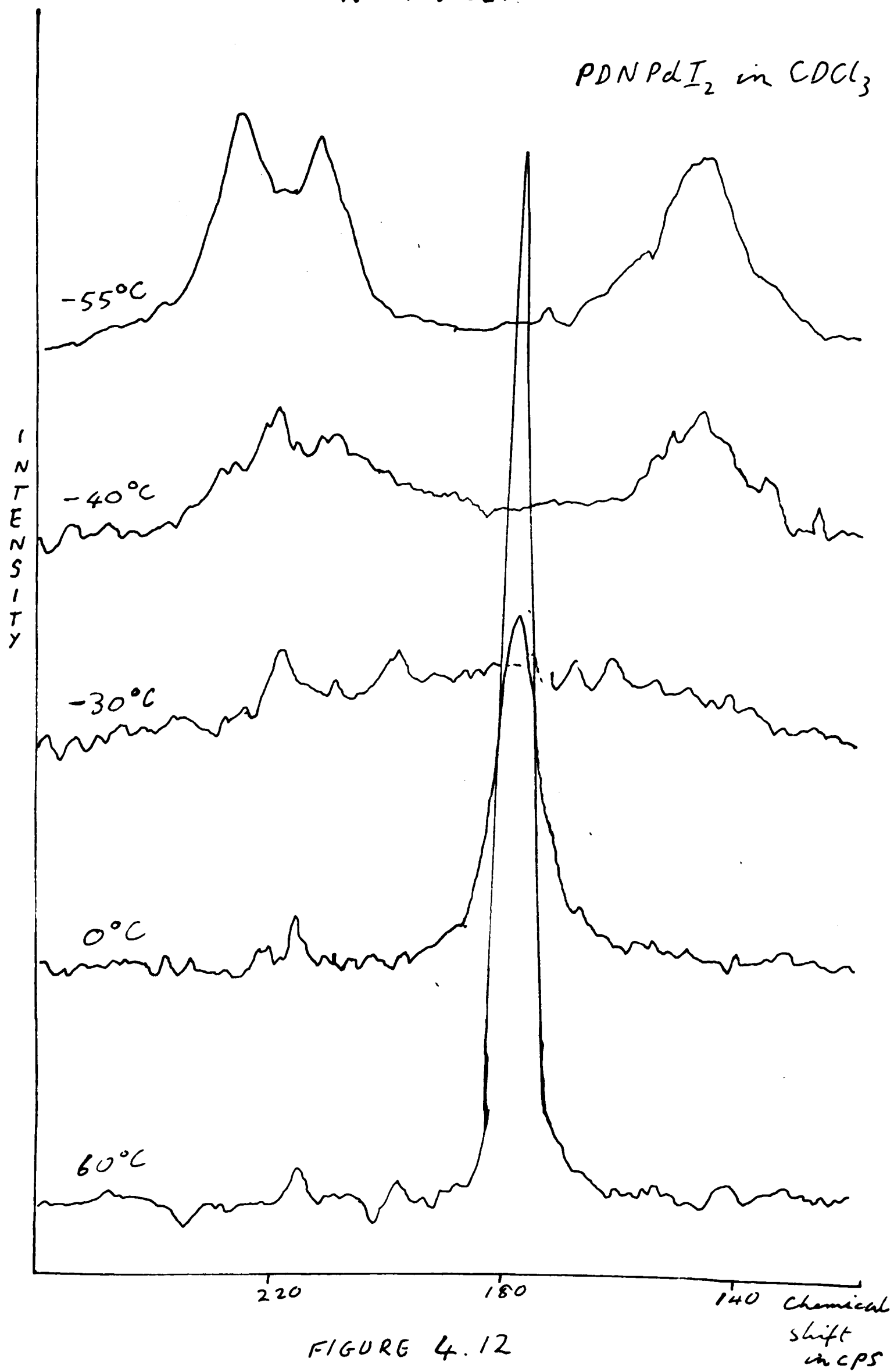
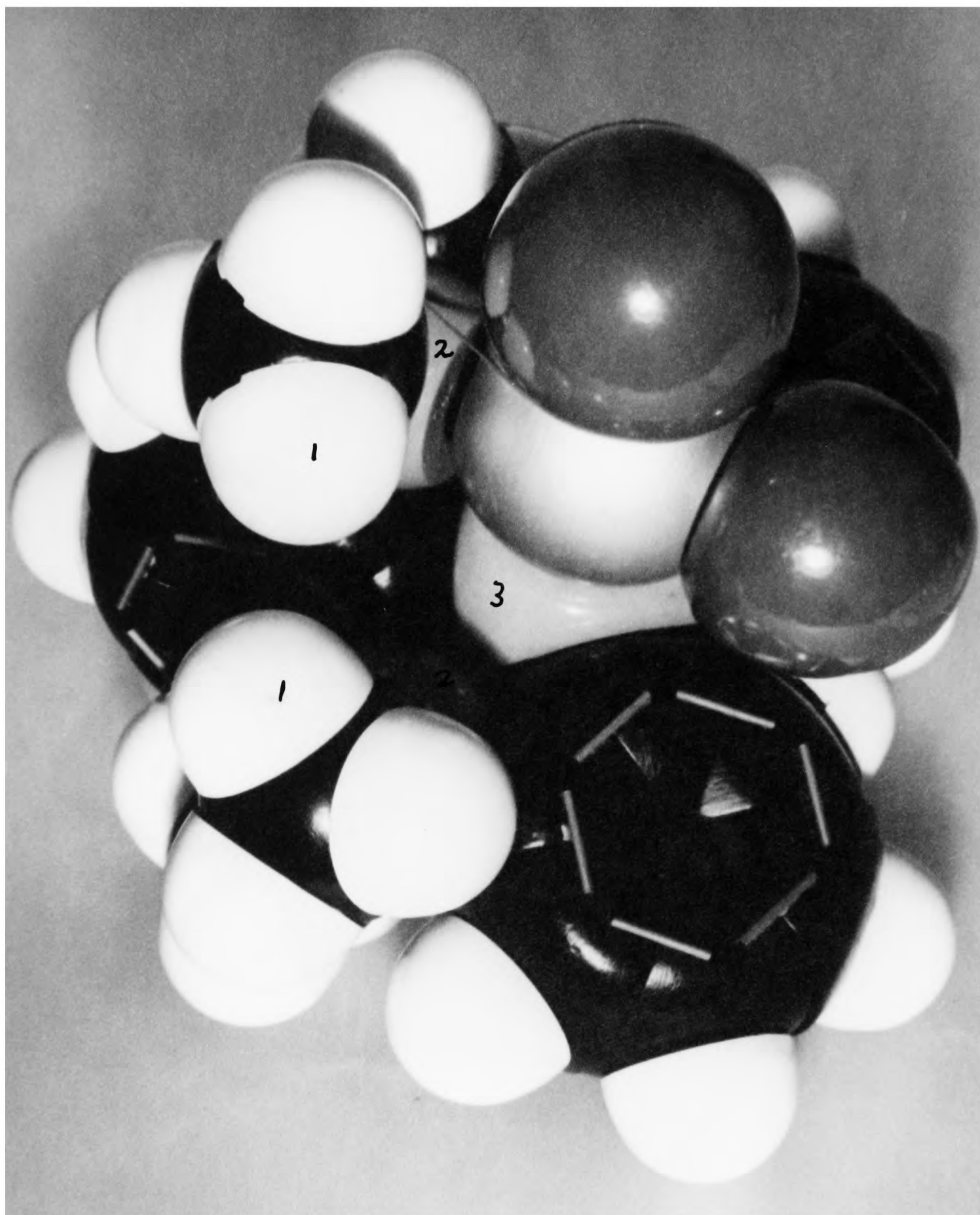
 PDNPdI_2 in CDCl_3 

FIGURE 4.12

was respectively 73.5 and 75.5 cps. further to lower fields (fig. 4.9). The coordinatively bound nitrogen is depleted of electrons and thus the shielding of the methyl protons is reduced. A similar but smaller lowering is observed for the protons of the aromatic rings attached to phosphorus in all the studied complexes. In the NMR. spectra of the PDN and PTN platinum complexes, the signal of the methyl protons attached to the unbound nitrogen atoms is shifted 14 to 19cps. to higher field than in the free ligand. The signal of those attached to the bound nitrogen atom are shifted 55 to 75 cps. to lower field (fig. 4.10).

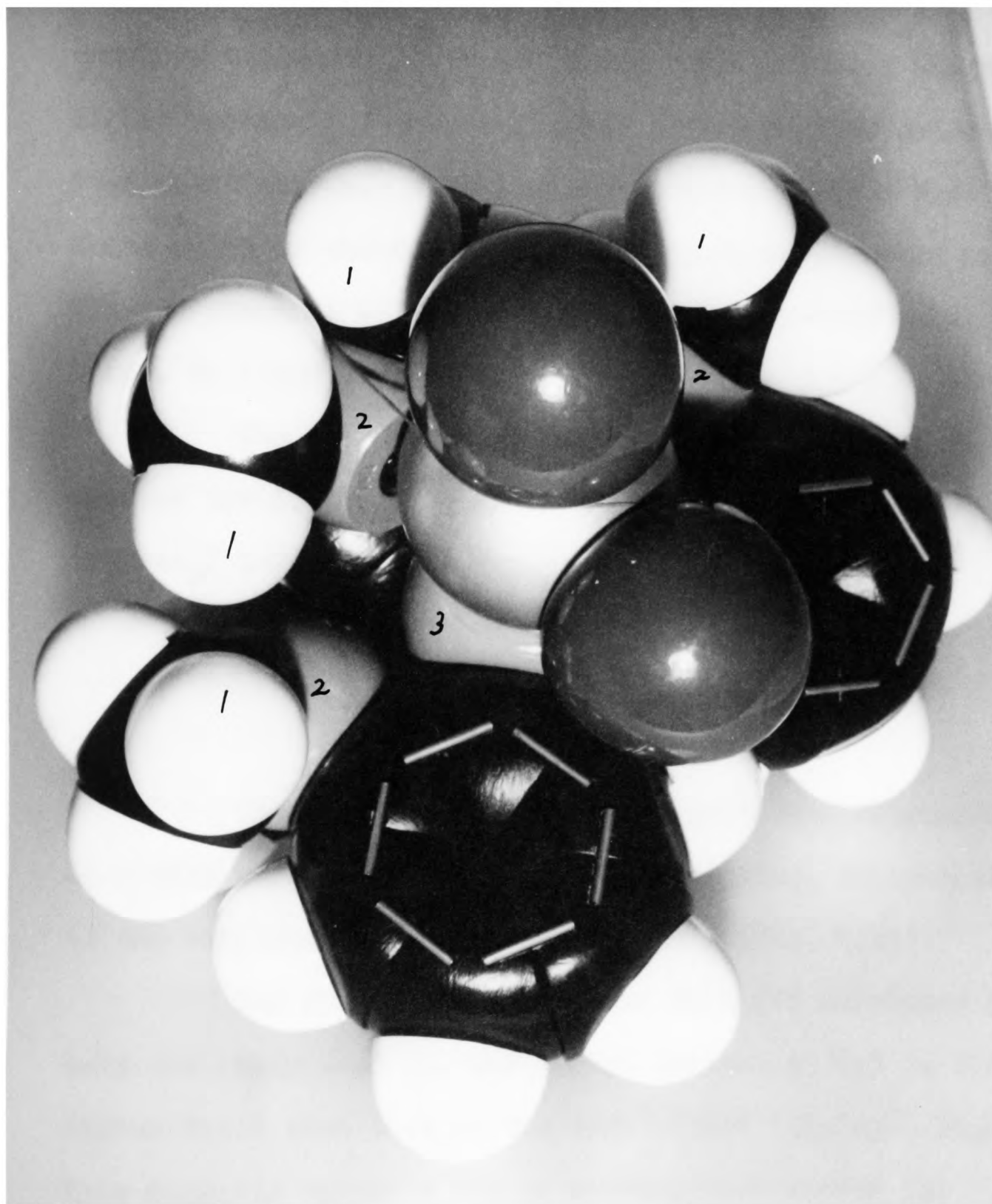
In the PDN complexes, due to the complete asymmetry of the molecule, the shielding of the two methyl groups attached to the coordinated nitrogen is different. In the NMR. spectra a different chemical shift results for the protons of the methyl group influenced by the unbound nitrogen. Similarly a different $^{195}\text{Pt-N-C-H}$ coupling constant is observed.

This may be explained as follows: the uncoordinated dimethylamino group in PDN influences the nearest methyl group on the bound nitrogen atoms so much that a distortion of the $\text{C}_{\text{ring}}-\text{N}-\text{C}_{\text{methyl}}$ angle results. Atomic models show this very clearly (fig's. 4.13,14). This splitting is not observed in the PTN complex since in this case both methyl



- 1 Interacting methyl groups
- 2 Nitrogen atoms
- 3 Phosphorus

Figure 4.13



- 1 Interacting methyl groups
- 2 Nitrogen atoms
- 3 Phosphorus atom

Figure 4.14

groups on the bound nitrogen atom are equally influenced by free -NH_2 groups.

Moreover, in the series PN- , PDN- , PTN-PtI_2 the coupling constants $^{195}\text{Pt-N-C-H}$ show an equivalent shift to higher values. These couplings provide further evidence for Pt-N coordination. The coupling gives rise to a pair of bands split by about 34cps, with respect to the main band. This corresponds well with Powell and Sheppard's value of 45cps. in $[\text{Pt}(\text{en})_2]^{+2}$ (61).

The approximate relative intensity ratios of methyl protons are in the case of $[\text{PDNPtX}_2]$ 1:1:2 and in the case of $[\text{PTNPtI}_2]$ 1:2.

2. PALLADIUM COMPLEXES

The NMR. spectra of the PN palladium dibromide and di-iodide were, except for the Pt-H coupling, fully analogous to the corresponding platinum compounds (fig. 4.11).

The PDN and PTN palladium dihalide complexes gave only one sharp band for the methyl protons at 6.5 to 20cps. higher field than that of the free ligand (fig's. 4.10,11). This suggests either a higher coordination number for palladium or a rapid exchange of the particular nitrogen atom bonded. The second alternative is confirmed when the

NMR. spectra were studied at lower temperatures. At -30°C the PBN palladium complexes showed a flat broad (ca. 100cps.) proton resonance signal for the methyl protons; at -53°C the spectra was fully analogous to that of the corresponding platinum complex with two signals for the 'complexed' methyl protons (fig. 4.12). The PTN palladium complexes gave only a broadening of the signal which was sharp at room temperature to (ca. 100cps.). The apparatus was not suitable for the study of the spectra at yet lower temperatures.

Phosphorus - proton spin splitting was never clearly discernable.

The wide range of physical measurements carried out on the Pt and Pd complexes of PTN, PBN and PN confirm that, in all of these complexes, the metal is coordinated to one phosphorus, one nitrogen and two halide donor groups. The σ -donor power of the remaining dimethylamino groups) in PTN and PBN is reduced to such an extent by coordination of two groups in the molecule that the methyl iodide quaternisation reaction does not occur. Clearly such deactivation explains the negligible coordinating power of such groups.

Thus the system with PTN, formally the equivalent of QAS and QP, does not give the same coordination number although the latter two compounds have tertiary aromatic arsine and phosphine groups.

B. Complexes of Nickel II

The nickel complexes of the three ligands were prepared by the general method of adding one mole of the nickel salt to one mole of the ligand in a suitable solvent. As most of the complexes were insoluble and precipitated immediately in ethanol, they were prepared in hot butanol. The products were still microcrystalline and in most cases could not be recrystallised. The PN and PDN iodide complexes were obtained as relatively large crystals. The alcohol solutions were deep red in all cases but the precipitated complexes varied in colour. The compounds prepared, together with their colours, decomposition points and conductivities in nitromethane are listed in Table 4.8. The analytical results confirmed the formulae listed in the table; the compounds were thus precipitated in the pure state.

It was possible that the compounds might have the formula $[P/N_2Ni]^{+2}[NiX_4]^{-2}$ rather than $[P/NNiX_2]$. However, the U/V spectrum (discussed below) showed no evidence of the $[NiX_4]^{-2}$ ion and heating the complex with a large excess of ligand gave no sign of formation of another complex. A di-perchlorate or halido-perchlorate complex of nickel II could not be isolated in any case.

The infra-red spectra of the nickel complexes show the band at ca. $2,800\text{cm.}^{-1}$ associated with the presence of an

TABLE 4.8

Physical Properties of Ni II and Co II complexes
of PTN, PDN and PN.

<u>Formula</u>	<u>Colour</u>	<u>Melting Point (°C)</u>	<u>Molar Cond. in Nitromethane at 20°C (mhos)</u>
[PTNNiCl ₂]	pale green	253 d.	1
[PTNNiBr ₂]	ochre	238	1
[PTNNiI ₂]	maroon	211.5	10.5
[PTNNi(SCN) ₂]	maroon	196	3.2
[PDNNiCl ₂]	olive green	238	28
[PDNNiBr ₂]	brown	225	29
[PDNNiI ₂]	black	209	56
[PNNiCl ₂]	brown	245	12.5
[PNNiBr ₂]	violet	238	19.2
[PNNiI ₂]	black	208	78
[PTNCoCl ₂]	royal blue	196	8.3
[PTNCoBr ₂]	blue	182	40*
[PDNCoCl ₂]	royal blue	210	32*
[PDNCoBr ₂]	green/blue	192	25.7
[PNCoCl ₂]	royal blue	254	19.2*
[PNCoBr ₂]	royal blue	219	24.4*

- d. compound decomposed
 1 compound insoluble in nitromethane
 * conductivity increased in presence of methyl iodide.

N-CH₃ group. This band is weaker than in the Pt and Pd complexes and is split into a doublet in all except the thiocyanate complex (2,780cm.⁻¹). The two peaks fall in the range 2,795-2,790cm.⁻¹ and 2,785-2,770cm.⁻¹ in both the PTN and PDN complexes. The peak is not observed in the PN complexes. In other respects the spectra in the sodium chloride region are similar to those of the Pt and Pd compounds and confirm the anhydrous nature of the complexes.

The infra-red spectra in the caesium bromide region were measured for all the complexes and are recorded in Table 4.9. The table shows clearly that the main distinction between the halides is in the 30-40 μ region.

The chlorides show two bands, often complex, in this region, whilst the bromide shows one or two at lower energy and the iodide none. These are tentatively assigned to the metal-halogen stretches. The appearance of two bands in the chloro-complexes suggests that here again the symmetric and asymmetric stretching modes of a cis complex are observed. The paramagnetic nature of the complexes (see later) makes square planar configuration unlikely and so it is possible that the complexes have either tetrahedral or cis-octahedral configuration on the infra-red evidence.

The conductivities of the complexes were measured in nitromethane and are recorded in Table 4.8. The PTN and

TABLE 4.9

Infrared Absorption Bands of P/N Nickel Complexes
in the range 15-40 μ .

[PTNNiCl ₂]	17.2-17.7-18.4s	22.1-22.4-23.2s	30-31vs
	19.3-19.7-20.2vs	25.4-25.7m	35-36.1vs
[PTNNiBr ₂]	same as chloride	21.9-22.2-22.5s	36.5s
	below 21 μ	23.2s	39.9s
[PTNNiI ₂]	same as chloride	21.7m 22.5m	
	below 21 μ	23.3m	
[PDNNiCl ₂]	17.4-17.9-18.4s	21m 25.6m	30.6-31.7vs
	19.4-19.8vs	22.2-22.7-23.8m	
[PDNNiBr ₂]	same as chloride below 30 μ		36.9s
[PDNNiI ₂]	same as chloride	20.2s 25.2w	
	below 20 μ	22.8-23.6m	
[PNNiCl ₂]	17.2-17.9-18.6s	22.3-22.5-23.5s	32vs
	19.5-20-20.6vs		33.5vs
[PNNiBr ₂]	16.3-16.8w	19.5-20-20.7vs	36.2-37.5vs
	18.0-18.6s	22.6s23.8m25.4w	
[PNNiI ₂]	16.2-16.7w17.8-18.5s	22.0m22.7m	
	19.5-19.9-20.7vs	23.7m25.8m	

vs, very strong s, strong
 m, medium w, weak

PdN chlorides and bromides both required heating and so increased dissociation may have occurred. It is of great interest to note that the PN iodide is a 1:1 electrolyte, the PdN iodide almost so in this solvent. One might expect the iodide ions to be weakly bound in nickel II. It is interesting to note that in bis-triphenyl phosphine nickel dichloride the Cl-Ni-Cl bond angle is 131° , due presumably to Cl-Cl repulsions. In the PN complexes the larger bulk of the iodide ion will create greater repulsions, thus considerably weakening the metal-halide bond. It is not obvious why this tendency should be greatest with PN but the $-NMe_2$ groups may sterically hinder the attack of solvent molecules in the other cases.

Magnetic measurements on the complexes are recorded in Table 4.10. The compounds were all paramagnetic with moments in the range 3.12-3.28 B.M. except for the PTN thiocyanate at 1.93. This molecule may well be on the borderline for a diamagnetic species. The moments of the other molecules confirm the triplet ground state but do not distinguish between 'octahedral' or 'tetrahedral' forms, as the latter would be strongly tetragonal. Both stereochemistries give rise to moments greater than the 'spin-only' value of 2.83 B.M.: Octahedral nickel frequently has $\mu_{\text{eff.}}$ 3.16-3.2 B.M. whilst tetrahedral nickel with a greater

TABLE 4.10

Magnetic Susceptibilities of some
PTN, PDN and PN complexes.

<u>Formula</u>	<u>χ_m uncorr.</u> <u>(cgs units)</u> <u>($\times 10^6$)</u>	<u>Diamagn.</u> <u>Corr.</u> <u>(cgs units)</u> <u>($\times 10^6$)</u>	<u>χ_m corr.</u> <u>(cgs units)</u> <u>($\times 10^6$)</u>	<u>$\mu_{eff.}$</u> <u>B.M.</u>	<u>T°K</u>
[PTNPdI ₂]	274.4	374.4	+100	-	297
[PTNHCl ₂]	3864	327	4191	3.12	289
[PTNHBr ₂]	4051/10amp.*	347	4398	3.23	296
[PTNHI ₂]	4095	379	4474	3.25	293
[PTNH(SCN) ₂]	1226	345	1571	1.93	295
[PDNHCl ₂]	4037	295	4332	3.20	293
[PDNHBr ₂]	4157	315	4472	3.25	293
[PDNHI ₂]	3271	347	3618	2.93	294
[PNHCl ₂]	4289	262	4551	3.28	293
[PNHBr ₂]	4199	282	4481	3.24	291
[PNHI ₂]	4115	304	4429	3.22	291
[PTNCoCl ₂]	8954	327	9281	4.71	297
[PTNCoBr ₂]	9173	347	9520	4.74	294
[PDNCoCl ₂]	8898	295	9193	4.67	296
[PDNCoBr ₂]	8666	315	8981	4.60	293
[PNCoCl ₂]	8115	262	8377	4.46	295
[PNCoBr ₂]	8128	282	8410	4.46	293

* also 4045/5amp.

spin-orbit coupling and greater orbital contribution gives such higher values. However, in the tetragonal molecules, of low symmetry, considered here, much of the orbital contribution will be quenched. In the more symmetric bis(butyldiphenylphosphine) nickel halides, which are approximately tetrahedral, moments of 3.16-3.40 B.M. were observed. The magnetic moment measurements, therefore, support a distorted tetrahedral assignment.

Finally, the ultraviolet absorption spectra of the complexes were ^{record}~~worked~~ both in methylene chloride solution and in the solid state. The features and extinction coefficients are recorded in Tables 4.3-5 (p's. 123-131) and the spectra are reproduced in figures 4.15-20. The $[\text{PTN}(\text{NiCl}_2)]$ was insoluble in all solvents.

Interpretation of these spectra is difficult. The low symmetry of the molecules makes a spectral assignment impossible and one may infer the stereochemistry of the metal from the general band distribution. Certain similarities and differences in the spectra may be noted. The solution spectra of the chloride and bromide are the same for PTN and PBN (fig's. 4.15,16) but these differ from the PN complexes (fig. 4.17). All the iodides are similar, however, and similar to the PN chloride and bromide. The non-bonded $-\text{NMe}_2$ groups of PTN and PBN discussed in Pt and Pd, will lie

UV SOLUTION SPECTRA.

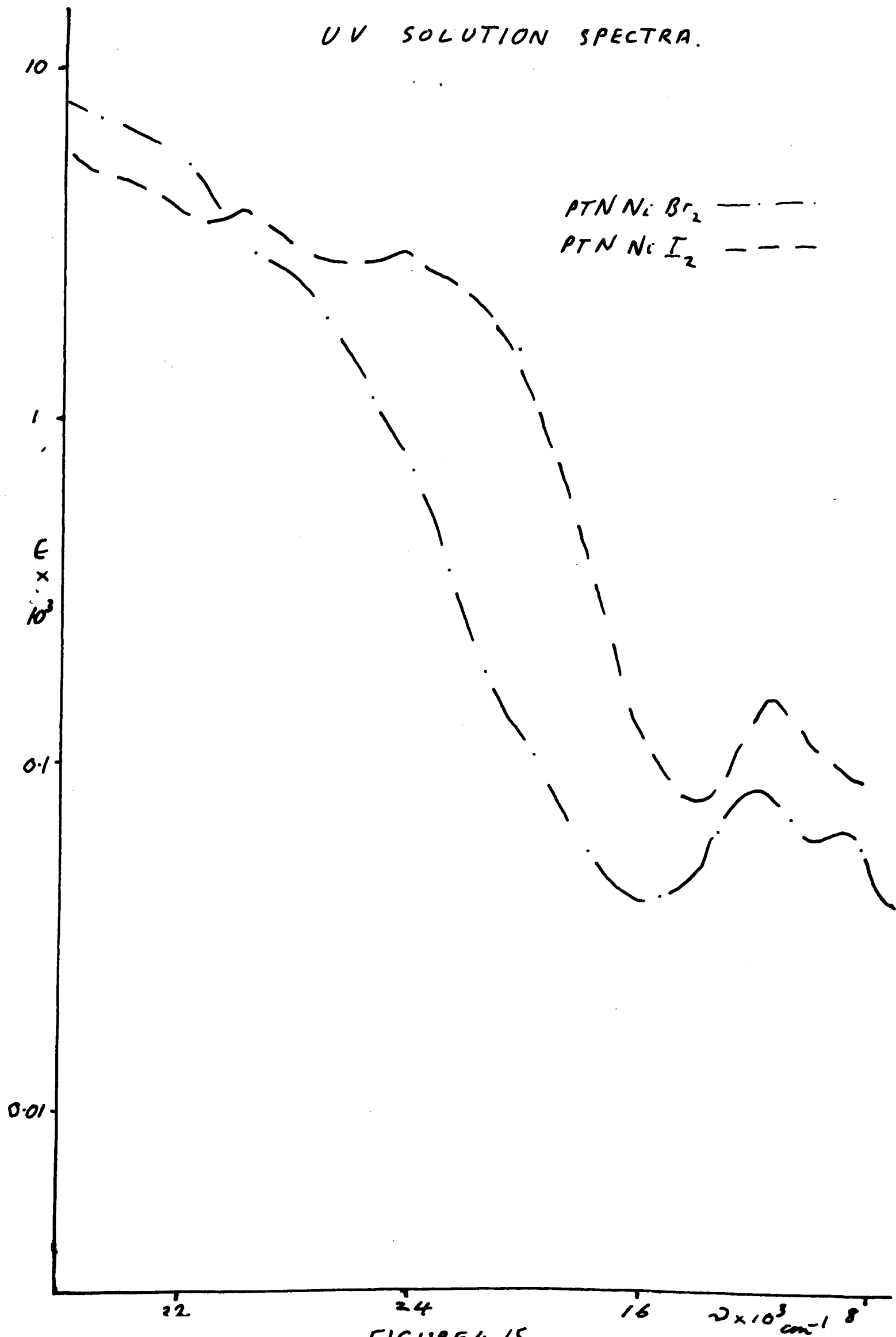


FIGURE 4.15

UV SOLUTION SPECTRA

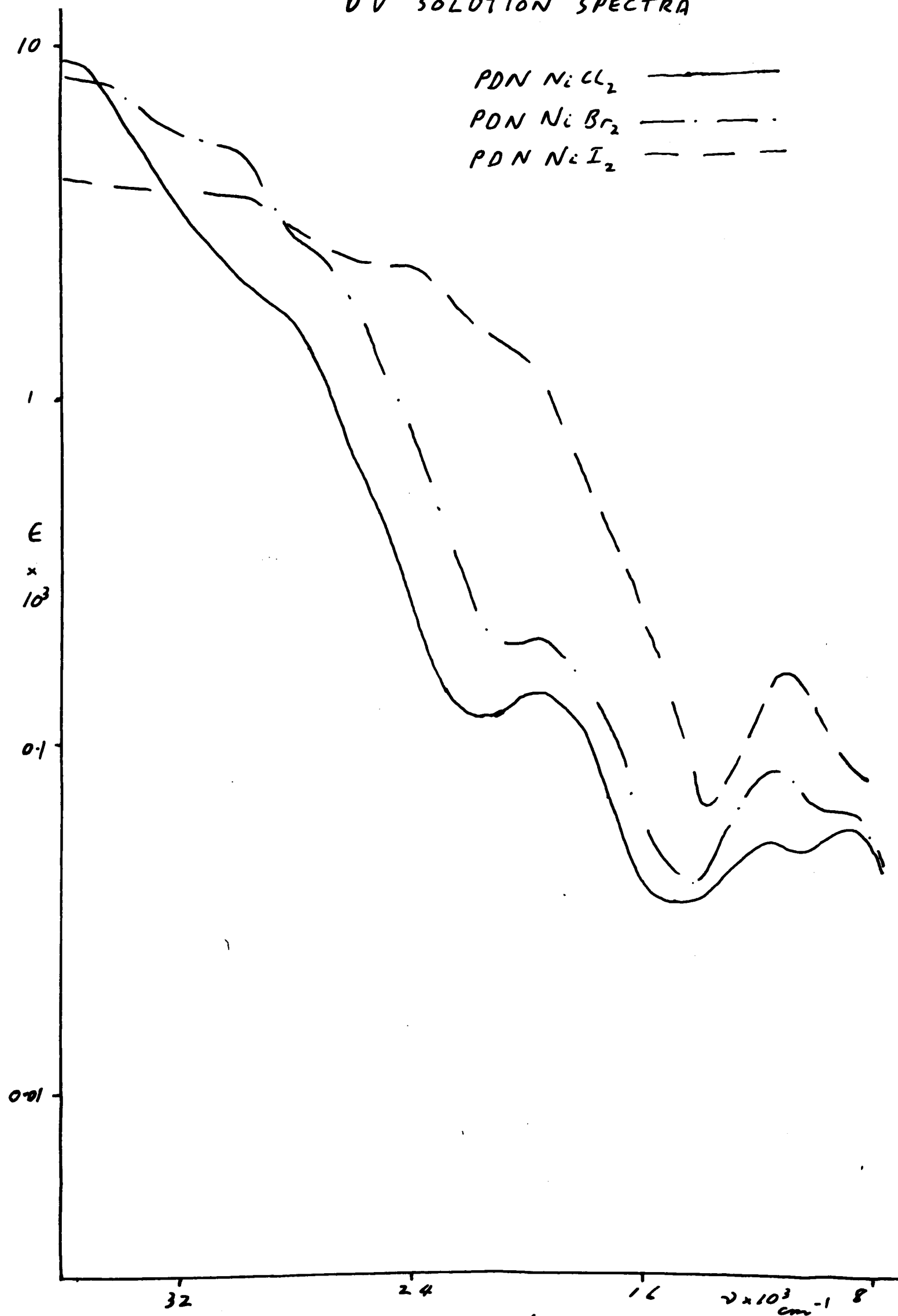
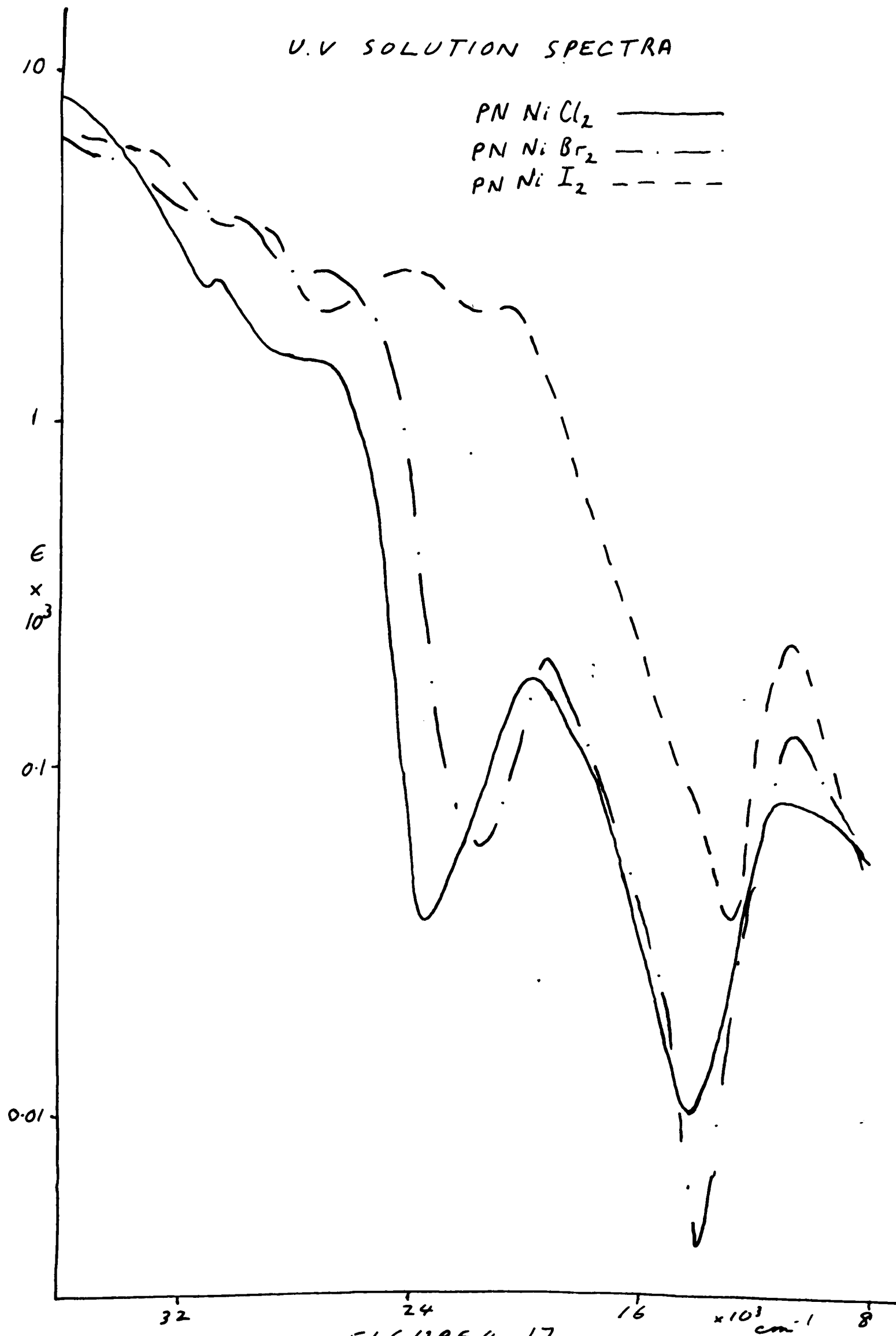
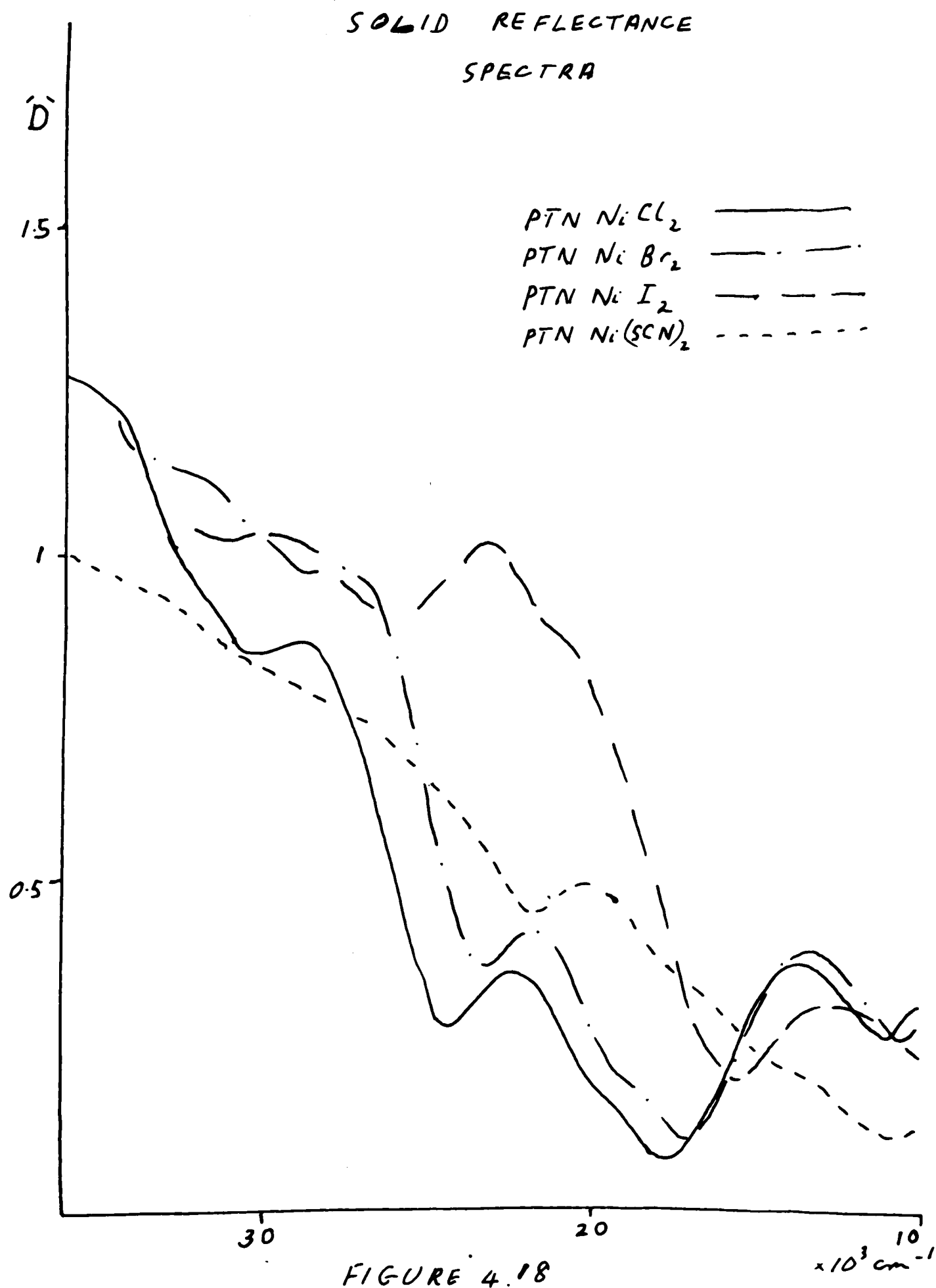
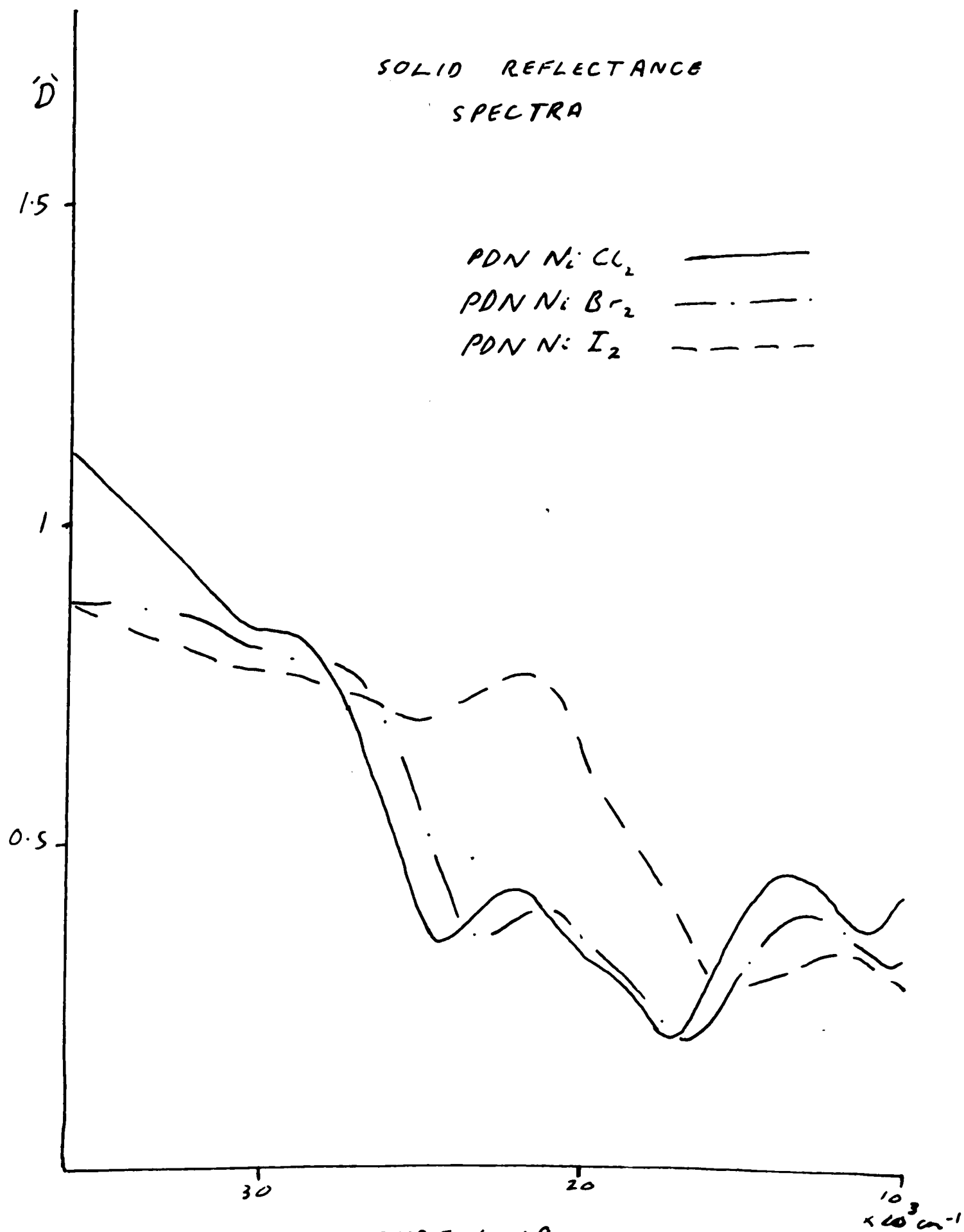


FIGURE 4.16

U.V SOLUTION SPECTRA







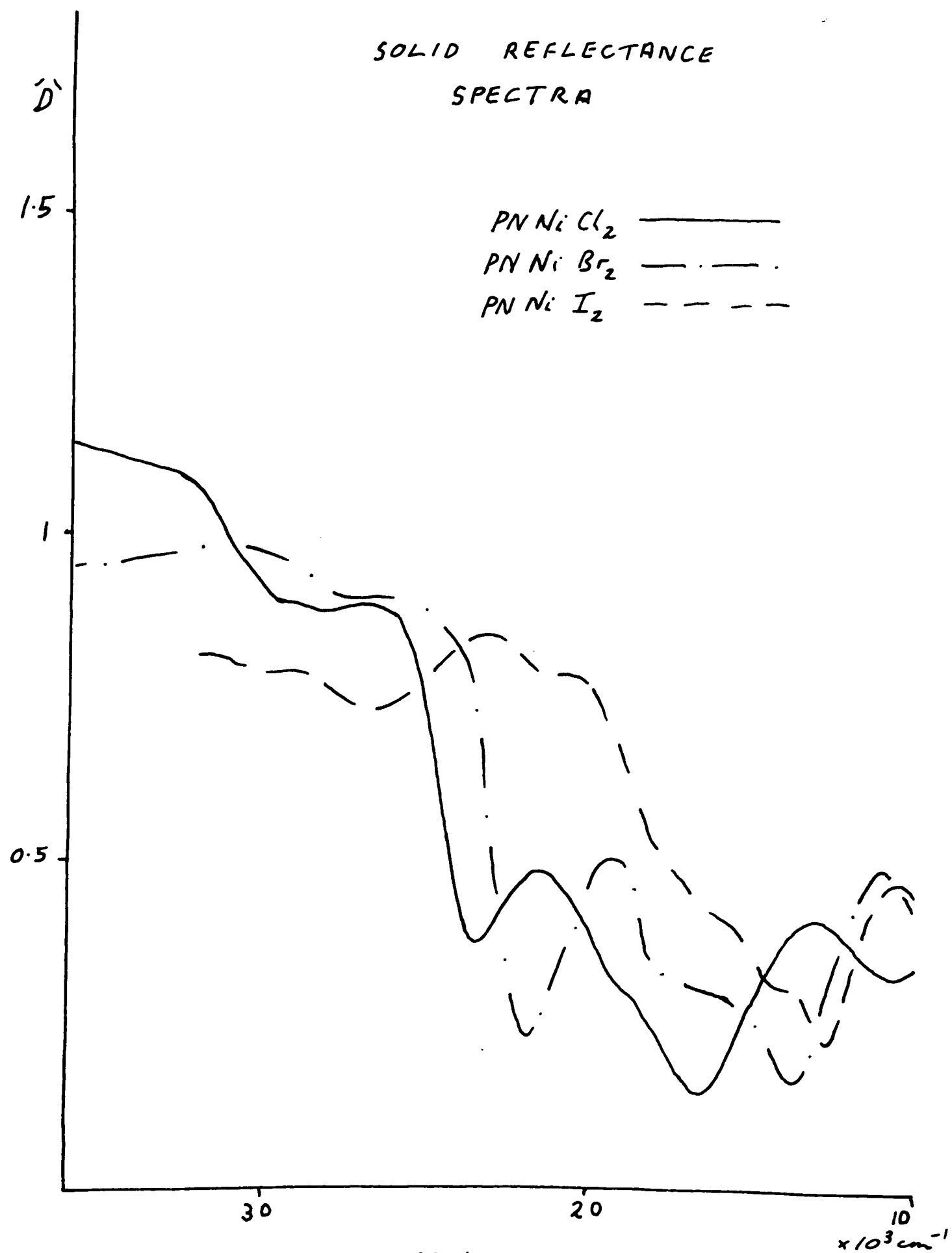
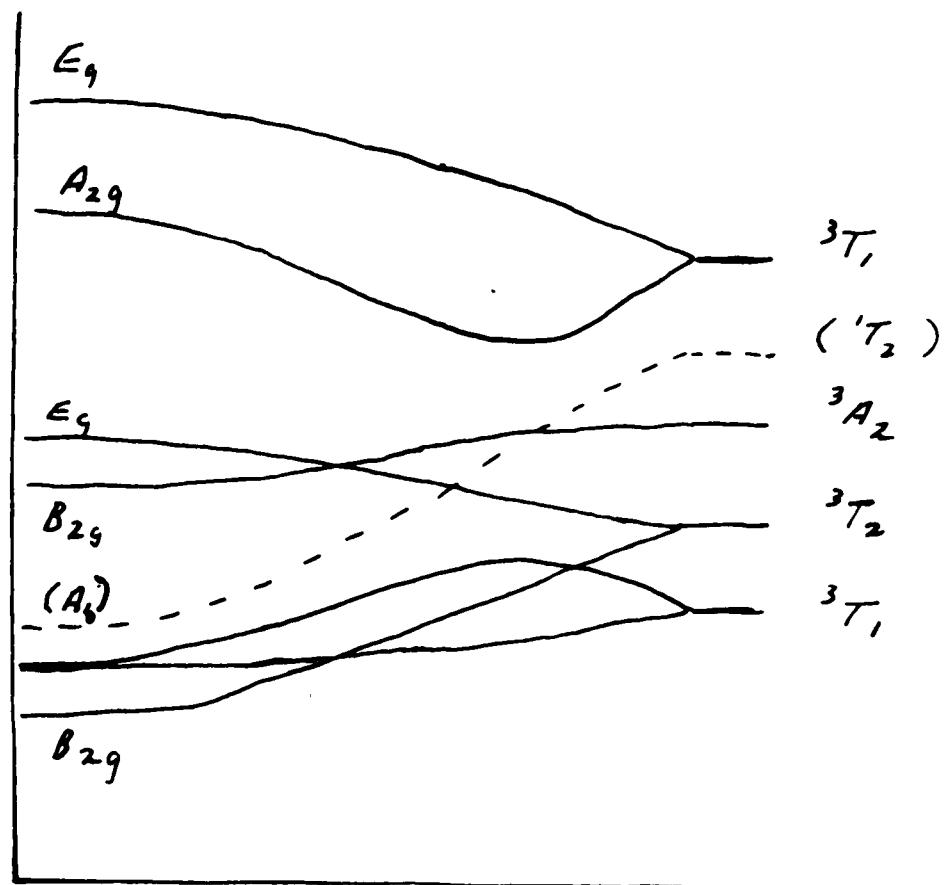


FIGURE 4. 20

in positions where they may interact with the nickel ion, certainly they will provide a steric hindrance to the approach of solvent in these cases and so the similarity of spectra is not unexpected. No such interaction or blocking is provided by PH. The similarity of the iodides suggests that such factors are outweighed here by protection due to the large size of the iodide ion - this being the same in each case.

Figure 4.21 shows the changes in relative energy of the low lying term systems as symmetry is changed from T_d to D_{4h} (72). Furlani calculated the expected bands and found two for T_d , at ca. 11,000 and 18,000 cm^{-1} and three for D_{2d} at ca. 11,000; 18,000 and 25,000 cm^{-1} (fig. 3.27). The PH nickel complexes certainly have bands at ca. 11,000; 19,800 and 28,000 cm^{-1} which could arise from an elongated tetrahedral stereochemistry.

In the solid state the situation is even more difficult as crystal packing must influence the spectra. However, some trends appear here as well. The chlorides all have similar solid spectra. The PH bromide differs from the others in that the band series at ca. 22,000 cm^{-1} is moved to lower energy, the PH iodide also differs from the PTH and PDH analogues. The solution spectra of the P/H complexes show similarities with the spectra of bis-butyl diphenyl phosphine complexes (9). These essentially tetrahedral complexes gave three distinct bands listed in Table 4.11.



$D_{4h} \rightarrow D_{2d} \rightarrow T_d$

Term systems (triplets + lowest singlet)
of Ni^{+2} ion as the symmetry changes
from D_{4h} to T_d

FIGURE 4.21

TABLE 4.11

	$\lambda_{\text{max.}}$	$\epsilon_{\text{max.}}$	$\lambda_{\text{max.}}$	$\epsilon_{\text{max.}}$	$\lambda_{\text{max.}}$	$\epsilon_{\text{max.}}$
$(\text{BuPh}_2\text{P})_2\text{NiCl}_2$	25,900	4,560	20,000	692	11,400	35.2
$(\text{BuPh}_2\text{P})_2\text{NiBr}_2$	24,200	5,660	18,200	476	11,380	117
$(\text{BuPh}_2\text{P})_2\text{NiI}_2$	25,000	3,460	(20,000 (16,500	sh	10,900	374
PNNiI_2	27,200	2,700	19,300	205	10,600	126

The weight of evidence, therefore, leads to the conclusion that the complexes exist in distorted tetrahedral arrangements. The low symmetry of the molecule does not permit spectral assignments but the tetragonal distortion is consistent with the low magnetic moments. Differences in the spectra may be attributed to interactions, either steric or electronic, with the 'free' nitrogen atoms. Thus the lower ligand field splitting in the first transition series permits a triplet ground state for the d^8 ion whilst the singlet square planar configuration is preferred for palladium and platinum. Because nickel has a smaller radius the ligand may span the approximately tetrahedral positions.

C. Complexes of Cobalt II

The cobalt compounds were prepared by the general method of adding one mole of the cobalt salt in hot ethanol to one mole of the ligand in hot ethanol. The solutions deposited blue crystals on cooling and these were recrystallised from ethanol. The complexes prepared, together with their colours, decomposition points and conductivities in nitromethane, are listed in Table 4.8 (p. 154). Analyses confirmed the formulae given in the table. No iodide complexes could be isolated.

The infra-red spectra of the complexes in the sodium chloride region were similar to those of the nickel analogues. The significant band at ca. $2,800\text{cm}^{-1}$ appears again in the PDN and PTN compounds and, as with nickel, it is a doublet at $2,790$; $2,778\text{cm}^{-1}$ in PTN and $2,790$; $2,774\text{cm}^{-1}$ in PDN. Again, the appearance of this band suggests that there are 'free' nitrogen atoms in the molecule.

The features of the infra-red spectra in the caesium bromide region are recorded in Table 4.12. The pattern of the spectra in the region $30-40\mu$ is of interest. The chlorides show bands at differing positions in the various compounds but of the same type as those previously tentatively assigned to metal-chlorine symmetric and asymmetric stretching frequencies. The assignment is supported by the marked

TABLE 4.12

Infra-red Absorption Spectra of Cobalt Complexes
in the range 15-40 μ .

[PTNCoCl ₂]	18.3-18.9-19.5m	22.2m22.7s23.4m	29.7-30.5s
	20-20.2m	25.8m27.2m	34.8vs
[PTNCoBr ₂]	17.4-18-18.7m	same as chloride	30.2w
		19-28 μ	37.1vs
[PDNCoCl ₂]	17.1m17.8-18.6s	21.1s22.6s	31sh-33vs
	19.4-19.8-20.2vs	24s26.1m	37.5m
[PDNCoBr ₂]	16.3-16.9w	same as chloride	27.3m37.5s
	17.7-18.3m18.6s	19-27 μ	29.2m40.3m
[PNCocl ₂]	16.3-16.9m18m	20.7vs22.6-22.8s	28.7vs
	18.6s19.6-20.2vs	24m25.3w	31.3vs
[PNCobr ₂]	same as chloride below 26 μ		36vs37.8w
			39w

vs, very strong
s, strong
m, medium
w, weak

movement of these bands to lower energies in the bromide complexes. Also the tetrahedral bis-triphenyl phosphine cobalt halides have bands in this region, thus the chloride has two, at 28.5μ ; 31.4μ ,s; and the bromide one at 36.1μ . This type of spectrum could, therefore, arise from a tetrahedral configuration.

The magnetic moments of the cobalt complexes are recorded in Table 4.10 (p.158). The value of μ_{eff} , 4.46-4.74 B.M., clearly shows that there are three ^{un-}paired electrons in all the complexes. Even so the value is much higher than that calculated on a spin-only basis of 3.89 B.M. The observed values may be compared with those of the CoX_4^{-2} anions where μ_{eff} is 4.59-4.77. Clearly spin-orbit coupling must be important here. The ground state of the ion in a tetrahedral field will be 4A_2 . Figure 4.22 shows the splitting of the free ion energy levels in a tetrahedral field. There will be configurational interaction between the 4T_1 states; further the spin-orbit coupling splits the 4T states. Mixing then occurs between the near J_0 states arising from 4T_2 and 4A_2 . Thus μ will increase. With cobalt, the ligand field splitting is greatest for chloride and so the iodide will have the greatest mixing as 4T_2 and 4A_2 are closest; and the highest μ - as is observed for CoX_4^{-2} . In the present compounds different amounts of quenching of the orbital

contribution will occur depending on the local stereochemistry and thus differences in the value of p are expected between the complexes of different ligands.

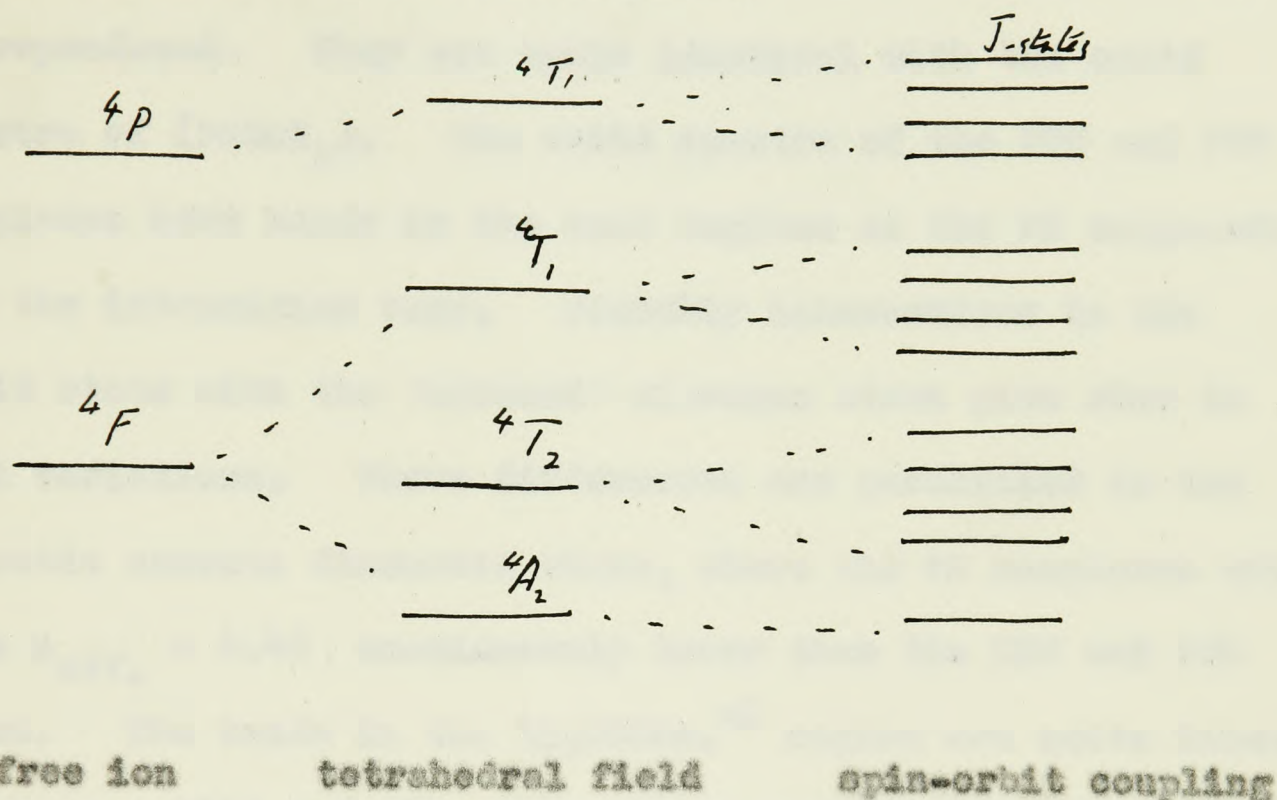


Figure 4.22

The conductivities of the complexes were measured in nitromethane and the compounds were found to be intermediate electrolytes with λ_m values ranging between 8 and 40. Clearly much solvolysis occurs in this solvent. There is an increase in conductivity in the presence of methyl iodide, in contrast with previous cases, and so it may be that considerable molecular rearrangement takes place.

The final evidence of the structure of the cobalt complexes comes from the ultraviolet absorption spectra. The features of the spectra are recorded in Tables 4.3-5

(p's. 123-131) and the spectra are reproduced in figures 4.23-26. The solution spectra of all the complexes in methylene chloride solution were identical and only one set is reproduced. They are again identical with the solid spectra of $[\text{PNCox}_2]$. The solid spectra of the PDN and PTN complexes have bands in the same regions as the PN compounds but the intensities vary. Probably interactions in the solid state with the "unbound" nitrogen atoms give rise to such variations. These differences are paralleled in the magnetic moments discussed above, where the PN complexes both have $\mu_{\text{eff.}} = 4.46$, considerably lower than the PDN and PTN cases. The bands in the $15,000\text{cm.}^{-1}$ region are quite intense ($\epsilon_{\text{max.}}$ ca. 200) and this supports an essentially tetrahedral description.

The features of the solution spectra are comparable with those of $[(\text{C}_4\text{H}_9)_2\text{N}]_2[\text{CoX}_4]$ (83). The general shape and distribution of bands is the same, the whole being shifted to higher energy by about $2,000\text{cm.}^{-1}$. The lower symmetry also increases the complexity slightly; thus in figure 4.22 A_2 transforms as A_2 but the T_1 levels transform as A_1 , B_1 and B_2 and the T_2 as A_2 , B_1 and B_2 in C_{2v} symmetry. Band groups rather than single transitions would be expected and are observed. This evidence does conclusively show that the complexes do not contain CoX_4^{-2} ions and further is consistent

UV SOLUTION SPECTRA.

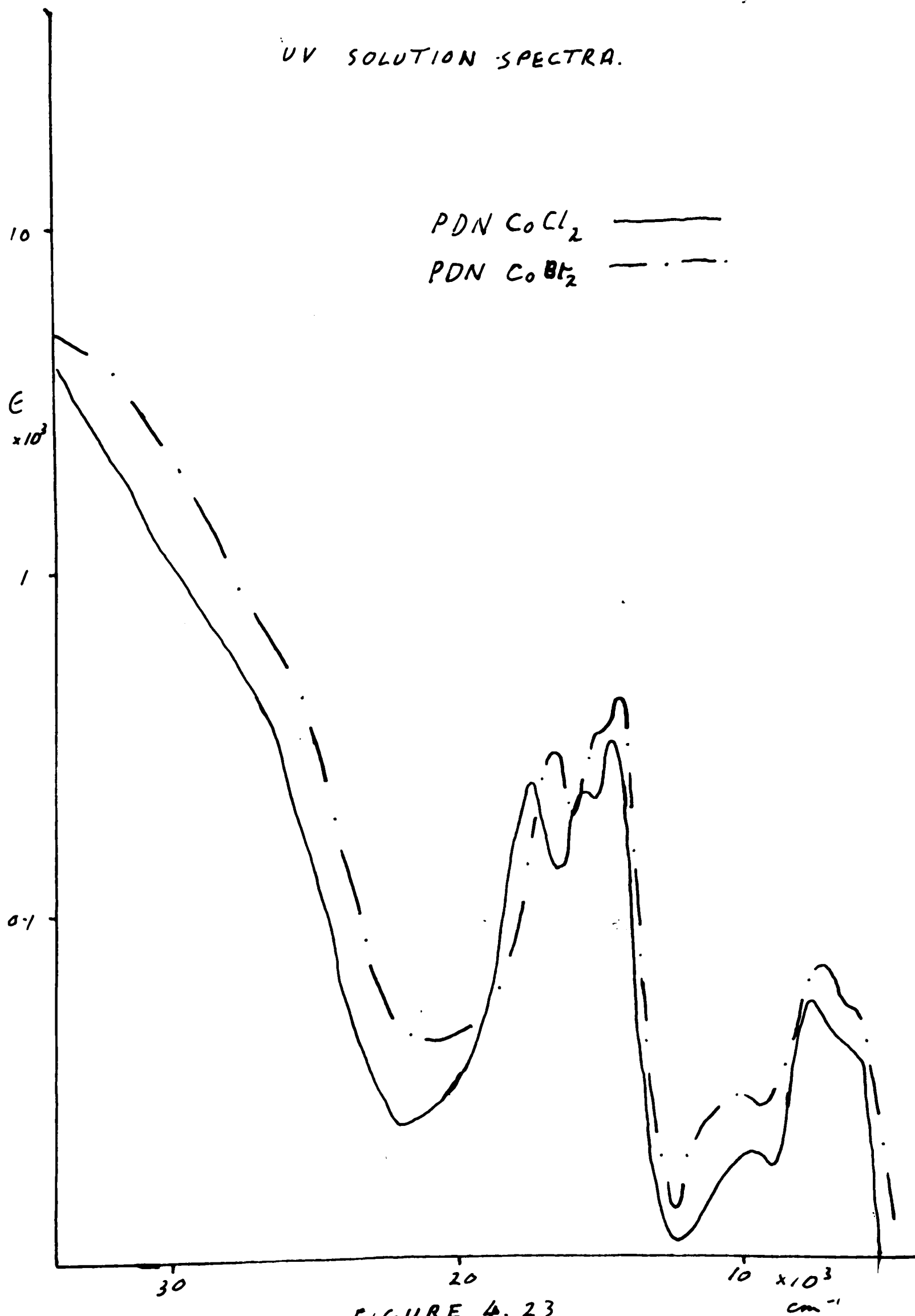


FIGURE 4.23

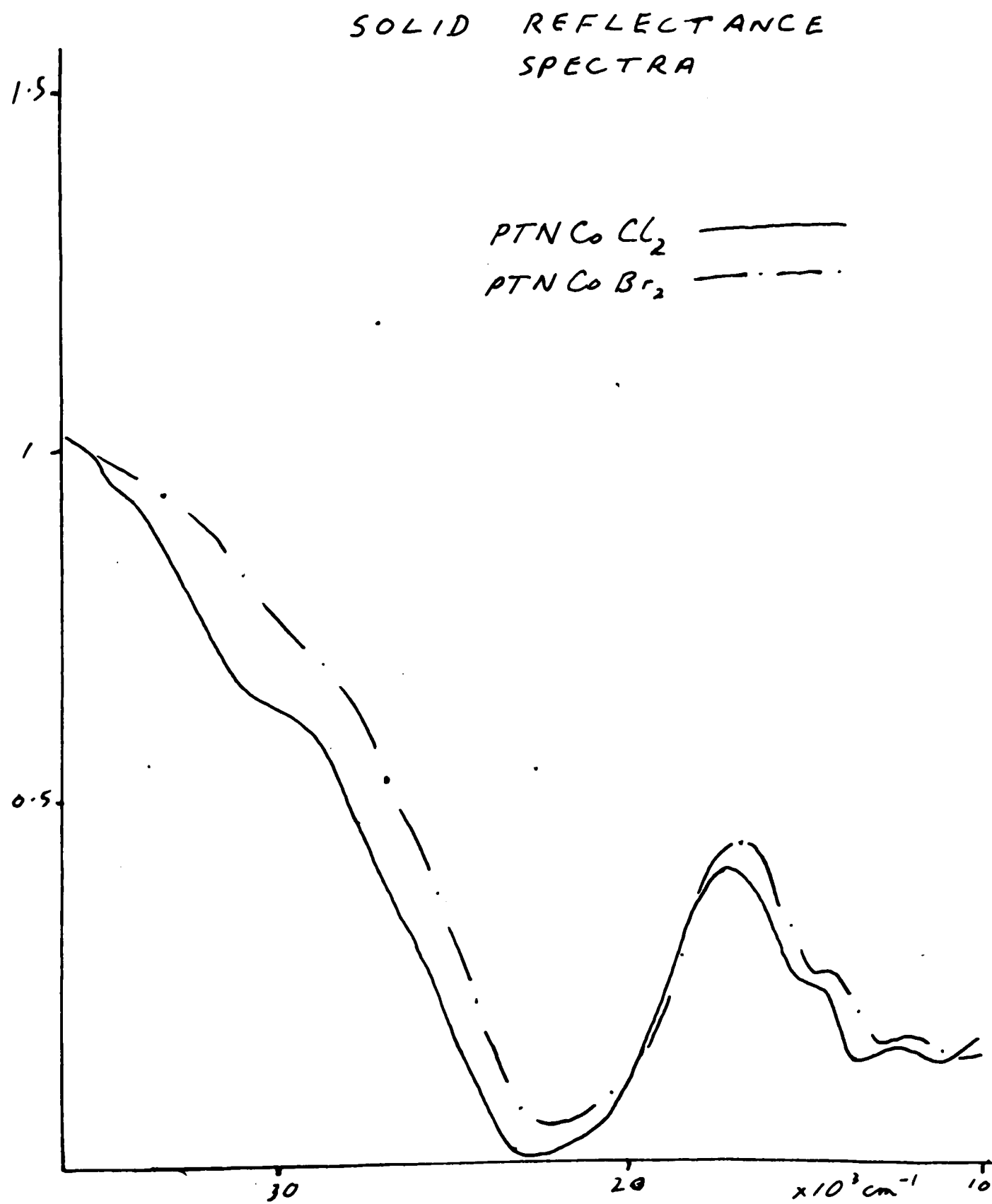


FIGURE 4.24

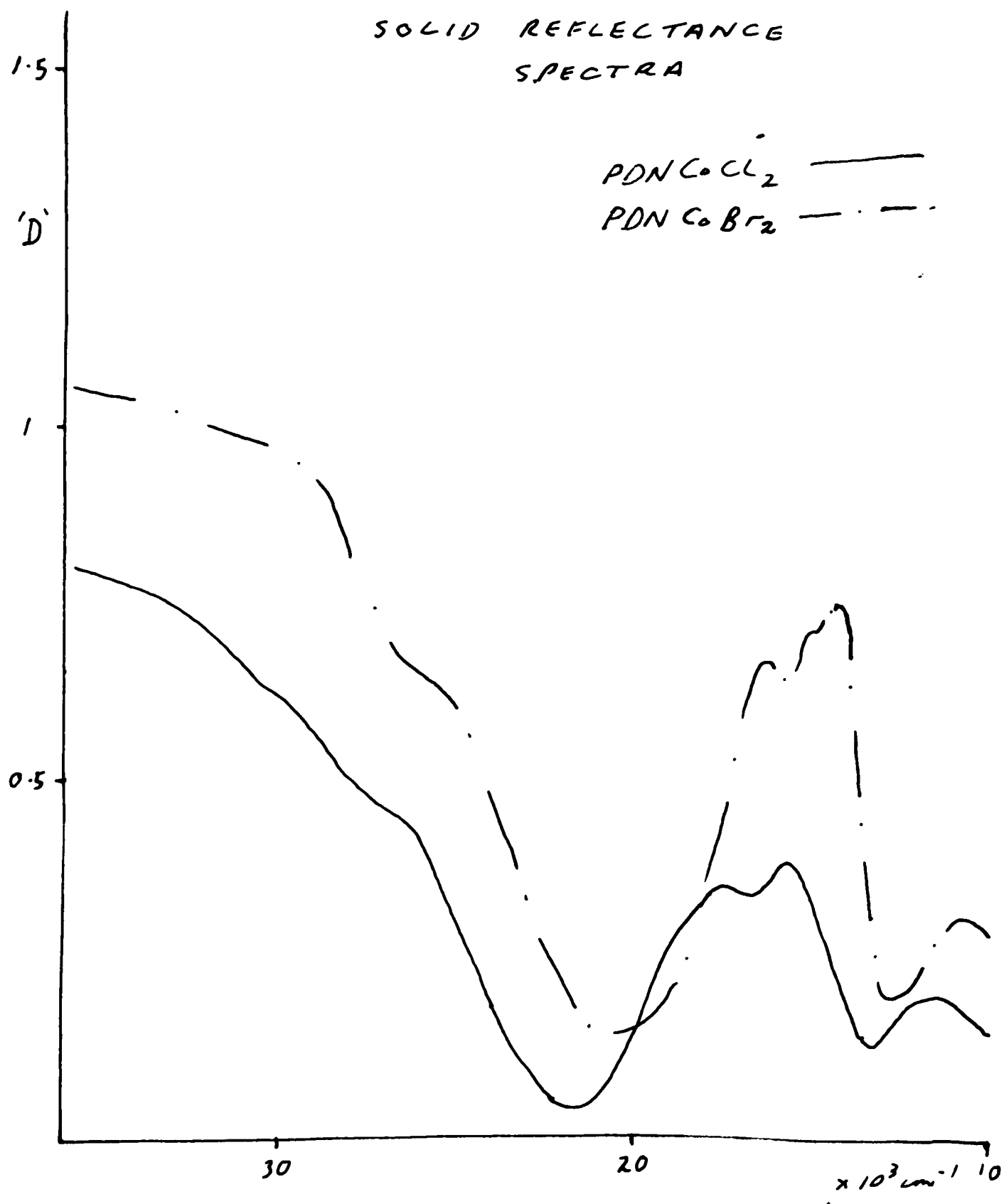


FIGURE 4.25

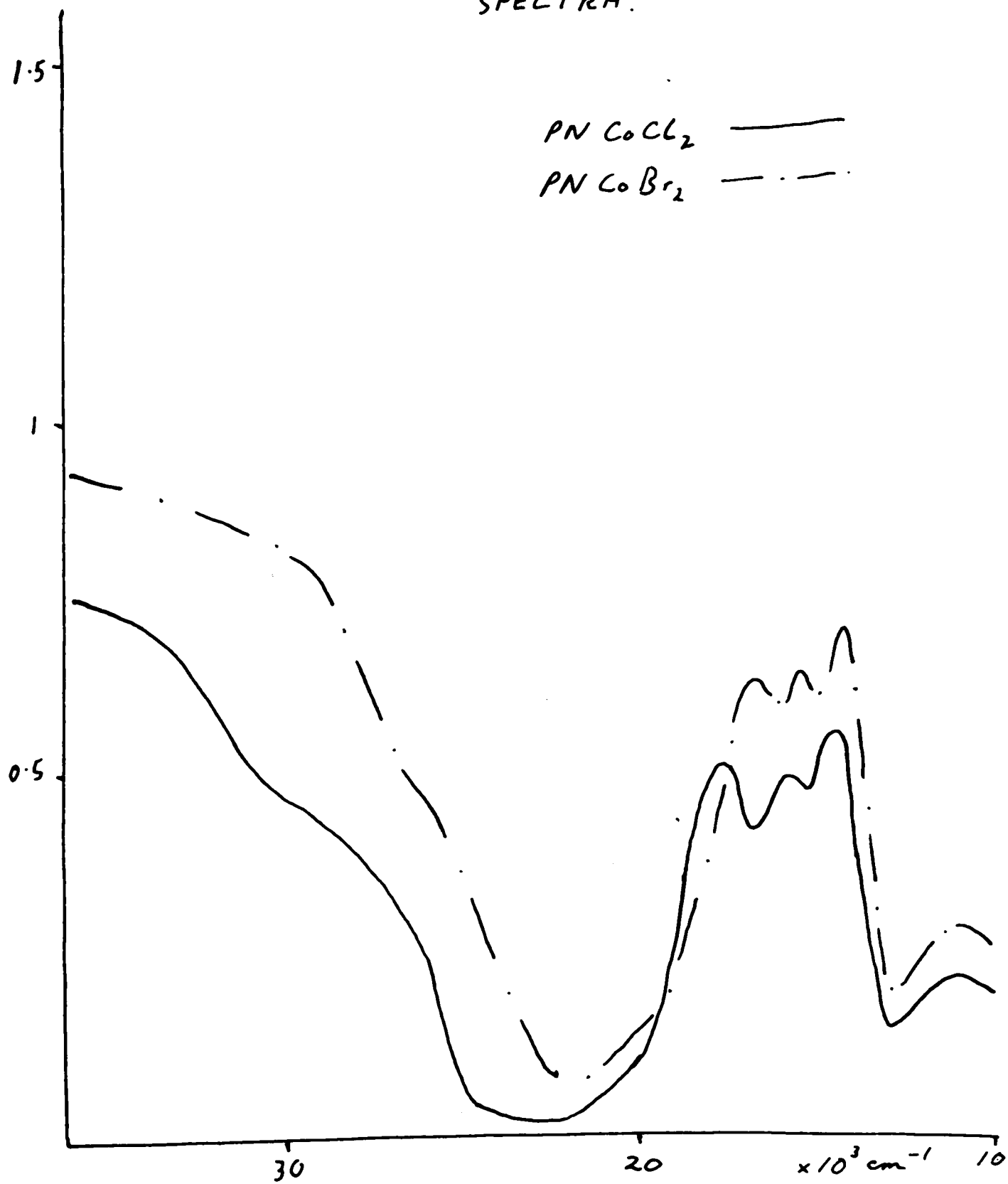
SOLID REFLECTANCE
SPECTRA.

FIGURE 4. 26

with the tetrahedral nature of the cobalt II in this range of complexes. As seen above, more interaction may occur in the PTN and PDM complexes in the solid state, but this is only qualitatively described. Ballhausen (81) assigns the band group at ca. $15,000\text{cm.}^{-1}$ to ${}^4A_2 \longrightarrow {}^4T_1$ (P) and that at ca. $7,000\text{cm.}^{-1}$ to ${}^4A_2 \longrightarrow {}^4T_1$ (F) in CoCl_4^{-2} . In the weak field of the tetrahedral molecule the first transition ${}^4A_2 \longrightarrow {}^4T_2$ should occur at about $4,000\text{cm.}^{-1}$ but this is not observed as the solvent absorbs in this region. The other main groups of absorptions correspond with the single transitions (81) for T_d symmetry.

An X-ray photograph of a crystal of $[\text{PNC}\text{CoCl}_2]$ was taken, and although no detailed work was carried out, the appearance of the photograph is not inconsistent with a tetrahedral stereochemistry.

The present complexes are thus similar to those of nickel in giving essentially tetrahedral species as shown by magnetic and spectral evidence. Here again the donor power of the tertiary amine is too low, even in the first transition series, to permit higher coordination number.

D. Complexes of Copper I

The copper compounds were prepared by the general method of refluxing equimolar quantities of the ligand and

cuprous salt for several hours in ethanol. The cuprous salt slowly dissolved to form a complex in solution. This was filtered hot and the product separated as large yellow or white crystals. The PN bromide and iodide formed only complexes containing two moles of PN one of copper but the other compounds were formed in 1:1 molar ratio. The products were all recrystallised from ethanol and their colours, melting points and conductivities in nitromethane are listed in Table 4.13. Analytical results confirmed the formulae given in the table.

The compounds are all true non-electrolytes in nitromethane except for the 2:1 species in which noticeable solvolysis occurs. Even here, however, the value of λ_m is well below that of a 1:1 electrolyte. The observation of an increase in conductivity on addition of methyl iodide in these latter compounds suggests that molecular rearrangement occurs in the solvent with the release of one of the ligand molecules.

The infra-red spectra of the cuprous complexes show the usual features for P/N compounds. The band at ca. $2,800\text{cm}^{-1}$ appears as a doublet in the PTN compounds, at $2,785$ and $2,775\text{cm}^{-1}$; in the PDN compounds as a single absorption at $2,780\text{cm}^{-1}$ and in the $(\text{PN})_2$ complexes the band is again observed at $2,780\text{cm}^{-1}$. The evidence suggests

TABLE 4.13

Physical Properties of Cu I complexes
of PTH, PDH and PH.

<u>Formula</u>	<u>Colour</u>	<u>Melting Point (°C)</u>	<u>Molar Condy. in Nitromethane at 20°C (mhos)</u>
[PTNCuCl]	lime green	171.5	5.6
[PTNCuBr]	yellow	175.5	6.3
[PTNCuI]	yellow	233	6.9
[PDNCuCl]	pale yellow	205-8 d.	3.7
[PDNCuBr]	pale yellow	219.5	5.2
[PDNCuI]	white	232.5	8.4
[PHCuCl]	pale green	168-9 d.	4.4
[(PH) ₂ CuBr]	white	224.5	21.2*
[(PH) ₂ CuI]	white	171	20*

* Conductivity increased in presence of methyl iodide.

d Compound decomposed.

that in this case, with all three ligands, there are uncoordinated nitrogen atoms. $[\text{PTNCuCl}]$ shows a doublet at 2,790; 2,782 cm^{-1} . It seems possible that even in the PTN complexes only the phosphorus atom is coordinated to give a two coordinate P-Cu-X molecule. Alternatively, the compounds may be polymeric.

The infra-red spectra in the caesium bromide region are recorded in Table 4.14. No clear pattern emerges from these although the band at ca. 31μ in PTNCuCl may be a Cu-Cl stretch. It appears at 38.3μ in the bromide. The spectra do not permit any structural deductions to be made. The d^{10} cuprous ions are necessarily diamagnetic and no magnetic measurements were performed. The ultraviolet absorption spectra of the cuprous complexes were measured in both the solution and solid states and are recorded in Tables 4.3-5 (p's. 123-131). Figures 4.27-29 show the solid reflectance spectra of the complexes; the solution spectra display no additional features and are not reproduced here. The 1:1 and 1:2 compounds show no notable features in the visible or near ultraviolet regions. There will be no ligand field d-d transitions in the d^{10} ion and so the bands observed must arise either from the ligands or from charge-transfer.

The available structural evidence for these compounds is scant and no deductions may be made. The

TABLE 4.13

Infra-red Absorption Spectra of Copper Complexes
in the range 15-40 μ .

[PTNCuCl]	15.1w17.9s	20.8-21.4m26.5m	29-29.8m
	18.7-19.3-19.7s	23.0-24.0s	31m
[PTNCuBr]	same as chloride below 25 μ	26.7m	38.3 broad m
[PTNCuI]	same as chloride	20.9-21.1s22.6m	
	below 20 μ	23.7-24.2s26.9m	
[PDNCuCl]	16.3w17.8-18.1m	21.2m22.9-23.2m	29.5w
	18.8-19.5-19.9-20.4s	24.1s27m	
[PDNCuBr]	16.2w17.4-17.8m	22.2s22.7m26.9m	29.5w
	18.7-19.4-19.8-20.2s	23.3-23.9s	
[PDNCuI]	16.2w17.7-18m	22.8-23.3m26.1m	29.5w
	18.9-19.2-19.9-20.5s	21.1w24.2m27.3w	
[PNCuCl]	16.2w17.8s	22.6-23m	25w
	18.7-19.6-20.5vs	24s26.4s	32.5w
[Ph ₃ PCuCl]	16.2w19.2-20vs	23m23.8w	
[(Ph) ₂ CuI]	16.2w17.9m18.8s	22.6-23-23.7m	
	19.1-19.8-20.6s	25w26w27w	
[Ph ₃ PCuI]	16.2w19.4-20-20.5vs	22.8m24.4-25m	

vs, very strong
s, strong
m, medium
w, weak

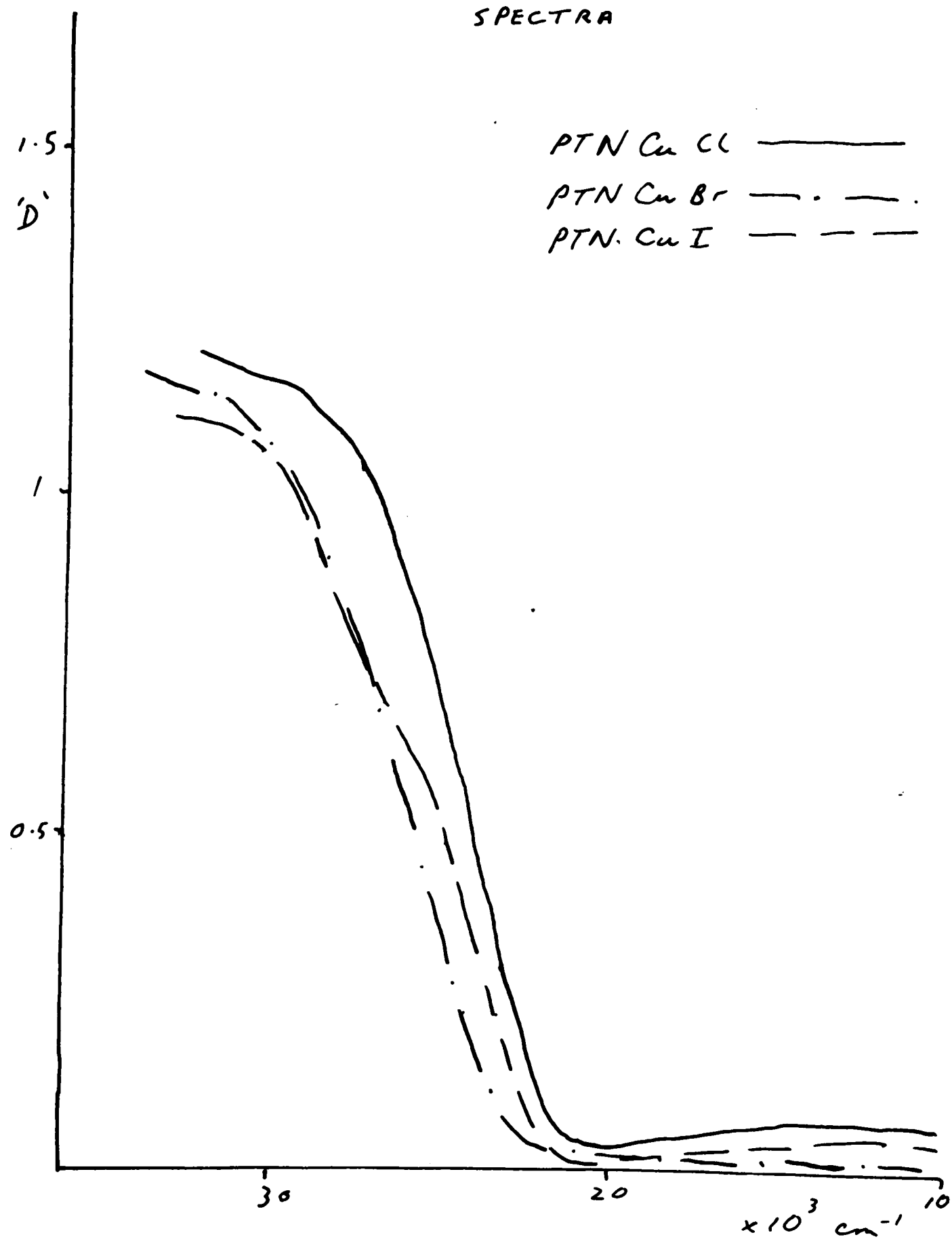
SOLID REFLECTANCE
SPECTRA

FIGURE 4.27

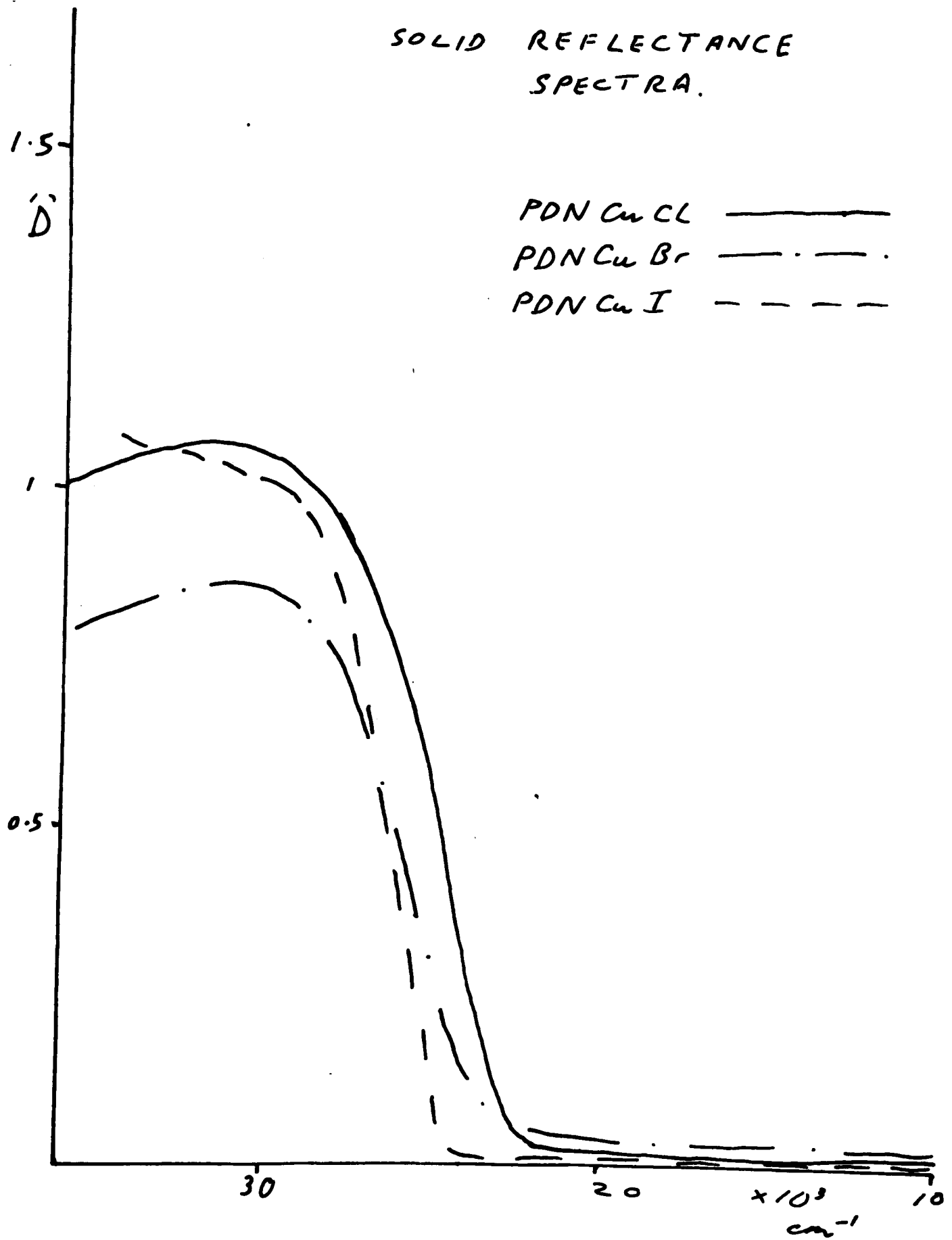


FIGURE 4.28

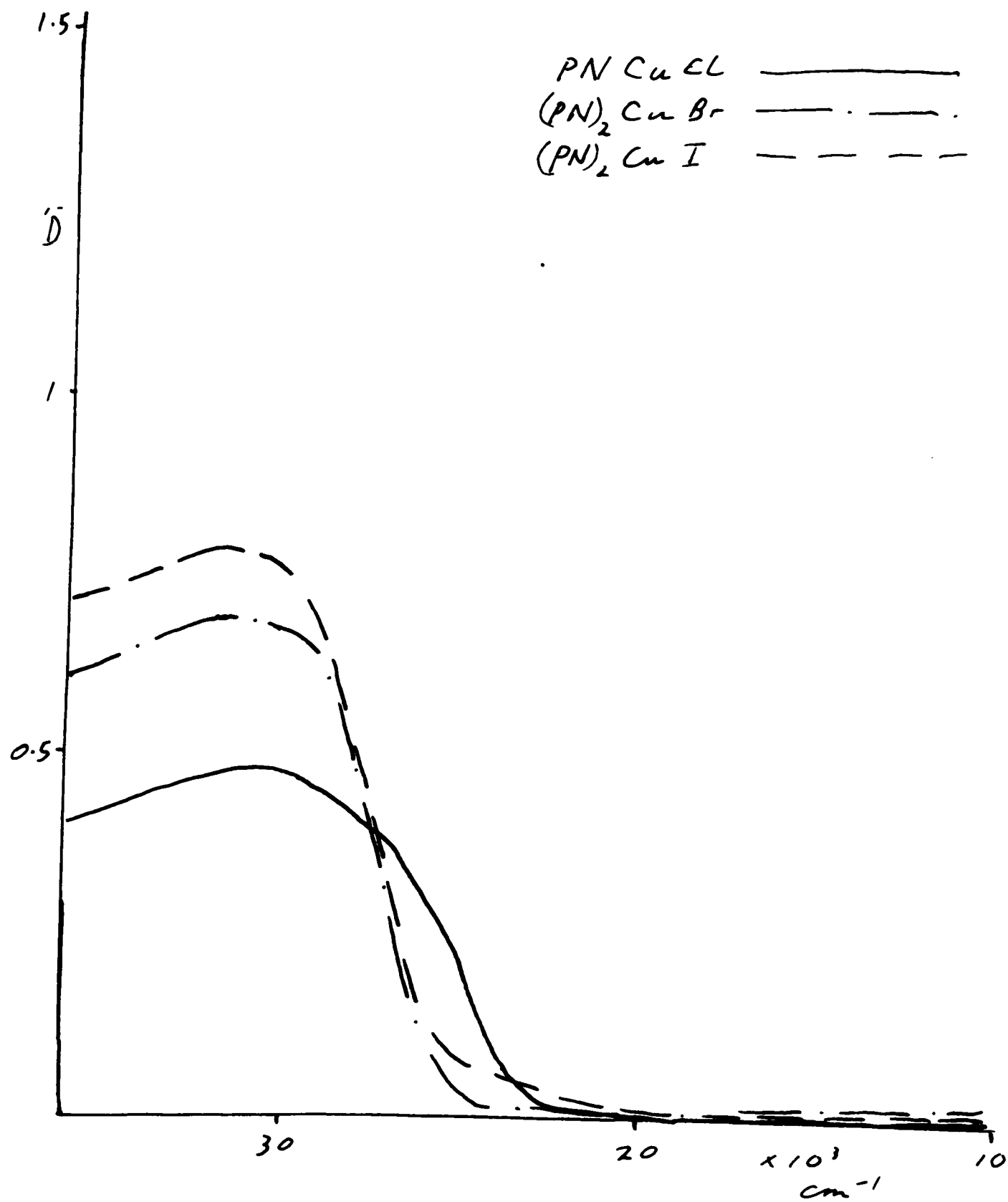
SOLID REFLECTANCE
SPECTRA.

FIGURE 4.29

compounds empirically $[R_3PCuI]$ may be analogous, however, as the present complexes would seem, on the infra-red evidence, to have only the phosphorus atom bound. X-ray analysis of the trialkyl phosphine compounds (84) showed them to be tetrameric. Four copper atoms were at the apices of a tetrahedron. Each copper was four-coordinate, being equidistant from three iodide ions at the mid-points, but raised above, the faces of the tetrahedra. The phosphine molecules were on the C_{3v} axes. X-ray analysis is required to make any predictions on the complexes of copper I as the evidence from physical measurements is insufficient.

EXHIBIT 10-10-10000

1. Attached herewith is a copy of the report of the

(1) [illegible]

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PART TWO

[illegible text]

(2) [illegible]

[illegible text]

CHAPTER V

PREPARATION OF THE LIGANDS

A. Attempted preparation of 1,2 dipentyl ethylene diamine.

(i) Esterification of hexanoic acid.

275ml. (2.2 moles) hexanoic acid was mixed with 225ml. (6 moles) methanol in a 1 litre flask and 25ml. concentrated sulphuric acid was added slowly with careful mixing. The mixture was refluxed for three-quarters of an hour during which time two layers separated. The product was poured into 2 litre cold water with stirring and the upper ester layer separated. This was washed successively with water twice, sodium bicarbonate solution twice and water twice, again. The ester was dried over calcium chloride and distilled, the fraction boiling at $149.5-152^{\circ}\text{C}$ being collected (recorded $149.5^{\circ}\text{C}/760\text{mm.}$). Yield = 265ml., 85%. The experiment was repeated with the same yield.

(ii) Acyclic condensation with methyl hexanoate.

Xylene was dried by refluxing over molten sodium in an atmosphere of nitrogen, a high speed stirrer being required to disperse the sodium, and the dry xylene was decanted for use.

23gm. (1 mole) sodium in 600ml. dry xylene was stirred rapidly at a controlled temperature of 105°C under nitrogen. 65gm. (.5 mole) methyl hexanoate was added slowly, at such a rate that the temperature did not exceed 110°C and the now viscous mixture was stirred for a further half an hour.

2 moles methanol were added slowly to decompose excess sodium, the whole allowed to cool to 80°C and 20ml. water were added to dissolve the sodium hydroxide. The xylene layer was separated and washed successively with water, twice, neutralised with hydrochloric acid (2N) and then this was neutralised with sodium bicarbonate solution. Finally the solution was washed with water and xylene removed by steam distillation. The impure yellow oil remaining was fractionated at 1.8-2mm. and gave three fractions boiling at $98-102^{\circ}\text{C}$; $103-112^{\circ}\text{C}$; greater than 112°C . All three showed hydroxyl and carbonyl bands in the infra-red spectrum though the spectrum was sharpest with the palest yellow first fraction. The products were used in attempts to make a crystalline derivative (A.iii.below). The mixture had gelled during the reaction so attempts were made to perform the reaction with more efficient stirrers and greater dilution. A "turbo-stirrer" with stator and rotor vanes of metal was tried unsuccessfully and the solution adopted was to use a

5 litre flanged flask with a large twisted wire stirrer, the reaction being performed with 4 mole sodium, 1.5 mole ester in 3 litre xylene.

Yield = 80gm., 52% acyloin Bpt. 85-89°C/.9mm.

The experiment was repeated twice giving 57 and 62% yields respectively.

(iii) Attempted preparation of canroin oxime.

10gm. (.05 mole) of the product from above was dissolved in 95% ethanol together with 6gm. hydroxylamine hydrochloride. Sodium hydroxide (11g., 30% aqueous solution) was added slowly with shaking and cooling. The mixture was then refluxed for five minutes, cooled and poured into 30ml. concentrated hydrochloric acid in 200ml. water. No crystalline oxime was formed, however, and the product was a brown oil. The experiment was repeated with longer refluxing times ($1\frac{1}{2}$ and 3 hours) but no crystalline product was formed. It is possible that the impurity in the starting material led to a complexity of products.

(iv) Attempted preparation of the α -diketone.

Two attempts were then made to oxidise the acyloin to the α -diketone with ammonium nitrate, but no pure product could be obtained.

60gm. crude acyloin, 50gm. ammonium nitrate, 1gm. cupric acetate and 350ml., 80% acetic acid were mixed and

warmed with stirring until all was dissolved. Slight cooling was required to control the evolution of nitrogen. The mixture was then refluxed for one and a half hours and cooled. No crystalline diketone separated, so the oily layer was extracted with ether, washed with sodium bicarbonate solution and with water, and the ethereal solution fractionated. Infra-red spectra indicated that oxidation was incomplete.

(v) Preparation of the osazone of caproin.

5ml. acyloin and 20ml. acetic acid were cooled to 0°C , it was found necessary to add a little propionic acid to prevent solidification. Pure, redistilled phenyl hydrazine (15ml.) was added slowly and the whole allowed to warm up to room temperature. The immediate, non-crystalline, yellow precipitate was broken up and the mixture left to stand overnight. A mass of white needles was filtered and washed with acetic acid, yield 3.25gm. The infra-red spectrum showed a $\text{C} = \text{N}$ stretching frequency and the absence of $\text{C} = \text{O}$ frequency as anticipated. The experiment was repeated twice and the product recrystallised twice from ethanol.

Total yield = 10.3gm. Mpt. 111.5°C

Analysis found C, 76.04; H, 9.17; N, 14.82%

$\text{C}_{24}\text{H}_{34}\text{N}_4$ requires C, 76.13; H, 9.07; N, 14.80%

(vi) Attempted reduction of the osazone to 1,2
dipentyl ethylene diamine.

(a) Reduction with aluminium amalgam.

Aluminium foil (.5g.) was shaken with 2% mercuric chloride solution for two minutes. While the solution still effervesced it was washed well with water and the osazone (.5g.) in 80% aqueous ethanol (10ml.) was added. The mixture was shaken overnight. The liquid was diluted with water and a red/brown oil extracted with ether. No diamine could be isolated from this oil.

(b) Reduction with hydrogen over a fresh platinum catalyst.

2g. dried carbon powder and 80ml. absolute ethanol were placed in a 500ml. flask. .2M sodium chloroplatinite (2ml.) in ethanol was added and a solution of 1M sodium borohydride in ethanol (10ml.) was injected through a serum cap. The mixture was stirred at 25°C with a magnetic stirrer and the platinum formed in the reaction deposited on the carbon. After one minute 8ml. concentrated hydrochloric acid was injected to form a hydrogen atmosphere. 40 millimole of the osazone in ethanol was slowly added with much stirring and the hydrogen pressure kept at about atmospheric pressure by slow addition of sodium borohydride over one and a half hours.

The solution was stirred overnight and the filtrate after removal of carbon was red/brown. Acidification produced

an emulsion and so the whole was treated with 5N sodium hydroxide until basic, and the oil extracted with ether. Fractionation of the product after drying gave two liquids. Neither formed complexes with nickel salts and the infra-red spectra showed that $\text{N}=\text{N}$ peaks were present and also some decomposition and presumably polymerisation had occurred. Two other attempts also failed and the synthesis was abandoned.

B. Preparation of meso-stilbene diamine

(i) Preparation of hydrobenzamide.

Benzaldehyde (125ml.) was shaken with .880 aqueous ammonia (60ml.) for five hours in a 600ml. Buchner flask. The outlet was sealed and a rubber bung held in place by wire. The white solid formed was filtered, washed with water and dried in vacuo, yield 90%. A small quantity was recrystallised from aqueous ethanol and melted at 101°C (recorded Mpt. 101°C). The experiment was repeated six times, each yielding about 100gm. of hydrobenzamide.

(ii) Preparation of anarin, 2,4,5 triphenyl-2-imidazoline.

Hydrobenzamide (100gm.) was heated in a 500ml. bolthead flask for five hours at $120-130^{\circ}\text{C}$ in an oil bath.

The liquid turned yellow and set to a glass on cooling. Prolonged heating (nine to ten hours) yielded a more crystalline product and this modification was adopted, the experiment being repeated six times.

(iii) Preparation of benzoyl acetyl stilbene diamine.

To the crude amarin (100gm.) was added acetic anhydride (175ml.) and freshly fused sodium acetate (3gm.) and the whole was refluxed on an oil bath for three hours. The dark yellow solution was decanted whilst hot into 25ml. concentrated hydrochloric acid in 300ml. water. After about one minute the crude product precipitated. Filtration and then extraction of impurities with two portions of boiling ethanol (100ml.) yielded a white finely divided precipitate of benzoyl acetyl stilbene diamine which was dried at 120°C , yield 45%. A small portion was recrystallised from nitrobenzene, Mpt. 318°C (recorded 316°C).

(iv) Hydrolysis to form the diamine.

50gm. crude benzoyl acetyl stilbene diamine was heated with a 500ml. water/600ml. concentrated sulphuric acid mixture and the whole steam-distilled for about four hours to remove the benzoic acid. When all the benzoic acid had distilled over the solution was cooled and neutralised with .880 ammonia, much ice being required to cool the reaction

mixture, as otherwise very low yields were obtained. An off-white precipitate was formed and filtered. This was dissolved in water and reprecipitated with solid sodium hydroxide to yield pure meso-stilbene diamine. Yields varied from 3 to 6gm. (10-20%).

Mpt. = 118.5°C , recorded 119.5°C

Analysis found C, 79.22; H, 7.55%

$\text{C}_{14}\text{H}_{16}\text{N}_2$ requires C, 79.14; H, 7.59%

C. Preparation of p,p'-isopropyl meso-stilbene diamine.

The method described above for meso-stilbene diamine was used. p-isopropyl benzaldehyde (150ml.) was shaken with 70ml. .880 ammonia for seven days. The milky, gluey product could not be crystallised and was used in the next stage after washing with water.

The above product was heated at $120-130^{\circ}\text{C}$ for five hours to yield the amarin. This was refluxed with acetic anhydride (180ml.) and sodium acetate (3gm.) for three hours and poured into N hydrochloric acid (300ml.). The dirty white precipitate formed was filtered and then boiled out with much ethanol to yield benzoyl acetyl p-isopropyl stilbene diamine. The overall yield from two batches was 150gm. A portion was recrystallised from nitrobenzene and melted at 268°C .

Hydrolysis of this to produce the diamine proved difficult and very low yields were obtained. 50gm. batches were steam-distilled with 500ml. water/600ml. concentrated sulphuric acid. Eight to nine hours were required to remove the benzoic acid and the brownish liquid had a tarry skin. The acid strength was modified to minimize oxidation and optimum conditions were found to be 530ml. acid/500ml. water. The acid solution was poured into 5 litre beakers full of ice and neutralised with .880 ammonia. The dirty white precipitate was filtered from this alkaline solution and was extracted twice with 400ml. boiling water. This led to the formation of further tarry products and was modified, the liquid being extracted with ethanol and precipitated from slightly alkaline solution with water. The amine was precipitated from this by addition of solid sodium hydroxide. Total yield from three batches = 3.3gm., Mpt. = 119°C .

Analysis found C, 81.01; H, 9.47%

$\text{C}_{20}\text{H}_{28}\text{N}_2$ requires C, 80.98; H, 9.51%

D. Preparation of tris-(o-dimethylaminophenyl)phosphine, PTN.

(1) Methylation of o-bromaniline.

100gm. o-bromaniline and 100ml. water were stirred in a 1 litre flask as 73gm. dimethyl sulphate was slowly added.

The mixture was stirred until it became homogeneous. The solution was neutralised with potassium hydroxide (25%) with cooling in an ice-bath. A second portion of dimethyl sulphate (73gm.) was then added, with stirring, and after standing for one hour the acid was neutralised and a slight excess of base was added. A third equivalent of dimethyl sulphate was added and the mixture left to stand for one hour. The oily layer was extracted with ether, washed with water, dried over potassium carbonate and fractionated.

Yield = of fraction 100-102°C/12mm. 75.5gm., 60%

The infra-red spectra showed strong peaks indicative of N-H and NH_2 groups. This impurity was removed by acetylation followed by fractionation.

160ml. of the impure product was refluxed with 10gm. acetic anhydride for three hours. After cooling, ether was added and the whole extracted with three 350ml. portions of 1:1 hydrochloric acid. The acid solution was neutralised with 30% aqueous sodium hydroxide on ice and the amine extracted with ether. The ethereal solution was dried over potassium carbonate and fractionated under nitrogen. The fraction boiling at 99-102°C/11mm. was collected and had no primary or secondary amine group; total yield = 100gm., 50%.

(11) Attempted preparation of PTN via the Grignard reagent.

The apparatus required; a 1 litre 3 neck flask, stirrer, condenser, and tap funnel was dried overnight at 120°C together with 9.5gm. magnesium turnings. Ether was dried with sodium and then stood over and decanted from phosphorus pentoxide.

The magnesium was placed in the flask with about 100ml. ether under nitrogen and about 15ml. of the 75gm. o-bromodimethyl aniline in 150ml. ether was added. The reaction was difficult to initiate; an iodine crystal and liquid bromine both being unsuccessful; and 1,2 dibromethane being required. As the Grignard reagent was formed the flask was cooled in an ice-bath to maintain the ether at a gentle refluxing temperature.

The mixture was stirred for a further hour after the addition was complete and then 17.2gm. (11ml.) phosphorus trichloride in 100ml. ether and cooled in ice was slowly added to the flask which was maintained at -10°C in an acetone/ CO_2 bath. The addition took two hours and the contents were stirred and allowed to warm up to room temperature overnight.

The mixture was hydrolyzed by 100gm. ammonium chloride in 350ml. boiled-out water and the ether layer

separated. From this no PIN could be isolated by fractionation or extraction techniques.

(iii) Preparation of PIN via the lithio derivative.

(a) Preparation of a solution of n-butyl lithium.

The reactive nature of this reagent makes it imperative that all apparatus be perfectly dry and that a dry inert atmosphere be maintained. It was found to be preferable to use argon rather than nitrogen for this atmosphere. All apparatus was dried overnight at 120°C. A 500ml. flask fitted with a mechanically sealed stirrer, condenser, tap funnel, low-temperature thermometer mounted in a rubber bung, and argon inlet were assembled. Dry ether (200ml.) was placed in the flask and lithium (9.4gm.) was added. Hartley (18) used lithium wire but it was found preferable to hammer the metal to a thin sheet and cut it into strips with scissors. Much less oxide coating of the metal was caused in this way and the reaction proceeded more smoothly. The whole was stirred and a few ml. of a solution of n-butyl bromide (55ml.) in dry ether (100ml.) added from the tap funnel. As soon as a slight cloudiness in the solution and bright spots on the lithium indicated that the reaction was initiated the whole was cooled to -20 to -40°C in an acetone/solid carbon dioxide bath and the remainder of the n-butyl bromide added over one hour. The solution was

then allowed to warm up to -10°C , stirred for half an hour and finally cooled to -65°C before filtration, through a glass wool plug and then a sintered glass filter, under argon into a graduated tap funnel. Connections were made using PVC tubing and the solution forced through the filters by argon pressure. The volume of the solution was noted and then the concentration of butyl lithium determined by the method of Gilman as follows:-

1. 5ml. of the solution was added to 10ml. water in a conical flask and the solution titrated against 0.2N hydrochloric acid using phenolphthalein indicator, thus giving the total hydrolysable lithium.

2. 5ml. of the solution was added to a solution of 1ml. benzyl chloride in 10ml. dry ether. This reacted with the butyl lithium thus:



After one minute the mixture was treated with 10ml. water and titrated with 0.2N hydrochloric acid using phenolphthalein. This titre gave the hydrolysable lithium not present as butyl lithium.

In the above experiment, titre 1 = 45.7ml. titre 2 = 8.9ml., thus the strength of the n-butyl lithium solution

was $\frac{36.8}{5} \times \frac{N}{5} = 1.47N$. The total volume of solution was 240ml. which represents a 74% yield.

(b) Preparation of tris-(o-dimethylaminophenyl)
phosphine, PTN.

The apparatus consisted of a 2 litre flask containing butyl lithium solution and fitted with a mechanically sealed stirrer, condenser, tap funnel, thermometer and argon inlet. A dry argon atmosphere was maintained during the experiment and phosphorus pentoxide tubes fitted to condenser and tap funnel. The flask contained .25 mole of butyl lithium in ether and .25 mole of o-bromodimethyl aniline (50gm.) in 100ml. dry ether was added over one hour at -20°C . The mixture was allowed to warm to room temperature and stirred for another hour. It was then cooled to -40°C and phosphorus trichloride (53ml.) in 50ml. dry ether added dropwise over one and a half hours. The mixture was again stirred for one hour at room temperature and then cooled in ice/water and hydrolyzed with normal hydrochloric acid until the whole was acid. The acid aqueous layer was separated and the ether washed with more acid. The combined acid was neutralised in ice water with concentrated sodium hydroxide solution. The light brown oil was extracted with ether, washed with water and the ether solution dried over potassium carbonate. Ether was removed

at the pump under argon and the off-white precipitate recrystallised twice from ethanol to give the required product.

Yield = 21gm., 30% Mpt. 109°C

Analysis found C, 73.51; H, 7.46; N, 10.70; P, 7.89%

$\text{C}_{24}\text{H}_{30}\text{N}_3\text{P}$ requires C, 73.63; H, 7.72; N, 10.74; P, 7.91%

E. Preparation of bis(o-dimethylaminophenyl)phenyl phosphine, PDN.

The preparation of PDN was similar to that of PTN except that phenyldichlorophosphine was added in the last stage rather than phosphorus trichloride:-

The quantities employed were as follows: 0.1 mole butyl lithium solution (65ml.); 20gm. o-bromodimethylaniline in 50ml. ether; 6.8ml. phenyldichlorophosphine in 50ml. dry ether. The product was recrystallised from 80% aqueous ethanol.

Yield = 14.5gm., 45% Mpt. 84.5°C

Analysis found C, 75.62; H, 7.08; N, 8.03; P, 8.94%

$\text{C}_{22}\text{H}_{25}\text{N}_2\text{P}$ requires C, 75.83; H, 7.21; N, 8.04; P, 8.89%

F. Preparation of o-dimethylaminophenyl diphenyl phosphine, PH.

The preparation of PH was as above except that diphenylchlorophosphine rather than phosphorus trichloride

was added at the last stage. The quantities employed were as follows:-

0.25 mole n-butyl lithium solution (165ml.); 50gm. o-bromodimethylaniline in 50ml. ether; 0.25 mole diphenylchlorophosphine (44ml.). The product was recrystallised from ethanol as white needles.

Yield = 37gm., 55% Mpt. 113.5

Analysis found C, 78.36; H, 6.78; N, 4.62; P, 10.17%

$C_{20}H_{20}NP$ requires C, 78.66; H, 6.61; N, 4.59; P, 10.15%.

CHAPTER VI

PREPARATION OF THE COMPLEXES

1. Complexes of meso-stilbene diamine, m-stien.

A. COMPLEXES OF COPPER

(i) m-stien cupric dichloride $[m\text{-stien}_2\text{CuCl}_2]\cdot\text{H}_2\text{O}$

0.171gm. cupric chloride dihydrate was dissolved in 10ml. water and added to 0.424gm. m-stien in 50ml. boiling water. The solution turned deep blue and was filtered and concentrated in a vacuum desiccator over $\text{c.H}_2\text{SO}_4$. The dark violet/blue crystals were recrystallised from methanol.

Yield = 0.376gm., 64% M.pt. 231.5°C

Analysis found C, 58.43; H, 5.91; N, 9.71%

$\text{C}_{28}\text{H}_{34}\text{Cl}_2\text{N}_4\text{OCu}$ requires C, 58.28; H, 5.94; N, 9.71%

(ii) m-stien cupric dibromide $[m\text{-stien}_2\text{CuBr}_2]\cdot\text{H}_2\text{O}$

Cupric bromide (0.135gm.) in 10ml. water was added to 0.212gm. m-stien in 100ml. boiling water and the solution filtered. On cooling and concentration violet crystals were produced and these were recrystallised from methanol. On

standing over concentrated sulphuric acid these could be converted into a green form and were recrystallised from dry methanol in this form.

Yield (total) = 0.17gm., 49% M.pt. 233°C (both forms)

Analysis found for violet crystals C, 50.06; H, 5.19;

N, 8.24; Cu, 9.5%

$\text{C}_{26}\text{H}_{34}\text{Br}_2\text{N}_4\text{OCu}$ requires C, 50.50; H, 5.15; N, 8.41; Cu 9.5%.

This is the monohydrate. The green form shows no peak due to water in the infra-red spectrum and is the anhydrous dibromide.

(iii) m-stien cupric di-iodide [$\text{m-stien}_2\text{CuI}_2$]

$[\text{m-stien}_2\text{CuCl}_2] \cdot \text{H}_2\text{O}$ (0.19gm.) was dissolved in 80ml. boiling water and 20gm. (4 equiv.) potassium iodide was added. The solution was filtered immediately and after two minutes yielded a green microcrystalline powder.

Yield = 0.12gm., 54% M.pt. 212.3°C

Analysis found C, 45.41; H, 4.28; N, 7.12; Cu, 8.5%

$\text{C}_{26}\text{H}_{32}\text{I}_2\text{N}_4\text{Cu}$ requires C, 45.32; H, 4.35; N, 7.15; Cu, 8.6%

(iv) m-stien cupric dithiocyanate [$\text{m-stien Cu}(\text{SCN})_2 \cdot \text{H}_2\text{O}$]

To a solution of 0.1gm. $[\text{m-stien}_2\text{CuCl}_2] \cdot \text{H}_2\text{O}$ in 50ml. boiling water was added a concentrated aqueous solution of ammonium thiocyanate. The solution turned pale blue, a pale blue powder separating on boiling. This was recrystallised from methanol.

Yield = 0.08gm., 73% M.pt. 161.5°C

Analysis found C, 57.72; H, 5.28; N, 13.72%

$C_{30}H_{34}N_6O_8Cu$ requires C, 57.91; H, 5.51; N, 13.50%

(v) m-stien cupric dinitrate [$m\text{-stien}_2Cu(NO_3)_2$]

0.121gm. cupric nitrate in 10ml. water and 0.212gm.

m-stien in 50ml. water were mixed hot and filtered. On cooling deep lilac crystals separated and could be recrystallised from aqueous ethanol.

Yield = 0.197gm., 61% M.pt. 215°C, d.

Analysis found C, 54.73; H, 5.34; N, 13.81; Cu, 10.8%

$C_{28}H_{32}N_6O_6Cu$ requires C, 54.94; H, 5.27; N, 13.73; Cu, 10.9%

(vi) m-stien cupric diperchlorate [$m\text{-stien}_2Cu(ClO_4)_2$]

An aqueous solution of cupric perchlorate was prepared by addition of perchloric acid to 0.104gm. copper carbonate. The light blue solution was filtered into 0.212gm. m-stien in 50ml. boiling water and the whole turned lilac. This was filtered and on standing pink/lilac crystals separated and were recrystallised from methanol.

Yield = 0.363gm., 77% M.pt. 246.5°C, d.

Analysis found C, 48.88; H, 4.72; N, 8.01%

$C_{28}H_{32}Cl_2N_4O_8Cu$ requires C, 48.95; H, 4.70; N, 8.16%

(vii) m-stien cupric sulphate [$m\text{-stien}_2CuSO_4 \cdot H_2O$]

0.125gm. cupric sulphate and 0.212gm. m-stien were mixed in 200ml. hot water. A violet precipitate formed

immediately and could not be recrystallised. It was Soxhlet extracted with water to give the pure product.

Yield = 0.116gm., 39% M.pt. 260.5°C

Analysis found C, 55.50; H, 5.72; N, 9.01; Cu, 10.7%

$C_{30}H_{34}N_4O_9Cu$ requires C, 55.85; H, 5.70; N, 9.31; Cu, 10.6%

(viii) m-stien cupric diacetate



Aqueous solutions (50ml.) of 0.212gm. m-stien and 0.091gm. cupric acetate were mixed hot, filtered and concentrated over $C.H_2SO_4$. Lilac crystals were recrystallised from methanol.

Yield = 0.133gm., 44% M.pt. 197°C

Analysis found C, 61.81; H, 6.30; N, 8.51; Cu, 10.1%

$C_{32}H_{40}N_4O_5Cu$ requires C, 61.57; H, 6.46; N, 8.98; Cu, 10.2%

(ix) m-stien cupric dioxalate



m-stien (0.212gm.) and 0.08gm. cupric oxalate were refluxed in 50ml. water for twenty minutes filtered hot and on standing violet crystals separated. This was Soxhlet extracted with water for purification.

Yield = 0.06gm., 18% M.pt. 210°C, d.

Analysis found C, 57.07; H, 5.70; N, 8.38%

$C_{32}H_{36}N_4O_9Cu$ requires C, 57.21; H, 5.51; N, 8.38%

B. COMPLEXES OF PALLADIUM(i) m-stien palladous dichloride [$m\text{-stien}_2\text{PdCl}_2$]

1.1gm. m-stien and 0.456gm. palladous chloride were refluxed in 70ml. ethanol for four hours. The solution was filtered whilst hot and on cooling a white product separated^{at} and was recrystallised from ethanol.

Yield = 0.414gm., 28% M.pt. 249-51°C, d.

Analysis found Pd, 15.6%

$\text{C}_{28}\text{H}_{32}\text{Cl}_2\text{N}_4\text{Pd}$ requires Pd, 17.6%. The infra-red spectrum showed presence of - OH groups and the peaks persisted, though were reduced in intensity, even after pumping at 10^{-4} mm./60°C for seven days. Reanalysis gave Pd, 16.9% suggesting the inclusion of 1.5 - 1.75 moles ethanol in the crystal lattice in the unpumped sample.

(ii) m-stien palladous dibromide [$m\text{-stien}_2\text{PdBr}_2$]

Palladous bromide was prepared by the reaction of palladium powder with bromine in the presence of one drop of concentrated nitric acid. Excess bromine was removed by blowing with compressed air. 0.424gm. m-stien and 0.278gm. palladous bromide were refluxed in 60ml. ethanol for five hours. Filtration and cooling yielded a cream/white product which was recrystallised from methanol.

Yield = 0.1gm., 14% M.pt. 248-50°C, d. Again the infra-

red spectrum showed strong - OH peaks which could not be completely removed by pumping.

Analysis found Pd, 13.93%; after pumping 15.0%

$C_{28}H_{32}Br_2N_4Pd$ requires Pd, 15.3%.

(iii) Attempted preparation of $[m\text{-stien}_2PdI_2]$

0.300gm. sodium iodide in ethanol (10ml.) was added to 0.19gm. sodium chloropalladite in ethanol (20ml.) and the solution filtered into 0.212gm. m-stien in 20ml. ethanol. The off-white precipitate formed immediately and filtered and recrystallised from methanol. No palladium was present in what was presumably an amine salt.

(iv) m-stien palladium dithiocyanate



Palladous thiocyanate was prepared by the addition of 2gm. potassium thiocyanate to 3gm. sodium chloropalladite in 50ml. water. An orange precipitate of the thiocyanate was filtered from the blood-red solution. 0.073gm. palladous thiocyanate and 0.141gm. m-stien were warmed in ethanol. A white precipitate formed and was recrystallised from ethanol. Yield = 0.1gm., 47% M.pt. $210^{\circ}C$, d.

Analysis found Pd, 15.9%; after pumping Pd, 16.3%

$C_{30}H_{32}N_6S_2Pd$ requires Pd, 16.4%

(v) m-stien palladous dinitrate $[m\text{-stien}_2Pd(NO_3)_2]$

The sample of palladous nitrate available was crude and so a solution of this in cold ethanol was filtered into

0.848gm. m-stien in 100ml. ethanol until the colour was no longer discharged. The white powdered precipitate formed was recrystallised from methanol.

Yield = 0.9gm., 83% M.pt. $271-3^{\circ}\text{C}$, d.

Analysis found Pd, 14.6%; after pumping 15.6%

$\text{C}_{28}\text{H}_{32}\text{N}_2\text{O}$ Pd requires Pd, 16.2%. Hydroxyl peaks were not completely removed from the infra-red spectrum by pumping.

2. Complexes of p,p'-isopropyl meso-stilbene diamine, p-stien.

A. COMPLEXES OF NICKEL

(1) p-stien nickel dichloride $[\text{p-stien}_2\text{NiCl}_2] \cdot 4\text{H}_2\text{O}$

To 1.20gm. p-stien in ethanol was added 0.474gm. nickel chloride hexahydrate in ethanol. The solution was filtered and concentrated to 30ml., and on standing bright-yellow crystals separated. These were recrystallised from ethanol.

Yield = 1.35gm., 85% M.pt. 197°C

Analysis found C, 60.10; H, 8.45; N, 6.96; Ni, 7.43; H_2O , 9.04%

$\text{C}_{40}\text{H}_{64}\text{Cl}_2\text{N}_4\text{Ni}$ requires C, 60.38; H, 8.12; N, 7.05; Ni, 7.38;

H_2O , 9.07%. The yellow material was thus the tetrahydrate.

The water of crystallisation was removed by pumping at 10^{-4} mm./ 60°C for three days and the resultant green powdered material was the anhydrous chloride.

Analysis found C, 66.31; H, 8.16; N, 7.93; Ni, 8.07%

$\text{C}_{40}\text{H}_{56}\text{Cl}_2\text{N}_4\text{Ni}$ requires C, 66.49; H, 7.81; N, 7.76; Ni, 8.12%

(11) p-stien nickel di-iodide [$\text{p-stien}_2\text{NiI}_2$]. $2\text{H}_2\text{O}$

An ethanolic solution of nickel iodide was prepared mixing 0.15gm. nickel nitrate and 0.158gm. sodium iodide in ethanol, concentrating to 5ml. and filtering the cold solution. This was added to 0.296gm. p-stien in 30ml. ethanol. A yellow crystalline precipitate slowly formed and was filtered and recrystallised from ethanol.

Yield = 0.29gm., 65% M.pt. 251.5°C

Analysis found C, 51.56; H, 6.43; N, 6.12; Ni, 6.17%

$\text{C}_{40}\text{H}_{60}\text{I}_2\text{N}_4\text{Ni}$ requires C, 51.03; H, 6.42; N, 5.95; Ni, 6.23%

The complex was thus the dihydrate. Pumping the complex, as previously, to remove lattice water caused a break-up of the crystals but no colour change in this case; the anhydrous iodide was produced.

Analysis found C, 52.62; H, 6.12; N, 6.54; Ni, 6.47%

$C_{40}H_{56}I_2N_4Ni$ requires C, 53.06; H, 6.23; N, 6.19; Ni, 6.48%

B. COMPLEXES OF PALLADIUM

(i) p-stien palladous dichloride



0.624gm. p-stien and 0.089gm. palladous chloride were refluxed for two hours in 50ml. ethanol. The solution was filtered from a small quantity of palladium metal and slow evaporation yielded a white powdered precipitate. This was recrystallised from methanol.

Yield = 0.26gm., 32% M.pt. $224-6^\circ C$, d.

Analysis found C, 59.30; H, 7.71; N, 6.83%

$C_{40}H_{60}Cl_2N_4O_2Pd$ requires C, 59.57; H, 7.52; N, 6.95%. On pumping the product for seven days at 10^{-4} mm./ $60^\circ C$ the

lattice water was lost and the white anhydrous $[p-stien_2PdCl_2]$ remained.

Analysis found C, 62.10; H, 7.80; N, 7.14%

$C_{40}H_{56}Cl_2N_4Pd$ requires C, 62.35; H, 7.33; N, 7.28%

(ii) p-stien palladous dibromide



p-stien (0.25gm.) and palladous bromide (0.11gm.) were refluxed in 50ml. ethanol for two hours and the solution filtered hot and concentrated to 20ml. On standing a white

powdered precipitate formed and was recrystallised from ethanol.

Yield = 0.11gm., 24% M.pt. 260°C , d.

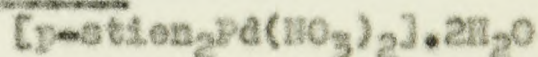
Analysis found C, 53.73; H, 6.78; N, 6.03%

$\text{C}_{40}\text{H}_{60}\text{Br}_2\text{N}_4\text{O}_2\text{Pd}$ requires C, 53.61; H, 6.76; N, 6.26%

(iii) Attempted preparation of [p-stien₂PdI₂]

0.312gm. p-stien refluxed with 0.180gm. palladous iodide and 0.1gm. KI in 50ml. ethanol yielded no solid product on evaporation of the filtrate to dryness. In each of several attempts brown oils and palladium metal were obtained.

(iv) p-stien palladous dinitrate



As with the m-stien complex an ethanolic solution of palladous nitrate was filtered into 0.25gm. p-stien in 30ml. ethanol until the colour just persisted. The solution was filtered and evaporated to small bulk. Addition of a little water produced a sticky white precipitate which was triturated with benzene to give a white powder.

Yield = 0.09gm., 25% M.pt. 262°C , d.

Analysis found C, 56.02; H, 7.14; N, 9.88%

$\text{C}_{40}\text{H}_{60}\text{N}_6\text{O}_8\text{Pd}$ requires C, 55.89; H, 7.02; N, 9.78%

C. COMPLEX OF COPPER

p-stien cupric dichloride [$p\text{-stien}_2\text{CuCl}_2$]. H_2O

p-stien (0.31gm.) and cupric chloride (0.085gm.) were mixed in 50ml. hot ethanol and the deep blue solution filtered. On standing a lilac powdered precipitate formed and was recrystallised from ethanol.

Yield = 0.21gm., 52% M.pt. 121°C , d.

Analysis found C, 64.30; H, 8.21; N, 7.60%

$\text{C}_{40}\text{H}_{58}\text{Cl}_2\text{N}_4\text{OCu}$ requires C, 64.12; H, 8.03; N, 7.73%

3. Complexes of tris(o-dimethylaminophenyl)phosphine, PTNA. COMPLEXES OF PLATINUM

(1) PTN platinumous dichloride [PTNPtCl_2]

0.455gm. Na_2PtCl_4 in 20ml. warm ethanol was filtered into a solution of 0.391gm. PTN in 20ml. hot ethanol. The solution was heated for two minutes and filtered to remove a

slight white precipitate. On standing a pale yellow crystalline precipitate formed and was recrystallised from n-butanol.

Yield = 0.269gm., 41% M.pt. 238°C , d.

Analysis found C, 43.88; H, 4.65; N, 6.27; P, 4.78; Pt, 29.51%

$\text{C}_{24}\text{H}_{30}\text{Cl}_2\text{N}_3\text{P}$ requires C, 43.83; H, 4.60; N, 6.40; P, 4.71; Pt, 29.69%

(ii) PTN platinumous dibromide $[\text{PTNPtBr}_2]$

A hot ethanolic solution of PTN platinumous chloride, prepared as above, was treated with 0.412gm. sodium bromide in 90% aqueous ethanol. The yellow solution (50ml.) was filtered after three hours to remove precipitated sodium chloride and the bromide slowly crystallised. The product was recrystallised from n-butanol as pale yellow needles.

Yield = 0.249gm., 33% M.pt. 232°C , d.

Analysis found C, 38.51; H, 4.06; N, 5.67; P, 4.23; Pt, 26.01%

$\text{C}_{24}\text{H}_{30}\text{Br}_2\text{N}_3\text{P}$ requires C, 38.61; H, 4.05; N, 5.63; P, 4.15; Pt, 26.15%

(iii) PTN platinumous di-iodide $[\text{PTNPTI}_2]$

A hot ethanolic solution of the dichloride, prepared as previously, was treated with 0.600gm. sodium iodide in 20ml. ethanol and filtered after five minutes. The chrome-yellow powdered precipitate was recrystallised from n-butanol.

Yield = 0.465gm., 55% M.pt. 216°C , d.

Analysis found C, 34.39; H, 3.69; N, 4.81; P, 3.61; Pt, 23.34%

$C_{24}H_{30}I_2N_3P$ requires C, 34.29; H, 3.60; N, 5.00; P, 3.69;

Pt, 23.23%

B. COMPLEXES OF PALLADIUM

(i) PTN palladous dichloride $[PTNPdCl_2]$

0.373gm. sodium chloropalladite in warm ethanol (20ml.) was filtered into 0.391gm. PTN in 20ml hot ethanol. The mixture was filtered after half an hour, and on standing for forty-eight hours two types of crystal separated as orange cubes and red needles. Phosphorus analysis on each was low so the whole was dissolved in a hot ethanol/butanol mixture and then evaporated to small bulk at the pump. A small quantity of yellow needles separated as $PTNPtCl_2$.

Yield = 0.08gm., 14% M.pt. $229^{\circ}C$, d.

Analysis found C, 50.89; H, 5.44; N, 7.28; P, 5.33%

$C_{24}H_{30}Cl_2N_3PPd$ requires C, 50.63; H, 5.31; N, 7.38; P, 5.44%

(ii) PTN palladous dibromide $[PTNPdBr_2]$

0.412gm. sodium bromide in 40ml. 90% aqueous ethanol was added to 0.373gm. Na_2PdCl_4 in 20ml. warm ethanol. The whole was then filtered into 0.391gm. PTN in 20ml. boiling ethanol. On standing overnight orange needles separated and were recrystallised from ethanol.

Yield = 0.406gm., 62% M.pt. $225^{\circ}C$, d.

Analysis found C, 43.65; H, 4.77; N, 6.32; P, 4.78%

$C_{24}H_{30}Br_2N_3PPd$ requires C, 43.80; H, 4.60; N, 6.39; P, 4.71%

(iii) PTN palladous di-iodide $[PTNPdI_2]$

0.600gm. NaI in 10ml. hot ethanol was added to 0.373gm. Na_2PdCl_4 in 20ml. ethanol and the mixture filtered into 0.391gm. PTN in 20ml. boiling ethanol. On standing, deep red needles separated from the dark solution. The complex was recrystallised from ethanol.

Yield = 0.32gm., 43% M.pt. $219^{\circ}C$, d.

Analysis found C, 38.53; H, 4.04; N, 5.92; P, 4.10, 4.18%

$C_{24}H_{30}I_2N_3PPd$ requires C, 38.32; H, 4.02; N, 5.59; P, 4.12%

C. COMPLEXES OF NICKEL

(1) PTN nickel dichloride $[PTNNiCl_2]$

0.238gm. $NiCl_2 \cdot 6H_2O$ in 20ml. ethanol was added to 0.391gm. PTN in 200ml. boiling butanol. The solution darkened in colour and then almost immediately a light green powder precipitated. This could not be dissolved in any solvent without decomposition.

Yield = 0.525gm., quantitative M.pt. $253^{\circ}C$, d.

Analysis found C, 56.06; H, 6.25; N, 8.50; P, 5.80; Ni, 11.18%

$C_{24}H_{30}Cl_2N_3PNi$ requires C, 55.32; H, 5.80; N, 8.06; P, 5.95;

Ni, 11.26%.

(ii) PTN nickel dibromide $[\text{PTNNiBr}_2]$

0.273gm. $\text{NiBr}_2 \cdot 3\text{H}_2\text{O}$ in hot butanol was added to 0.391gm. PTN in 200ml. boiling butanol. The colour darkened and over half an hour ochre-coloured needles precipitated. This could not be recrystallised.

Yield = 0.590gm., quantitative M.pt. 238°C .

Analysis found C, 48.23; H, 5.07; N, 6.80; P, 5.11; Ni, 9.41%

$\text{C}_{24}\text{H}_{30}\text{Br}_2\text{N}_3\text{PNi}$ requires C, 47.25; H, 4.96; N, 6.89; P, 5.08; Ni, 9.62%.

(iii) PTN nickel di-iodide $[\text{PTNNiI}_2]$

Commercial nickel iodide was found to be almost completely insoluble in ethanol, and so an ethanolic solution of this was prepared as follows: 0.325gm. sodium iodide in 20ml. butanol was added to 0.291gm. nickel nitrate in hot butanol. The iodide solution was cooled and filtered from the precipitated sodium nitrate into 0.391gm. PTN in 50ml. hot butanol, maroon needles slowly separated from the dark solution and were recrystallised from benzene.

Yield = 0.360gm., 53% M.pt. 211.5°C

Analysis found C, 40.78; H, 4.32; N, 6.26; P, 4.44; Ni, 8.52%

$\text{C}_{24}\text{H}_{30}\text{I}_2\text{N}_3\text{PNi}$ requires C, 40.94; H, 4.30; N, 5.98; P, 4.40; Ni, 8.34%

(iv) PTN nickel dithiocyanate $[\text{PTNNi}(\text{SCN})_2]$

0.194gm. potassium thiocyanate in 30ml. butanol was added to 0.291gm. nickel nitrate, hexahydrate, in 10ml. butanol.

The cold thiocyanate solution was filtered into 0.391gm. PTM in 20ml. hot butanol. A deep brown solution was formed but no precipitate separated. Evaporation at the pump gave a brown glass. Extraction with benzene gave a brown solution together with a small quantity of green crystals. From the solution maroon needles separated and were recrystallised from ethanol.

Yield = 0.09gm., 16% M.pt. 196°C , d.

Analysis found for maroon needles C, 55.54; H, 5.47; N, 12.26; P, 5.36; Ni, 10.48%

found for green powder C, 59.47; H, 5.69; N, 10.88; P, 4.70; Ni, 9.92%

$\text{C}_{26}\text{H}_{30}\text{N}_5\text{PS}_2\text{Ni}$ requires C, 55.14; H, 5.34; N, 12.36; P, 5.47; Ni, 10.36%

D. COMPLEXES OF COBALT

(1) PTM Cobalt dichloride $[\text{PTMCoCl}_2]$

0.238gm. cobalt chloride hexahydrate in 60ml. hot ethanol was added to 0.391gm. PTM in 20ml. boiling ethanol. On standing a royal blue crystalline precipitate slowly separated and was recrystallised from ethanol.

Yield = 0.462gm., 88% M.pt. 196°C

Analysis found C, 54.51; H, 5.80; N, 8.06; P, 6.02; Co, 11.38%

$\text{C}_{24}\text{H}_{30}\text{Cl}_2\text{N}_3\text{PCo}$ requires C, 55.29; H, 5.80; N, 8.06; P, 5.94; Co, 11.31%.

(ii) PTN Cobalt dibromide [PTNCoBr₂]

0.327gm. CoBr₂·6H₂O in 15ml. hot ethanol was added to 0.391gm. PTN in 15ml. boiling ethanol. The resultant deep blue solution slowly yielded blue crystals, which were recrystallized from ethanol.

Yield = 0.412gm., 68% M.pt. 182°C

Analysis found C, 47.5; H, 5.37; N, 6.62; P, 5.04; Co, 9.72%

C₂₄H₃₀Br₂N₃PCo requires C, 47.23; H, 4.96; N, 6.88; P, 5.08; Co, 9.66%

(iii) Attempted preparation of [PTNCoI₂]

An ethanolic solution of cobalt iodide was prepared by mixing 0.584gm. cobaltous nitrate and 0.30gm. sodium iodide in ethanol (20ml.). The cold solution was filtered and added to 0.782gm. PTN in 30ml ethanol. The hot solution was green, indicating complex formation, but on cooling the ligand crystallised out, concentration of the solution also led to decomposition.

E. COMPLEXES OF COPPER(1) PTN cuprous chloride [PTNCuCl]

Cuprous chloride was purified by precipitation from solution in concentrated hydrochloric acid by dilution with water, and was washed with water, ethanol and ether. 0.391gm. PTN was refluxed in 50ml. ethanol with 0.099gm. cuprous

chloride for three hours. The solution was concentrated to 10mls. at the pump and on standing lime green/yellow crystals were formed and recrystallised from ethanol.

Yield = 0.157gm., 27% M.pt. 171.5°C

Analysis found C, 57.95; H, 5.63; N, 8.77; P, 6.37%

$\text{C}_{24}\text{H}_{30}\text{ClN}_3\text{PCu}$ requires C, 58.77; H, 6.16; N, 8.57; P, 6.32%

(ii) PTN cuprous bromide [PTNCuBr]

0.391gm. PTN was refluxed with 0.145gm. CuBr in 50ml. ethanol for three hours. The solution evaporated at the pump and the yellow crystalline product recrystallised from ethanol.

Yield = 0.11gm., 20% M.pt. 175.5°C

Analysis found C, 53.77; H, 5.68; N, 7.82; P, 5.83%

$\text{C}_{24}\text{H}_{30}\text{BrN}_3\text{PCu}$ requires C, 53.88; H, 5.65; N, 7.86; P, 5.79%

(iii) PTN cuprous iodide [PTNCuI]

0.190gm. CuI was refluxed with 0.391gm. PTN in 50ml. ethanol. The solution was filtered and large yellow crystals separated on standing. The product was recrystallised from ethanol.

Yield = 0.32gm., 55% M.pt. 233°C

Analysis found C, 48.89; H, 5.75; N, 7.11; P, 5.28%

$\text{C}_{24}\text{H}_{30}\text{IN}_3\text{PCu}$ requires C, 49.53; H, 5.20; N, 7.22; P, 5.32%

4. Complexes of bis-(o-dimethylaminophenyl)phenyl phosphine, PDN

A. COMPLEXES OF PLATINUM

(i) PDN platinumous dichloride [PDNPtCl₂]

0.455gm. Na₂PtCl₄ in 30ml. warm ethanol was filtered into a solution of 0.347gm. PDN in 30ml. boiling ethanol. An immediate off-white precipitate was formed which was unchanged on prolonged refluxing. This was filtered and washed with water, ethanol and ether. The complex was purified by dissolving in methylene chloride and recrystallising from a methylene chloride/ethanol mixture, after filtration from a small quantity of platinum, as cream coloured microcrystals.

Yield = 0.325gm., 53% M.pt. 274°C

Analysis found C, 43.10; H, 4.11; N, 4.55; P, 5.07; Pt, 31.99%

C₂₂H₂₅Cl₂N₂Pt requires C, 43.00; H, 4.10; N, 4.56; P, 5.04;

Pt, 31.77%

(ii) PDN platinumous dibromide [PDNPtBr₂]

Sodium chloroplatinite (0.91gm.) and sodium bromide (0.824gm.) were mixed in 30ml. 90% aqueous ethanol. The cold bromoplatinite solution was filtered and added to 0.694gm. PDN in 30ml. boiling ethanol. Very pale yellow crystals separated after a few minutes and were recrystallised from methylene chloride/ethanol, the ethanol containing some sodium bromide.

Yield = 1.06gm., 76% M.pt. 272.5°C

Analysis found C, 37.38; H, 3.56; N, 3.65; P, 4.46; Pt, 27.90%

$C_{22}H_{25}Br_2N_2Pt$ requires C, 37.56; H, 3.58; N, 3.98; P, 4.40;

Pt, 27.75%

(iii) PDN platinumous di-iodide $[PDNPtI_2]$

0.600gm. sodium iodide in 10ml. ethanol was added to 0.455gm. Na_2PtCl_4 in 30ml. cold ethanol and the Na_2PtI_4 solution filtered and added to 0.347gm. PDN in 30ml. boiling ethanol. A yellow crystalline precipitate rapidly formed and was filtered and washed with water and methanol and dried. The product was recrystallised from ethanol/methylene chloride. Yield = 0.53gm., 66%. However, this product gave high analyses for P and Pt after repeated recrystallisations, errors increasing with the number of recrystallisations. Examination of the CsBr infra-red spectrum showed a peak at ca. 30 μ assigned to a Pt-Cl stretch, which increased in intensity with the number of recrystallisations. Presumably chloride ions are introduced from the methylene chloride. The substance was, therefore, dissolved in methylene chloride, filtered to remove a little metallic platinum and added to an ethanolic solution of sodium iodide; evaporation of the methylene chloride yielded chrome-yellow crystals of the pure product. Washing with water removed traces of sodium iodide. Yield = 0.46gm., 58% M.pt. 263.5°C

Analysis found C, 32.96; H, 3.14; N, 3.50; P, 3.92; Pt, 24.62%

$C_{22}H_{25}I_2N_2PPt$ requires C, 33.13; H, 3.16; N, 3.51; P, 3.88;

Pt, 24.48%.

B. COMPLEXES OF PALLADIUM

(i) PDN palladous dichloride $[PDNPdCl_2]$

0.522gm. PDN in 50ml. hot ethanol were mixed with 0.563gm. Na_2PdCl_4 in 50ml. ethanol. The deep orange solution was filtered and slowly yielded yellow microcrystalline precipitate. This was recrystallised twice from a mixture of methylene chloride and ethanol.

Yield = 0.61gm., 77% M.pt. $274^{\circ}C$

Analysis found C, 50.37; H, 4.53; N, 4.95; P, 5.98%

$C_{22}H_{25}Cl_2N_2PPd$ requires C, 50.23; H, 4.79; N, 5.33; P, 5.90%

(ii) PDN palladous dibromide $[PDNPdBr_2]$

0.417gm. NaBr in ethanol was added to 0.373gm.

Na_2PdCl_4 in ethanol and the bromopalladite solution filtered into 0.347gm. PDN in hot ethanol. The yellow solution (50ml.) slowly deposited a deep yellow crystalline precipitate, which was recrystallised from ethanol.

Yield = 0.47gm., 76% M.pt. $263^{\circ}C$, d.

Analysis found C, 43.61; H, 4.08; N, 4.75; P, 5.15%

$C_{22}H_{25}Br_2N_2PPd$ requires C, 42.97; H, 4.09; N, 4.56; P, 5.04%

(111) PDN palladous di-iodide $[\text{PDNPdI}_2]$

Ethanollic solutions (30ml.) of 0.373gm. Na_2PdCl_4 and 0.600gm. NaI were mixed and filtered into 0.347gm. PDN in hot ethanol (30ml.). On standing deep red needles separated and were recrystallised from ethanol.

Yield = 0.55gm., 78% M.pt. 254.5°C

Analysis found C, 37.22; H, 3.48; N, 3.68; P, 4.46%

$\text{C}_{22}\text{H}_{25}\text{I}_2\text{N}_2\text{Pd}$ requires C, 37.27; H, 3.55; N, 3.95; P, 4.37%

C. COMPLEXES OF NICKEL(1) PDN nickel dichloride $[\text{PDNNiCl}_2]$

Hot butanolic solutions of 0.238gm. $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ and 0.347gm. PDN were mixed. The dark red solution (200ml.) slowly deposited olive needles. The substance was sparingly soluble in solvents for recrystallisation, but the original precipitate proved to be analytically pure.

Yield = 0.242gm., 51% M.pt. 238°C

Analysis found C, 55.02; H, 5.48; N, 5.65; P, 6.55; Ni, 12.20%

$\text{C}_{22}\text{H}_{25}\text{Cl}_2\text{N}_2\text{Ni}$ requires C, 55.27; H, 5.27; N, 5.86; P, 6.48;

Ni, 12.28%

(11) PDN nickel dibromide $[\text{PDNNiBr}_2]$

0.273gm. $\text{NiBr}_2 \cdot 3\text{H}_2\text{O}$ in hot butanol was added to 0.347gm. PDN in hot butanol (200ml.). The deep red solution yielded a brown microcrystalline precipitate which could not be recrystallised.

Yield = 0.415gm., 73% M.pt. 225°C

Analysis found C, 46.79; H, 4.64; N, 4.83; P, 5.45; Ni, 10.30%

$C_{22}H_{25}Br_2N_2PW_i$ requires C, 46.60; H, 4.45; N, 4.94; P, 5.49;

Ni, 10.35%

(iii) PDN nickel di-iodide $[PDNNiI_2]$

0.281gm. $Ni(NO_3)_2 \cdot 6H_2O$ and 0.325gm. NaI were mixed in 20ml. cold butanol and the resultant NiI_2 solution was filtered into 0.347gm. PDN in 50ml. hot butanol. A black crystalline precipitate rapidly formed and was recrystallised from propanol.

Yield = 0.215gm., 32% M.pt. 209°C

Analysis found C, 40.05; H, 3.97; N, 4.60; P, 4.67; Ni, 8.92%

$C_{22}H_{25}I_2N_2PW_i$ requires C, 40.00; H, 3.81; N, 4.24; P, 4.69;

Ni, 8.88%

D. COMPLEXES OF COBALT

(i) PDN cobalt dichloride $[PDNCoCl_2]$

Hot ethanolic solutions of 0.526gm. PDN and 0.408gm. $CoCl_2 \cdot 6H_2O$ (30ml.) were mixed and left to stand for three hours. A deep blue crystalline precipitate formed and this was recrystallised from ethanol/methylene chloride.

Yield = 0.38gm., 58% M.pt. 210°C

Analysis found C, 55.05; H, 5.23; N, 6.03; P, 6.48, 6.56;

Co, 12.25%

$C_{22}H_{25}Cl_2N_2PCo$ requires C, 55.24; H, 5.27; N, 5.86; P, 6.65;
Co, 12.32%

(ii) PDN cobalt dibromide $[PDNCoBr_2]$

0.694gm. PDN in ethanol (20ml.) was mixed with 0.654gm. cobalt bromide hexhydrate in ethanol (10ml.). On standing green/blue crystals separated and were recrystallised from ethanol.

Yield = 0.47gm., 42% M.pt. $192^{\circ}C$

Analysis found C, 46.41; H, 4.49; N, 4.92; P, 5.46; Co, 10.52%

$C_{22}H_{25}Br_2N_2PCo$ requires C, 46.58; H, 4.44; N, 4.94; P, 5.48;
Co, 10.41%

(iii) Attempted preparation of $[PDNCoI_2]$

An ethanolic solution (20ml.) of cobaltous iodide was prepared, as before, from $Co(NO_3)_2 \cdot 6H_2O$ (0.584gm.) and NaI (0.30gm.). This was added to 0.694gm. PDN in 30ml. ethanol but, as with the PTN derivative, ligand crystallised out on cooling or concentration of the solution.

E. COMPLEXES OF COPPER

(i) PDN cuprous chloride $[PDNCuCl]$

0.694gm. PDN and 0.198gm. cuprous chloride were refluxed in 50ml. ethanol for four hours. The pale yellow solution was filtered hot and on cooling pale yellow crystals separated. These were recrystallised from ethanol.

Yield = 0.17gm., 20% M.pt. 205-8°C, d.

Analysis found C, 59.05; H, 5.47; N, 6.16; P, 7.04%

$C_{22}H_{25}ClN_2PCu$ requires C, 59.05; H, 5.63; N, 6.26; P, 6.92%

(ii) PDN cuprous bromide [PDNCuBr]

0.347gm. PDN and 0.143gm. CuBr were refluxed for four hours in 50ml. ethanol. The pale yellow solution was filtered and on standing very pale yellow crystals separated and were recrystallised from ethanol.

Yield = 0.34gm., 70% M.pt. 219.5°C

Analysis found C, 52.71; H, 5.12; N, 5.95; P, 6.35%

$C_{22}H_{25}BrN_2PCu$ requires C, 52.58; H, 5.30; N, 6.04; P, 6.30%

(iii) PDN cuprous iodide [PDNCuI]

0.347gm. PDN and 0.190gm. CuI were refluxed for four hours in 50ml. ethanol. The filtrate yielded a white crystalline precipitate which was recrystallised from ethanol.

Yield = 0.385gm., 72% M.pt. 232.5°C

Analysis found C, 48.0; H, 4.68; N, 5.20; P, 5.74%

$C_{22}H_{25}IN_2PCu$ requires C, 48.02; H, 4.71; N, 5.28; P, 5.75%

5. Complexes of o-dimethylaminophenyl diphenyl phosphine, PNA. COMPLEXES OF PLATINUM(i) PN platinumous dichloride $[\text{PNPtCl}_2]$

Warm ethanolic solutions of (50ml.) 0.462gm. PN and 0.683gm. $\text{Na}_2\text{PtCl}_4 \cdot 3\text{H}_2\text{O}$ were mixed and an amorphous off-white precipitate was produced. Both P and Pt analyses for this substance were bad and so recrystallisation was attempted by filtering a methylene chloride solution into alcohol and boiling off the CH_2Cl_2 . This produced platinum metal and so the experiment was repeated in the cold; methylene chloride being removed at the pump to yield a cream microcrystalline product.

Yield = 0.81gm., after recrystallisation 0.404gm., 48%

M.pt. 295°C

Analysis found C, 42.15; H, 3.48; N, 2.57; P, 5.42; Pt, 34.23%

$\text{C}_{20}\text{H}_{20}\text{Cl}_2\text{NPt}$ requires C, 42.03; H, 3.53; N, 2.45; P, 5.43;

Pt, 34.16%

(ii) PN platinumous dibromide $[\text{PNPtBr}_2]$

Sodium chloroplatinite (0.630gm.) and sodium bromide (0.55gm.) were mixed in 20ml. 90% aqueous ethanol and solution filtered and mixed with 0.410gm. PN in 30ml. hot ethanol. A very pale crystalline precipitate formed rapidly and this was

recrystallised from a methylene chloride-ethanol mixture, the ethanol containing some sodium bromide. The product was washed carefully with water and methanol to remove any traces of sodium bromide.

Yield = 0.56gm., 64% M.pt. 285°C , d.

Analysis found C, 36.58; H, 2.88; N, 2.19; P, 4.67; Pt, 29.62%

$\text{C}_{20}\text{H}_{20}\text{Br}_2\text{P}^+\text{Pt}$ requires C, 36.37; H, 3.05; N, 2.12; P, 4.69;

Pt, 29.56%

(iii) PN platinumous di-iodide $[\text{PNPtI}_2]$

0.683gm. $\text{Na}_2\text{PtCl}_4 \cdot 3\text{H}_2\text{O}$ and 0.9gm. NaI were mixed in ethanol and the cold solution (30ml.) filtered into 0.462gm. PN in 30ml. hot ethanol. An immediate ochre precipitate redissolved on boiling and chrome-yellow needles began to form. The product was extracted several times with 100ml. hot ethanol and the pure product thus obtained.

Yield = 0.61gm., 55% M.pt. 279°C

Analysis found C, 31.91; H, 2.86; N, 1.61; P, 4.16; Pt, 26.00%

$\text{C}_{20}\text{H}_{20}\text{I}_2\text{NPt}$ requires C, 31.84; H, 2.67; N, 1.86; P, 4.11;

Pt, 25.88%

B. COMPLEXES OF PALLADIUM

(1) PN palladous dichloride $[\text{PNPdCl}_2]$

0.462gm. PN was dissolved in 30ml. hot ethanol and 0.563gm. $\text{Na}_2\text{PdCl}_4 \cdot 3\text{H}_2\text{O}$ in 30ml. ethanol filtered into the solution. A chrome-yellow crystalline precipitate slowly

formed and was recrystallised from ethanol/methylene chloride, three recrystallisations were required to produce analytically pure material.

Yield = 0.4gm, 55% M.pt. 287-288°C, d.

Analysis found C, 49.84; H, 4.04; N, 3.08; P, 6.45%

$C_{20}H_{20}Cl_2NPPd$ requires C, 49.73; H, 4.17; N, 2.90; P, 6.41%

(ii) PN palladous dibromide $[PNPdBr_2]$

0.760gm. sodium chloropalladite and 0.824gm. sodium bromide were mixed in 90% aqueous ethanol (20ml.) and the solution filtered. This was added to 0.610gm. PN in 30ml. boiling ethanol and the solution deposited yellow crystals. These were recrystallised from dichloromethane/ethanol in the presence of sodium bromide.

Yield = 0.82gm., 73% M.pt. 284-5°C, d.

Analysis found C, 34.39; H, 3.69; N, 2.48; P, 5.35%

$C_{20}H_{20}Br_2NPPd$ requires C, 42.00; H, 3.53; N, 2.45; P, 5.41%

(iii) PN palladous di-iodide $[PNPdI_2]$

Ethanollic solutions of 0.56gm. $Na_2PdCl_4 \cdot 3H_2O$ and 0.9gm. NaI were mixed and filtered into 0.462gm. PN in hot ethanol (total volume, 60ml.). Red needles precipitated and were recrystallised from ethanol.

Yield = 0.89gm., 89% M.pt. 268°C

Analysis found C, 35.88; H, 3.12; N, 2.37; P, 4.70%

$C_{20}H_{20}I_2NPPd$ requires C, 36.07; H, 3.03; N, 2.10; P, 4.65%

C. COMPLEXES OF NICKEL(i) PN nickel dichloride $[PNNiCl_2]$

0.616gm. PN in hot butanol (200ml.) and 0.476gm. $NiCl_2 \cdot 6H_2O$ in butanol were mixed. The deep red solution deposited the brown microcrystalline product after three minutes. This could not be recrystallised.

Yield = 0.772gm., 89% M.pt. $245^\circ C$, d.

Analysis found C, 54.39; H, 4.55; N, 3.14; P, 7.08;

Ni, 13.27, 13.35%

$C_{20}H_{20}Cl_2NNi$ requires C, 55.22; H, 4.63; N, 3.22; P, 7.12;

Ni, 13.49%

(ii) PN nickel dibromide $[PNNiBr_2]$

Butanolic solutions (150ml.) of 0.616gm. PN and 0.546gm. $NiBr_2 \cdot 3H_2O$ were mixed and the deep red solution yielded a violet microcrystalline precipitate which could not be recrystallised.

Yield = 0.80gm., 77% M.pt. $238^\circ C$

Analysis found C, 45.97; H, 4.17; N, 2.82; P, 5.82; Ni, 11.15%

$C_{20}H_{20}Br_2NNi$ requires C, 45.85; H, 3.85; N, 2.67; P, 5.91;

Ni, 11.20%

(iii) PN nickel di-iodide $[PNNiI_2]$

NiI_2 was prepared by mixing ethanolic solutions of 0.582gm. $Ni(NO_3)_2 \cdot 6H_2O$ and 0.650gm. NaI, evaporating to

ca. 20ml. and filtering the cold solution. This was mixed rapidly with 0.616gm. PN in 20ml. hot ethanol and slowly yielded a black crystalline product from the deep red solution. This was analytically pure.

Yield = 0.58gm., 48% M.pt. 208°C

Analysis found C, 38.77; H, 3.48; N, 2.05; P, 5.01; Ni, 9.58%

$\text{C}_{20}\text{H}_{20}\text{I}_2\text{NPNi}$ requires C, 38.87; H, 3.26; N, 2.27; P, 5.01;
Ni, 9.50%

D. COMPLEXES OF COBALT

(i) PN cobalt dichloride $[\text{PNCoCl}_2]$

A mixture of 0.238gm. $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and 0.308gm. PN in ethanol gave a blue solution which was reduced in bulk to 20ml. at the pump. On cooling a blue crystalline precipitate separated. This was recrystallised from ethanol.

Yield = 0.216gm., 50% M.pt. 254°C

Analysis found C, 55.02; H, 4.47; N, 3.27; P, 7.04; Co, 13.46%

$\text{C}_{20}\text{H}_{20}\text{Cl}_2\text{NPCo}$ requires C, 55.19; H, 4.63; N, 3.22; P, 7.12;
Co, 13.54%

(ii) PN cobalt dibromide $[\text{PNCoBr}_2]$

Hot ethanolic solutions (30ml.) of 0.654gm. cobaltous bromide and 0.610gm. PN were mixed. The hot solution was filtered and, on standing, royal blue crystals separated and were recrystallised from ethanol.

Yield = 0.827gm., 78% M.pt. 219°C

Analysis found C, 45.62; H, 3.88; N, 2.76; P, 5.96; Co, 11.14%

$C_{20}H_{20}Br_2NPCo$ requires C, 45.83; H, 3.85; N, 2.67; P, 5.91;

Co, 11.22%

(iii) Attempted preparation of $[PNCuI_2]$

An ethanolic solution of CuI_2 prepared as previously was added to 0.610gm. PN in 30ml. ethanol. Again cooling and concentration of the solution led to precipitation of the free ligand.

E. COMPLEXES OF COPPER

(i) PN cuprous chloride $[PNCuCl]$

0.099gm. purified $CuCl$ and 0.305gm. PN were refluxed in 50ml. ethanol for four hours. The solution was filtered and the very pale green product recrystallised from ethanol.

Yield = 0.175gm., 43% M.pt. 168-9°C, d.

Analysis found C, 59.34; H, 5.00; N, 3.58; P, 7.70%

$C_{20}H_{20}ClNPCu$ requires C, 59.40; H, 4.99; N, 3.46; P, 7.67%

(ii) PN cuprous bromide $[(PN)_2CuBr]$

The preparation of $[PNCuBr]$ was attempted, refluxing 0.286gm. cuprous bromide with 0.610gm. PN in 50ml. ethanol for four hours. The hot solution was filtered and the white product which separated on cooling was recrystallised from ethanol.

This was shown to have the composition $[(\text{PN})_2\text{CuBr}]$.

Yield = 0.5gm., 67% M.pt. 224.5°C

Analysis found C, 63.57; H, 5.26; N, 3.55; P, 8.26%

$\text{C}_{40}\text{H}_{40}\text{BrN}_2\text{P}_2\text{Cu}$ requires C, 63.70; H, 5.34; N, 3.71; P, 8.23%

(iii) PN cuprous iodide $[(\text{PN})_2\text{CuI}]$

As above, attempted preparation of $[\text{PNCuI}]$ led to the formation of $[(\text{PN})_2\text{CuI}]$. 0.610gm. PN and 0.380gm. cuprous iodide were refluxed in 100ml. ethanol for four hours. The solution was filtered hot from some CuI and on cooling a white product separated. This was recrystallised from ethanol.

Yield = 0.32gm., 40% M.pt. 178°C , d.

Analysis found C, 59.76; H, 5.22; N, 3.35; P, 7.66%

$\text{C}_{40}\text{H}_{40}\text{IN}_2\text{P}_2\text{Cu}$ requires C, 59.96; H, 5.03; N, 3.50; P, 7.74%

(iv) Triphenylphosphine cuprous chloride
 $[(\text{C}_6\text{H}_5)_3\text{PCuCl}]$

Triphenyl phosphine (2.25gm.) and cuprous chloride (0.85gm.) were refluxed in ethanol (100ml.) for four hours. The solution was filtered hot and on cooling a white precipitate separated. This was recrystallised as white needles from methylene chloride/ethanol.

Yield = 2.58gm., 85% M.pt. 228.5°C

Analysis found C, 59.77; H, 4.18; P, 8.62%

$\text{C}_{18}\text{H}_{15}\text{ClPCu}$ requires C, 59.84; H, 4.19; P, 8.58%.

CHAPTER VII

ANALYTICAL METHODS

Micro-analytical methods were employed as only small quantities of pure compounds were prepared. Spectrophotometric methods were used and absorbance measured on a Unicam S.P.500 Spectrophotometer in 1 cm. "Infrasil" cells. "AnalaR" reagents were used throughout.

1. PLATINUM

Platinum was determined colorimetrically by the method described in "Chemical Analysis" by E. B. Sandell (83). The method was modified to allow the weighing out of larger quantities. It was found to be unnecessary to evaporate the acid ashing solutions to dryness to remove nitric acid as described by Sandell. Heating to small bulk in a Kjeldahl flask with hydrochloric acid several times, was found to be adequate.

The complex (10-20mg.) was heated with nitric acid (3ml.) and perchloric acid (3ml.) in a 100ml. Kjeldahl flask for two hours. The bulk was then reduced by vigorous heating until the perchloric acid fumed strongly. After cooling,

the solution was heated with three successive portions of concentrated hydrochloric acid (5ml.). The resulting solution was washed into a 500ml. volumetric flask with 50ml. hydrochloric acid and with distilled water. 100ml. of a stock solution of stannous chloride was added and the volume made up to 500ml. with distilled water, then being just less than 2M in hydrochloric acid. After at least twenty minutes the optical density was measured against a reagent blank at 403mμ.

Solutions: Acids used were A.R. grade. Stannous Chloride: The stock solution, molar in stannous chloride and 3.5M in hydrochloric acid was prepared by dissolving 920gm. $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ (A.R. grade) in 1,300ml. hydrochloric acid and diluting to 4 litres. The solution turned cloudy during dilution but gentle warming yielded a clear stock solution.

Calibration Curve: A series of solutions was prepared using Johnson and Matthey 'Specpure' ammonium chloroplatinate as a standard. A graph of absorbance at 403mμ against platinum concentration was found to obey Beer's Law over the range 0 - 40p.p.m., at least.

Interference: Nitric acid interferes but is completely removed by the above ashing method. Perchloric acid, hydrochloric acid, phosphorus and halogen caused no interference.

Theory: Treatment of an acidic solution of tetravalent platinum with stannous chloride solution yields yellow to orange products of uncertain constitution. The intensity of the colour is very dependent on the acid concentration. The maximum intensity occurs at about 0.3M HCl but the colour is more stable at acidities greater than 0.7M. The stannous chloride concentration has little effect on the colour intensity and a large excess is used. At low acidity small amounts of stannic chloride affect the colour but this has no effect in the 2M solution used.

2. PALLADIUM

The method of Menis and Rains (86) was employed. It could not be used to yield results with a spread of less than 3% and so later complexes were not analysed for palladium. Samples of the complexes expected to contain about 1mg. palladium were digested in evaporating basins with 6ml. mixed nitric and perchloric acids and then twice with 5ml. hydrochloric acid. The resulting solution was washed into a 500ml. volumetric flask with 20ml. hydrochloric acid and distilled water, 50ml. absolute alcohol were added and the whole diluted to about 400ml. with distilled water. Immediately before measuring the absorbance the α -furyl dioxime reagent was prepared and 20ml. added to the flask, the volume being made up to 500ml. with distilled water. The

absorbance was measured at 420m μ against a reagent blank and the maximum reading taken, after about four minutes.

Solutions: The α -furyl dioxime solution is unstable and was prepared immediately before use, it consisted of 1gm. α -furyl dioxime dissolved in 50ml. absolute alcohol and made up to 100ml. with distilled water.

Calibration Curve: Solutions were prepared using Johnson and Matthey "Specpure" ammonium chloropalladite and a graph of absorbance against Pd concentration at 420m μ plotted. It was a linear function up to 1mg. Pd in the solution.

Interference: Other elements present in the complexes caused no interference. However, the colour-producing complex tended to precipitate on the cell walls during measurement, this tendency increasing with Pd concentration and it was necessary to check the cell with a blank between solutions. The colour developed over two to three minutes and then faded more slowly. Thus a maximum reading must be taken.

3. NICKEL

Nickel was determined by the dimethylglyoxime - oxidising agent method of Claassen (87). 10-15mg. of complex was heated strongly for two hours with 4ml. mixed nitric and perchloric acids in a 30ml. Kjeldahl flask to destroy organic

matter. The solution was washed into a 250ml. beaker and neutralised with 2N sodium hydroxide solution. The following reagents were added: 2ml. citric acid (10% solution in water); 6ml. potassium persulphate (2% solution in cold water); 30ml. sodium hydroxide 2N; 4ml. dimethylglyoxime (1% solution in ethanol). The solution was heated in a water bath at 70-80°C for seven to eight minutes, cooled and made up to 500ml. in a volumetric flask with distilled water. The optical density of the red solution was measured at 465mμ against a reagent blank.

Calibration Curve: "Analar" nickel ammonium sulphate was used as a standard and solutions prepared. Beer's Law was obeyed up to 1.6mg. nickel.

Interference: No interference was observed from varying amounts of nitric or perchloric acids or other elements present in the complexes.

Theory: The nature of the coloured species is in doubt. A suggestion (88) that it is a complex of nickel II with an oxidation product of dimethylglyoxime is countered with by one (89) that it contains nickel III and dimethylglyoxime. Claassen (87) suggests that the ratio of nickel to dimethylglyoxime is 1:4 but gives neither structure nor oxidation state.

4. COBALT

The method of McNaught (90) was used, involving the formation of a red complex with nitroso - R salt (sodium 1-nitroso-2-hydroxynaphthalene-3,6-disulphonate).

The complex (10-15mg.) was heated for two hours with 4ml. mixed nitric and perchloric acids in a 30ml. Kjeldahl flask to destroy organic matter and the solution made up to 250ml. with distilled water. A 25ml. portion was treated with: 2.5ml. concentrated hydrochloric acid; 2.5ml. nitric acid (10%); 5ml. nitroso-R salt (0.2% aqueous solution); 10g. sodium acetate (hydrated). The solution was shaken to mix the reagents and heated in a boiling water bath for one minute, nitric acid (10ml.) added and the whole heated for a further minute. The solution was allowed to cool in the dark, made up to 100ml. and the absorbance measured at 500mμ against a reagent blank.

Calibration Curve: "AnalaR" cobalt chloride hexahydrate was weighed out as a standard and treated as above. Beer's Law was obeyed by solutions containing up to 10μg. of cobalt.

Interference: Neither nitric and perchloric acids nor other elements present interfered.

Theory: A complex anion is formed, soluble in water and stable in acid solution. The structure of this is

probably octahedral though doubt exists as to the oxidation state of the cobalt, being either II or III. The complex is only formed at $\text{pH} > 2.5$ and the purpose of the sodium acetate is to act as a buffer during complex formation, thereafter the addition of concentrated nitric acid will destroy complexes of other transition metal ions, if present. The solutions were allowed to cool in the dark before their absorbances were measured, because Olson (91) reports a fading of the colour in daylight.

5. COPPER

Volumetric estimation

(1) The method described in Volumetric Analysis (92) was used, ferrous iron being oxidised to the ferric state by cupric ions present and in the presence of thiocyanate, then back-titrated against standard mercurous nitrate.

The ferrous ammonium sulphate solution used as a reagent was shown to deteriorate overnight and so a fresh sample was prepared and the solutions standardised each day.

A 25ml. portion of standard ca. 0.01 N cupric sulphate solution was taken and 10ml. of the ferrous ammonium sulphate solution added (slight excess). Addition of 2ml. ammonium thiocyanate turned the solution red and it was made up to 0.5N in nitric acid by addition of 12ml. 2N nitric acid. A further 25ml. nitric acid (0.5N) was added to bring the

final volume up to 100ml, and the mixture titrated against standard mercurous nitrate until the colour was just discharged. The last 2ml. was added slowly, allowing about fifteen seconds between drops. Reproducible standardisation titres were obtained using this procedure.

The complex (0.12-0.15gm.) was weighed accurately and dissolved in 25ml. water; the other reagents were added as above. The blood-red solution was titrated with standard mercurous solution as above.

Solutions: 10ml. ferrous ammonium sulphate (1.2gm. in 100ml.); 2ml. ammonium thiocyanate (40% aqueous solution); mercurous nitrate 0.01N in 0.5N nitric acid.

Interference: No interference was observed from the amine or anions present.

This method gave good results but required ca. 0.5gm. pure complex to yield three titres and was thus impracticable as a general method. The method was attempted using 0.005 and 0.002N mercurous nitrate but the end point was no longer well defined under these conditions.

(11) The complexometric titration method of Malat and Suk (93) was used. The method involved titration of the unknown copper solution against a standard solution of disodium ethylene diamine tetra-acetic acid (EDTA.). This was first standardised by titration with a known bismuth solution.

Acidified bismuth nitrate solution (25ml.) was diluted to about 50ml. with water and 3 to 5 drops of pyrocatechol violet indicator added. The pH was then adjusted to 2-3 with 0.5N aqueous ammonia, until the solution had a blue rather than purple tint. This was titrated against the EDTA, until the solution turned yellow, just after a transient purple colour. The EDTA, was standardised by this method both at 0.1N and 0.002N concentrations.

The standardisation was then checked using a standard copper sulphate solution. To 50ml. of the solution (containing less than 10mg. copper) was added 0.5gm. ammonium nitrate, 4-5 drops indicator and the acidity adjusted with 0.5N aqueous ammonia until a blue colour just appeared. 1.5gm. sodium acetate was added and the whole titrated against standard EDTA. Correlation was fair (±2%), the weakness in the method lying in difficulties in estimating the blue to green transition at the end point.

The complex was treated as above, 20-30mg. being titrated against 0.002N EDTA. However, at this concentration results were not within the required limits.

Solutions: Disodium EDTA. dihydrate (37.21g./litre); bismuth nitrate (2.42gm./125ml. 0.5N nitric acid and dilute to 500ml. with water); pyrocatechol violet (0.1gm./100ml. water).

Interference: No interference was caused by the amine present. There is, however, interference from fluoride, chloride, phosphate, oxalate, artrate and citrate.

(iii) Recourse was then made to the colorimetric determination using dithizone as the reagent (41). This method involved extraction of copper from 0.1N acid solution by dithizone in carbon tetrachloride and measuring the colour of the organic phase.

5.7mg. copper complex was decomposed by ashing with mixed acid and with hydrochloric acid and then made up to 500ml. in 0.1N hydrochloric acid. 25ml. of this was diluted to 250ml. and 10ml. of the solution was placed in a pear-shaped stoppered flask. 5ml. 0.004% dithizone was added and the mixture shaken mechanically for two minutes, stood for one minute and the majority of the CCl_4 layer pipetted into a clean dry 1cm. cell. The solution was measured at 535m μ against a reagent blank.

Solutions: The 0.004% dithizone was prepared daily by dilution of a 0.01% solution in carbon tetrachloride which was stored in the dark.

Calibration Curve: This was constructed using a series of standard solutions of copper sulphate. Problems were encountered in that the slope of the curve was low. The 0.004% dithizone concentration used gave a better curve than the published method.

Interference: The wet-ashing method described gave rise to no interference. One problem encountered was the separation of water droplets on the cell faces from the CCl_4 solution. This was overcome by using warm cells. However, this method was limited by the low slope of the calibration curve and gave results with a spread of $\pm 2-3\%$.

6. PHOSPHORUS

The "heteromolybdenum blue" method was used. This was developed in this laboratory from the original method of Magnusson (94).

The complex (ca. 10mg.) was decomposed by heating for *two* hours in a 100ml. Kjeldahl flask with perchloric acid (5ml.) and a little ammonium vanadate (ca. 10mg.). The latter acts as a redox catalyst. The solution was transferred to a 250ml. volumetric flask. A 25ml. portion of this solution in a 100ml. flask was treated successively with concentrated sulphuric acid (3ml.), sodium molybdate solution (5ml.) and reductant solution 'R' (5ml.). The whole was diluted to ca. 80ml. with distilled water and the flasks heated in a boiling water-bath for seven to eight minutes to develop the blue colour, lead rings being used to weigh down the flasks. The flasks were cooled in a cold water-bath and made up to the mark.

The colours were determined at 825m μ against a reagent blank. The peak of the absorbance curve is rather sharp and it is advisable to set the wave-length scale to the absorbance maximum in the region 820-835m μ as the wave-length scale on the S.P.500 spectrophotometer used is only of $\pm 2-3\%$ accuracy.

Solutions: The sodium molybdate reagent contained 6gm. sodium molybdate dihydrate per 100ml.

The reductant 'R' was prepared by dissolving 76gm. sodium sulphate in 400ml. distilled water with slight warming. The solution was allowed to cool and 1gm. 1-amino-2-naphthol-4-sulphonic acid added. The reductant was then filtered into a dark bottle and was stable for one week.

Calibration Curve: The calibration substance used was disodium hydrogen phosphate which was treated as above. Beer's Law was obeyed up to 0.1mg. phosphorus in test solutions.

Interference: No interference was observed from perchlorate or vanadate, nor from any other elements present. The platinum complexes gave a cloudy solution but a 25ml. portion treated to develop the colour yielded a clear blue final solution, and analysis of a mixture of sodium phosphate and ammonium chloroplatinate gave accurate results.

Theory: The addition of sodium molybdate to the phosphorus solution gives a heteropolymolybdiphosphate, possibly of the structure $[\text{PMo}_{12}\text{O}_{40}]^{-3}$. This is reduced by the sodium sulphite to yield molybdenum blue. The structure of this is ^{not} known and it may or may not contain phosphorus. The same colour is given by arsenic with an identical calibration curve; and the molybdate can be reduced to the blue compound in the absence of phosphorus though this is less easy. Under the given conditions of acidity only the phosphorus-containing compound is reduced by the method described.

7. WATER

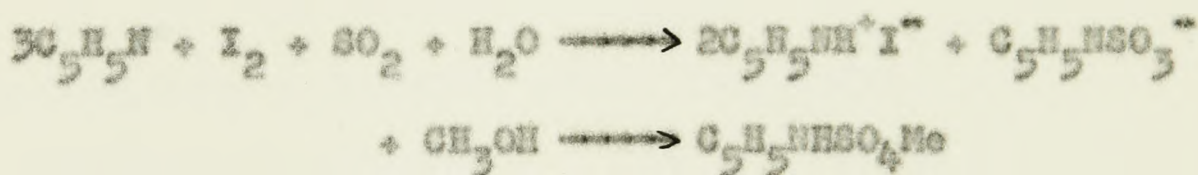
Water was determined by the Karl Fisher method using a commercial apparatus. 0.2-0.3gm. of complex was weighed accurately and quickly transferred to the enclosed beaker of the apparatus which was flushed with dry nitrogen. It was dissolved in 25ml. dry methanol and titrated with Karl Fischer reagent to the electrometric end-point. The amount of water present in the methanol was determined by a second titre. The Karl Fischer reagent was standardised as described below and thus the percentage water in the unknown was determined. This method was found to give an accuracy of 42% with fresh reagents, but suffered from the disadvantage of requiring large quantities of complex and so was not used generally.

Solutions: Karl Fischer reagent: consists of 3 moles SO_2 , 1 mole iodine, 10 moles pyridine in 100 volumes anhydrous methanol.

Standard solution of water in methanol: a 1 litre glass stoppered flask was filled to about 900ml. with anhydrous (less than 0.1% water) methanol and thermostatted at 25°C . About 15gm. water were accurately weighed into this and the volume made up with more methanol.

Calibration: The reagent was standardised using the standard methanol solution and this was checked against a known weight of pure sodium D-tartrate dihydrate.

Theory: The reaction between the reagent and water may be formulated:-



The reaction is followed electrometrically with a pair of bright platinum electrodes. Current flows as long as iodine is present as excess reagent to remove hydrogen and depolarise the electrodes. The solution was stirred with a magnetic stirrer during the titration.

8. CARBON, HYDROGEN and NITROGEN

Analyses for these elements were carried out by Dr. A. Bernhardt at the Max-Planck-Institut, ["]Mulheim,

West Germany. Carbon and hydrogen were determined gravimetrically as CO_2 and H_2O following combustion and the nitrogen by Dumas' method.

CHAPTER VIII

PHYSICAL MEASUREMENTS

1. Conductivity Measurements

These were carried out in approximately $10^{-3}M$ solutions of the complexes. The solvents used were redistilled nitrobenzene, nitromethane and acetonitrile. A cell having vertical electrodes of dark platinum was used for all measurements.

The cell constant was checked for each series by comparison with a standard pair of electrodes and was of the order of 0.3(0.29-0.34). Further confirmation using a standard aqueous solution of potassium chloride was performed occasionally. The temperature of the measurements was recorded.

2. Infra-red absorption spectra

The infra-red spectra of the complexes were recorded on a Perkin-Elmer model 221 spectrophotometer in the ranges 4,000-650 cm^{-1} (sodium chloride optics) and

14-40 μ (caesium bromide optics). The complexes were dispersed in nujol or hexachlorobutadiene mulls, between sodium chloride plates for the former region and on polythene discs between caesium bromide plates for the latter. Some of the infra-red spectra were taken by a laboratory technician. The assignments of observed bands were based on those given for similar compounds by Bellamy (95) and Cross (64).

3. Visible and Ultraviolet Absorption Spectra

The solid reflectance spectra were measured over the range 10,000-35,000 cm^{-1} on a manually operated S.P.500 Unicam spectrophotometer. The instrument was fitted with an S.P.540 diffuse reflection attachment and a disc of magnesium carbonate of the same area was used as a reference substance. The sample was finely ground in an agate mortar and spread on filter paper for the determination. Many of the complexes had strong absorption peaks in the range of the instrument and dilution of these with KCl led to a sharper, clearer spectrum. The complex was ground for ten minutes in an agate mortar with Analar KCl to give a ca.10% solution in solid potassium chloride. The spectra were plotted on an arbitrary density scale 'D' having no quantitative significance.

Solution spectra were determined on a S.P.700 Unicam recording spectrophotometer using 1cm. silica cells over the range $4,000-54,000\text{cm.}^{-1}$, the limits of range for individual solvents being less than these. The solutions were between 10^{-3} and 10^{-5} molar, the concentrations being adjusted to keep the optical density between 0.1 and 0.9.

4. Nuclear Magnetic Resonance Spectra

The NMR. Spectra of the platinum and palladium halide complexes of PN, PDN and PTN were investigated.

The solvents used were methylene chloride and, where necessary, deuteriochloroform. The results quoted in Table 4.7(p.142) for chemical shifts are given relative to an internal standard of tetramethylsilane as shifts to lower field in cps. The coupling constants are also given in cps. The spectrometer used was a Varian analytical NMR. spectrometer, Model A.60 with variable temperature system V-6057.

5. Magnetic Measurements

Magnetic susceptibilities were determined on a Faraday balance constructed in this laboratory by J. P. Day and J. G. Smith (96). An inhomogeneous magnetic field was generated by an electromagnet with wedge-shaped pole pieces. The sample (ca. 15mg.) was placed in a silica bucket

suspended between the poles of the magnet on a Sartorius microgravimetric balance. The displacement of the sample was nullified by an electric current passing through coils and providing a restoring force to the balance beam. The sample was weighed with the magnet current off and then again with current on. The weight was recorded by a pen recorder as the magnet was slowly lowered passed the sample. In this way a reproducible maximum deflection better than 0.5% was obtained. Measurements were carried out in vacuo except for the p-stien nickel compounds which dehydrated under these conditions. The apparatus was fitted with heating and cooling systems for determination of temperature dependence of the magnetism. Use was made of the high temperature range in a thermogravimetric determination of the amount of solvent in $[p\text{-stien}_2\text{NiCl}_2]$. The compound was weighed before and after pumping at 10^{-1} mm./60°C and the loss of weight determined.

In a Faraday balance, the gram susceptibility of the sample is given by the equation:

$$\chi_g = \frac{F}{W_g H \frac{dH}{dx}} \dots\dots\dots (1)$$

where F = force exerted on sample = change in weight of sample ΔW_g

W_s = weight of sample
 H^{dH}/dx = product of field strength and field gradient along the axis of symmetry of the field.

ΔW_s is known, since the deflection of the bucket alone may be determined and subtracted from the observed deflection; W_s is the observed weight less the weight of the bucket, and H^{dH}/dx must be determined using a series of standards where the value of χ_g is known accurately. The balance was calibrated with sodium chloride and the calibration checked with cobalt mercury thiocyanate. The value of χ_g obtained from equation (1), was multiplied by the molecular weight of the complex to give the molar susceptibility χ_M (uncorrected). This was then corrected for the diamagnetic contribution of the component atoms and ions from Pascal's constants (97) to give $\chi_{M \text{ corr.}}$ the true value of χ_M .

The effective magnetic moment is related to the molar susceptibility by the equation:

$$\chi_M = \frac{\mu_{\text{eff.}}^2 N_A^2}{3 k T} \dots\dots\dots (2)$$

where $\mu_{\text{eff.}}$ = the effective magnetic moment

N = Avogadro's number

T = absolute temperature, $^{\circ}\text{K}$.

β = Bohr magneton, $\frac{eh}{4mc}$

The magnetic moment was expressed in units of Bohr magnetons.

No correction was made for temperature independent paramagnetism.

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