SYNTHETIC AND PHYSICAL STUDIES OF METAL COMPLEXES WITH AMBIDENTATE PYRIMIDINE LIGANDS

by

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ABSTRACT

Complexes of pyrimidines containing exocyclic oxygen or sulphur atoms at the 2-position have been prepared and characterised to investigate the coordination properties of these ambidentate ligands. Complexes with molybdenum in a range of oxidation states were prepared giving a variety of types of product. Platinum(II) complexes, both with and without coordinating halide groups, were prepared and studied using conventional physical techniques, again the ligands showed diversity in their mode of coordination.

X-ray crystallography has been used to solve the structures of 3 complexes and an unusual crystallographic problem posed by bis(4,6-dimethylpyrimidine-2-thionato)platinum(II) is discussed.

A number of heteronuclear complexes containing Pt-M-Pt linear arrays (M=Mn,Cu,Co,Ni,Fe) with bridging pyrimidine bases have been studied using e.p.r, diffuse electronic and Mössbauer spectroscopy, to probe the electronic environment of the central metal atom. A related complex containing Pt-Cu units bridged by 1-methyluracil has also been investigated using e.p.r. and shows an unexpected magnetic exchange interaction between neighbouring copper sites.

ACKNOWLEDGEMENTS

I have been fortunate in that, throughout this project, the people I worked with were always willing to give advice when it was sought. I am particularly indebted to Dr. D.M.L. Goodgame for his guidance and support throughout the project. I am also most grateful to Dr. A.C. Skapski who supervised my crystallographic work. Many thanks are also due to Dr. B. Lippert who provided such interesting complexes to probe spectroscopically and was willing to share them. Without the help of these people this thesis would undoubtedly be very different.

Many other people have influenced me during the course of this work, their contributions range from technical support and specialist advice to criticism, ideas and good company. Thanks are due to all of them.

Finally, the award of a Science and Engineering Research Council Studentship is gratefully acknowledged.

R.W.R.

To My Family

To My Friends.

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ABBREVIATIONS

2OPymH	Pyrimidine-2-one
1Me2OPym	1-Methylpyrimidine-2-one
$4,6Me_2$2OPymH	4,6-Dimethylpyrimidine-2-one
$1,4,6Me_3$2OPym	1,4,6-Trimethylpyrimidine-2-one
2SPymH	Pyrimidine-2-thione
1Me2SPym	1-Methylpyrimidine-2-thione
$4,6Me_2$2SPymH	4,6-Dimethylpyrimidine-2-thione
$1,4,6Me_3$2SPym	1,4,6-Trimethylpyrimidine-2-thione
py	Pyridine
acacH	2,4-Pentanedione
pyz	Pyridazine
en	1,2-diaminoethane
1MeTH	1-Methylthymine
1MeUH	1-Methyluracil
1MeCH	1-Methylcytosine
2,2dmp	2,2-Dimethoxypropane
1,1,3,3tep	1,1,3,3-Tetraethoxypropane

CHAPTER 1

INTRODUCTION

1.1 OVERVIEW

The metal complexes of pyrimidinones and pyrimidinethiones are of particular interest because they provide an opportunity to study the coordination of N/O and N/S ambidentate donor systems while, at the same time, they can provide insight into the interactions between metals and some biologically relevant molecules.

The aims of the work presented here were to synthesize some new transition metal complexes of these ligands, to probe such complexes using a variety of spectroscopic and other physical techniques, and to investigate the possible reactivity of some of them. So, although the biochemical relevance was borne in mind, the primary source of interest in these ligands for this study was in the unusual chemical structures and behaviour their complexes might possess.

1.2 THE LIGANDS

The pyrimidines are a very important group of heterocyclic compounds and have been subject to much study over many years because of their occurrence in living systems and because some of their derivatives

show biological activity.

Pyrimidine chemistry is extensive; the accounts by Brown [1,2] provide an excellent survey of the subject while, more recently, Hurst has produced a useful introduction to the field with particular emphasis on the biological and biochemical aspects [3]. A brief discussion of some of the important basic properties of the pyrimidines used in the work presented here is given below, while the books referred to above give a much more complete description.

The numbering system associated with pyrimidine ligands is shown in Figure 1.2, together with some representative structures of ligands used in this work. As well as systematic names, some pyrimidine derivatives have trivial names which are in common use; the structures of such ligands which were used in this project are shown in Figure 1.3.

1.2.1 Important Properties

The ligands studied in this work all have at least one exocyclic group, the ring always being substituted at the 2-position, ortho to the two ring nitrogens, by oxygen or sulphur. An important feature of some of these ligands is their tautomerism. For example, pyrimidine-2-one exists in an equilibrium between two tautomeric forms (Figure 1.1 below).

Figure 1.1 Tautomerism of Pyrimidine-2-one.

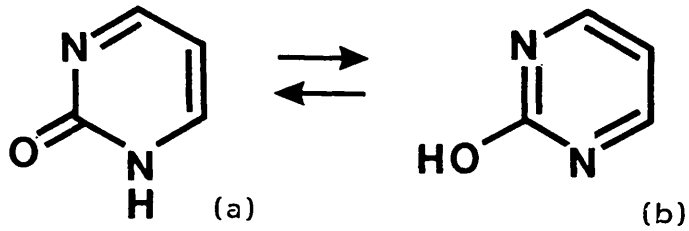
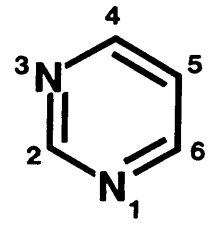
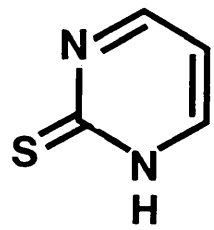


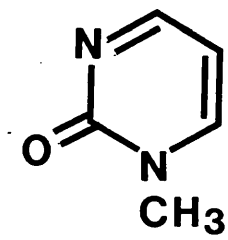
Figure 1.2 Representative Structures Of Ligands Used In This Project.



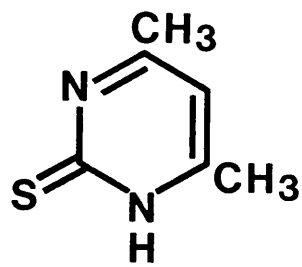
Pym



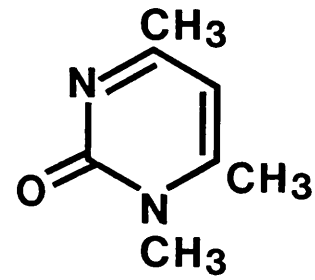
2SPymH



1Me2OPym

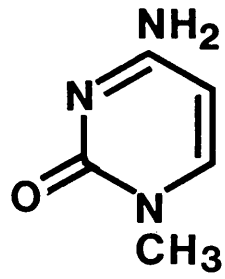


4, $6Me_2$2SPymH

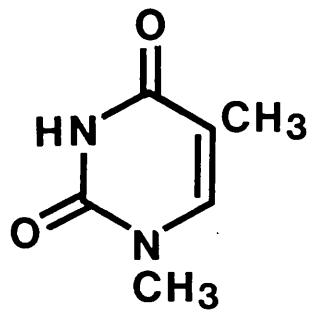


1, 4, $6Me_3$2OPym

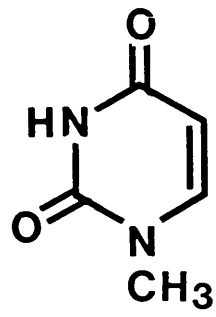
Figure 1.3 Ligands With Trivial Names Used In This Project.



1-Methylcytosine



1-Methylthymine



1-Methyluracil

Early studies suggested that pyrimidinones existed largely as the pyrimidinol form (Figure 1.1b) [4], but later work using i.r. and UV spectroscopy showed that they existed predominantly in the pyrimidinone form (Figl.1a) [5,6]. This has been confirmed more recently by using n.m.r. [7]. Similarly, the pyrimidine-2-thiones exist in the thione, rather than the thiol form [8]. A review of the tautomerism of biologically important pyrimidines has been published [9] and a more general account of the tautomerism of heterocycles is also available [10].

Pyrimidinones and thiones with an proton at N(1) will ionize as acids. Pyrimidine-2-one has an acidic pK_a of 9.17 while pyrimidine-2-thione is more acidic with pK_a 7.14. Ring methylation reduces the acidity of the molecules. Pyrimidine-2-one is a stronger base than pyrimidine (basic pK_a 2.24 compared with 1.31) but rather weaker than pyridine (pK_a 5.2), pyrimidine-2-thione is less basic with pK_a 1.35 and, again, methylation increases basicity. Obviously the N-methylated molecules do not have the options of acidic ionization or tautomerism open to them.

1.2.2 Biological Importance Of The Pyrimidines

Pyrimidines are major constituents of DNA and RNA, used in nature in the genetic material in cell reproduction and protein synthesis. The most common of the pyrimidines are thymine, uracil and cytosine (Fig 1.3). In addition to these extremely important compounds, pyrimidines are widespread in nature in a wide variety of forms too numerous to review here. There are a number of excellent books and reviews available, however [1-3,11,12].

1.2.3 Commercial Value Of Pyrimidines

Pyrimidines form the basis for a large number of pharmaceuticals. Thiouracil shows antithyroid activity [14], diaminopyrimidines are used as antimalarials [15], pyrimidine-2-thione itself shows antibacterial and antitumour action [16], while the barbiturates have been used medically for many years. Pyrimidines have also found use in pest control and as agricultural chemicals [17,18].

1.3 MODES OF COORDINATION

The pyrimidine-2-ones and -thiones have the capacity to coordinate to metals in a surprising variety of ways when one considers the simplicity of these molecules. Examples of almost every conceivable coordination mode have been established for this 'family' of ligands.

1.3.1 Complexes Of Pyrimidinones And Pyrimidinethiones

The molecules may act as simple, monodentate ligands, coordinating solely by the exocyclic oxygen or sulphur atom - as is the case with (Me)(2SPym)Hg and $CuCl(2SPymH)_2$ [19,20].

The N(3) nitrogen atom is available as a donor in both the N-methylated ligands and those which have a hydrogen at the N(1) position - the 'proton-labile' ligands. In some cases only the ring nitrogen coordinates e.g. in the complex $Cu(2OPymH)_4[ClO_4]_2$, which has been structurally characterised as the ethanol solvate [21]. N(3) coordination has also been shown for the acetone solvate of the complex $Zn(1Me2SPym)_4[ClO_4]_2$ [22].

For the deprotonated ligands, N(1) and the exocyclic O/S may coordinate simultaneously, either to the same metal, giving a chelate complex such as $Co(4,6Me_2 2SPym)_3$ (isolated as the acetone solvate) [23], or to two metal centres - acting as a bidentate bridge, as in $Mo_2(4,6Me_2 2SPym)_4$ [24].

Finally there is the unusual case of $Cu_4(1Me2SPym)_6[BF_4]_4$ where the planar array of copper(I) atoms is linked by the six ligands in three different coordination modes. One pair of ligands act as monodentate sulphur donors, another pair bridge pairs of copper atoms via the exocyclic sulphur group while the final pair also bridge two copper centres via sulphur but at the same time bind to a third copper atom via the non-methylated nitrogen [25].

1.3.2 Metal Complexes With Other Pyrimidine Bases, Nucleosides And Nucleotides.

In recent years, with the growth of biochemistry and molecular biology, inorganic chemists have become increasingly interested in the interaction of metal ions with various biological molecules, especially aminoacids, polypeptides and proteins - as possible models of metalloenzymes - and with nucleotides, nucleosides and their related bases because of their importance in protein synthesis and in cell reproduction.

An important group of complexes with pyrimidine-based ligands is that of their platinum complexes. Interest has been aroused chiefly because of the antitumour action of some platinum chemicals - these complexes are discussed more fully in chapters 2 and 4.

Other work of note in this field is that of Kistenmacher et al. who have characterised a number of pyrimidine-based complexes of copper and silver [26-30]. The copper(I) complex of bis(2-pyrimidyl)disuphide is known. The ligand bridges the copper centres via nitrogen, giving rise to polymeric sheets [31]. Organometallic complexes with pyrimidine ligands have been isolated e.g. $2,4S_2Pym[Ti(\eta^5Mecp)_2]$ - the dithiopyrimidinate chelating each titanium via N and S [32].

Recently, interest has grown in the complexes of nucleotides and nucleosides with transition metals [33-35]. Platinum complexes in this class are discussed in chapter 4.

Thus it may be seen that the study of the complexes of the pyrimidinones and thiones is of interest because of their diverse coordination chemistry and because of their relationship to a large group of biologically active molecules. The work here describes the synthesis and characterisation of some complexes of these ligands with platinum and molybdenum, together with a spectroscopic study of a number of mixed-metal complexes with the metal centres bridged by pyrimidine-based ligands.

CHAPTER 2

PLATINUM COMPOUNDS

Previous studies of the complexes of the 2-oxo- and 2-mercapto-pyrimidine ligands had been restricted mainly to those of first row transition elements [36,37]. As part of the present work we wished to study the complexes of some of the heavier metals with these ligands.

Platinum was selected for investigation for a number of reasons. Platinum(II) represents a fairly simple system, almost invariably forming square planar complexes. Much work has been done analysing the *trans* effect and *trans*-influence of various donor molecules in such complexes. Square-planar complexes of Ni(II), Pd(II) and Pt(II) have been studied in depth as they catalyse a large number of reactions [38]. Interest has been further stimulated by the discovery of the anti-tumour activity of *cis*-$Pt(NH_3)_2Cl_2$ and other *cis*-$PtCl_2L_2$ complexes (L= neutral N-donor ligand) [39-44]. Much work has also been carried out investigating the platinum complexes of nucleic acid bases, nucleosides and nucleotides - this is discussed in chapter 4.

More recently, attention has been focussed on platinum complexes which consist of linear stacks of square-planar platinum moieties with extended metal-metal interactions along, but not between, the stacks. Such complexes exhibit highly anisotropic "one-dimensional" conductive properties [45].

2.1 PLATINUM IN OXIDATION STATE +2

Platinum is most commonly found in the +2 oxidation state. In this oxidation state the main coordination geometry is square planar. Divalent platinum, having eight d-electrons, thus leaves one orbital ($d_{x^2-y^2}$) vacant.

K_2PtCl_4 provides a useful, water-soluble source of platinum(II) while $[PtI_4]^{2-}$ is more susceptible to reaction, the iodide ions being more labile than chloride.

An important feature of substitution reactions of platinum(II) complexes is the trans effect. This is the effect of a coordinated group on the rate of the substitution reactions of ligands opposite to it in a metal complex [47]. The cause of the trans effect has been a source of debate but it seems to be a combination of two ligand properties. Ligands exhibit a large trans effect if they are strong σ-donors or high π-acceptors, an approximate order of decreasing labilising ability is:

$C_2H_4 \approx CN^- > R_3P > SC(NH_2)_2 > I^- > Br^- > Cl^- > NH_3 \approx py > OH^- > H_2O$

A series of experiments was carried out reacting K_2PtCl_4 and $[PtI_4]^{2-}$ with a number of pyrimidinones and thiones. The results of these experiments are summarised in Table 2.1.

Table 2.1 Platinum Complexes of Pyrimidine-2-ones and -thiones

Platinum Source / Ligand	K_2PtCl_4	$[PtI_4]^{2-}$
2OPymH	$PtCl_2L_2$	PtI_2L_2
1Me2OPym	$PtCl_2L_2$	PtI_2L_2
$4,6Me_2$2OPymH	$PtCl_2L_2$	-
$1,4,6Me_3$2OPym	$PtCl_2L_2$	-
2SPymH	$PtL'_2Cl_{0.8}$	$(PtL'_2I)_2$
1Me2SPym	$PtCl_2L_2$	PtI_2L
$4,6Me_2$2SPymH	PtL'_2	PtL'_2
$1,4,6Me_3$2SPym	$PtCl_2L_2$	-

L′ represents deprotonated ligand in the table above.

Table 2.2 Infrared Absorptions For Platinum Complexes In The Region 300-400cm^{-1}

Complex	Observed peaks (cm^{-1})
$PtCl_2(2OPymH)_2$	337, 345
$PtCl_2(1Me2OPym)_2$	337
$PtCl_2(4,6Me_2 2OPymH)_2$	325 (broad)
$PtCl_2(1,4,6Me_3 2OPym)_2$	323, 318 (shoulder)
$PtCl_{0.8}(2SPym)_2$	300
$PtCl_2(1Me2SPym)_2$	324
$Pt(4,6Me_2 2SPym)_2$	-
$PtCl_2(1,4,6Me_3 2SPym)$	318, 310 (shoulder)

2.1.1 Complexes With Pyrimidine-2-ones.

As expected, the reactions of K_2PtCl_4 with pyrimidine-2-ones yielded complexes of stoichiometry $PtCl_2L_2$ in each case. The infrared spectrum of the complex with 2OPymH showed the Pt-Cl stretching modes resolved into two components, both strong, at 336 and 346cm^{-1}. This is indicative of the complex being in the cis-configuration, the bands observed being tne A_1 and B_2 modes. The other compounds each showed a broad, strong band (width at half-height typically 25cm^{-1}) which were not resolved into two distinct components. Even so, these compounds are tentatively assigned the cis-configuration as the ligands would certainly bind via nitrogen and the kinetic trans effect would favour the formation of the cis-isomer. This reasoning assumes that the steric effect of the first-bound ligand does not interfere with further ligand substitution to such an extent as to overcome the trans effect. There are many cases known where similarly substituted pyrimidine rings have been shown to bind in the cis-configuration (e.g. 1MeUra and 1MeThy - see chapter 4) so it is not unreasonable to predict that that configuration is favoured here.

The iodide analogues of the 2OPymH and 1Me2OPym complexes were isolated but the more heavily substituted pyrimidinones did not yield complexes before platinum started to deposit from the $[PtI_4]^{2-}$ solutions. The greater methyl substitution of these ligands would be expected to make the nitrogen a better σ-donor (by the inductive effect) so the slowness in complex formation for these complexes must be due to steric effects. For the iodide complexes which were isolated the Pt-I bands could not be observed in the infrared spectrum as they were at too low a frequency. The configuration for these complexes is assumed to be cis for the reasons given above for

the chloride complexes.

2.1.2 Complexes With Pyrimidine-2-thiones.

The pyrimidinethiones provided some rather more interesting chemistry than the oxygen analogues. Reactions of K_2PtCl_4 with the N-methylated pyrimidinethiones yielded yellow products, which resembled their oxygen analogues in having $PtCl_2L_2$ stoichiometry. The metal-halogen bands were at slightly lower frequency ($324cm^{-1}$ for the 1Me2SPym complex and $318cm^{-1}$ for the $1,4,6Me_3$2SPym compound) than for the corresponding oxygen compounds, but, again, the band could not be resolved into more than one distinct component, although the spectrum of $PtCl_2(1,4,6Me_3 2SPym)_2$ showed a shoulder at c.a. $310cm^{-1}$.

The ligands presumably coordinate via sulphur (as with thiourea and K_2PtCl_4); the <u>trans</u> effect would then be expected to favour formation of the <u>trans</u> compound. If <u>trans</u> were the favoured configuration, there should only be one infrared-active Pt-Cl stretch , assuming that the resulting complex was rigorously centrosymmetric. The shoulder observed in the Pt-Cl stretching region would seem to indicate a <u>cis</u> configuration, but, without other evidence or precedent, no definite assignment can be made. As the $1,4,6Me_3$2SPym is heavily substituted it is possible that the second band may be a ligand band activated on coordination, or the molecule, even if in the <u>trans</u> configuration, may not be rigorously centrosymmetric allowing two Pt-Cl stretches to be observed.

2.1.2.1 Reactions With Pyrimidine-2-thione - Reaction of K_2PtCl_4 with 2SPymH gave a yellow precipitate which redissolved rapidly in the reaction mixture before a scarlet compound, analysing as $Pt(2SPym)_2Cl_{0.8}$ was formed. More interesting still, was the reaction of $[PtI_4]^{2-}$ with 2SPymH in hot methanol/water. (A compound with similar stoichiometry was obtained by carrying out the reaction with K_2PtCl_4 anaerobically.) Again a yellow precipitate formed in seconds but rapidly re-dissolved as the reaction mixture became deep crimson-red. On standing, a red powder precipitated and, when the mother liquor was refrigerated, very dark red crystals formed. Both the crystals and the red powder analysed as $Pt(2SPym)_2I$. When the reaction was carried out anaerobically the yellow primary product was isolated. This was quite stable in air when dry, analysed as $Pt(2SPym)_2$, and did not decompose on stirring in methanol/water. The diamagnetic crystals of $Pt(2SPym)_2I$ were stable in air, virtually insoluble in water but partially soluble in alcohol. The crystals were suitable for crystallography and so the structure of this complex was solved using X-ray methods.

2.1.2.2 Crystal Data For $Pt_2(2SPym)_4I_2$ - $C_{16}H_{12}I_2N_8Pt_2S_4$, $\underline{M}$=1088.6, monoclinic, $\underline{a}$=15.874(4), $\underline{b}$=9.729(2), $\underline{c}$=15.983(3)Å, β=98.02(2)°, $\underline{U}$=2444.2Å^3 (at 18°C), space group $P2_1/c$, Z=4, D_c=2.96gcm^{-3}. X-ray diffraction data consisted of 2505 independent reflections (to θ=50°) of which 461 were "unobserved". The structure was solved by Patterson and Fourier methods, and least-squares refinement reached R=0.043.

The structure, shown in figures 2.1 and 2.2, was found to be binuclear. The two platinum atoms are each bound to the four bridging 2SPym ligands and one iodine atom. The 2SPym ligands form a cis-planar array of two sulphur and two nitrogen donors at each platinum centre with the iodine atoms occupying the terminal positions of the dimer.

The PtN_2S_2 planes are not fully eclipsed; there is a c.a. 26° twist about the Pt-Pt axis. Five of the atoms in the PtN_2S_2I coordination sphere around each platinum lie in a closely octahedral arrangement, but the iodine atoms are displaced by c.a. 7° from the Pt-Pt axis. This perturbation from octahedral coordination is caused by steric interaction between the iodines and the H(6) protons on the pyrimidine rings.

Figure 2.1 Structure of $Pt_2(2SPym)_4I_2$

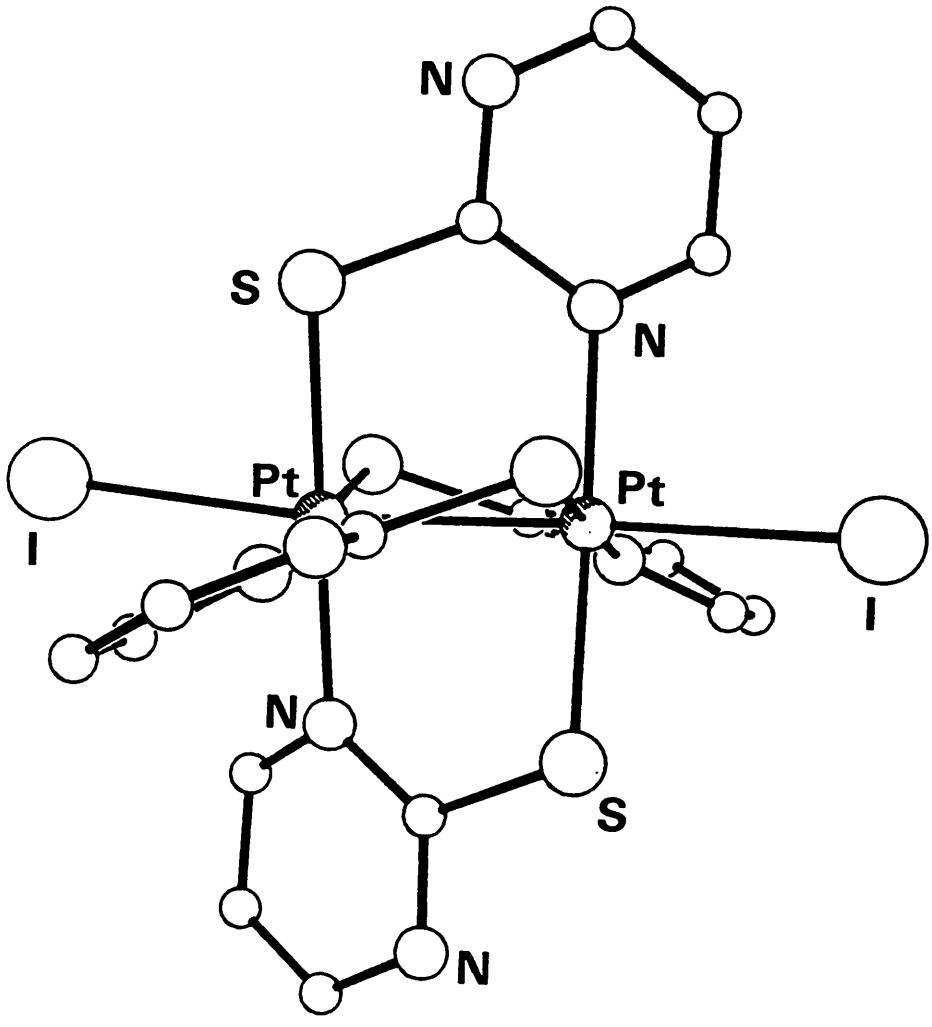


Figure 2.2 Structure of $Pt_2(2SPym)_4I_2$ Viewed Along The Pt-Pt Axis

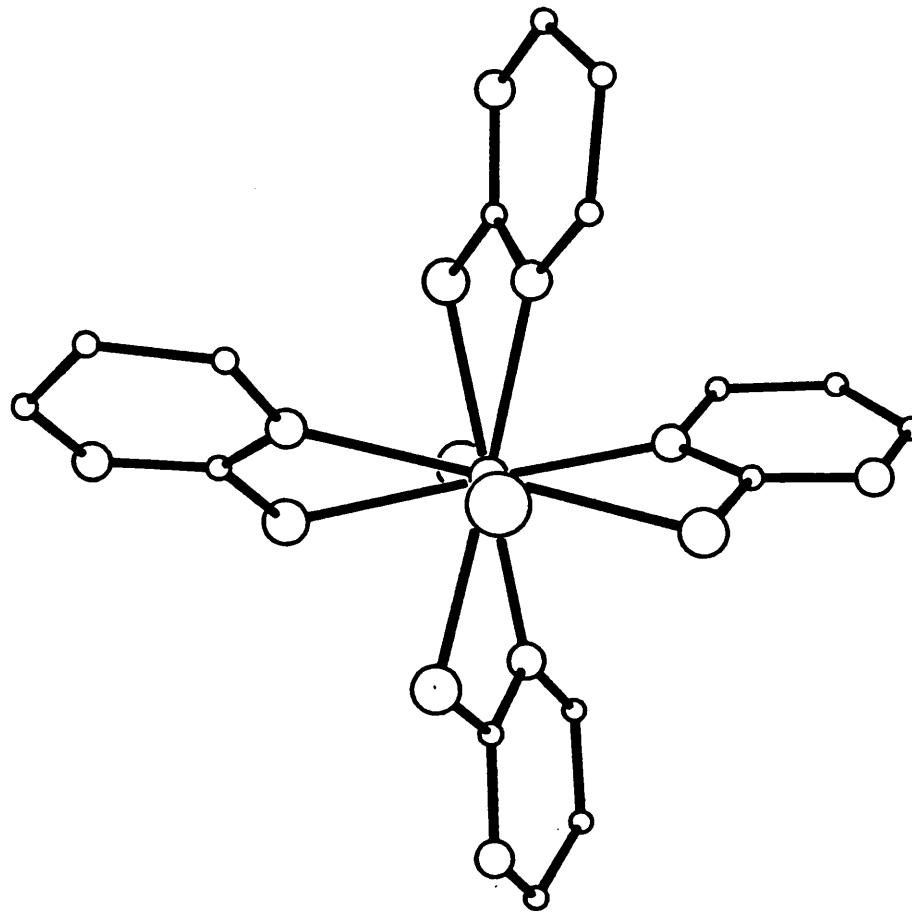


Table 2.3 Selected Bond Angles And Bond Distances For $Pt_2(2SPym)_4I_2$.

Mean Bond Lengths Around Platinum (Å)

Pt-Pt′	2.554	Pt-I	2.774(7)
Pt-S	2.294(7)	Pt-N	2.109(17)

Mean Bond Angles Around Platinum (Degrees)

Pt′-Pt-I	173.2(8)	Pt′-Pt-S	89.6(2)
Pt′-Pt-N	90.1(5)	I-Pt-S	85.7(11)
I-Pt-N	94.7(10)	S-Pt-S	90.0(11)
S-Pt-N	90.4(15)	S-Pt-N	178.8(6)
N-Pt-N	89.3(8)		

Mean Ligand Bond Distances (Å)

S-C(2)	1.707(22)	N(1)-C(2)	1.371(4)
C(2)-N(3)	1.345(20)	N(3)-C(4)	1.332(31)
C(4)-C(5)	1.366(38)	C(5)-C(6)	1.365(32)
C(6)-N(1)	1.310(11)		

Mean Ligand Bond Angles (Degrees)

Pt-S-C(2)	106.2(7)	Pt′-N(1)-C(2)	119.8(16)
Pt′-N(1)-C(6)	122.9(16)	C(2)-N(1)-C(6)	117.3(17)
N(1)-C(2)-S(1)	124.2(19)	N(1)-C(2)-N(3)	121.8(25)
S(1)-C(2)-N(3)	114.0(12)	C(2)-N(3)-C(4)	118.2(22)
N(3)-C(4)-C(5)	122.1(12)	C(4)-C(5)-C(6)	116.5(19)
C(5)-C(6)-N(1)	123.2(25)		

Metal-metal interactions between platinum atoms in square planar complexes have been recognised for about 25 years. It was in 1957 that Rundle described such interactions in compounds such as "Magnus green salt" and similar "stacked" polymers [48]. Interest has recently been re-awakened in these compounds because of their potential "one-dimensional" anisotropic conductivity (both thermal and electrical).

The Rundle model assumes hybridisation of the filled d_{z^2} and empty p_z orbitals producing four σ orbitals : a_{1g} , a_{1u}, a^*_{1g} , and a^*_{1u}. The strength of any M-M bond would, then, depend on the metal-metal distance and the difference in energy between the nd_{z^2} and $(n+1)p_z$ orbitals. Such a σ bond would not completely describe the metal-metal interactions, however, as it does not specify the relative orientation of one metal-ligand coordination plane relative to the other. In the extremes the two metal-ligand planes could be eclipsed or staggered. The resulting conformation in the present structure lies between these extremes, resulting from competing forces; electronic and steric. A staggered symmetry allows a small net δ bonding from hybridization of d_{xy} and $d_{x^2-y^2}$ orbitals and minimises electron pair repulsion between δ orbital electrons. A fully staggered (45° relative rotation of one square) would, however, require the ligands to be twisted further away from a position where they were each coplanar with the Pt-Pt vector. This would, in turn, require the platinum atoms to approach each other more closely and may result in electron repulsion between the metal centres. A more flexible ligand, or one with a slightly larger "bite", might well have allowed a more staggered conformation.

In synthesising a "sulphur-rich" platinum(II) cumate Fackler et al. produced quantities of another product identified as $Pt_2(dtcum)_4$ [49]. The complex consists of two platinum atoms, each bound to one chelating ligand and to two bridging ligands. Other dithioarylacid complexes of platinum(II) have since been described as dimers on the basis of infrared spectroscopy [50]. Browall et al. synthesised $M_2(S_2C_2H_2)_4$ M=Pd or Pt [51]. In those compounds none of the ligands bridged, but the complexes were found to crystallise in dimeric units with the PtS_4 units lying directly above each other, the sulphur atoms at the vertices of a slightly distorted cube.

Since then, a number of complexes have been structurally characterised which show evidence for a platinum-platinum bond. Table 2.4 shows those complexes with platinum in oxidation state +3. One main class within this table is the set of compounds where two $[Pt(NH_3)_2]^{3+}$ moieties are linked by two pyridonate ligands with additional small anionic ligands binding to the axial platinum sites. The other main class is that of the quadruply-bridged structures where the two platinum atoms are linked by four oxygen donors.

Table 2.4 Pt-Pt Distances For Some Platinum(III) Dimers

Compound	Pt-Pt Distance	Reference
$Pt_2(NH_3)_4(C_5H_4NO)_2(NO_3)_2^{2+}$	2.547Å	[52]
$Pt_2(NH_3)_4(C_5H_4NO)_2(NO_2)_2^{2+}$	2.575Å	[52]
$Pt_2(Me)_4(\gamma\text{-pic})_2(CF_3CO_2)_2$	2.557Å	[53]
$K_2[Pt_2(SO_4)_4(H_2O)_2]$	2.466Å	[54]
$Na_2[Pt_2(HPO_4)_4(H_2O)_2]$	2.486Å	[55]
$Pt_2(NH_3)_4(C_5H_4NO)_2(NO_3)^{3+}$	2.539Å	[56]
$K_2[Pt(SO_4)_4(OSMe_2)_2]4H_2O$	2.471Å	[57]
$Pt_2(pop)_4Cl_2^{4-}$	2.695Å	[58]
$Pt_2(2SPym)_4I_2$	2.554Å	This work

More recently Bellitto et al. have characterised quadruply-bridged platinum dimers with sulphur donors (dithioactetate) [59,60]. In their work $Pt_2(CH_3CSS)_4I_n$ (n=0, 1, 2) have all been isolated although only the structures of the n=0 (Pt-Pt=2.767Å [59]), and n=1 (Pt-Pt=2.677Å [60]) compounds have been solved crystallographically. Complexes such as these had previously been prepared by oxidative addition to a pre-formed dimer [56,58,60] or by further oxidation of an already partially oxidised Pt(II)/Pt(III) polynuclear species [56].

There are a number of variables to bear in mind when comparing the Pt-Pt distances.of these different compounds. Firstly, we must consider the oxidation state of the platinum, the trend being for similar complexes to have decreasing Pt-Pt bond distance as the platinum oxidation state shifts from +2 to +3 [56,61]. Secondly, we should consider the donor groups of the bridging molecules. The Pt-Pt distance in $Pt_2(2SPym)_4I_2$ lies between those of quadruply bridged Pt(III) dimers with O-donor bridges [57,62] and that for $Pt(pop)_4Cl_2^{4-}$, where the bridges are phosphorus donors. Finally we may consider the effect of the terminal iodide groups. It has been shown that an increased <u>trans</u> influence in axial donors to Pt(III) dimers results in a significant lengthening of the metal-metal bond [40].

Comparison of $Pt_2(2SPym)_4I_2$ with the dithioacetate complexes prepared by Bellitto et al. [59,60] is reasonable, as the ligands in all three compounds have a small bite and are soft donors. We see a progression of Pt-Pt bond distances in Table 2.5.

Table 2.5 Effect Of Oxidation State On Pt-Pt Distance In Selected Dimers

Compound	Oxidn.State	Pt-Pt Distance
$Pt_2(dta)_4$	2	2.767 Å
$Pt_2(dta)_4I$	2.5	2.677 Å
$Pt_2(2SPym)_4I_2$	3	2.554 Å

2.1.2.3 Reactions With 4,6Dimethyl-Pyrimidine-2-thione - The orange $Pt(4,6Me_2 2SPym)_2$ was a powder when formed in water/methanol, but, by using a two-phase water/CH_2Cl_2 system, crystals were obtained and these were subjected to X-ray cystallographic invstigation.

Figure 2.3 Possible Structures Of Pt $(4,6Me_2 2SPym)_2$

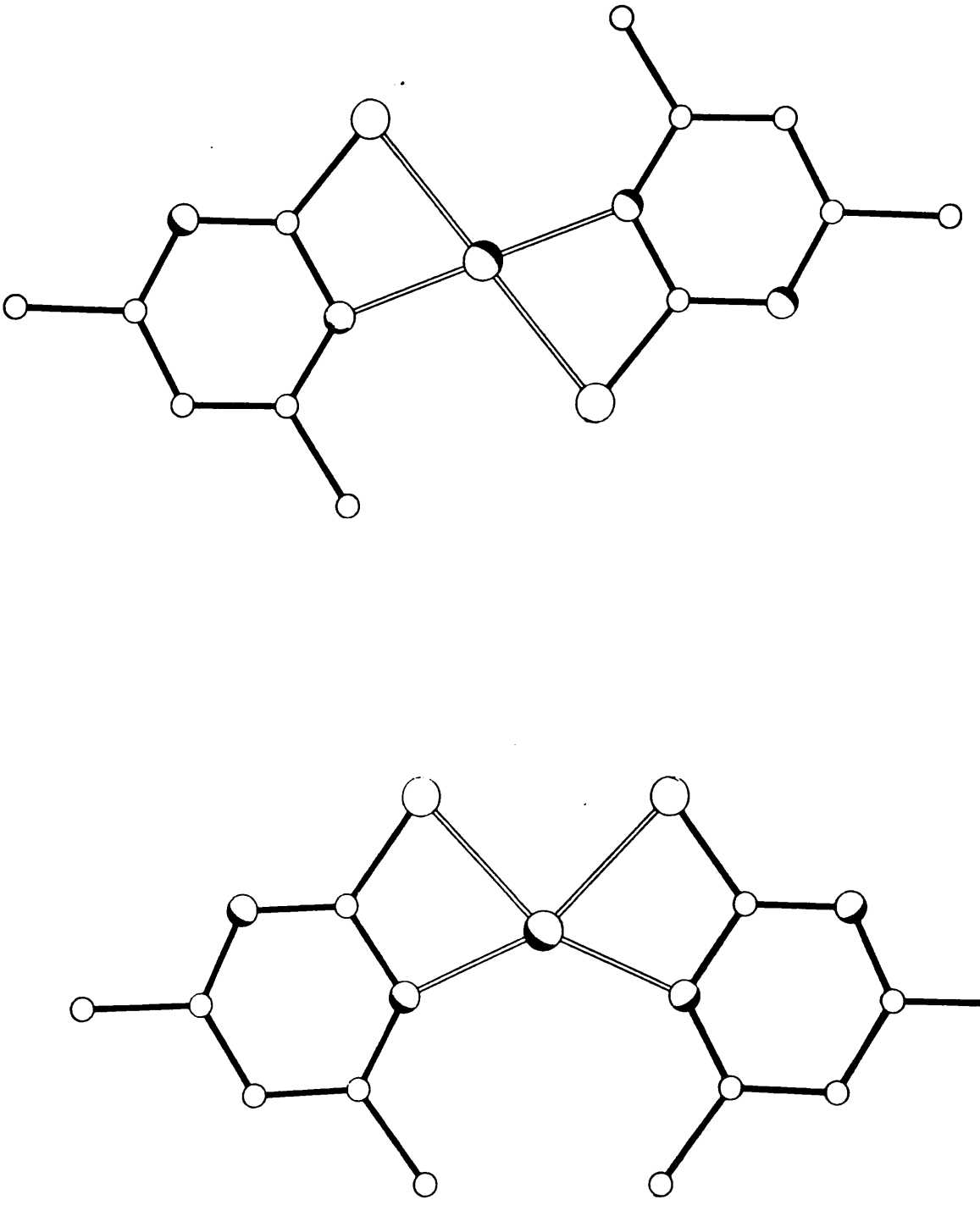


Table 2.6 Bond Angles And Bond Lengths For $Pt(4,6Me_2 2SPym)_2$

Bond Lengths (Å)

Pt-S	2.345(4)	Pt-N1	1.998(13)
S-C2	1.702(13)	N1-C2	1.387(19)
N1-C6	1.325(20)	N3-C2	1.360(19)
N3-C4	1.321(18)	C4-C5	1.358(19)
C4-C7	1.540(19)	C6-C5	1.360(20)
C6-C8	1.512(18)		

Bond Angles (Degrees)

S-Pt-N1	71.1(4)	Pt-S-C2	78.9(5)
Pt-N1-C2	99.8(10)	Pt-N1-C6	141.8(12)
C2-N1-C6	118.4(12)	C2-N3-C4	116.1(11)
S-C2-N1	110.2(11)	S-C2-N3	127.3(9)
N1-C2-N3	122.5(11)	N3-C4-C5	123.8(13)
N3-C4-C7	116.2(13)	C5-C4-C7	120.1(13)
C4-C5-C6	118.7(12)	N1-C6-C5	120.6(12)
N1-C6-C8	115.8(13)	C5-C6-C8	123.6(11)

2.1.2.4 Crystal Data For $Pt(4,6Me_2 2SPym)_2$ - $C_{12}H_{14}N_4Pt_1S_2$, $\underline{M}$=473.4, monoclinic, $\underline{a}$=15.645(2), $\underline{b}$=13.128(2), $\underline{c}$=3.5045(3)Å, β=99.78(1)°, $\underline{U}$=709.3Å^3 (at 18° C), space group probably C2/m, Z=2, D_c=2.22gcm^{-3}. X-ray diffraction data consisted of 1041 independent reflections (to θ=57°) of which 524 were "unobserved". Patterson and Fourier methods were used in attempt to solve the structure, least-squares refinement reaching R=0.016.

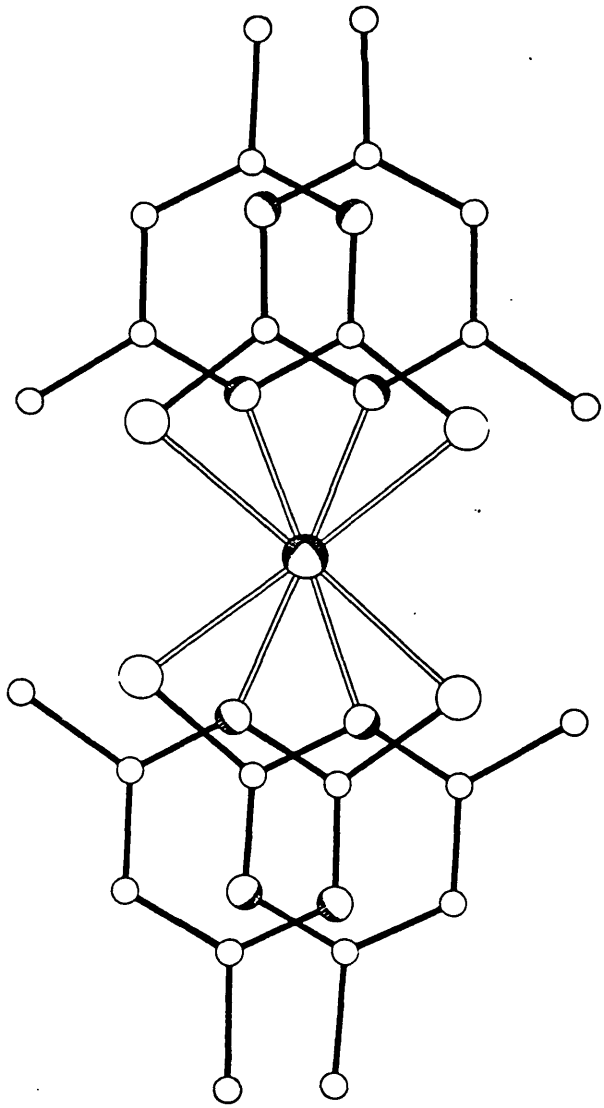
One immediately notices the extremely short $\underline{c}$ axis at 3.5045Å. This reflects the expected planarity of the PtL_2 complex, with the molecule lying in the ab plane. Another important point is the fact that the space group was not determined with certainty. The reasons for this are described below.

When beginning the process of structure determination for C face centred monoclinic structures with the pattern of reflections observed here (h+k=2n) one has to make a "blind" initial decision for the space group: C2, Cm or C2/m. In this case the first attempt at refinement was made assuming space group C2, implying a $\underline{cis}$ configuration for the complex. This refined to R=0.0215 but the anisotropic thermal parameters for three of the ring atoms (N(1), N(3) and C(2)) were "non-positive definite" i.e. they were physically impossible. Using an isotropic thermal description for those atoms gave an R-factor of 0.0241.

The other possibility, considering the overall size and shape of the molecule, was that the structure was disordered, with a resultant space group C2/m. With these conditions imposed, the anisotropic thermal parameters all became satisfactory and the R-factor dropped to the very low value of 0.0160. Thus an accurate description of the structure of the asymmetric unit was obtained but

that unit was $Pt_{1/2}(L)$ and by invoking the disorder the molecule could not be assigned cis- or trans stereochemistry. The effect of invoking disorder is that one obtains the superposed structure of the component states see Figure 2.4

Figure 2.4 Structure Resulting from disorder of $Pt(4,6Me\ 2SPym)_2$



Consideration of the diagram shows that it can be regarded equally well as a superposition of two trans structures or two cis structures.

So although the R-factor was extremely low and the thermal parameters indicated that this was a good description of the asymmetric unit, possibly the most important feature of the structure of the complex, whether it was cis or trans, could not be determined directly. Fig 2.3 shows the possible structures of the molecule while Table 2.6 gives bond angles and bond lengths for the half-molecule. The N(1)-C-S angle is only 110.2° and N(3)-C-S is 127.3°, showing distortion from those angles expected for the free ligand. This distortion allows a greater overlap with the metal orbitals by increasing the C(2)-S-Pt and C(2)-N(1)Pt angles.

Whether the complex is cis or trans the S-Pt-N angle is 71.1° with a bite of 2.541Å. If the molecule had the trans configuration the other angles at platinum (S-Pt-N(1)′) would be 108.9° (S-Pt-S′ and N-Pt-N′ being 180° by symmetry). If the cis form was preferred then S-Pt-S′ would be 84.9° and N-Pt-N′ would be 133.0°. All of these bond lengths and angles are quite feasible and no deductions about the cis/trans nature of the molecule can be made from them. One indirect method of assigning the stereochemistry might have been to investigate the angles about C(6). In the cis orientation the methyl groups attached to C(6) would be expected to approach each other. This could be reflected in an opening of the N(1)-C(6)-C(8) angle (>120°) and closing of the C(5)-C(6)-C(8) angle (<120°). In fact what we see is N(1)-C(6)-C(8) 115.8° and C(5)-C(6)-C(8) 123.6°, i.e. the observed angles are displaced from 120° in the opposite direction to that expected if there were steric repulsive forces between the approaching methyl groups. On the other hand, the

minimum nonbonding approach observed between the protons on opposing methyl groups in this orientation is 2.035Å which is not impossible. Also, in the trans orientation there is no obvious reason why these angles should be displaced from 120° at all.

Proton n.m.r. studies would not be able to elucidate the structure, and work with other nuclei would require a large amount of background work to be carried out, investigating coupling constants for platinum compounds of known orientation before one would know even whether the technique was a sensitive enough probe to apply to the problem in hand. Vibrational spectroscopy for this complex is hampered by coupling and no definite assignments can be made for any of the "Pt-N" or "Pt-S" modes. Dipole moment measurements could not be made (the trans form, being centrosymmetric, would have zero dipole moment while the cis form would not) as the complex is not soluble in nonpolar solvents. It seems that there is no readily available technique which can unravel this problem.

2.1.3 Conclusions

2SPymH is the only ligand in the set of eight pyrimidine ligands used in this study to show a tendency to form dimeric complex. The reaction with K_2PtCl_4 follows a similar route to that with $[PtI_4]^{2-}$, the PtL_2 complex was isolated from both reaction mixtures when the reactions were carried out anaerobically, but the final product is a diamagnetic solid with unusual stoichiometry. The PtL_2 species forms first in both cases, followed by aerobic oxidation to give the di-/polymeric species. Why should 2SPymH be the only ligand studied to give the well defined dinuclear species? The answer comes in several parts providing a useful summary of the results.

Firstly, the pyrimidine-2-one ligands show no ability to displace halides from platinum to bind via oxygen - the nitrogen sites are the primary donors to Pt(II) for these ligands. In the platinum blues and other polynuclear platinum species where hydroxypyrimidines and hydroxypyridines bind via nitrigen and oxygen the platinum source is $Pt(NH_3)_2(H_2O)_2^{2+}$ where the aquo groups are easily displaced.

The pyrimidinethiones, however, have nitrogen and sulphur donors. Here the sulphur is expected to be the primary donor to Pt(II) but the nitrogen donor groups are also strong enough to displace the halides. The N-methylpyrimidines are unable to generate an anionic charge easily and so we find that they produce the simple $PtCl_2L_2$ complexes with K_2PtCl_4. Their reactions with $[PtI_4]^{2-}$ are unclear - the steric hindrance of the trimethylated ligand prevents complex formation of a stable complex before the platinum is reduced to Pt(0) (as with $1,4,6Me_3$2OPym.) The 1Me2SPym ligand gives PtI_2L, this compound may be polynuclear but N,S chelation is also quite possible.

The PtL_2 product formed by $4,6Me_2$2SPym does not go on to form a dimeric product - possibly for two reasons. Firstly, the inductive effect of the methyl groups would tend to make the sulphur and nitrogen atoms better donors than in the 2SPym ligand. When the PtL_2 complex is formed then, there would be less tendency for the Pt-S or Pt-N bonds to break to give rise to the dimeric or polymeric species. Also, considering the $Pt_2(2SPym)_4I_2$ complex, it was noted that there was a steric interaction between the terminal iodide groups and the H(6) protons of the pyrimidine rings. With $4,6Me_2$2SPym these protons are replaced by methyl groups. If an analogous $Pt_2(4,6Me_2SPym)_4I_2$ complex were to form, the displacement

of the iodide from the Pt-Pt axis would be magnified, decreasing the Pt-I bond strength and, indeed there would be an appreciable Me(6)...Me(6) interaction between adjacent ligands. For these reasons, then, 2SPymH alone, among the ligands studied, forms a dimeric complex with $[PtX_4]^{2-}$ (X=Cl or I). It would be interesting to compare the structure of $Pt_2(2SPym)_4I_2$ with those of complexes with other, closely related ligands, in detail. The ligands would contain a six-membered ring with nitrogen at the 1-position and a mercapto group substituted at the 2-position. The 6-position would probably have to be unsubstituted to allow a dimeric complex to form. A series of experiments could be carried out to determine the effect of substitution at the 4- and 5-positions and the effect of further nitrogen atoms in the ring itself. Another field ripe for study is the electrochemistry of these complexes which would be expected to show a stepwise oxidation, at least part of the way along the path: [Pt(II),Pt(II)] <--> [Pt(II)Pt(III)] <--> . . . [Pt(III)Pt(IV)] <--> [Pt(IV)Pt(IV)]. Reaction of $Pt_2(2SPym)_4I_2$ with the yellow $Pt(2SPym)_2$ or with other planar $Pt(chelate)_2$ neutral complexes in an attempt to generate complexes of the type $\dagger IPt\text{-}(2SPym)_4\,PtIPt(chelate)_2\dagger_n$ which might show extended interactions along the [Pt...Pt...I] stacks with consequent "one-dimensional" properties.

CHAPTER 3

MOLYBDENUM COMPLEXES

3.1 MOLYBDENUM COORDINATION CHEMISTRY

As one of the objectives of the studies was to investigate the possibility of forming complexes of potential catalytic activity, an obvious candidate for the metal centre was molybdenum.

The reasons for this choice of metal were that molybdenum complexes are known to have :

1. a range of formal oxidation states accessible to the metal; 0, 2, 3, 4, 5 and 6 all being well known, with extensive chemistry within and between these states,

2. a range of coordination numbers, typically from four to eight,

3. an involvement in a range of enzyme catalysed reactions.

It was hoped a range of new molybdenum compounds could be made with the ligands studied here and that investigations of their chemical reactivity, for instance in redox processes, would yield catalytic systems.

It is not feasible to provide a comprehensive review of molybdenum coordination chemistry here, the review presented concentrates on those areas which are of direct relevance to this project. Some excellent reviews [63-66] are available which provide starting points for a more complete survey.

Several convenient molybdenum starting materials (molybdenum hexacarbonyl, molybdenum(V) chloride, molybdenum trioxide and a range of molybdate salts) are commercially available and were purchased, while others were synthesised. Dimolybdenumtetraacetate, bis(2,4-pentanedionato)dioxomolybdenum(VI) and diammoniumaquo-pentachloromolybdenum(III) were prepared using published routes, while an improved synthesis for tris(pyridine)trichloro-molybdenum(III) was used.

3.1.1 Molybdenum In Oxidation State (VI)

3.1.1.1 Structure - In the vast majority of compounds of molybdenum(VI) the metal centre is multiply bonded to one or more oxygen atoms. The monomeric complexes in this class include, for example, $MoOF_4$ [67], $MoO_2(acac)_2$ [68], $MoO_3(dien)$ [69] and L_2MoO_4 (L= cyclohexylammonium cation) [70]. This list also provides examples of the range of the number of terminally bound oxygen atoms. The largest group of oxo-complexes of molybdenum(VI) is that of the six-coordinate complexes containing the MoO_2^{2+} group, sometimes referred to as the molybdenyl unit. Many such compounds have been structurally investigated [71-80].

The coordination geometry around molybdenum in these complexes is almost invariably quasi-octahedral with the terminal oxygen atoms occupying cis positions with respect to each other. The oxygens repel each other away from 'true' octahedral sites so that the

O_t-Mo-O_t angle is generally c.a. 110°-120°. The main exceptions to this arrangement are the complexes with hydroxylamine-type ligands where, although the molybdenum is still six coordinate, the geometry is based on tetrahedral, rather than octahedral, symmetry [81,82].

In molybdenum-oxo complexes the terminally bound oxygens exhibit a trans effect towards additionally bound ligands; for example in the compound $MoO_2(acac)_2$ [68] the Mo-O(ligand) bond trans to the terminal oxo groups have an average length of 2.20Å while those trans to another ligand oxygen are shorter (1.98 Å). A similar effect is seen in the compound $(Et_2NCS_2)_2MoO_2$ [74,83] where the diethyldithiocarbamate ligands chelate the molybdenum in a cis orientation as expected. Here the Mo-S bonds trans to the oxo groups are 2.64Å and those trans to sulphur atoms are 2.45Å. The dithiocarbamate complex is of interest because it incorporates two four-membered chelate rings in the structure with a bite angle at the metal of 68.5° (S-Mo-S). This may be compared with the very small bite (59.1°) found for the 2-substituted pyrimidine ligands seen in the complex $Co(2SPym)_2Cl_2$

3.1.1.2 Synthesis -

Complexes of the form $MoO_2(R_2dtc)_2$ had previously been prepared by Malatesta [84] and Moore et al. [85] by acidification of basic aqueous solutions containing the molybdate ion and the appropriate ligand.

Another general method of synthesis for cis-dioxo complexes of molybdenum(VI) has been to use a ligand replacement reaction with $MoO_2(acac)_2$ as starting material. This approach has been used by Stieffel et al. with various bi- and tetradentate ligands yielding MoO_2L_2 and MoO_2L respectively [72].

Closely related to this method of preparation is the use of the octamolybdate $(Bu_4N)_4Mo_8O_{26}$. This has been used to give increased yield over the reactions of $MoO_2(acac)_2$ [124] but the products are generally similar. Ammonium paramolybdate has also been used in the synthesis of $[MoO_2]^{2+}$ complexes [125] but the yields using this reactant are lower than when $MoO_2(acac)_2$ is used.

3.1.2 MOLYBDENUM IN OXIDATION STATE (III)

Trivalent chromium complexes have been investigated at great length but molybdenum(III) complexes, unlike the chromium compounds, are susceptible to oxidation by air and other mild oxidants. The trihalides of molybdenum exist as extended lattices. Trivalent compounds of the form $Mo(SR)_3$ have been reported [86] but are not well characterised.

Monomeric molybdenum(III) complexes have a $4d^3$ configuration and octahedral coordination has been confirmed in most cases. Compounds of the type $MoX_3(NAr)_3$ (X= Cl, Br; NAr= py or pic) invariably crystallise as the meridinal isomer. No substantial differences in the Mo-N bond lengths, comparing Mo-N trans to Mo-N with Mo-N trans to Mo-X, are found in the solid state, showing that there is no strong trans influence in these compounds [87-90].

Mononuclear complexes of molybdenum(III) with bidentate ligands have not been extensively explored.

3.1.2.1 Synthesis - Two useful starting materials in the investigation of Mo(III) proved to be ammonium aquopentachloro-molybdenum(III) and tris(pyridine)trichloromolybdenum(III). $(NH_4)_2[MoCl_5(H_2O)]$ is prepared from dimolybdenumtetraacetate by the reaction:

$$Mo_2(OAc)_4 + HCl_{(aq)} + O_2 \longrightarrow MoCl_5(H_2O)^{2-} + MoCl_6^{3-}$$

Hydrolysis of $[MoCl_6]^{3-}$ leads to the production of pure $[MoCl_5(H_2O)]^{2-}$ which may then be isolated as the ammonium salt, while saturation of the solution with hydrogen chloride gas gives rise to the $MoCl_6^{3-}$ species [91].

Complexes of the type MoX_3L_3, for instance $MoCl_3py_3$, have previously been prepared by reaction of MoX_3 or the $[MoX_6]^{3-}$ species with a donor ligand [92]. An improved synthetic route to $MoCl_3py_3$ is presented in the experimental section of this thesis.

3.1.3 MOLYBDENUM IN OXIDATION STATE (0)

3.1.3.1 Structure - In $Mo(CO)_6$ the metal has a formal oxidation state of zero. The complex generally reacts either by ligand substitution or by an oxidative process.

Ligand substitution reactions have been performed with a huge variety of neutral donor ligands. Degrees of substitution vary, the general reaction simply being :

$$[Mo(CO)_6] + nL \longrightarrow [Mo(CO)_{6-n}L_n] + nCO$$

It has been found that for sigma donor ligands n= 1-3. Further substitution is hindered by a build up of electron density at the metal centre, due to the sigma donation, which can only be dissipated by the CO ligands. For sigma donors with a capacity to accept back donation via π-orbitals this restriction is lifted and for small ligands with high π-acceptor properties substitution may proceed to completion. Thus for sigma donor / pi acceptor ligands n can equal 1 - 6. Indeed, with the ligand PF_3 the whole range of $[Mo(CO)_{6-n}(PF_3)_n]$ complexes is known [93]. With larger ligands substitution does not proceed to completion, for example only the complexes $[Mo(CO)_{6-n}(PMe_3)_n]$ (n= 1, 2, 3) are known for trimethyl-

phosphine [94]. Another important class of molybdenum carbonyl complexes is that of pi-donor / pi-acceptor ligands but these have no relevance to the present study.

There are a number of ways in which one could view the pyrimidine ligands when reacting with molybdenum hexacarbonyl. Firstly, they might be regarded as being predominantly an aromatic nitrogen donor ligand, the exocyclic groups having little effect. If this were so they would be expected to behave in a similar fashion to pyridine. Although such aromatic amines can act as pi-acceptors, in most cases such acceptance appears to be limited and so complex formation is attributed primarily to sigma bonding.

Conversely one can concentrate on the exocyclic coordinating group and temporarily consider the ring to be coordinatively inert. The lower Lewis basicity of oxygen would make N sigma donor bonds more effective than O-bonds but O-donor complexes are known for molybdenum(0) e.g. $[Mo(CO)_5(OEt_2)]$ [95] and $[Mo(CO)_4acac]^-$ [96]. Sulphur ligands generally coordinate more strongly to molybdenum than do the corresponding oxygen species [97]. The thioketone complex $[Mo(CO)_5(S{=}CMe_2)]$ has been reported [98]. The crystal structure of its chromium analogue has an M - S bond length of 2.377 Å [99]. It therefore appears to be quite feasible for any of the potentially coordinating groups of the pyrimidine ligands to bond to zerovalent molybdenum. It is possible that both ring nitrogen and exocyclic oxygen or sulphur could coordinate. The chelating acac group in $[Mo(CO)_4(acac)]^-$ has already been mentioned and complexes containing nitrogen chelating ligands abound, typical examples being $[Mo(CO)_4(en)]$ and $[Mo(CO)_{6-2n}(bipy)_n]$ (n= 1, 2, 3) [100].

The products described above assume that no oxidation state changes occur on reacting $Mo(CO)_6$ with the ligands, i.e. the processes are simple ligand substitution. This is not always the case. The reaction with acetylacetone, for instance, may proceed further to give $Mo(acac)_3$. There are generally two routes for chemical oxidation of molybdenum carbonyl complexes, namely oxidation by halogen incorporating halide ligation, or reaction with an organic substrate containing a labile proton as indicated by the scheme below:

$$Mo(CO)_6 + nHL \longrightarrow MoL_n + (n/2)H_2 + 6CO$$

Such reactions with potentially bidentate sulphur donors may give rise to high coordination numbers e.g. $[Mo(CO)_n(S_2CNEt_2)_2]$ (n= 2, 3) [101,102]. A large number of complexes of the type $[Mo_2L_4]$ are known. The classic example is dimolybdenumtetraacetate [103] but more recently the structure of $Mo_2(4,6\text{-}Me_2 2SPym)_4$ has been published [104].

3.2 EXPERIMENTS WITH MOLYBDENUM(III)

Investigations of the reactions of molybdenum(III) were limited to reacting the ligands with $(NH_4)_2[MoCl_5(H_2O)]$ in water and with $MoCl_3py_3$ in methanol respectively.

Reactions of $(NH_4)_2[MoCl_5(H_2O)]$ in water were fairly fruitless. No new products were isolated on refluxing the reactants or allowing them to stand for months. Reactions with the proton-labile sulphur ligands were shown to occur by colour changes in solution on heating the reaction mixture. The red solutions tended to deepen quickly (1-2 minutes) to a dark brown colour on heating in air, however pure, dry products were not obtained. Infrared spectra seemed to indicate that the products may have been MoL_4 but they could not be

adequately characterised when first synthesised.

Reaction of $MoCl_3py_3$ with the 2S- and 2O- pyrimidine ligands in methanol gave identical results regardless of whether the conditions were aerobic or anaerobic. No reaction was observed with any ligands except the 2-mercaptopyrimidines with labile protons, namely 2SPymH and $4,6Me_2$2SPymH.

Those mixtures which did not react showed no colour change on prolonged heating. Some breakdown of the original $MoCl_3py_3$ was indicated by the release of pyridine. Very small amounts of pale brown powder were sometimes formed in the hot solutions but the amount was too small to characterise and cooling only produced unreacted ligand.

In the positive reactions, however, the original yellow solutions became intense purple/red within two minutes of starting to reflux. On allowing the red solutions to cool, pleochroic crystals formed slowly from the 2SPymH reaction but no solid could be isolated in a pure state from the reaction mixture containing $4,6Me_2$2SPymH.

The crystals obtained from the reaction of $MoCl_3py_3$ with 2SPymH analysed as $Mo(2SPym)_4$; they were dark, metallic green by reflected light but transmitted as a deep red colour. The crystals would not re-dissolve to give a dark red solution similar to the reaction mixture but would only dissolve slightly to give a pale red solution. The solid was diamagnetic (Gouy method) but saturated solutions were not concentrated enough to give proton n.m.r. signals even using Fourier Transform n.m.r. The crystals were most soluble in chloroform and ethanol, they were very slightly soluble in polar organic solvents and benzene but were insoluble in alkanes.

The infrared spectrum showed loss of the Mo--Cl stretches and the ligand C--S stretch was unshifted, indicating weak coordination or chelation. Recrystallisation was hampered by the low solubility of the compound but, after repeated experiments a crystal suitable for X-ray crystallography was found.

3.2.1 Crystal Data For $Mo(2SPym)_4$

$Mo_2C_{32}H_{24}N_{16}S_8.0.5(CH_3OH)$, M=1097.0, triclinic, a=8.995(1), b=9.325(1), c=25.289(4)Å, α =82.039(12)°, β =83.503(12)°, γ =88.192(12)°, U=2086.99 Å^3 (at 18°C), space group $P\bar{1}$, Z=2, D =1.75gcm^{-3}. X-ray diffraction data consisted of 4274 independent reflections (to θ=50°) of which 230 were 'unobserved'.

Figure 3.1 Structure $Mo(2SPym)_4$

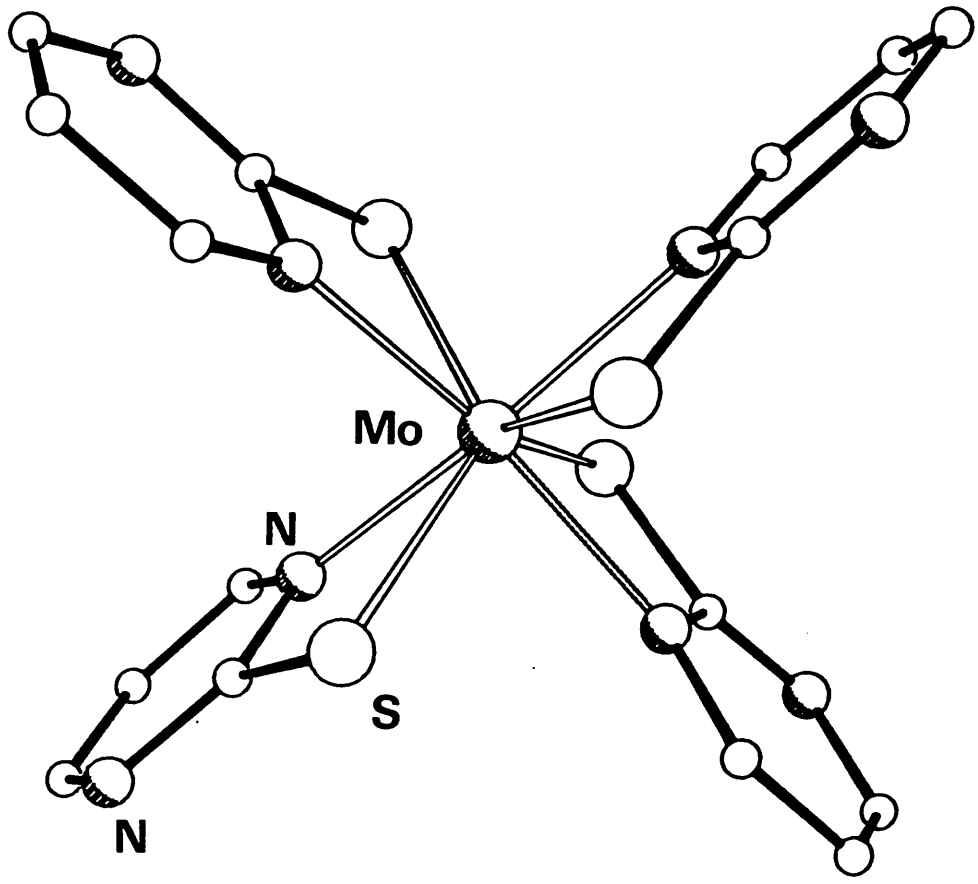


Table 3.1 Mean Bond Angles And Bond Lengths

For $Mo(2SPym)_4$

Bond Lengths (Å)

Mo1-S112	2.526(1)	Mo2-S212	2.526(1)
Mo1-S122	2.527(1)	Mo2-S222	2.515(1)
Mo1-S132	2.517(1)	Mo2-S232	2.523(1)
Mo1-S142	2.518(1)	Mo2-S242	2.527(1)
Mo1-N111	2.184(4)	Mo2-N211	2.168(3)
Mo1-N121	2.171(4)	Mo2-N221	2.188(4)
Mo1-N131	2.171(4)	Mo2-N231	2.171(3)
Mo1-N141	2.186(3)	Mo2-N241	2.185(3)

Mean Bond Lengths for Ligands (Å)

S-C2	1.719(4)	N1-C2	1.354(7)
N1-C2	1.354(7)	C2-N3	1.321(9)
N3-C4	1.341(12)	C4-C5	1.363(10)
C5-C6	1.367(6)	C6-N1	1.342(6)

Hydrogen bond between the disordered methanol oxygen (O1 and O2) and N123 2.983(2) Å

Bond Angles Around Molybdenum (degrees)

S112-Mo1-S122	133.9(1)	S212-Mo2-S222	130.5(1)
S112-Mo1-S132	129.0(1)	S212-Mo2-S232	72.1(1)
S112-Mo1-S142	70.9(1)	S212-Mo2-S242	133.0(1)
S112-Mo1-N111	63.6(1)	S212-Mo2-N211	64.0(1)
S112-Mo1-N121	83.1(1)	S212-Mo2-N221	82.0(1)
S112-Mo1-N131	81.5(1)	S212-Mo2-N231	136.1(1)
S112-Mo1-N141	134.5(1)	S212-Mo2-N241	81.6(1)
S122-Mo1-S132	71.4(1)	S222-Mo2-S232	131.8(1)
S122-Mo1-S142	128.9(1)	S222-Mo2-S242	71.6(1)
S122-Mo1-N111	83.2(1)	S222-Mo2-N211	81.8(1)
S122-Mo1-N121	63.6(1)	S222-Mo2-N221	64.0(1)
S122-Mo1-N131	135.2(1)	S222-Mo2-N231	80.7(1)
S122-Mo1-N141	81.4(1)	S222-Mo2-N241	135.3(1)
S132-Mo1-S142	134.1(1)	S322-Mo2-S242	128.6(1)
S132-Mo1-N111	82.4(1)	S322-Mo2-N211	136.1(1)
S132-Mo1-N121	134.7(1)	S322-Mo2-N321	82.6(1)
S132-Mo1-N131	64.0(1)	S322-Mo2-N231	64.1(1)
S132-Mo1-N141	83.9(1)	S322-Mo2-N241	82.6(1)
S142-Mo1-N111	134.2(1)	S422-Mo2-N211	83.9(1)
S142-Mo1-N121	81.8(1)	S422-Mo2-N421	135.5(1)
S142-Mo1-N131	83.1(1)	S422-Mo2-N231	81.0(1)
S142-Mo1-N141	63.7(1)	S422-Mo2-N241	63.9(1)

Bond Angles Around Molybdenum (degrees) continued.

N111-Mo1-N121	87.7(1)	N211-Mo2-N421	92.5(1)
N111-Mo1-N131	94.9(1)	N211-Mo2-N231	159.8(1)
N111-Mo1-N141	162.0(1)	N211-Mo2-N241	89.5(1)
N121-Mo1-N131	161.2(1)	N221-Mo2-N231	88.9(1)
N121-Mo1-N141	93.7(1)	N221-Mo2-N241	160.6(1)
N131-Mo1-N141	89.6(1)	N231-Mo2-N241	95.8(1)

Mean Bond Angles For Ligands (degrees)

Mo-S-C2	82.2(1)	Mo-N1-C2	105.3(4)
Mo-N1-C6	137.4(4)	C2-N1-C6	117.3(4)
S-C2-N1	108.5(3)	S-C2-N3	125.4(6)
N1-C2-N3	126.0(5)	C2-N3-C4	114.7(7)
N3-C4-C5	123.7(5)	C4-C5-C6	117.9(4)
C5-C6-N1	119.9(3)		

Each asymmetric unit contains two molybdenum atoms with the surrounding ligands bound almost identically. Each molybdenum atom is bound to four 2SPym molecules, each acting as a bidentate chelating N,S donor (Fig 3.1). The four ligands occupy two planes which are mutually perpendicular and contain the molybdenum atom on their intersection. The molybdenum atom is eight coordinate with virtual D_{2d} symmetry.

Eight coordinate molybdenum is known for a variety of compounds: $[Mo(CN)_7(H_2O)]^{4-}$, $[Mo(CN)_8]^{4-}$, $Mo(Me_2dtc)_4$ etc. [105]. Considerable interest has been shown in attempting to understand the factors which govern ligand arrangements in eight coordinate complexes [106-108].

The two principal modes of eight coordination for discrete complexes - neglecting those which assume that cyclopentadienyl groups can occupy three coordination sites - are the square antiprism and the dodecahedron. The square antiprism may be visualised as the result of rotating one face of a cube by 45° relative to the opposite face, while keeping the two faces parallel. The dodecahedron (or, more precisely, the triangulated dodecahedron) is composed of two interpenetrating distorted tetrahedra (bisphenoids), one elongated and the other flattened such that the eight ligand sites are equally divided into equivalent sets of four, A and B respectively [109]. The important difference between these two arrangements is that the square antiprism sites are all equivalent while the dodecahedral vertex sites are not, being divided into two bisphenoidal sets with each site equivalent only to the other three sites in the same set.

Figure 3.2 Dodecahedral Structure In $Mo(2SPym)_4$

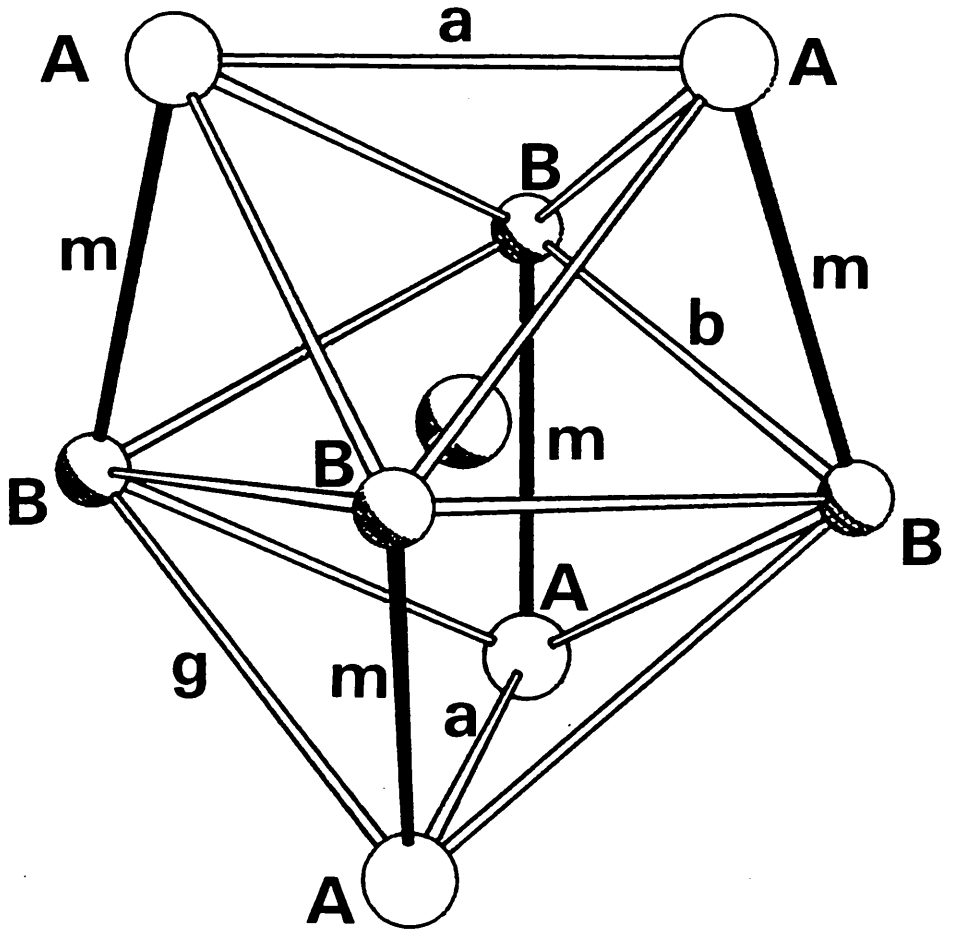


Figure 3.2 shows the molybdenum and the coordinating atoms for a single MoL_4 unit. The atoms have been joined to show the dodecahedral nature of the coordination sphere. The solid lines join atoms from a common ligand while open lines complete the dodecahedron. The shaded atoms are molybdenum (at the centre) and nitrogen, while the unshaded atoms are sulphur.

The vertices and edges are labelled conventionally [109]. The two sets of equivalent vertices are labelled A and B respectively; The eighteen edges are distributed among four classes: a(2), b(4), m(4) and g(8). The centre of the polyhedron (the molybdenum site) is the point of intersection of three mutually orthogonal symmetry axes, the $\bar{4}$ axis and a pair of twofold axes.

It has been shown that there is little difference between the energies of the dodecahedral arrangement and the square antiprism unless other factors, such as the formation of chelate rings come into play. Indeed $M(CN)_8^{n-}$ (M= Mo,W) (n= 3,4) ion geometry varies with changes in counter-ion and on changing from crystalline to solution phases [105,110,111].

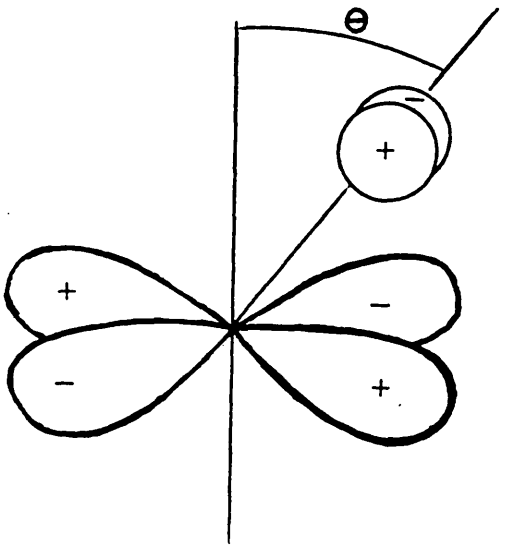
When the ligands chelate, especially if the bite is small, coordination tends to be dodecahedral with the ligands spanning the m edges giving a structure of the mmmm type, although this is not always the case [112].

If, as is the case with 2SPym, the chelating ligands have different donor groups at different coordination sites (i.e. the nitrogen and sulphur atoms in the molybdenum coordination sphere in this complex), then each metal-ligand group within the complex is asymmetric. There are six possible isomers for such systems [107] but consideration of metal-ligand σ and π bonding factors using

molecular orbital calculations suggests that π bonding is the predominant factor in determining which donor atoms reside at each site [113]. Burdett, Hoffman and Fay's extensive calculations concerning these structures [113] lead to the following:

In the dodecahedral structure the lowest lying d orbital is the σ nonbonding $d_{x^2-y^2}$. The overlap of a ligand $\pi_\perp$ orbital with this $d_{x^2-y^2}$ orbital depends on Θ, the angle the resultant bond makes with the eventual $\bar{4}$ axis (Figure 3.3).

Figure 3.3 Overlap Of Ligand π orbital With Metal $d_{x^2-y^2}$ Orbital



The largest interaction will be for ligands with the largest values of Θ, i.e. the B-site ligands. So, if the interaction leads to an overall stabilisation, as is the case for a d^2 metal with a π-acceptor or a d^0 metal with a π-donor (Figure 3.4) then the π-bonding ligands should enter the B sites to maximise orbital overlap.

If, on the other hand, the effect is a destabilising one (Figure 3.5) then the donors should prefer the A sites.

Figure 3.4 Stabilising Metal ligand Interaction.

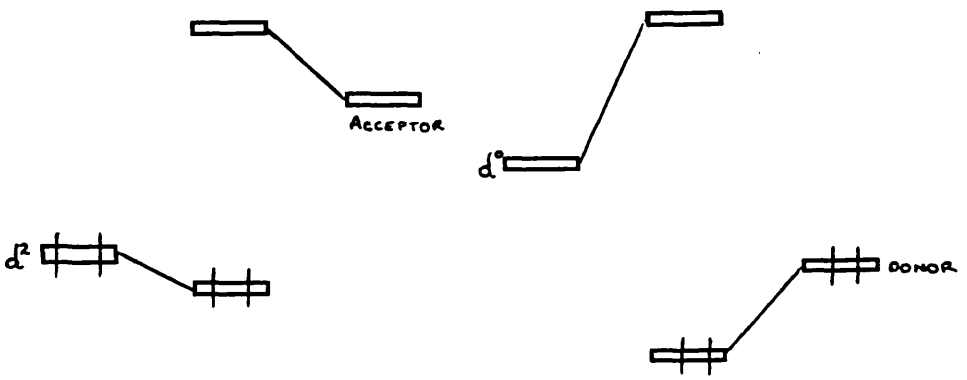
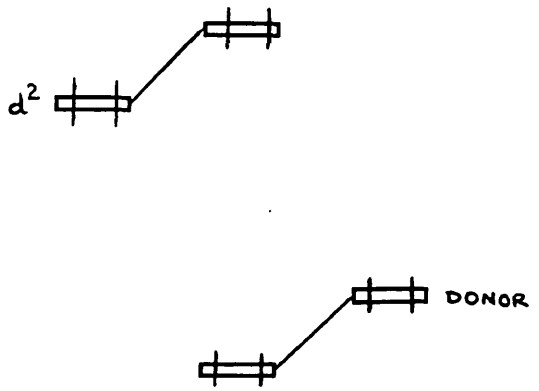


Figure 3.5 Destabilising Metal Ligand Interaction



$\pi_{//}$ orbitals have no overlap with the $d_{x^2-y^2}$ orbital, so a π ligand with a single π orbital should align itself in the $\perp$ orientation if the potential π-bonding would cause stabilisation, but in the // direction if π-interaction would be destabilising. As well as these electronic effects one must take into account the steric constraints. As already mentioned, the mmmm chelation pattern of dodecahedral coordination is an excellent choice from

steric considerations [109].

The overall conclusions are that for 2SPym, where we expect the nitrogen atom to be the better π acceptor, the coordinating nitrogen atoms should be found in the B positions and the sulphur atoms in the A positions. The structure shows this prediction to be borne out in the present compound.

The mean Mo-S and Mo-N distances are 2.522 Å and 2.181 Å repectively. The mean lengths of the m edges are 2.510 Å. The angles Θ_A and Θ_B (defined as the angles between the unique $\bar{4}$ axis of the idealised dodecahedron and the bonds which extend from the metal to the dodecahedral A and B sites respectively) have the mean values of 35.8° and 80.3° respectively.

The former value is typical of dodecahedral complexes where Θ_A generally has values between 30° and 40°. Θ_B is somewhat larger than the usual values, which are more commonly 72°. This more common, smaller, Θ_B value corresponds to a potential energy minimum when steric constraints are small. However, when the bite size of the ligand is small Θ_B values are typically > 80° [114-120]. The structural parameters for this compound are very similar to those found for the analogous tungsten(IV) complex [121].

In addition to the two MoL_4 units, the asymmetric unit in the crystal contained a methanol of crystallisation at half occupancy with disorder of the OH group which occupied positions consistent with hydrogen bonding to N(3) of one of the pyrimidine rings.

As a result of this work, similar experiments were attempted using a range of N-heteroaromatic compounds containing an exocyclic sulphur and a labile proton. The ligands used were: 2SpyH,

dithiouracil, 2-mercaptopurine, 6-mercaptopurine and 2-thiobarbituric acid.

Of these, the only successful reaction was that with 2-mercaptopyridine which yielded an almost identical looking product analysing as MoL_4. The physical properties were similar to $Mo(2SPym)_4$ and it was assumed that the molecular structure would also be mmmm dodecahedral with sulphurs occupying the A sites. The other ligands either did not react or gave unusual stoichiometries, perhaps indicating polymerisation. However in these cases the yields were much lower than for the reactions giving the MoL_4 products.

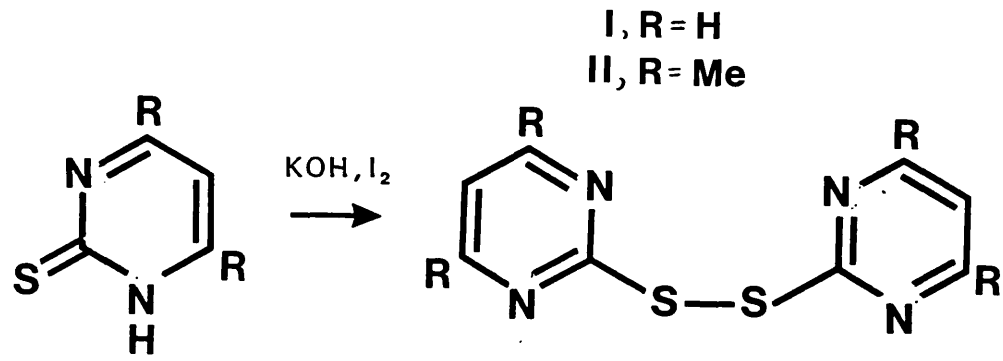
3.3 EXPERIMENTS WITH MOLYBDENUM(0)

In an attempt to obtain a more soluble molybdenum(IV) species, to enable n.m.r. investigation, repeated attempts were made to isolate the $Mo(4,6Me_2 2SPym)_4$ complex. The previous difficulty in isolating a solid compound seemed to imply a greater solubility of product. In the ensuing experiments it was found that $Mo(CO)_6$ reacted with 2SPymH to give $Mo(2SPym)_4$ slowly and in poorer yield than that for the $MoCl_3py_3$/2SPymH reaction. A similar reaction of $4,6Me_2$2SPymH with $Mo(CO)_6$ in benzene yielded some purple solution but purple solid, analysing as MoL_4, was only obtained in poor yield. To try to improve the yield of these experiments a different strategy was employed.

In order to form a complex MoL_4 from $Mo(CO)_6$ the molybdenum must undergo a four electron oxidation. To facilitate this oxidation the pyrimidine ligand was added in the form of the appropriate disulphide (I and II in the Figure 3.6),synthesised by iodine oxidation of the parent ligand.

The disulphide could then act as an oxidising agent itself, generating the mercaptopyrimidinate in situ as the molybdenum oxidised. This method proved most successful, giving $Mo(2SPym)_4$ in good yield and yielding a dark solid which analysed as $Mo(4,6Me_2 2SPym)_4$ with the dimethylated ligand derivative. The $Mo(4,6Me_2 2SPym)_4$ would not redissolve, however, to give an intensly coloured solution, either in benzene or in alcohol. The liquor from the reaction mixture was dark purple but, on carrying out the reaction in deuterated benzene and running the magnetic resonance spectra on the liquor no signal was seen for molybdenum or for protons.

Figure 3.6 Oxidation Of Pyrimidinethiones



A possible explanation for this is that the Mo(IV) complex is not the species responsible for the intense colouration of the methanol and benzene reaction mixtures. It is known, for instance, that reaction of $Na4,6Me_2 2SPym$ with $Mo(CO)_6$ in benzene gives the dinuclear compound $Mo_2(\mu\text{-}4,6Me_2 2SPym)_4$ [104]. This complex crystallises from a red solution and may be responsible for the intense colour in the solutions. It is also possible that other species may be present as the redox process proceeds and it may be that paramagnetic species broaden any n.m.r. bands which might otherwise have been observed.

Reactions of $Mo(CO)_6$ with various ligands in refluxing benzene gave two types of product. With proton-labile sulphur ligands the dark red colouration of the reaction mixture which gives MoL_4 was produced, as has already been described. $Mo(CO)_6$ reacted with the proton-labile oxygen ligands to give scarlet solutions and a little red solid. The products were, however, extremely air sensitive, both in solution and as the solid, quickly darkening on contact with air to give a black intractable mass.

Three of the four N-methylated ligands reacted with molybdenumhexacarbonyl. 1Me2OPym and $1,4,6Me_3$2OPym both reacted to give scarlet crystalline solids with the stoichiometry $Mo(CO)_4L_2$. $1,4,6Me_3$2SPym gave orange crystals with analysis results consistent with $Mo(CO)_5L$. The complex $Mo(CO)_4(1Me2OPym)_2$ was stable for days in air while $Mo(CO)_4(1,4,6Me_3 2OPym)_2$ and $Mo(CO)_5(1,4,6Me_3 2SPym)$ were unstable over periods of more than a few hours, darkening to brown, tarry solids.

As none of the crystals was suitable for X-ray crystallographic studies the probable structures were assigned on the basis of infrared spectra. In the case of the $Mo(CO)_4L_2$ complexes, the shifts of the ring carbonyl vibrations to higher frequency on forming these complexes are consistent with bonding via nitrogen, leading to the conclusion that the ligands were binding in a monodentate mode.

For a complex $Mo(CO)_4L_2$, where L is a monodentate ligand, <u>cis</u> and <u>trans</u> isomers are possible.The <u>cis</u> configuration has a site symmetry of C_{2v} and all the normal modes of vibration for the carbonyl groups are both infrared and Raman active.

These normal modes are $2a_1 + b_1 + b_2$; they appear generally as a sharp $a_1(1)$ mode of medium intensity followed by a complex set of bands which may not always be resolved into the remaining carbonyl normal vibrations. The trans isomer, on the other hand, has a site symmetry at molybdenum of D_{4h} and so the normal modes of vibration would be $a_{1g} + b_{1g} + e_u$. The a_{1g} and b_{1g} modes would be Raman active and the e_u mode infrared active (the centre of symmetry implies that no vibration should, by simple group theoretical calculations, appear in both the Raman and infrared spectra). In practise, the infrared spectra of such compounds typically have one intense carbonyl band, assigned as the e_u mode. In some cases very much weaker absorptions, corresponding to the Raman active bands, are observed in the infrared spectrum at higher frequency than the e_u mode. Such transitions may become allowed, with a small transition probability, as a result of the geometry about the molybdenum centre not being rigorously D_{4h}, which is clearly unlikely to be the case when one considers the complex as a whole rather than just the coordination sphere around molybdenum.

In fact $Mo(CO)_4(1Me2OPym)_2$, run as a KBr disc shows an infrared spectrum quite typical of a cis-$Mo(CO)_4L_2$ system. It has a sharp, medium intensity band (a_1) at 2013 cm^{-1} and three other bands, well resolved and with roughly equal intensity, at 1890,1848 and 1802 cm^{-1}. Comparison of these results with those found for the complex $Mo(CO)_4py_2$ [122] shows similarity in the spread and relative intensities of the bands. Combining infrared and microanalytical results, the complex is assigned as cis-$Mo(CO)_4(1Me2OPym)_2$, with ligands binding via N(3).

Generally, care must be taken when comparing infrared spectra of compounds in different physical states. The results given by Kraihanzel and Cotton [122] were almost all for solutions of molybdenum complexes in solution, in which intermolecular interactions are reduced. When the i.r. spectrum of a nitromethane solution of $Mo(CO)_4(1Me2OPym)_2$ was obtained, a dramatic change in the form of the spectrum was observed, indicating that a structural change had occurred on dissolving the complex.

The most striking feature of the spectrum was a high intensity band at 1940 cm^{-1}, with weaker absorbances at 2078 and 1892cm^{-1} and a slight shoulder to the main peak at 1946cm^{-1}. Comparison of this spectrum with published results for complexes of the type $Mo(CO)_4L_2$ leads to the assignment of the observed dissolved species as being trans-$Mo(CO)_4(1Me2OPym)_2$.

The strong absorbance at 1946 cm^{-1} is assigned to the doubly degenerate infrared active e_u mode. Slight asymmetry in the molecule may partially lift the degeneracy of the e_u mode giving rise to the observed shoulder. Similarly the asymmetry leads to a partial lifting of the Raman selection rules allowing the symmetric stretches to be discerned in the infrared. The spectrum could also be interpreted as a $Mo(CO)_5L$ spectrum but it is difficult to see how such a complex could form without forming other carbonyl species which would complicate the observed simple spectrum.

Accurate spectroscopy of the other carbonyl complexes was hampered by their instability, especially in the heat of the i.r. beam. The 1,4,6$Me_3$2OPym product (as solid) gave a strong, broad band at 1900cm^{-1}, possibly indicating the trans isomer - as may be expected from the larger steric effect of the trimethylated ligand.

$Mo(CO)_5(1,4,6Me_32SPym)$ decomposed rapidly in the i.r. beam, showing a sharp peak at $2015cm^{-1}$ and a broad, poorly resolved peak between 1800 and $1900cm^{-1}$.

3.4 EXPERIMENTS WITH MOLYBDENUM(V) AND (VI)

In order to investigate the reactions of molybdenum(V) with the pyrimidine ligands, two approaches were used. The first consisted of direct reaction of the ligand or its sodium salt with molybdenum(V) chloride in a suitable solvent. The second was to generate Mo(V) in an aqueous environment by the action of dithionite on a molybdate solution.

3.4.1 Reactions With Molybdenum(V) Chloride

The reactions with molybdenum(V) chloride were hampered by its reactivity towards solvents suitable for the ligands. Molybdenum(V) chloride is a reactive solid which decomposes, liberating HCl, on contact with moist air. Even under an inert atmosphere, however, no solvent could be found which would dissolve the solid without reacting with it. Further research revealed the paper by Kepert and Mandyczewsky [123] who outline the different types of reaction which occur between $MoCl_5$ and various solvents.

Hydrogen chloride is evolved when molybdenum(V) chloride comes into contact with solvents containing OH or NH groups; reduction/ disproportionation may give rise to molybdenum(IV) compounds e.g. $MoCl_42(THF)$, which is formed when $MoCl_5$ is dissolved in tetrahydrofuran; oxygen abstraction occurs with such compounds as THF, DMSO and acetone. Benzene, alkanes, pyridine and nitriles give rise to low-valent molybdenum. Solutions in dioxan and in carbon tetrachloride are somewhat more stable, but neither of these was a

good solvent for the pyrimidine ligands.

Some tentative experiments were carried out using $4,6Me_2$2SPymH in dichloromethane but this yielded an extremely air-sensitive, finely divided brown product. Eventually it was decided that even if a suitable solvent were found, the reactivity of the molybdenum(V) chloride may well have been such that the oxygen/sulphur would have been abstracted from the pyrimidine ligands, destroying their ambidentate nature. For these reasons the experiments with molybdenum(V) chloride were discontinued.

3.4.2 Reactions With Molybdates

Malatesta [84,126] and Moore et al. [127] have produced oxomolybdenum complexes of dithiocarbamates with molybdenum in oxidation states (V) and (VI). The former were synthesised by generation of Mo(V) <u>in situ</u> using an acidic molybdate solution and dithionite as a reducing agent. The molybdenum(VI) complexes were formed by neutralisation of acidic ligand solutions in the presence of the molybdate ion. More recently, similar experiments have been carried out using tetrabutylammonium octamolybdate and ammonium paramolybdate as the molybdenum source [124,125].

In corresponding experiments with the pyrimidinones and pyrimidinethiones no reactions were observed. Neutralisation of acidic molybdate solutions containing 2SPymH and $4,6Me_2$2SPymH (or rather their hydrochloride form, considering the low pH (<4)) produced the ligands in quantitative yield independent of the temperature of the reactions (which were carried out at 0°C, ambient temperature and at c.a. 70°C).

The oxygen analogues, being water soluble, did not precipitate on neutralisation but did not form complexes either. On reducing the neutral solutions virtually to dryness no evidence of coordination was found in the infrared spectra of the solids, which crystallised on cooling. These solids were, in each case, free ligand, sometimes with some molybdate impurity.

Similar results were obtained in the presence of dithionite and when octamolybdate was used as the molybdenum source.

3.4.3 Experiments With Bis(2,4-pentanedionato)dioxomolybdenum(VI)

Bis(2,4-pentanedionato)dioxomolybdenum(VI) ($MoO_2(acac)_2$) is a useful source of the cis-dioxomolybdenum(VI) unit. It is easily synthesised from 2,4-pentanedione and molybdenum trioxide and is readily soluble in methanol [128]. Although the solid is reasonably stable, solutions of the compound decompose, from an initial orange to yellow and eventually colourless solution in alcohols and, more rapidly, to blue/green solutions in aprotic solvents such as benzene, chloroform and acetonitrile. Thus $MoO_2(acac)_2$ must either be added directly, as a solid, to a ligand solution or it may be dissolved first but should be used immediately to minimise side reactions.

$MoO_2(acac)_2$ has been used by others in the synthesis of various oxomolybdenum complexes [124,125,129]. Typically the $MoO_2(acac)_2$ is reacted with the ligand in an alcohol solution resulting in a simple ligand replacement.

Reaction of each of the hydroxy and mercaptopyrimidine ligands with $MoO_2(acac)_2$ was attempted, using dry, degassed methanol as the solvent and carrying out the reactions under nitrogen.

Only one of the ligands showed any signs of reacting, this was $4,6Me_2$2SPym. All the other reactions showed no difference in colour when compared with a control experiment without ligand and only impure solids were deposited on concentrating the reaction mixtures. Such solids showed infrared peaks consistent with the free ligand together with some additional peaks. The solids appeared impure and the microanalysis (C,H,N) results approached those of the free ligand. Such results indicate that complex formation with these ligands is not favoured, the impurity evident in the infrared spectra is assumed to be a breakdown product of the $MoO_2(acac)_2$.

The reaction mixture using $4,6Me_2$2SPymH gave a dark maroon coloured solution, within five minutes of mixing the $MoO_2(acac)_2$ and the ligand solutions. On refluxing, this colour intensified to purple.

Various attempts were made to isolate the purple compound. Concentration of the solution followed by cooling gave an orange solid (see below), but no purple product. Evaporating the reaction mixture to dryness under reduced pressure gave a pale solid, containing unreacted ligand, which did not regenerate the purple colour when redissolved in methanol. Addition of bulky anions or cations (BPh_4^-,NBu_4^+ and Cs^+) did not yield a solid or change the colour of the solution. Similarly, oxidising and reducing reagents did not give a solid product although BH_4^- caused a deepening of the purple colour, reverting to the original purple-red as effervescence subsided. Reaction with triphenylphosphine gave a similar darkening

in colour.

The original purple-red solution was found to be sensitive to moisture. If water was added in quantity the red colour was lost instantly, liberating free ligand as a precipitate. On allowing the dark red solution to stand for a week the colour faded to orange and orange crystals were deposited. The C, H and N microanalysis results were consistent with $MoO_3L.nMeOH$, n=2.5 or 3, although both these formulations were found to be incorrect at a later stage. The experiment was repeated with the addition of 2,2dmp to scavenge any water, as it was considered that the slow fading of the purple solution to orange may have been reflecting a partial decomposition due to moisture reaching the reaction mixture. However the reaction followed a similar course and yielded an identical product (by analysis and infrared spectroscopy)

The orange solid was diamagnetic and its n.m.r and i.r spectra, indicated that coordination of the thione ligand had taken place, i.e. the product was not simply a complex molybdate with protonated ligands present as counter-cations. Detailed interpretation of the i.r. spectrum was not straightforward due to its complex nature. E.p.r. spectroscopy of the red reaction mixture (as frozen solution) indicated the presence of some paramagnetic species but these signals were very weak and dependent on the length of time the reaction had proceeded before freezing. Control solutions containing $MoO_2(acac)_2$ but no ligand showed very similar signals in the e.p.r. spectrum (X-band) and so these could not be attributed to complex formation.

Crystals formed by these original reaction mixtures were too small and flat to be suitable for X-ray structure determination. Suitable crystals were obtained, however, by carrying out the reactions at much higher concentrations than those previously used. At these increased concentrations small clusters of crystals formed in a few days and by breaking up these groups a crystal was eventually selected. The structure is shown in figures 3.7 and 3.8.

Crystal Data For $Mo_2O_3S(4,6Me_2SPym)_2MeOH$

$Mo_2C_{13}H_{18}N_4O_4S_3$, M=582.4, orthorhombic, $\underline{a}$=7.484(1), $\underline{b}$=16.267(5), $\underline{c}$=34.023(9) Å, U=4142.0 Å^3 (at 18°C), space group Pbnb (No.56), $\underline{Z}$=8, D =1.87 gcm^{-3}. The structure was solved by Patterson and Fourier methods and least squares refinement reached R=0.042. X-ray diffraction data consisted of 2664 independent reflections (to θ=52°) of which 502 were 'unobserved'.

The complex is dinuclear (Fig 3.7) with the molybdenum atoms linked via one oxo- and one sulphido bridge. Each molybdenum is also bound to one terminal oxygen and to a $4,6Me_2SPym$ ligand which chelates via sulphur and nitrogen. The presence of the mixed μ(O,S) bridge is interesting as the sulphur must have been abstracted from excess ligand. Additionally in each dimeric unit there is a molecule of methanol coordinated to one molybdenum centre.

Figure 3.7 Structure of $Mo_2O_3S(4,6Me_2SPym)_2MeOH$

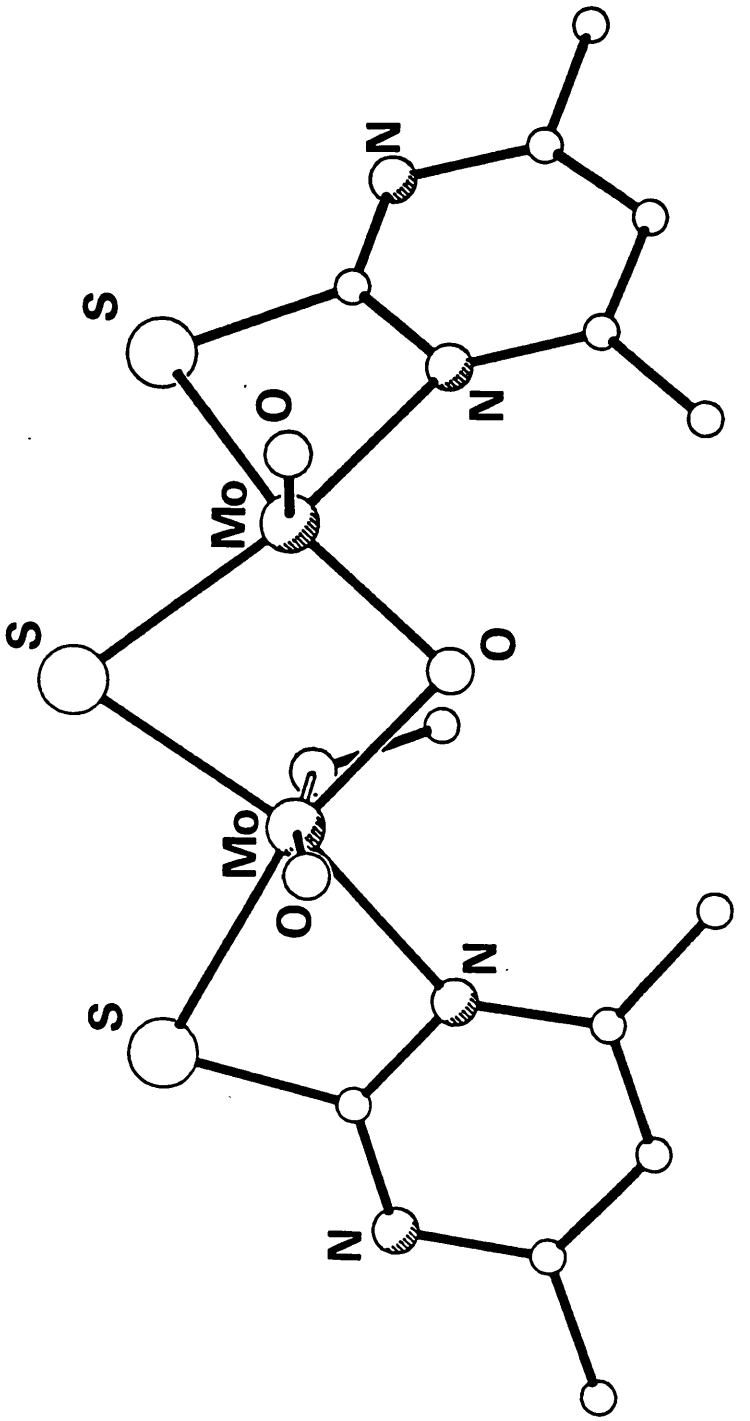
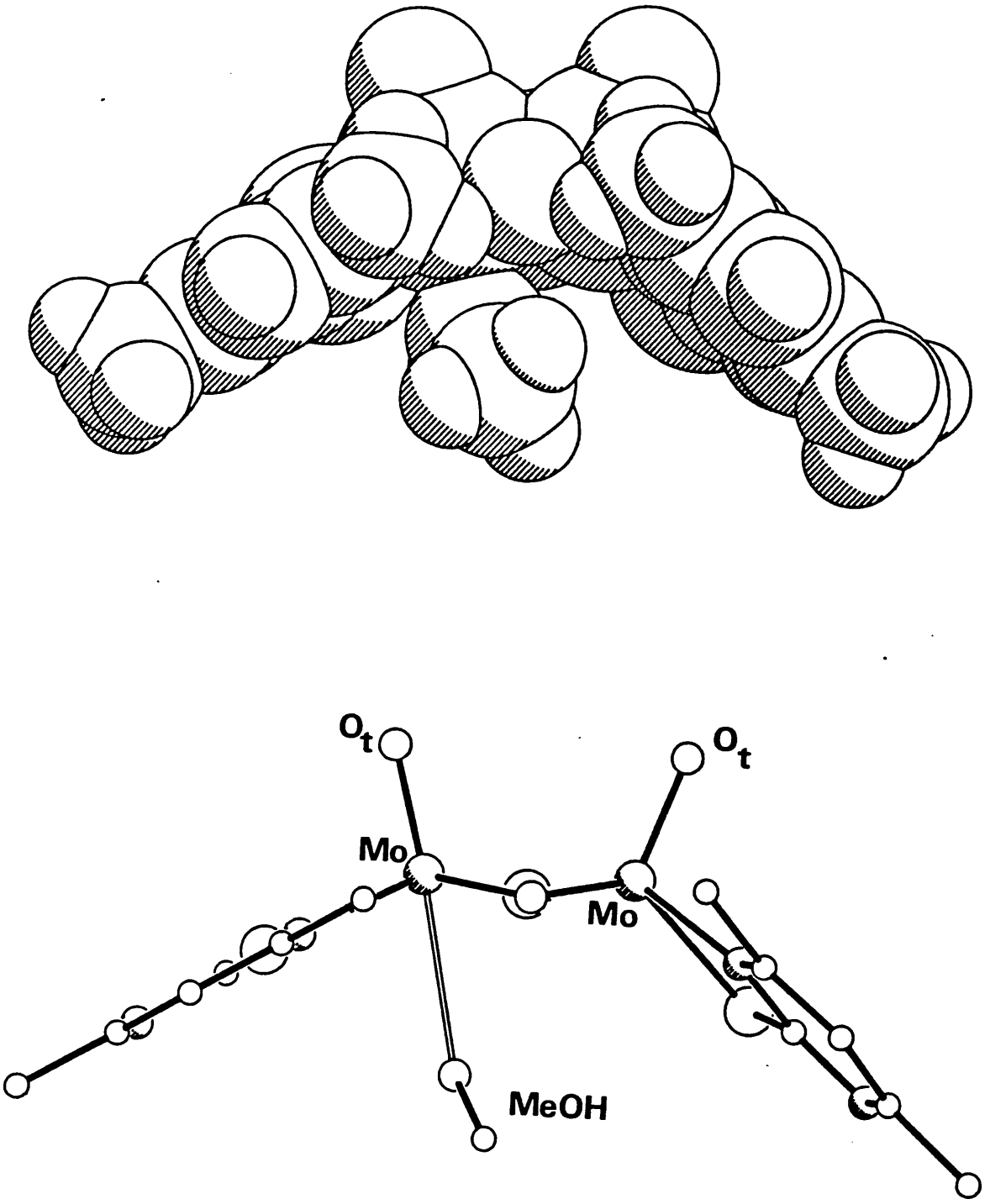


Figure 3.8 $Mo_2O_3S(4,6Me_2SPym)_2MeOH$ Showing Methanol Coordination



Molybdenum(V) complexes of the type $\{[Mo(O)L]_2O_xS_{2-x}\}$, where L is a dithiochelating ligand and x=0 or 1 have been known for some time [130], although few crystallographic studies of such complexes have been reported. Those structures which have been published are structurally very similar to complexes containing the more common $Mo_2O_4^{2+}$ core [130-135]. For such $Mo_2O_4^{2+}$ complexes, the stereochemistry around the molybdenum atoms, which are commonly either both five coordinate or both six coordinate (neglecting any Mo-Mo bond as part of the coordination sphere), has been rationalised as being the result of three effects [63].

Firstly, each molybdenum atom lies out of the plane of its 'basal' donor atoms (in this case the two bridging atoms and the chelating N, S donors). The strong Mo-O_t bond defining the local tetragonal axis is largely responsible for this effect although it should be noted that SCFMO calculations have indicated that in this type of complex there is significant bonding between the terminal oxygen atoms and the 'opposite' molybdenum atoms in the same molecule (e.g. between Mo(1) and $O_t(2)$ in this complex). Such an interaction would also be expected to produce this sort of distortion [137].

The two molybdenum atoms and the bridging atoms are not coplanar; the μO and μS atoms are displaced away from the terminal oxygens such that the angle between the planes defined by μO-Mo1-μS and μO-Mo2-μS is 160°. This displacement of the bridging atoms allows the molybdenum atoms to approach each other more closely than would a planar arrangement, without unduly contracting the Mo-μ(O,S)-Mo angles. The resulting Mo-Mo distance of 2.660(1) Å, together with the Mo-μO-Mo and Mo-μS-Mo angles of 87.6(2)° and 69.9(1)° indicate the presence of a metal-metal bond. Additional

evidence for a Mo-Mo interaction is provided by the magnetic properties of the compound. Neither solid nor frozen solutions gave an e.p.r. signal at X-band, the solid was shown to be diamagnetic by Evans' balance measurements, and deuterochloroform solutions showed sharp proton n.m.r. signals. Molybdenum(V), unless strongly coupled, would be paramagnetic. If this were the case we would expect a consequent broadening of the n.m.r. signals and, possibly, the appearance of e.p.r. signals, at least at low temperature.

The bonding scheme may be qualitatively described as follows. The $4d_{x^2-y^2}$, $4d_{z^2}$, 5s, $5p_x$, $5p_y$ and $5p_z$ orbitals are used in sigma bonding to the various ligands, the z axis being defined by the Mo-O_t vector. The $4d_{xz}$ and $4d_{yz}$ are then used in π-bonding to the terminal oxygen leaving one unpaired electron in each molybdenum $4d_{xy}$ orbital. These orbitals, however, are oriented in such a way as to allow direct overlap with consequent Mo-Mo bonding (Fig 3.9)

Figure 3.9 Mo-Mo Orbital Overlap For The Mo(V) Dimer

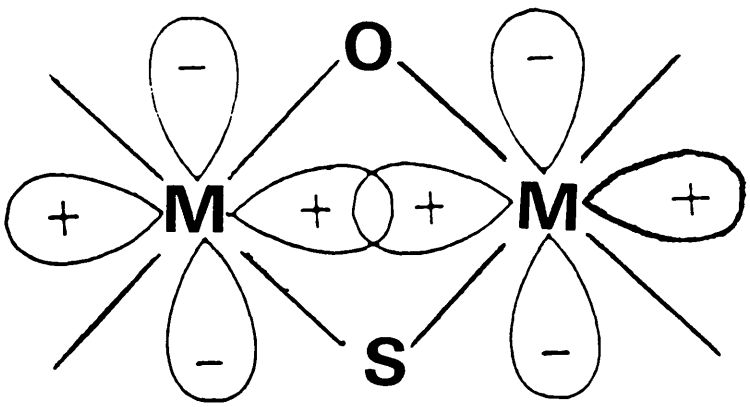


Table 3.2 Bond Angles And Bond Lengths For $Mo_2O_3S(4,6Me_2SPym)_2MeOH$

Bond Lengths (Å)

Mo1-Mo2	2.660(1)	Mo1-S1	2.435(3)
Mo1-S3	2.319(2)	Mo1-O1	1.911(5)
Mo1-O11	1.664(6)	Mo1-N11	2.180(7)
Mo2-S2	2.489(2)	Mo2-S3	2.321(3)
Mo2-O1	1.933(5)	Mo2-O21	1.670(6)
Mo2-N21	2.209(7)	Mo2-O2	2.535(6)
S1-C12	1.751(9)	S2-C22	1.738(8)
N21-C22	1.360(10)	N21-C26	1.340(11)
N23-C22	1.332(10)	N23-C24	1.343(11)
N11-C16	1.340(11)	N11-C12	1.364(12)
C16-C18	1.498(14)	C16-C15	1.367(13)
N13-C14	1.341(12)	N13-C12	1.303(12)
C26-C25	1.367(13)	C26-C28	1.488(13)
C24-C25	1.393(12)	C24-C27	1.481(12)
C15-C14	1.376(13)	C14-C17	1.474(14)
O2-C2	1.419(12)		

Bond Angles (Degrees)

Mo2-Mo1-S1	128.3(1)	Mo2-Mo1-S3	55.0(1)
S1-Mo1-S3	86.5(1)	Mo2-Mo1-O1	46.5(2)
S1-Mo1-O1	131.2(2)	S3-Mo1-O1	100.2(2)
Mo2-Mo1-O11	111.2(2)	S1-Mo1-O11	112.4(2)
S3-Mo1-O11	106.8(2)	O1-Mo1-O11	111.6(3)
Mo2-Mo1-N11	127.9(2)	S1-Mo1-N11	66.7(2)
S3-Mo1-N11	146.6(2)	O1-Mo1-N11	84.6(2)
O11-Mo1-N11	101.8(3)		
Mo1-Mo2-S2	141.3(1)		
Mo1-Mo2-S3	55.0(1)	S2-Mo2-S3	91.5(1)
Mo1-Mo2-O1	45.9(2)	S2-Mo2-O1	145.9(2)
S3-Mo2-O1	99.5(2)	Mo1-Mo2-O21	104.8(2)
S2-Mo2-O21	102.6(2)	S3-Mo2-O21	106.0(2)
O1-Mo2-O21	105.1(3)	Mo1-Mo2-N21	134.6(2)
S2-Mo2-N21	66.1(2)	S3-Mo2-N21	150.4(2)
O1-Mo2-N21	90.6(2)	O21-Mo2-N21	98.0(3)
Mo1-Mo2-O2	79.1(1)	S2-Mo2-O2	77.3(2)
S3-Mo2-O2	81.7(1)	O1-Mo2-O2	72.6(2)
O21-Mo2-O2	172.3(3)	N21-Mo2-O2	74.8(2)

Bond Angles (Degrees) continued

Mo1-S1-C12	82.3(3)	Mo2-S2-C22	81.1(3)
Mo1-S3-Mo2	70.0(1)	Mo1-O1-Mo2	87.6(2)
Mo2-N21-C22	101.0(5)	Mo2-N21-C26	138.9(6)
C22-N21-C26	120.1(7)	C22-N23-C24	117.2(7)
Mo1-N11-C16	140.4(6)	Mo1-N11-C12	102.0(5)
C16-N11-C12	117.6(8)	N11-C16-C18	117.2(8)
N11-C16-C15	118.9(9)	C18-C16-C15	123.9(8)
C14-N13-C12	115.6(8)	S2-C22-N21	111.7(6)
S2-C22-N23	124.1(6)	N21-C22-N23	124.1(7)
N21-C26-C25	117.0(8)	N21-C26-C28	118.4(8)
C25-C26-C28	124.6(9)	N23-C24-C25	119.8(7)
N23-C24-C27	118.3(8)	C25-C24-C27	121.9(8)
C26-C25-C24	121.9(8)	C16-C15-C14	119.6(8)
N13-C14-C15	121.9(8)	N13-C14-C17	115.6(8)
C15-C14-C17	122.5(8)	S1-C12-N11	109.0(6)
S1-C12-N13	124.6(7)	N11-C12-N13	126.4(8)
Mo2-O2-C2	129.5(5)		

The Mo-Mo distance lies nicely between typical M-M distances for complexes containing the MoO_2Mo bridge (e.g. 2.55 Å for $Mo_2O_4(histidine)_2$ [138]) and those containing the MoS_2Mo bridge (e.g. 2.82 Å for $Mo_2O_2S_2(histidine)_2$ [139]). As the geometries of these complexes are very similar, the differences in bond lengths may be directly attributed to the larger steric effects of sulphur compared to those of oxygen.

Finally, it will be noticed that the terminal oxygens are bent back from each other (Mo-Mo-O_t > 90°). If this were not the case then the $O_t \bullet\bullet\bullet O_t$ distance would be 2.66 Å (i.e. the Mo-Mo distance) which is shorter than the Van der Waals contact distance of 2.80 Å. Thus tetragonal distortion, Mo-Mo bonding and O_t-O_t repulsion contribute to the basic geometry of the $OMo_\mu(O,S)MoO^{2+}$ unit.

$Mo_2O_3S(4,6Me_2 2SPym)_2MeOH$ has some additional structural features which perturb this straightforward structural description however. Firstly, the $4,6Me_2 2SPym$ ligands chelate via N and S. In previously reported complexes containing an $OMo(X,Y)MoO^{2+}$ [X=O,S; Y=O,S] core the chelating ligands have invariably been of a single donor type. Secondly, a molecule of methanol is bound to one of the molybdenum atoms, trans to the terminal oxygen (this is well defined and not a disordered solvent molecule). Both these features would be expected to affect the structure of the complex and, indeed, some structural effects are observed when we investigate the molecule in more detail.

Although both Mo atoms have a square based pyramidal environment, with the metal atom lying out of the plane of the basal donor atoms bonded to it and towards its associated terminal oxygen, the geometries around the two metals are appreciably different.

Mo(1) lies 0.68 Å above the mean plane of its basal donor atoms, while Mo(2), having methanol bound to the sixth coordination site, is only 0.51 Å above the corresponding plane in the other half of the molecule, so that it approaches octahedral geometry with a concomitant opening of the equatorial angles. Although the sulphido-bridge remains symmetrically disposed between the molybdenum atoms, the oxo- bridge lies towards Mo(1); [Mo(1)-μO = 1.910(6) Å, Mo(2)-μO = 1.932(5) Å]. There is a slight lengthening of the Mo-N bond as a result of methanol coordination (Table 3.2), but the largest effect is seen in the Mo-S(ligand) distances: [2.435(3) Å for Mo(1)-S(1) and 2.489(2) Å for Mo(2)-S(2)]. There is no significant lengthening of the Mo-O bond as a result of methanol coordination and the oxygen atoms remain eclipsed (O(11)-Mo(1)-Mo(2)-O(21) torsion angle= 2.8°). An almost linear hydrogen bond exists between the methanol oxygen and the N(23) of the adjacent dimer.

Several complexes are now known which contain this type of 'core' and which have solvent or other molecules bound to give either symmetrical or asymmetric adducts, with at least one molybdenum atom being six-coordinate.

The first such compound to be reported was $Mo_2O_3(NH)(S_2P(OC_2H_5)_2]_2$ [131]. This compound, containing a mixed μ(O), μ(NH) bridge, showed THF bound asymmetrically to one molybdenum atom ($Mo\text{-}O_{THF}$ =2.633(3) Å). The THF is loosely bound, as suggested by the long $Mo\text{-}O_{THF}$ distance, and is lost from the solid at room temperature.

More recently there have been a series of publications by Drew et al. [132-134] who reported the structures of various 1:1 adducts of the type $Mo_2O_3S(S_2P(Oi\text{-}Pr)_2)_2L$, obtained by adding N-heteroaromatic ligands to $Mo_2O_3S(S_2P(Oi\text{-}Pr)_2)_2$.

When L = pyridine the product is symmetrical with Mo-N distances of 2.97 and 2.93 Å, the pyridine ring being almost coplanar with the bridging oxygen and sulphur atoms. Although this $Mo\text{-}N_{py}$ distance is long, the presence of a bonding interaction is inferred from the changes in conformation around molybdenum on addition of the pyridine [132].

When L = pyrimidine the N-ligand is found in a similar orientation to that of the pyridine in the previous compound, but it is preferentially bound to one molybdenum (Mo-N=2.86 Å) and consequent differences between the coordination geometries of the two molybdenum atoms result [134].

The most recently reported structure is that of the pyridazine adduct [133]. Here, however, the mode of binding is somewhat different, as the plane of the pyz molecule lies parallel to the Mo-Mo vector and each molybdenum atom is bound to a separate pyz nitrogen, forming a Mo-N-N-Mo bridge (Mo-N=2.58 Å).

In $Mo_2O_3S(4,6Me_2SPym)_2MeOH$ the $Mo\text{-}O_{MeOH}$ distance is 2.535(6) Å, which is much shorter than for the previously reported asymmetric complexes. The strength of the Mo-L interaction should depend on both the ligand basicity and steric factors [133]. Pyridine, being more basic than methanol, would be expected to bind more strongly to molybdenum than does methanol, all other things being equal. However there are two other major differences between the $Mo_2O_3S(S_2(Oi\text{-}Pr)_2)_2L$ compounds and $Mo_2O_3S(4,6Me_2SPym)_2MeOH$.

Firstly the $Mo_2O_3S(4,6Me_2SPym)_2$ unit is very open around the vacant molybdenum sites due to the planarity of the pyrimidine ligands, whereas in Drew's compounds the alkoxy chains must hinder the approach of an additional ligand to some degree. The other factor is the small size of the methanol which also reduces steric interactions between the incoming molecule and the molybdenum complex. It can readily be seen in the space-filling diagram (Fig. 3.8) how easily the methanol can approach the molybdenum centres.

An interesting point arises from this in relation to Drew's work. He states that although the molybdenum atoms in complexes of the type $[\{Mo(O)(X)\}_2(O)_x(S)_{2-x}]$ (X=dtc or phosphorodithioate, $S_2P(OR)_2^-$) are five coordinate and appear to be coordinatively unsaturated, they are regarded as showing little tendency to form adducts, except by oxidative addition. He then infers that adduct formation with certain phosphorodithioate complexes is facilitated by the presence of a "molecular crevice" formed by the ligands' alkyl chains. However, no such crevice exists in $Mo_2O_3S(4,6Me_2SPym)_2MeOH$ and yet methanol binds firmly to the sixth coordination site of one of the molybdenum atoms.

Investigation of the literature shows that direct attempts to synthesise adducts of this sort were not attempted before Drew's work and that the assertion that such adduct formation is generally not favoured may be mistaken. In the literature which Drew cites, many of the reactions were deliberately aimed at oxidative addition, using substrates which could undergo facile reduction. The attempts at adduct formation using pyridine reported by Mitchell and Scarle were not carried out on a preformed dimeric species but on $MoO(Et_2dtc)_2$ in chloroform solution [140]. In such an experiment formation of a dimeric adduct is most unlikely.

It is thus debateable whether the "molecular crevice" in the phosphorodithioate complexes facilitates adduct formation or whether the alkyl chains actually hinder close approach of potential donor molecules to the molybdenum core. If the alkyl chains were regarded as acting to "squeeze out" the donor molecule by steric repulsion, this would rationalise the long Mo-N distances reported by Drew when compared with the shorter $Mo\text{-}O_{MeOH}$ distance in the present compound where such interactions must be nearly at a minimum.

There is certainly no obvious reason why $Mo_2O_3S(4,6Me_2 2SPym)_2 py$ should not be formed by reacting the methanol adduct with pyridine and this is recommended for future work.

CHAPTER 4

MIXED-METAL COMPLEXES OF PYRIMIDINE LIGANDS

4.1 INTRODUCTION

As mentioned in the chapter 2, it has been well established that the biological activity of platinum(II) antitumour agents is related to their binding to DNA. As a result of this, considerable interest has been generated in the binding of cis-$Pt(NH_3)_2^{2+}$ and the cis-$PtCl_2$ unit to various nucleotides, nucleosides and bases of nucleic acids, and to related model compounds[141-143].

Recently Lippert has undertaken an extensive program aimed at synthesising and characterising products formed by the interaction of cis-diammineplatinum(II) and related residues with the four major bases of DNA: cytosine, thymine, adenine and guanine [144-158].

As a result of work using 1-MeThy as a model for the nucleoside thymidine, Lippert was not only able to isolate the expected cis-$Pt(NH_3)_2(1MeThy)_2$ but also, with the addition of excess "cis-$Pt(NH_3)_2(H_2O)_2^{2+}$", a dimeric platinum complex with a "head-to-head" arrangement of the ligands [159]. Further work led to the synthesis of complexes of the type $[(NH_3)_2Pt(1MeThy)_2M(1MeThy)_2Pt(NH_3)_2]$ with M= silver(I) [160] or manganese(II) [161]. In this type of compound the metals were

generally found to be held in a linear array, the ligands binding to platinum via N(3) and by exocyclic oxygen, probably O(4), to the hetero metal.

The introduction of paramagnetic manganese(II) in the latter compound made it a natural candidate for probing by e.p.r. spectroscopy. Although the structure of the compound had been solved crystallographically, e.p.r. could provide further information by describing the nature of any distortion in the ligand field about the manganese centre, thus permitting a study of the effects on the central atom of the two axially disposed platinum atoms.

In later work Lippert used 1MeUra as a model for both uridine and thymidine, instead of 1MeThy. One reason for this may have been that the polynuclear complexes with 1MeThy gave somewhat equivocal structures when solved crystallographically due to a pseudo twofold axis of symmetry through N(3) and C(6).

Much the same sort of complex was obtained with 1MeUra as had been made with 1MeThy. Introduction of copper as the secondary metal again gave rise to species which, in principle, could be studied effectively using e.p.r. spectroscopy. Using this technique we have examined a range of copper-1MeU-platinum systems, each containing a Pt-Cu-Pt linear array, allowing the effects of the counter anions and of replacing some of the ligands with the related 1MeC to be gauged. During these studies, slight irregularities in some of the spectra led us to wonder whether the samples might not be completely pure. Possible impurities were the corresponding cis-$[(NH_3)_2PtL_2Cu(H_2O)_2]^{2+}$ complexes. The compound cis-$[(NH_3)_2Pt(1MeU)_2Cu(H_2O)_2]SO_4.4.5(H_2O)$ had already been isolated

using an excess of Cu^{2+} and had been shown crystallographically to contain pairs of [Pt,Cu] units arranged in a "head-to-head" fashion [162]. E.p.r. spectroscopy of this compound has now revealed an unexpected Cu-Cu interaction.

Synthesis and e.p.r. spectroscopy of cis-$[(NH_3)_2Pt(1MeT)_2Cu(1MeT)_2Pt(NH_3)_2](NO_3)_2$ has permitted a direct comparison to be made with the original results for the manganese complex providing a correlation between the manganese and copper systems. More recently Lippert has incorporated further metals in similar compounds containing the [Pt,M,Pt] moiety (M= Fe(III), Ni(II), Co(II)) [163]. We have studied the e.p.r. spectra of the iron(III) complex for comparison with Mn(II) and the electronic spectra of the nickel(II) and cobalt(II) complexes, to examine the unusual ligand fields about the central metal ions in these compounds.

4.2 E.P.R SPECTROSCOPY OF A (PT,MN,PT) COMPLEX OF 1-METHYLTHYMINE

X-ray crystallography has shown that the complex cis-$[(NH_3)_2Pt(1MeT)_2Mn(1MeT)_2Pt(NH_3)_2]Cl_2.10H_2O$ (I) contains a linear Pt(II)Mn(II)Pt(II) array with the coordination geometry around the manganese being centrosymmetric as described in table 4.1

Table 4.1 - Bond lengths and angles around manganese

Mn - Pt	2.704 Å	O(4)-Mn-O(4)′	94.5°
Mn - O(4)	2.103 Å	Pt-Mn-O(4)	82.2°
Mn - O(4)′	2.158 Å	Pt-Mn-O(4)′	101.1°

(Data from reference [161])

E.p.r. spectroscopy provides an excellent method for probing the symmetry of the ligand field around high spin manganese(II). Departures from cubic symmetry are described by zero-field splitting parameters D and E; D is a measure of axial and E rhombic distortions in the ligand field. The parameter λ (=E/D) is generally used in associated calculations. By a judicious choice of axes we may always have $\lambda < 1/3$.

The X-band (9.50GHz) spectrum of a polycrystalline sample of (I) was extremely simple, consisting of a strong band at 121.3mT (Fig 4.1(A)). Such a spectrum is consistent with a very high D value and a low λ value. The asymmetry in the derivative peak suggested that $\lambda \neq 0$.

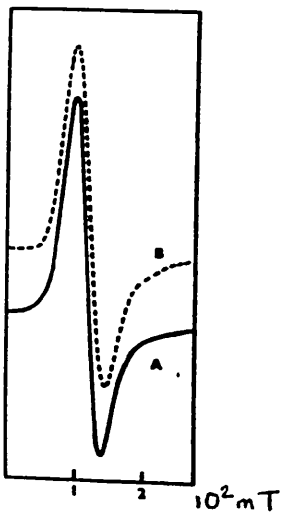
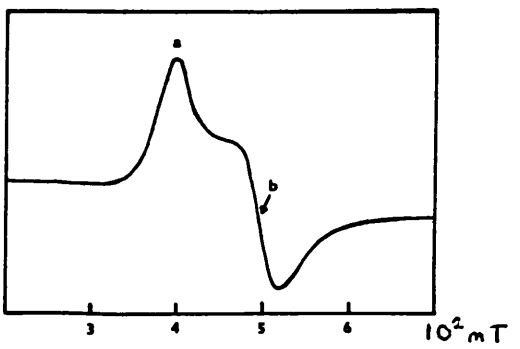


Figure 4.1 X-Band (9.50GHz) Spectrum Of The Pt_2Mn complex (I)
A, Experimental
B, Simulated for
$D=1.9cm^{-1}$, $\lambda=0.026$

On changing the microwave frequency from X-band to Q-band (35.98GHz) we were able to resolve the band into two components at 399.3 and 496.2mT. These field strengths correspond to the peak a and crossover b (Fig 4.2) respectively.

Figure 4.2 Q-Band (35.98GHz) spectrum of the Pt_2Mn complex (I)



The Q-band spectrum also showed a weak, poorly resolved band at c.a. 1.31T.

Derivation of the D and λ values from the positions of these transitions was achieved with the aid of the computer program ESRS [164] which calculates transition fields and produces simulated spectra for given values of D, λ, working frequency etc.

By running a series of simulations of the Q-band spectrum and noting the effect of D and λ on the axial transition fields the experimental fields could be approached iteratively.

In the first instance, the evaluation of λ was based on the separation of the x and y components, rather than on their absolute positions. This separation could be measured fairly accurately at Q-band, and the low value thus obtained was consistent with the small rhombic distortion about the manganese found from the crystallographic study (Table 4.1). The determination of D could not be as precise as that of λ because of the simplicity of the spectrum, together with the fact that at large values of D the resonance fields of the x and y components become decreasingly sensitive towards changes in D.

The final, calculated, value of D should be regarded as something of a lower limit to the actual value. Certainly D cannot be significantly lower than $1.9cm^{-1}$, as below this value high field transitions, showing pronounced D-dependence would be expected to be observed [165-166]. At high values of D these bands move to fields beyond the range of conventional spectrometers.

Table 4.2 Q-Band (35.98GHz) transitions for the Pt_2Mn complex (I)

Observed field /mT	Calculated field for $D=1.9cm^{-1}$, $\lambda=0.026$ /mT	Axis
399.3	396.1	y
496.3	491.9	x
1310*	1311	z

*Broad, weak band.

The transition at c.a. 1310mT is itself very D-dependent but, because of the weakness and broadness of the observed transition at this field, the close agreement between the observed and calculated transition fields along the z axis (Table 4.2) should be regarded as fortuitous rather than of high significance.

Even if the measured D value of $1.9cm^{-1}$ were slightly low, it is still significantly higher than those reported in the literature for other very strongly distorted six-coordinate manganese(II) compounds (e.g. for the trans N_4I_2 donor set in $Zn(Mn)(N_2H_4)_2I_2$, $D=1.21cm^{-1}$ [166] and for the trans O_4I_2 donor set in $[Zn(Mn)]B_7IO_{13}$, $D=0.624cm^{-1}$ [167]) The Mn-O distances in (I) are quite normal and the in-plane ligand field would be expected to be slightly weaker than that generated by four nitrogen donor atoms in such compounds as $M(N_2H_4)_2I_2$ [166] or $M(4\text{-Mepy})_4I_2$ [165].

We therefore conclude that the presence of the platinum(II) in axial positions in (I) produces a significantly greater tetragonal distortion than those present in well established MnN_4I_2 or MnO_4I_2 coordination spheres.

While the e.p.r. measurements on this Pt,Mn,Pt system provided a useful measure of the magnitude of D there was no way of telling from the simple spectra obtained whether the distortion represented an axial compression or elongation. Fortunately, closely analogous compounds with copper as the central atom of the Pt,M,Pt array were available and e.p.r. measurements of these compounds provided a simple method of determining the nature of the axial distortion.

4.3 E.P.R SPECTROSCOPY OF SOME PLATINUM/COPPER MIXED-METAL COMPLEXES WITH NUCLEOSIDE MODEL COMPOUNDS

When discussing the e.p.r spectroscopy of these platinum-copper systems it is useful to consider first the electronic structures and e.p.r. spectra of some more conventional complexes of divalent copper.

Strictly octahedral Cu^{2+} (d^9), would possess a degenerate ^2E_g electronic ground state. Jahn-Teller distortions produce a more stable electronic structure so that Cu(II) is usually found in a tetragonal environment - commonly with four strongly bound equatorial ligands and one or two axial ligands. Such an axial elongation gives the $d_{x^2-y^2}$ orbital as the highest energy metal-centred orbital so that it is this orbital which contains the unpaired electron. Axially compressed systems are rarer than the elongated ones and have d_{z^2} as the half-occupied metal orbital.

The spin Hamiltonian for Cu(II) in cubic symmetry is given by

$$H_s = g\beta_e S.H + AS.I \quad (1)$$

For an axially symmetric system this becomes

$$H_s = g_{//}\beta_e H_z S_z + g_{\perp}\beta_e(H_x S_x + H_y S_y) + \text{hyperfine terms} \quad (2)$$

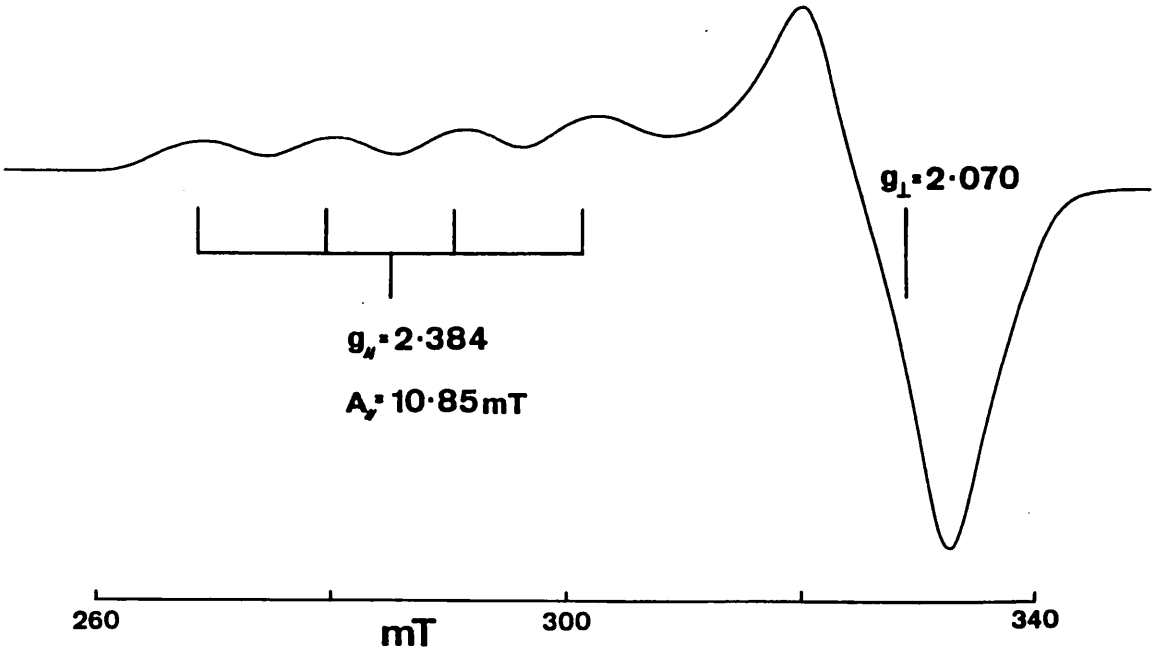
Thus we expect, neglecting any hyperfine terms, two resonance fields giving two g values by the energy equation

$$h\nu = \Delta E = g\beta H \qquad (3)$$

The net effect is that if there is an axial elongation around the copper then $g_{//} > g_{\perp}$ while for the axially compressed case $g_{\perp} < g_{//}$. Cis-$[(NH_3)_2Pt(1MeU)(1MeC)Cu(1MeU)(1MeC)Pt(NH_3)_2](NO_3)_4 \cdot nH_2O$ (II) and cis-$[(NH_3)_2Pt(1MeU)_2Cu(1MeU)_2Pt(NH_3)_2]^{4+}$, both as the sulphate dodecahydrate (III) and the nitrate hexahydrate (IV) were investigated by e.p.r. spectroscopy to determine the direction of the distortion provided by the axially disposed platinum atoms. The structure of (II) had been solved crystallographically and had been shown, as expected, to contain a linear Pt-Cu-Pt array similar to that found in the manganese compound (I) [163].

The compound cis-$[(NH_3)_2Pt(1MeT)_2Cu(1MeT)_2Pt(NH_3)_2](SO_4) \cdot H_2O$ (V) was synthesised and its spectra studied to give a closer link between the results obtained for the manganese system and those obtained for the copper complexes.

Figure 4.3 X-Band spectrum of the Pt-Cu-Pt complex (II)



The X-band spectrum of a polycrystalline sample of II is shown in figure 4.3 together with the positions of the calculated transition fields for the g and A values given. The $g_{//}$ absorption (at c.a. 287mT) is split into four components by the copper nuclear hyperfine interaction and is at lower field than the $g_{\perp}$ band (at 330mT). This immediately indicates a tetragonal elongation of the ligand field about the Cu(II) ion.

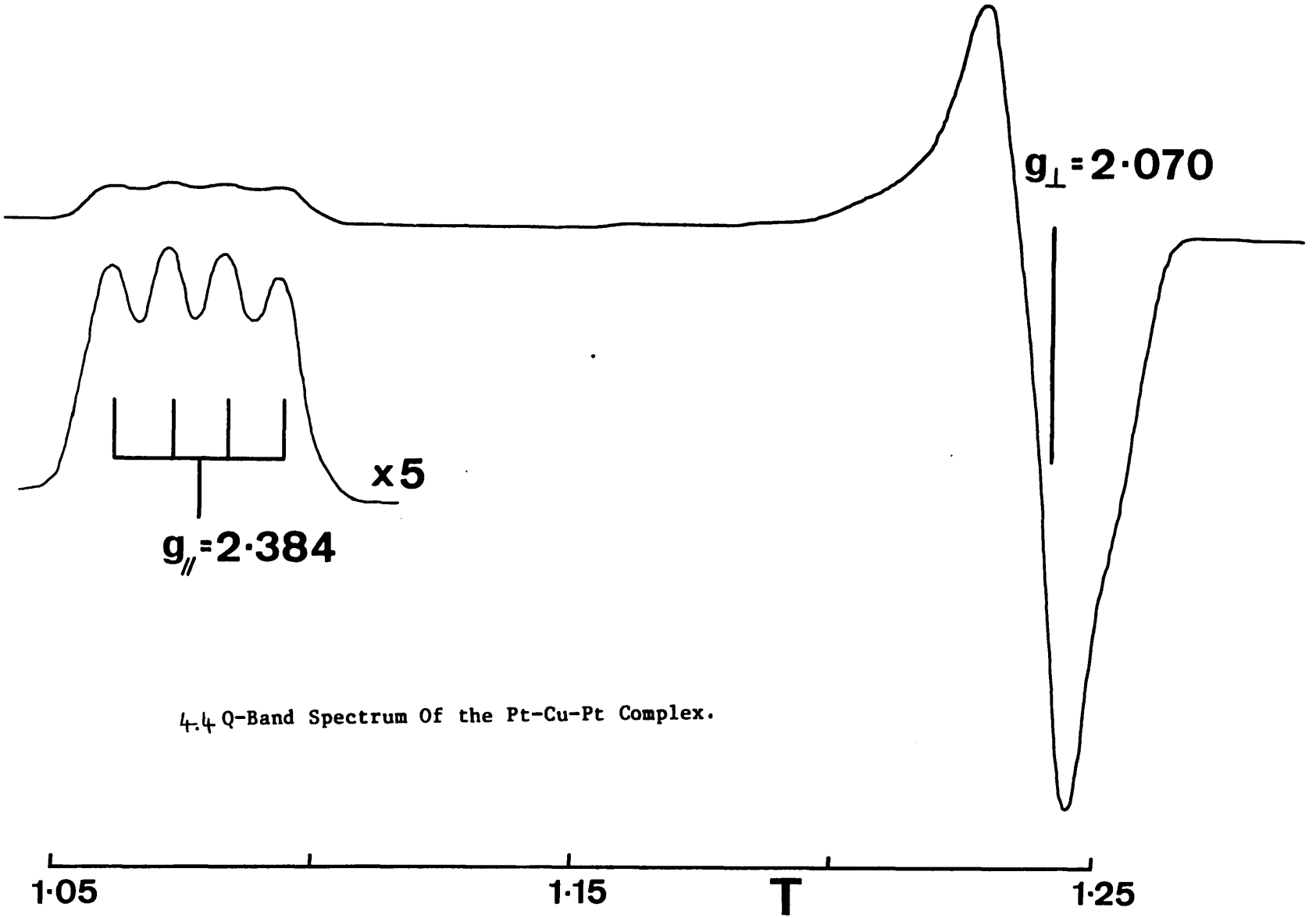
At Q-band frequency (35.98GHz), the $g_{//}$ set of transitions was completely separated from the $g_{\perp}$ region of the spectrum with the $g_{//}$ and $g_{\perp}$ signals centred at 1085mT and 1240mT respectively (Figure 4.4). From the results at both X and Q band $g_{//}$, $g_{\perp}$ and $A_{//}$ were calculated. A corellation between the observed transition fields and those expected for the calculated parameters is shown in table 4.3.

Table 4.3 Transition fields (mT) for

cis-$[(NH_3)_2Pt(1MeU)(1MeC)Cu(1MeU)(1MeC)Pt(NH_3)_2](NO_3)_4$

$g_{//}$ = 2.384 $g_{\perp}$ = 2.070 $A_{//}$ = 10.85mT

X-Band (9.514GHz)		Q-Band (35.980GHz)	
Calculated	Observed	Calculated	Observed
268.8	269.2	1062.0	1059.9
279.7	280.1	1072.9	1070.7
290.5	291.3	1083.7	1081.6
301.4	302.5	1094.6	1091.7
328.4	329.3	1241.9	1239.1



4.4 Q-Band Spectrum Of the Pt-Cu-Pt Complex.

X-ray studies of the compound show that there is a small rhombic distortion to the almost tetragonal field about the copper(II) centre, the Cu-O distances being 1.984Å for O_{MeC} and 1.943 for O_{MeU}. This distortion is not readily apparent in the $g_{\perp}$ signal, although close inspection does reveal a slight asymmetry in the absorption. The e.p.r. spectra of (III) and (IV) are very similar to those of (II). This supports the suggestion made by Neugebauer and Lippert [162] that they also contain a Pt-M-Pt array with square-planar coordination of each metal to the ligands. The results are shown in table 4.4.

Comparison of (III) with (IV) shows that there is little anion dependence. However replacement of two of the four 1MeU ligands by 1MeC, as in (II), causes an increase in $g_{//}$ and $g_{\perp}$ while reducing $A_{//}$ from 12.25 to 10.85mT. One cannot confidently correlate these differences with structural changes on replacing the ligand, however, without X-ray information about (III) or (IV).

Table 4.4 - Transition fields (mT) for

cis-$[(NH_3)_2Pt(1MeU)_2Cu(1MeU)_2Pt(NH_3)_2]$

Sulphate dodecahydrate (III)

$g_{//}$ = 2.367 $g_{\perp}$ = 2.058 $A_{//}$ = 12.14mT

X-Band (9.514GHz)		Q-Band (35.980GHz)	
Calculated	Observed	Calculated	Observed
268.9	268.6	1067.9	1068.6
281.0	280.6	1080.1	1080.9
293.2	292.6	1092.2	1093.2
305.3	304.6	1104.3	1105.4
330.3	330.2	1249.2	1249.2

Nitrate hexahydrate (IV)

$g_{//}$ = 2.362 $g_{\perp}$ = 2.056 $A_{//}$ = 12.38mT

X-Band (9.514GHz)		Q-Band (35.980GHz)	
Calculated	Observed	Calculated	Observed
269.2	269.8	1069.9	1069.2
281.6	281.9	1082.3	1081.8
294.0	293.9	1094.7	1094.7
306.4	306.3	1107.1	1107.0
330.6	331.3	1250.5	1249.7

Studies of these compounds were hampered by the difficulty in obtaining the ligands and the fact that the multi-step nature of the synthesis, together with separation of isomers, of the heteronuclear complexes made the yields low. Experiments attempting to use structurally related ligands such as 2OPymH, 4,6$Me_2$2OPymH, 2OpyH and 6Me2OpyH all failed to give the desired heteronuclear complexes. Eventually a source of 1MeThy was located and it was decided that the most useful compound to make was the copper analogue of the original manganese compound, as this would provide a useful final link between the previous copper studies and those of the Mn(II) complex.

cis-$[[(NH_3)_2Pt(1MeT)_2Cu(1MeT)_2Pt(NH_3)_2](SO_4) \cdot H_2O$ (V) was produced as a yellow, water soluble powder. As expected, the X- and Q-band e.p.r. spectra were similar to those for the other copper complexes (Table 4.5) Changing from 1MeU to 1MeT as a ligand, comparing (III) with (V) for instance, raises $g_{//}$ and $g_{\perp}$ while $A_{//}$ was lowered. This is the same pattern of changes as was observed when two 1MeU ligands were replaced by 1MeC but again we cannot expect accurately to account for these changes without further detailed crystallography.

Table 4.5 Transition fields (mT) for

cis-[[$(NH_3)_2$Pt(1MeT)$_2$Cu(1MeT)$_2$Pt$(NH_3)_2$](SO$_4$)

$g_{//}$ = 2.390 $g_{\perp}$ = 2.063 $A_{//}$ = 11.59mT

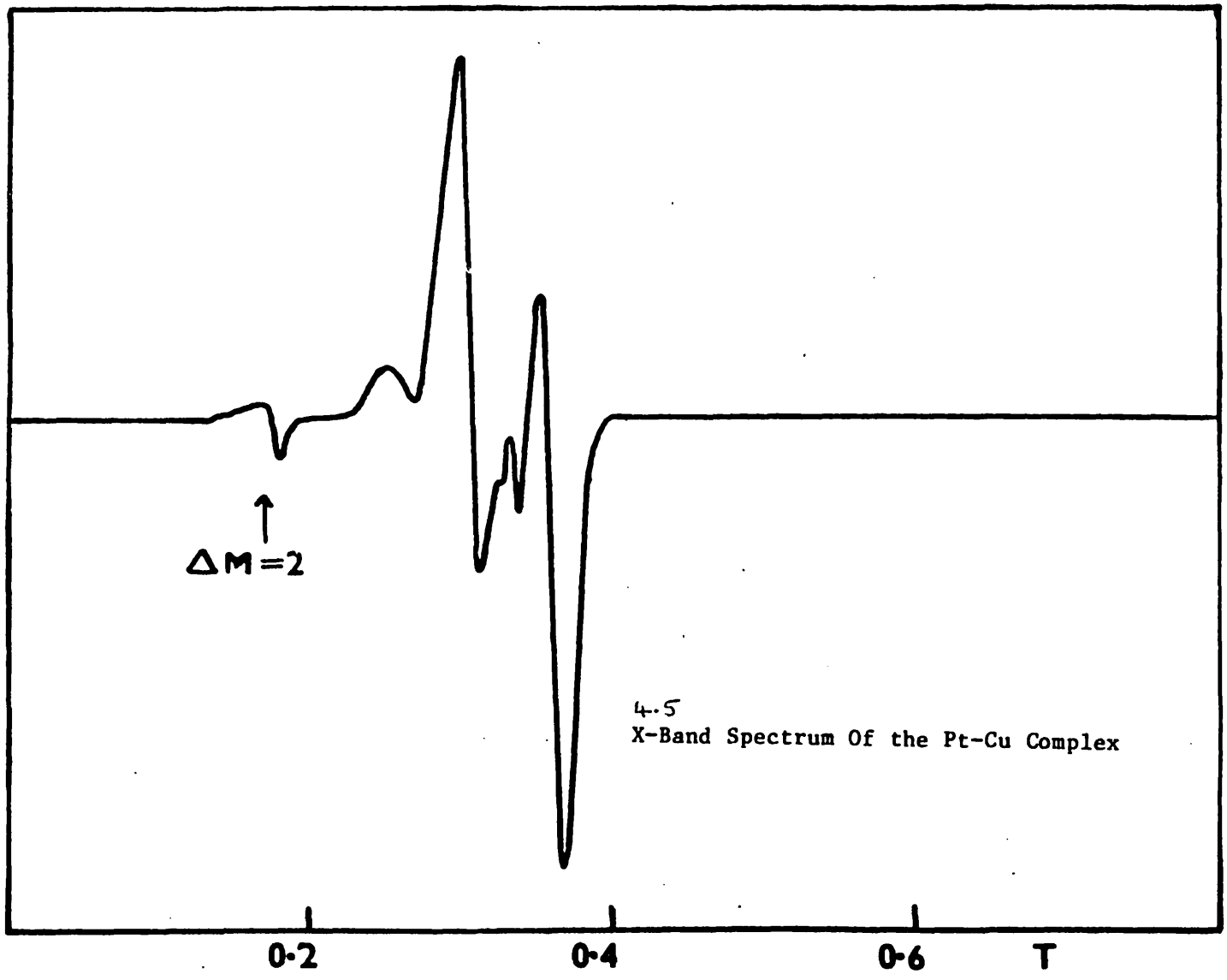
X-Band (9.514GHz)		Q-Band (35.980GHz)	
Calculated	Observed	Calculated	Observed
266.0	267.2	1060.0	1057.8
277.6	277.5	1071.6	1070.3
289.2	290.3	1083.2	1082.0
300.8	300.8	1094.8	1094.1
328.4	329.4	1248.2	1244.5

Study of the e.p.r spectra of compounds III and IV at high gain showed small shoulders on the $g_{\perp}$ components. Two possible causes were : (a) partial dehydration of the samples, giving rise to a subtle change in the stereochemical environment at the copper centre, or (b) the presence of an impurity. The latter possibility seemed reasonable because Lippert and Neugebauer had shown that the trinuclaer complexes are not the only products which one may obtain by reaction of cis-$(NH_3)_2$Pt(nucleobase)$_2$ with heterometal ions. Both bimetallic and pentametallic structures have been isolated [162,168]. The dimeric unit cis-[$(NH_3)_2$Pt(1MeU)$_2$Cu$(H_2O)_2$]$_2$ is formed when an excess of copper sulphate is reacted with the cis-$(NH_3)_2$Pt(1MeU)$_2$ unit [162]. If the situation is an equilibrium between the various species it would not be unreasonable to expect to find traces of the dimeric unit in the trimeric sample. To investigate this possibility the e.p.r. spectra of the dimeric

species, as the sulphate (VI), were measured.

It had been previously shown that, in the sulphate salt the cations pack as pairs in a centrosymmetric "head-to-head" arrangement. At the time when the structure was solved the separation of 3.483Å between the copper atoms in the cation pairs was regarded as being too great for there to be any significant interaction. E.p.r. measurements have now shown that this conclusion was not correct.

The X-band spectrum (figure 4.5) of a polycrystalline sample of (VI) is typical of those found for dipolar coupled pairs of Cu(II) ions [169]. Coupling between copper(II) sites perturbs the magnetic ground state of the Cu(II) centres. In the limit of strong interaction a Cu-Cu bond would exist, the electrons would have their spins paired in the bonding orbital, and the compound would be diamagnetic. An indirect, weaker interaction is found when bridging ligands form a superexchange pathway leading to a coupling of the unpaired spin states.



4.5
X-Band Spectrum Of the Pt-Cu Complex

In this system, however, there is no superexchange pathway so we approach a limit where 2J-->0. Here the e.p.r. spectrum is perturbed by dipolar coupling of the spins. As the spins couple we obtain an S=1 system. Assuming, to begin with, that the e.p.r. spectrum can be considered as arising simply within the triplet state we may use the spin Hamiltonian described below for the S=1 system in a distorted octahedral field.

$$H_s = \beta H.gS + D(S_z - 2/3) + E(S_x^2 - S_y^2) + \text{hyperfine terms} \quad (4)$$

where D and E are zero-field spiltting parameters as described for the Mn(II) system. Wasserman et al. have derived a set of equations for the six $\Delta M_s=1$ transitions expected for randomly oriented triplet molecules which appeared to be valid for inorganic molecules [170].

$$BX_1 = (g_e/g_x) \times [(B_0 - D' + E') \times (B_0 + 2E')] \quad (5a)$$

$$BY_1 = (g_e/g_y) \times [(B_0 - D' - E') \times (B_0 - 2E')] \quad (5b)$$

$$BZ_1 = (g_e/g_z) \times [(B_0 - D') - E'] \quad (5c)$$

$$BX_2 = (g_e/g_x) \times [(B_0 + D' + E') \times (B_0 - 2E')] \quad (5d)$$

$$BY_2 = (g_e/g_y) \times [(B_0 + D' - E') \times (B_0 + 2E')] \quad (5e)$$

$$BZ_2 = (g_e/g_z) \times [(B_0 + D') - E'] \quad (5f)$$

In these equations g_e is the free electron g value =2.0023, B_0 stands for the magnetic field expected for the free electron resonance while D' and E' are the zero-field splitting parameters expressed in T and are related to D and E by :

$$D(cm^{-1}) = D'(T) \times 2.0023 \times \beta \text{ with } \beta = 0.4669 cm^{-1}/T$$

A computer program was written which used these equations to give transition fields for the various sets of parameters. The program has the facility to allow any one of the parameters to be varied through a defined range and, by using the program, it was found that the effect of E' was negligible when calculating the BZ

transition fields. This meant that we could substitute $E'=0$ into equations (5c) and (5f) without introducing any great innaccuracy. We thus obtained the simplified equations.

From 5c $BZ_1 = (g_e/g_x)\ |(B_0 - D')|$ (6)

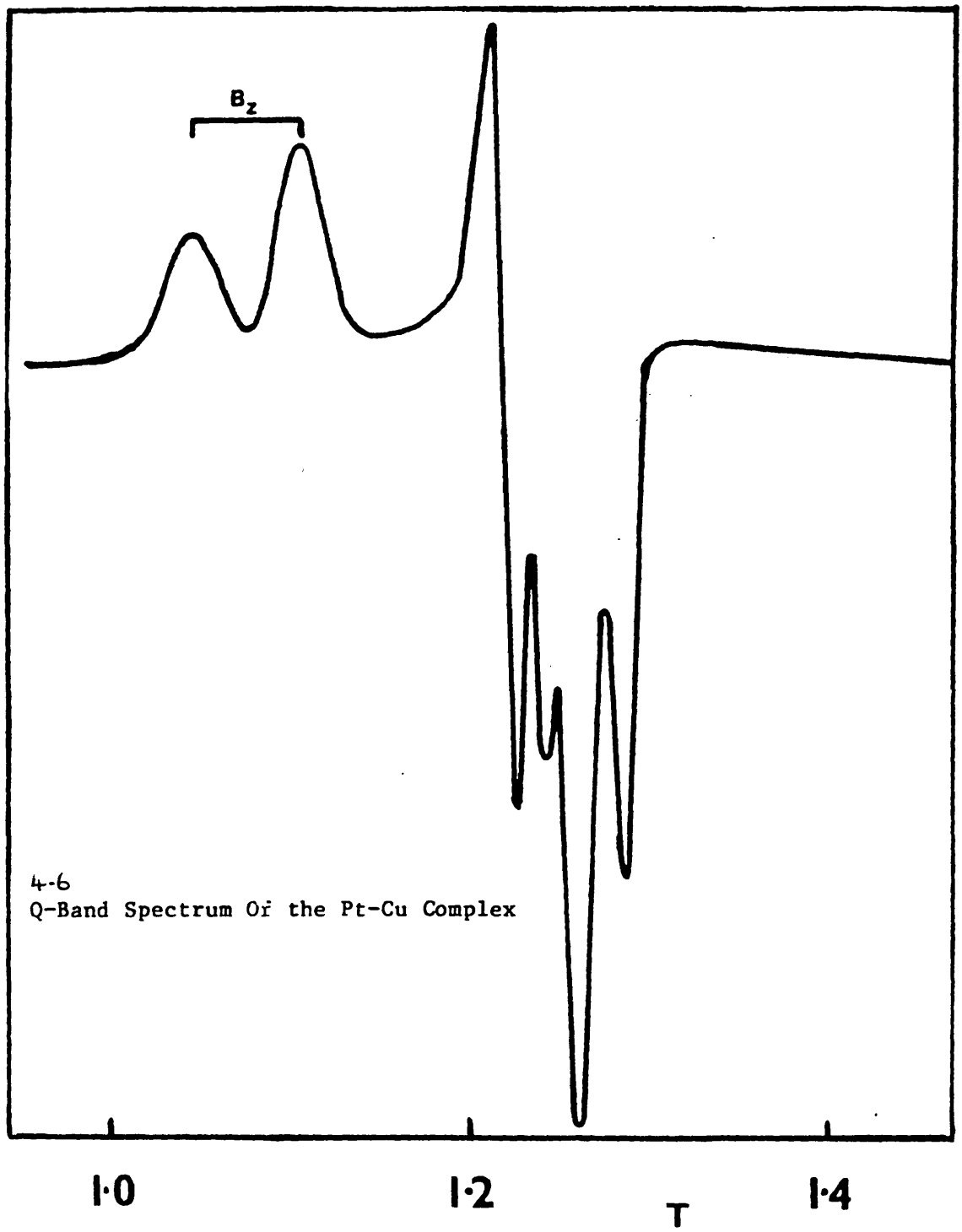
From 5f $BZ_2 = (g_e/g_x)\ |(B_0 + D')|$ (7)

The sign of D' cannot be determined by use of these equations as a change of sign of D' merely swaps the assignments of the Z_1 and Z_2 transitions. Assuming, for the moment, that D' is positive and, as is almost certainly the case, $D'<B$ we arrive at an analytical solution to D'

$$D' = (B_{Z_2} - B_{Z_1})B\ /(B_{Z_1} + B_{Z_2}) \quad (8)$$

So by measuring the Z transition fields we may arrive at a value of D' and hence D. In the Q-band spectrum of (VI) (Figure 4.6) the two Z components, unsplit by copper nuclear hyperfine interaction, are seen at 1049 and 1108 mT, corresponding to $|D|=0.033cm^{-1}$.

The complexity of the rest of the spectrum makes band locations difficult and without single crystal studies band assignment is impossible. The differences between the different possible band assignments were quite small however. A typical set of values for the various parameters is $g_x=2.068$, $g_y=2.059$, $g_z=2.384$, $D'=35mT$ and $E'=9mT$ giving $D=0.033cm^{-1}$ and $E = 0.009cm^{-1}$. The z transition fields are marked on figure 4.6



4-6
Q-Band Spectrum Of the Pt-Cu Complex

4.3.1 The Nature Of D In $Cis[(NH_3)_2Pt(1MeU)_2Cu(H_2O)_2]^{2+}$

For simple systems one can calculate the contributions to D from dipolar and exchange coupling terms fairly easily. However there are several complications which make accurate calculations more difficult in our case. Generally

$$D = D_{EX} + D_{DIP} \quad (9)$$

Where D_{EX} and D_{DIP} are the exchange and dipolar coupling terms. D_{DIP} is always negative but D_{EX} may be either positive or negative and we cannot tell from the peak positions the sign of the observed D. For an axial system

$$D_{DIP} \propto (g_{//}^2 + g_{\perp}^2/2)/r^3 \quad (10)$$

Where r is the separation between the two paramagnetic centres. For our system r=3.483Å $g_{//}$=2.384 and $g_{\perp}=(g_x+g_y)/2$=2.064. Taking the constant of proportionality as 0.45 when D is in cm^{-1} and r in Å [171]. We have for our system $D_{DIP} = -0.083cm^{-1}$ while our observed $|D|=0.033cm^{-1}$. This implies that $D_{EX}=+0.050$ or $D_{EX}=+0.116\ cm^{-1}$. This compares with, for instance, copper(II)acetate where D_{EX} has been measured as $0.54cm^{-1}$ [171].

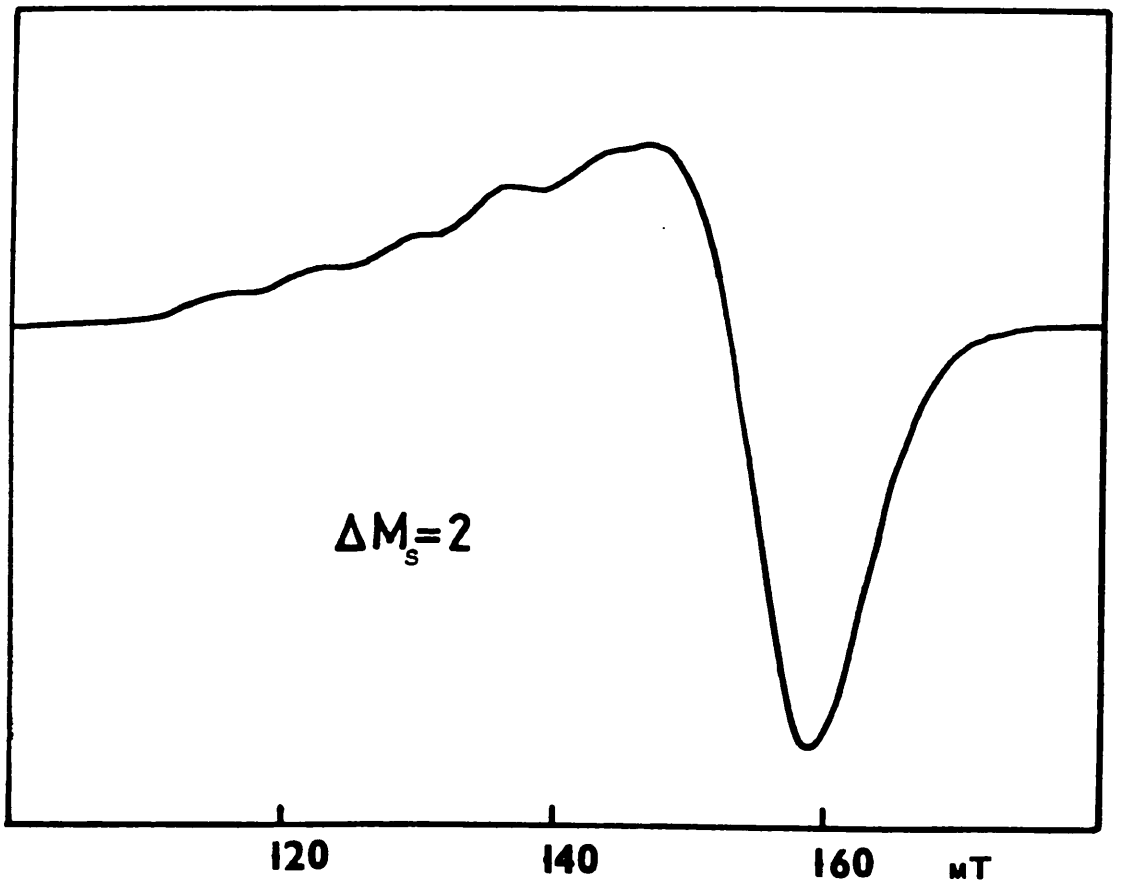
Finally it should be noted that the calculations shown above assume that the systems are linear whereas, in fact, they are not; the Pt-Cu fragments are parallel but each fragment is offset from being colinear with its neighbour. This causes an increase in the complexity of the calculations and necessitates full simulations for accurate deductions to be made. The crystals available were not suitable for single crystal e.p.r. studies and the powder data were not accurate enough to warrant a full calculation for this single compound. We can say, though, that there is a weak coupling between the copper sites and that we expect any exchange interaction to be antiferromagnetic.

4.3.2 The $\Delta M_s=2$ Transition

The transition which can be seen at c.a. 140mT at X-band is due to the $\Delta m_s=2$ transition. This transition is formally forbidden at high fields but at lower fields a certain degree of mixing of the states occurs, the wavefunction becoming a linear combination of the high field states. In these cases the $\Delta m_s=\pm1$ selection rule does not apply as one cannot apply m_s values to the mixed states. It can be seen in figure 4.8 that the $\Delta m_s=2$ transition is split by hyperfine interactions from both copper centres.

Figure 4.7

$\Delta m_s=2$ Region Of The X-Band Spectrum Of The Pt,Cu Compound



It is interesting to note in passing that the $\Delta m_s=2$ transition is not observed at Q-band frequency even at very high gain, this effect has been noted in another copper dimer $Cu_2(adenine)_4$ and is probably general for such systems. The reason for this reduction in intensity stems from the way the signals arise in the first place, as a "breaking" of the selection rule of $\Delta m_s=\pm1$.

At higher fields the eigenfunctions of the Hamiltonian become more like those for $\hat{S}_z$ and so the transition becomes "forbidden". We should not, however, regard this allowed/forbidden label as an on/off situation; just as the degree of mixing of the spin states rises continuously as H is lowered, becoming maximum when H=0, so the "forbiddenness" of the $\Delta m_s=2$ transition should be expected to be lifted in a continuous fashion, the intensity rising as H, or the operating frequency, is lowered.

4.4 OTHER (PT,M,PT) COMPLEXES

Three further compounds were investigated spectroscopically. All were of the type cis-$[(NH_3)_2Pt(1MeU)_2M^n(1MeU)_2Pt(NH_3)_2](NO_3)_n.xH_2O$, with n=3, M=Fe,(VII); n=2, M=Ni,(VIII); n=2, M=Co (IX).

4.4.1 E.p.r. Spectroscopy

The e.p.r. spectrum of the iron(III) complex was extremely similar to that of the manganese(II) compound (I), showing a single asymmetric absorption at X-band at 1140mT. This was not unexpected as high spin iron(III) is a d^5 system like manganese(II). Thus we deduce, as before, a high D value and a low E value.

4.4.2 Electronic Spectroscopy

Examination of the electronic spectra of these compounds (VII, VIII and IX) provided an independent check on the nature of the distortion of the ligand field of the central metal atom and also yielded spectral information on what appear to be some of the most distorted examples of a nominally six-coordinate environment for these metal ions.

Again the samples were microcrystalline and unsuitable for single crystal spectroscopy but reflectance spectra of good quality were obtained in the 400-2200nm region (Figure 4.8). The sharp bands marked (*) in the 1400-2200nm range are ligand vibrational overtones and combinations, being identified by their invariance on changing the central metal ion. Only in the case of the lowest energy d-d band of the nickel complex was there significant overlap of the vibrational and d-d bands, and then only by the weak vibrational set at 1400-1700nm, which are seen as small additional features on that d-d band (Fig 4.8A).

Considering the spectrum of the nickel complex first, the d-d band energies of which are listed in table 4.6. Analysis of the d-d spectra of tetragonally distorted six-coordinate nickel(II) complexes is now well documented. Two of the most severely distorted ligand fields are in the compounds $Ni(py)_4I_2$ [172] and $Ni(pyrazole)_4Br_2$ [173]. The reported band energies and assignments (in D_{4h}) for these compounds are also listed in Table 4.6 for direct comparison with the results for the Pt-Ni-Pt complex. (An O_h-D_{4h} correlation diagram for the high-spin levels arising for d^7 and d^8 is shown in Figure 4.9).

Figure 4.8 Electronic Spectra Of Some Pt-M-Pt Complexes

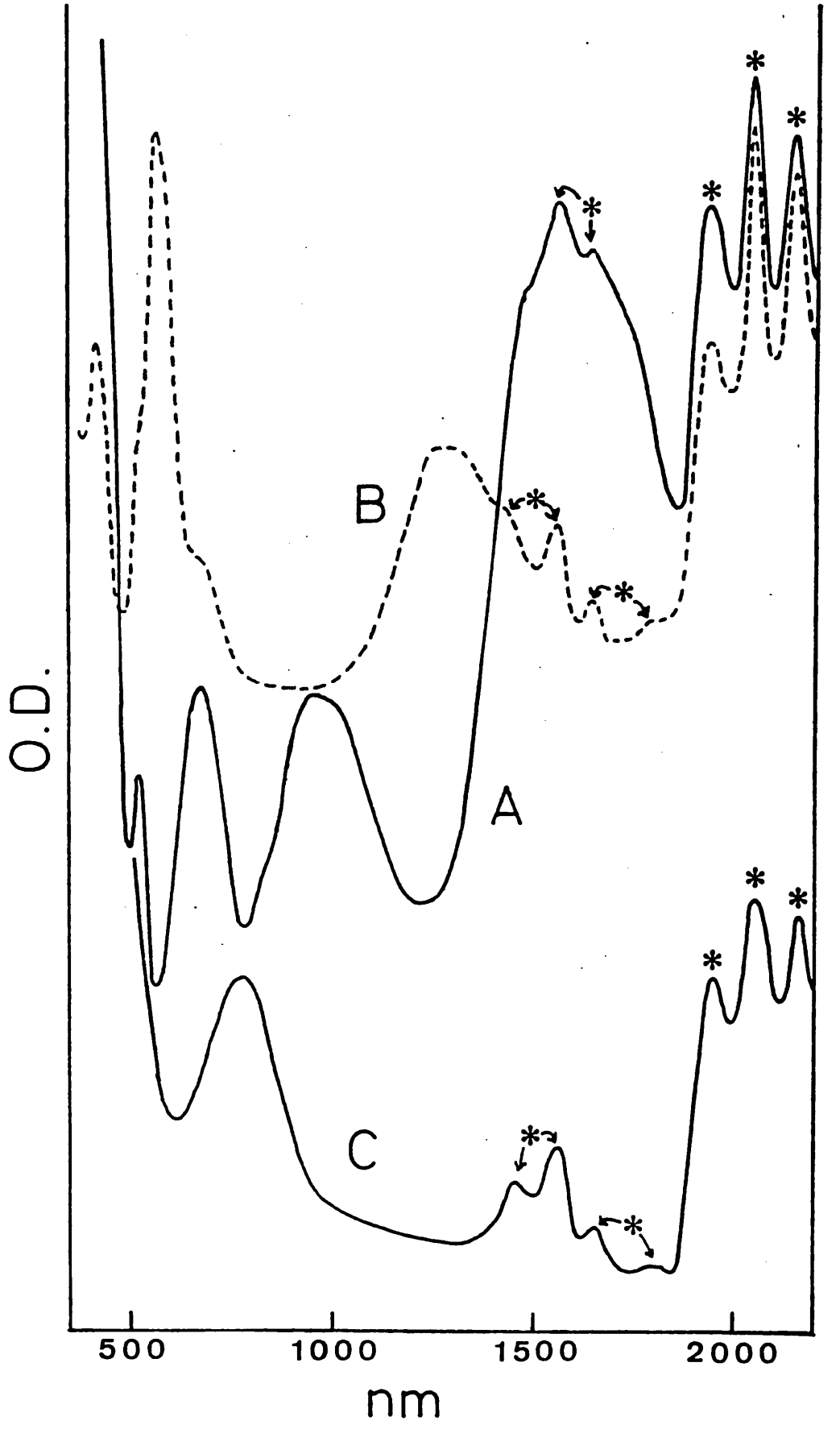
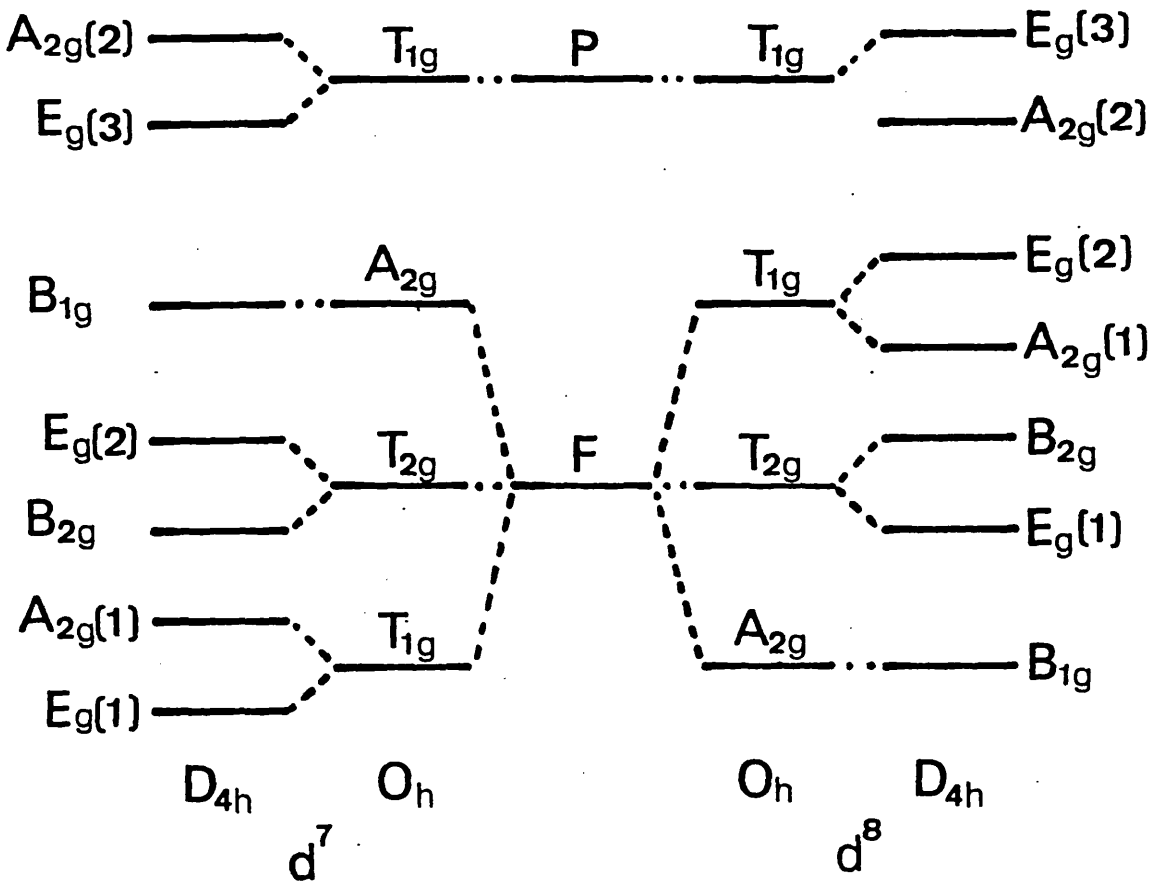


Figure 4.9 Correlation Diagram For High Spin d^7 and d^8



The ligand fields generated by the exocyclic oxygen atoms in uracil, thymine and related ligands are known to be low [174-175]; significantly less than those produced by pyridine or pyrazole. Accordingly, the average ligand field in the Pt-M-Pt complexes should be quite weak as well as very distorted. The weakness of the overall field is also demonstrated by the electronic spectrum of the cobalt(II) complex described later.

The strong band at 6250 cm^{-1} in the spectrum of the nickel complex is readily assigned as $^3B_{1g} \rightarrow {}^3E_g(1)$. Three bands (from the transitions $^3B_{1g} \rightarrow {}^3B_{2g}$, $^3A_{2g}(1)$ and $^3E_g(2)$) would be expected in the 7000-16,000 cm^{-1} region, but only two were observed, at about 10,000 cm^{-1} and at 14,500 cm^{-1}. The former band is asymmetric and becomes more so on cooling to c.a. 80K, but the absorption could not be reliably resolved into two components. The $^3B_{2g}$ and $^3A_{2g}(1)$ levels are known to lie close together in $Ni(py)_4I_2$ and $Ni(pyrazole)_4Br_2$, with $^3B_{2g} < {}^3A_{2g}(1)$. The corresponding levels, $^3B_2$ and $^3A_2(1)$ are also closely spaced in the square pyramidal (C_{4v}) complex [Ni(2-methylimidazole)$_4$Br]Br, but in that case $^3B_2$ (at 11,600cm^{-1}) lies above $^3A_2(1)$ (at 10,300cm^{-1}) [176].

The Pt-Ni-Pt complex appears to represent the intermediate situation where the $^3B_{2g}$ and $^3A_{2g}(1)$ levels are too close to be resolved without the use of polarised light. Assignment of the 14,500cm^{-1} band as either $^3B_{2g}$ or $^3A_{2g}(1)$ would be quite at variance with the results for other compounds given in Table 4.6. This problem does not arise with the assignment of the 14,500cm^{-1} band as $^3B_{1g} \rightarrow {}^3E_g(2)$. The remaining band, at 18,700cm , is probably $^3B_{1g} \rightarrow {}^3A_{2g}(2)$ but, in view of Hitchman's observation [176] of the relatively high intensity of the $^3B_1 \rightarrow {}^1E(1)$ band at 17,300cm^{-1} in the spectrum of [Ni(2-methylimidazole)$_4$Br]Br, one cannot rule out an

alternative assignment as $^3B_{1g} \rightarrow {}^1E_g(1)$ for this 18,700cm^{-1} band.

The spectrum of the Pt-Co^{II}-Pt complex (Fig4.10B) has only one d-d band in the 4500-12,500cm^{-1} region and this is at low energy (7750cm^{-1}) for a nominally six-coordinate Co(II) species.

The spectra of strongly tetragonally distorted six-coordinate cobalt(II) complexes have received less detailed attention than their nickel(II) analogues. The effects of the tetragonal distortion of the ligand field on the terms arising for the cubic d^7 case and the relative order of the component levels have been discussed, inter alia, by Lever [177]. Splitting of the original $^4T_{2g}$ term into the components $^4E_g(2)$ and $^4B_{2g}$ is quite sensitive to the extent of the distortion of the field from O_h symmetry.The spectra of compounds of the type CoL_4X_2 (L= heterocyclic amine; X=Cl, Br, I), in which the field is quite distorted but of only weak to moderate mean strength, have the transitions to $^4E_g(2)$ and $^4B_{2g}$ in the 5000-9000cm^{-1} region. There is, however, some disagreement as to the assignment of the two bands in this region for closely related compounds. Some workers [178,179] place $^4E_g(2) > {}^4B_{2g}$ while others [180] prefer $^4E_g(2) < {}^4B_{2g}$. From low temperature single crystal spectroscopy, Lever [181] assigns $^4E_g(1) \rightarrow {}^4B_{2g}$ at 6325cm^{-1} and $^4E_g(1) \rightarrow {}^4E_g(2)$ at 9270cm^{-1} for $[Co(EtNHCH_2CH_2NH\ Et)_2\ Br_2]$, in which the diamine contributes no π-component to the equatorial field.

Table 4.6 Electronic Spectral Band Energies For Pt-M-Pt Complexes And Some Reference Compounds

Compound	Band maxima (cm^{-1})[a]					
	$^3E_g(1)$	$^3B_{2g}$	$^3A_{2g}(1)$	$^3E_g(2)$	$^3A_{2g}(2)$	$^3E_g(3)$
Pt-Ni-Pt	6250	10,100[h]		14,500	18,700	i
$Ni(pyrazole)_4Br_2$[b]	7240	10,900	12,000	15,900	25,800[j]	
$Ni(pyridine)_4I_2$[c]	7905	11,834	13,158	16,393	(23,977)[k]	(25,164)[k]
$[Ni(2\text{-}Meim)_4Br]Br$[d]	5150	11,600	10,300	15,300	22,800	24,800

	$^4B_{2g}$	$^4E_g(2)$	$^4B_{1g}$	$^4E_g(3)$	$^4A_{2g}(2)$
Pt-Co-Pt	ℓ	7750	14,300	17,400	23,500
$Co(MPZ)_4I_2$[e]	(6294)[m]	8600	n	17,950	24,500
$Co(s\text{-}Et_2en)_2Br_2$[f]	6325	9270	17,630	18,700	21,470
				19,300	

	$^5A_{1g}$	$^5B_{1g}$
$Pt\text{-}Fe^{II}\text{-}Pt$	ℓ	12,900
$Fe(MPZ)_4I_2$[e]	4700	12,850
$Fe(IQ)_4I_2$[g]	5900	11,750

Notes for table 4.6 (a).Upper level designations are for D_{4h} symmetry except for $[Ni(2\text{-Meim})_4Br]Br$ (C_{4v}) for which g notation in the designations should be deleted. (b) See [173]. (c) See [172]. (d) See ref [176]; 2-Meim = 2-methylimidazole. (e) See [179]; MPZ = 3(5)-methylpyrazole. (f) See [181]; s-Et_2en = $EtNHCH_2CH_2NHEt$. (g) See [184]; IQ = isoquinoline. (h) Asymmetric band. (i) Hidden under U.V. absorption. (j) Components not resolved experimentally. Calculated values from [176]: 25,120cm^{-1} ($^3A_{2g}(2)$), 27,100($^3E_g(3)$). (k) Calculated values from [172]; experimental band energies not reported. (l) Not observed above 4500cm^{-1} . (m) Calculated value from [179]. (n) Not reported

Notwithstanding the question of the order of the $^4E_g(2)$ and $^4B_{2g}$ levels in the compounds referred to above, the observation of only one band (at 7750cm^{-1}) for Pt-Co-Pt in the 4500-12,500cm^{-1} region shows that the ligand field distortion experienced by the cobalt(II) ion in this compound is large, and also that the average field is weak. Making the reasonable assumption that here DQ(axial) < DQ(equatorial), the 7750cm^{-1} band may be assigned to the transition to $^4E_g(2)$. That to $^4B_{2g}$ either lies below 4500cm^{-1} or is very weak and is obscured by the vibrational bands in the region 4500 to 5250cm^{-1} . (The reverse assignment would require a very low value for the equatorial ligand field produced by the exocyclic oxygen atoms).

The assignments of the other bands are given in Table 4.6. The weakness of the transition to $^4B_{1g}$ is as expected [182], as are the relative intensities of the bands assigned to $^4E_g(3)$ and $^4A_{2g}(2)$. The splitting of the original $^4T_{1g}(P)$ level is large and is similar to those observed for the strongly tetragonally distorted compounds [Co 3(5)-methylpyrazole$_4X_2$] (X=Br, I) [179]. (Bands for the iodide, from [179], are given in Table 4.6 for comparison).

Assignment of the spectrum of Pt-Fe(II)-Pt (Fig 4.10C) is straightforward. The ^5E_g level arising for high-spin d^6 in O_h symmetry splits into $^5A_{1g}$ + $^5B_{1g}$ in D_{4h}, and the effects of a tetragonal distortion on the spectra of six-coordinate iron(II) complexes are well documented [179,184]. In practice both transitions are generally intense enough for them to be detected in the region where vibrational bands also contribute, though the latter can sometimes reduce the precision with which the band maxima can be determined. Examples of compounds in which the tetragonal distortion is particularly large are FeL_4I_2 (L= 3(5)-methylpyrazole [179] or isoquinoline [184]) and the reported band energies for those compounds are listed in Table 4.6.

As in the case of the nickel and cobalt analogues, the Pt-Fe(II)-Pt complex represents a more distorted situation than the quoted reference compounds, so that the lower energy component ($^5A_{1g}$) has moved below the limit of study (4500cm^{-1}). This $^5A_{1g}$ level is particularly sensitive to the degree of axial distortion and in the limiting case of a high-spin square configuration, as in the mineral gillespite [185], it becomes the ground state.

4.4.3 Mössbauer Spectroscopy Of Pt-Fe(II)-Pt

The Mössbauer spectrum of the complex with iron(II) gave a noisy spectrum, but was resolved into a well defined quadrupole doublet with no additional features. The isomer shift δ was 0.952 $\pm$ 0.007 mms^{-1} indicating a high spin (S=2) Fe(II) complex. The observed shift was lower than the values expected for comparable octahedral complexes; typically c.a. 1.2 to 1.4 mms^{-1}, suggesting 4-fold coordination. The quadrupole splitting Δ = 2.045+0.007mms^{-1}, which is relatively low, again indicating a fourfold geometry with the sixth electron in $|xz\rangle$ or $|yz\rangle$ orbitals. Although the absolute degree of distortion could not be inferred from these measurements the distortion indicated was in agreement with that observed when using the other spectroscopic techniques.

4.5 SUMMARY

All of the spectroscopic techniques employed indicate a large distortion about the central metal atom in these Pt-M-Pt complexes. The next step in further quantifying this distortion would probably require that single crystal spectroscopic techniques be employed.

CHAPTER 5

EXPERIMENTAL

5.1 GENERAL

Analyses were carried out by the Microanalytical Laboratory, Imperial College. Infrared spectra were recorded using a Perkin-Elmer 683 (4000-200cm^{-1}). Diffuse reflectance spectra were measured in the region 400-2200nm on a Beckman DK2 spectrometer and Cary 14 spectrometer. E.p.r. measurements were made on two spectrometers: X-band measurements were made using a Varian E12 spectrometer operating at about 9.5 GHz. The Q-band machine comprised a Varian 36 GHz microwave system and field controller with a Newport instruments type-F magnet.

5.2 CRYSTALLOGRAPHIC METHODS

For a crystal to be suitable for the collection of X-ray diffraction data it must be the correct size, it must be a single, untwinned crystal, and it must be undistorted. The 'correct' size for a crystal depends somewhat on the atomic composition of the compound, heavier atoms increase absorption and so a smaller crystal is required, crystals were generally chosen with dimensions in the range 0.1 to 0.5mm in each direction. Use of a polarising microscope with 'cross' Nicols enabled twinned cystals to be

identified. Twinned crystals show themselves by having both light and dark regions at the same time as they are rotated about an axis normal to the plane of the polariser, while a single crystal is uniformly dark or light.

Data was collected on a Nicolet R3m on-line four-circle diffractometer at 18°C using CuK_α radiation (λ=1.5418Å) with a graphite monochromator. The crystal was mounted in the goniometer and centred by eye. A polaroid rotation photograph was taken and the distances between corresponding spots in the resulting diffraction pattern were entered into the diffractometer control to enable the search for reflections and the centring procedure to begin. When the reflections corresponding to the 'spots' on the photograph had been located, the orientation matrix was calculated together with the lattice parameters and their standard deviations.

Full data collection followed using the ω-scan technique, and monitoring two strong reflections as references every 50 reflections.

The calculations were carried out using the SHELXTL program system [187]. The heavy atoms were located using Patterson synthesis and the lighter atoms were located using difference Fourier synthesis maps. Absorption corrections were carried out using the crystal shape defined by indexing the observed crystal faces. Where this was impossible, for $Mo(2SPym)_4$, an empirical absorption correction was applied based on 36 psi scan measurements for ten representative reflections. Least-squares refinement was by the block cascade method typical of the SHELXTL system. A weighting scheme of the type

$$\omega = 1/[(\sigma F_o)^2 + cF_o^2]$$

was applied, where c is a refinable parameter. The reliability index R is defined by

$$R = \sum |F_o - F_c| \; / \sum |F_o|$$

where F_o and F_c are the observed and calculated structure factors.

5.3 SYNTHESES

5.3.1 Ligands

Published methods were used as the bases for the syntheses of the following ligands: 1Me2SPym [188], 1,4,6$Me_3$2SPym [189], 2OPym [190, 191], 1Me2OPym [188], and 1,4,6$Me_3$2OPym [192]. The methods described by Jeeves [36] were used for the ligands 4,6$Me_2$2SPym and 4,6$Me_2$2OPym. Three slight modifications to these methods were generally used:

1. Preparation of N-methyl pyrimidinones was carried out under an inert atmosphere. The oxygen-bearing ligands slowly discoloured in air (over a period of a few weeks), presumably by the absorption of carbon dioxide. Syntheses of these ligands in air sometimes failed, with the production of a brown, tarry substance, this was never observed when the reactions were carried out in an inert atmosphere.

2. All reactions were carried out using a 100% excess of the "three carbon fragment" source of the pyrimidine ring. It has been shown that 2-hydroxy and 2-mercaptopyrimidines form complexes with urea and thiourea [190, 193, 194] and this was sometimes observed when using published preparative methods. Use of an excess of 1,1,3,3tep or acacH overcame this problem.

3. Neutralisation of the mercaptopyrimidine hydrochloride products was carried out using aqueous sodium carbonate. The ligand was then extracted into chloroform, the chloroform dried over sodium sulphate, filtered and evaporated to dryness under reduced pressure. The ligand was then recrystallised from benzene or ethanol/ether and dried in vacuo at c.a. 50°C. This method proved much quicker than those published and consistently gave high quality products whereas use of a strong base sometimes destroyed the ligands.

The ligand disulphides were prepared using standard iodine oxidation as described below.

Bis(4,6-dipyrimidin-2-yl)disulphide

4,6$Me_2$2SPymH (2.80g, 20mmol) was added, as a fine powder, to a methanolic solution of KOH (1.122g, 20mmol in 15cm^3), whilenitrogen was bubbled through the mixture. Iodine (2.538g, 10mmol in methanol (20cm^3)) was added, dropwise, with stirring. As the iodine was added, a white precipitate formed. The solution was reduced to dryness, extracted with benzene (50cm^3), which was washed with water (3x10cm^3), dried with sodium sulphate and reduced to dryness giving the disulphide as a white crystalline solid.

Yield 2.08g, 75%

Calc. C 51.77% H 5.07% N 20.13%

Found C 52.04% H 5.09% N 20.23%

M.p. 150-153°C Literature 150-155°C [195]

Dipyrimidin-2-yl disulphide

A method similar to that described above was employed, using 2SPymH(2.243g, 20mmol) to give the corresponding disulphide as a pale yellow solid.

Yield 1.48g, 67%

Calc. C 43.23% H 2.72% N 25.21%

Found C 43.61% H 2.83% N 25.29%

M.p. 132-134° C Literature 136° C [195]

5.3.2 Platinum Preparations

Platinum complexes were synthesised using the two general methods described below.

K_2PtCl_4 (1.660g, 4.0mmol) was dissolved in water (c.a.40cm^3). The solution was then divided into eight equal aliquots. Each portion was used for a separate experiment as described below.

$PtCl_2(2OPymH)_2$

2OPymH (0.105g, 1.1mmol) was dissolved in water (5cm^3). The K_2PtCl_4 solution was added with stirring and a yellow precipitate started to form within 1 minute. The mixture was stirred in the dark, overnight, before collecting the yellow microcrystalline solid which was washed with water (2x5cm^3) and ethanol (5cm^3), and air-dried. (This method is reffered to in future as method I)

Yield 0.214g 93%

Calc. C 20.97% H 1.76% N 12.23%

Found C 20.78% H 1.74% N 11.75%

$PtCl_2(1Me2OPym)_2$

This was prepared using method I except that the ligand (0.121g, 1.1mmol) was dissolved in $10cm^3$ of water. The yellow precipitate started to form after c.a. 15 seconds.

Yield 0.222g 91%

Calc. C 24.70% H 2.49% N 11.52%

Found C 24.44% H 2.45% N 11.05%

$PtCl_2(4,6Me_2OPymH)_2$

This was prepared using method I with 0.137g, 1.1mmol ligand. The yellow precipitate started to form after c.a. 5 minutes.

Yield 0.225g 88%

Calc. C 28.03% H 3.14% N 10.89%

Found C 27.66% H 3.08% N 10.36%

$PtCl_2(1,4,6Me_3OPym)_2 2H_2O$

This was prepared using method I. The orange/yellow precipitate started to form after c.a. 5 minutes.

Yield 0.143g 49%

Calc. C 29.07% H 4.18% N 9.69%

Found C 28.75% H 3.48% N 9.59%

$Pt(2SPym)_2Cl_{0.8}$

The K_2PtCl_4 solution was added to a solution of 2SPymH (0.112g, 1mmol) in hot methanol ($150cm^3$). A yellow precipitate formed almost instantly. The heat was removed but stirring continued and the precipitate rapidly re-dissolved, producing a scarlet solution and precipitate within 5 minutes. The brilliant scarlet precipitate was collected after 15 hours at room temperature. The solid, which was

insoluble in alcohols, water, ether, benzene and chlorinated solvents, was washed with water ($10cm^3$) and ethanol (2 x $10cm^3$) and vacuum dried.

Yield 0.173g 78%

Calc. C 21.55% H 1.36% N 12.57% Cl 6.36%

Found C 21.88% H 1.38% N 12.82% Cl 6.34%

$\underline{PtCl_2(1Me2SPym)_2}$

This compound was best prepared by adding an aqueous solution of K_2PtCl_4 (0.103g, 0.25mmol in $15cm^3$) to a solution of 1Me2SPym in CH_2Cl_2 (0.063g, 0.5mmol in $15cm^3$). The mixture was shaken once and left in the dark at room temperature overnight. The yellow precipitate was collected, washed with water (2x$5cm^3$) and ethanol ($5cm^3$) and air-dried. (This method is referred to as method II).

Yield 0.084g 65%

Calc. C 23.17% H 2.33% N 10.81%

Found C 23.09% H 2.21% N 10.52%

For preparations employing the $[PtI_4]^{2-}$ ion, K_2PtCl_4 (0.5mmol) was dissolved in water ($5cm^3$). A saturated aqueous solution of potassium iodide (0.33g, 2mmol) was added and the mixture was stirred for 45s before adding to a ligand solution as in the method above.

$\underline{PtI_2(2OPymH)_2}$

2OPymH (0.105g, 1.1mmol) was dissolved in water ($5cm^3$). The $[PtI_4]^{2-}$ solution was added with stirring and a yellow precipitate started to form within 2 minutes. The mixture was stirred in the dark, overnight, before collecting the yellow microcrystalline solid which was washed with water (2x$5cm^3$) and ethanol ($5cm^3$), and

air-dried. (this method is referred to in future as method III)

Yield 0·187g 58%

Calc. C 14.99% H 1.26% N 8.74%

Found C 14·84 % H 1·32 % N 8·65 %

$PtI_2(1Me2OPym)_2$

This compound was prepared using method III except that the ligand was dissolved in $10cm^3$ of water. Yellow precipitate began to form within 2 minutes.

Yield 0·161g 48%

Calc. C 17.95% H 1.81% N 8.37%

Found C 17·76 % H 1·90 % N 8·25 %

$Pt_2(2SPym)_4I_2$

The $[PtI_4]^{2-}$ solution was added to a solution of 2SPymH (0.112g, 1mmol) in hot methanol ($150cm^3$). A yellow precipitate formed almost instantly. The heat was removed but stirring continued and the precipitate rapidly re-dissolved, darkening to give a crimson solution which produced a red precipitate after 10 minutes. A portion of the liquor ($25cm^3$) was decanted and both samples were refrigerated for c.a. 70 hours. After this period the decanted liquor had produced dark green crystals with a metallic lustre while the remainder of the reaction mixture contained both crystals and the red powder. Microanalysis and infrared spectroscopy showed the crystals and powder to be the same compound.

Yield 0.272g 85%

Calc. C 17.65% H 1.11% N 10.29% I 23.32

Found (Crystals) C 18.00% H 1.19% N 10.20% I 23.36

Found (Powder) C 17.84% H 1.15% N 10.24%

Pt(2SPym)$_2$ This complex was prepared by either of the methods described above for $Pt_2(2SPym)_4 I_2$ or $Pt(2SPym)_2 Cl_{0.8}$ but using anaerobic conditions. The solutions were degassed and mixed under a nitrogen atmosphere with nitrogen bubbling gently through the hot reaction mixture. The reaction mixture developed the yellow precipitate as before but, under these conditions, it did not re-dissolve. When cool, the solid was filtered anaerobically and washed with degassed 1:1 water/alcohol. The yellow powdery product did not react with air and did not decompose when heated as a suspension in water/methanol. The solid analysed as PtL_2 in each case.

Yield (From chloride) 0.120g 58%

Yield (From iodide) 0.113g 54%

Calc. C 23.02% H 1.45% N 13.42%

Found (From chloride) C 22.86% H 1.48% N 13.36%

Found (From iodide) C 22.73% H 1.37% N 13.28%

Pt(1Me2SPym)I_2 This was prepared using method III, dissolving the ligand (0.139g 1.1mmol) in 25cm^3 MeOH.

Yield 0.194g 68%

Calc. C 10.44% H 1.05% N 4.87%

Found C 11.07% H 1.09% N 4.98%

$Pt(4,6Me_2 2SPym)_2$ (Crystals)

Crystals of this compound were prepared using method II in a graduated cylinder, to give a lower area to the interface between the two phases.

Yield 0.098g 83%

Calc. C 30.44% H 2.98% N 11.83%

Found C 30.51% H 2.89% N 11.57%

This compound was readily attained as a powder by using methods I or III, in each case the ligand was dissolved in $50cm^3$ MeOH.

Yield method I 0.223g 94%

Yield method III 0.156g 66%

5.3.3 Molybdenum Preparations

Molybdenum hexacarbonyl, molybdenum(V) chloride and sodium molybdate were purchased and bis(2,4-pentanedionato)dioxomolybdenum(VI) was prepared using the method of Fernelius et al. [128].

$[(n\text{-}Bu)_4N]_4Mo_8O_{26}$

Aqueous solutions of sodium molybdate ($NaMoO_4.2H_2O$, 9.68g, 0.04mol in $100cm^3$ - acidified to pH3.0 with 2M hydrochloric acid) and tetra-n-butyl ammonium chloride ($nBu_4N(Cl)$, 6.51g, 0.022mol in $200cm^3$) were mixed together and the reaction mixture cooled to 0°C. The precipitate was filtered after an hour, washed with ice-cold water, ethanol and ether and air-dried.

Yield 9.30 g 86 %

Calc. C 35.70 % H 6.74 % N 2.60 %

Found C 35.11 % H 6.85 % N 2.55 %

$\underline{MoCl_3py_3}$

Trichlorotris(pyridine)molybdenum(III) has previously been prepared from K_3MoCl_6 and pyridine [92]. Use of the dehydrating agent 2,2dmp allows $(NH_4)_2MoCl_5H_2O$ to be used in place of K_3MoCl_6. This makes the synthesis of $MoCl_3py_3$ more efficient both interms of the overall yield and time as $(NH_4)_2MoCl_5H_2O$ is simpler to make than the hexachloro complex [91-93].

Pyridine (50ml, c.a. 0.6mol), 2,2dmp ($5cm^3$, c.a. 0.04mol) and $(NH_4)_2MoCl_5(H_2O)$ (6.55, 0.02mol) [93] were refluxed for 3 hours under dry nitrogen. The mixture was allowed to cool and then poured into $300cm^3$ of water with vigorous stirring. After stirring for 2 hours the product was filtered off, washed with $1000cm^3$ of water, air dried and then dried at 100-110°C under a slow stream of dry nitrogen.

Yield 7.630g 87%

Calc. C 40.98% H 3.44% N 9.56%

Found C 40.84% H 3.41% N 9.41%

Reactions with $MoCl_3py_3$ followed a general method (IV). The ligand (2.2mmol) was dissoved in boiling methanol ($100cm^3$) under reflux. $MoCl_3py_3$ (0.20g, 0.5mmol) was suspended in methanol (110ml) and added directly to the refluxing ligand solution. The reaction mixture was refluxed for 3 hours or overnight. The mixture was refrigerated and any solid products were analysed.

$\underline{Mo(2SPym)_4}$

This was obtained using the general method IV, refluxing overnight. Crystals suitable for X-ray work were produced by lagging the reaction vessel with glass wool, allowing it cool to room temperature slowly before refrigerating. The crystals appeared to be metallic, reflecting green, close inspection revealed them to transmit red light and crystals crushed on a white tile gave a red streak.

Yield 0.154g 55%

Calc. C 35.55% H 2.24% N 20.73% S 23.72

Found C 35.57% H 2.39% N 20.02% S 23.12

The same product was obtained in poor yield (c.a. 20%) by refluxing $Mo(CO)_6$ (0.246g 1mmol) with 2SPymH (0.448g 4mmol) in benzene (c.a. $50cm^3$). An increased yield (70%) was obtained by reacting $Mo(CO)_6$ (0.246g, 1mmol) with dipyrimidin-2-yl disulphide (0.444g 2mmol), refluxing them in benzene ($50cm^3$) for 18 hours. The product with this method did not form in such good crystals as when $MoCl_3py_3$ was employed. Compounds were shown by infrared and microanalysis to be the same compound.

$\underline{Mo(2SPy)_4}$

This compound was obtained using method IV with 2SPyH (0.445g, 4mmol), cooling slowly overnight to room temperature before collecting dark green crystals with a metallic lustre.

Yield 0.137g 51%

Calc. C 44.77% H 3.01% N 10.44%

Found C 44.39% H 2.93% N 10.28%

$\underline{Mo(4,6Me_2 2SPym)_4}$

Bis(4,6-dipyrimidin-2-yl)disulphide (0.577g, 2mmol) was dissolved in degassed benzene (15cm^3)and refluxed under nitrogen for 15 minutes. The degassed solution was allowed to cool until boiling ceased. $Mo(CO)_6$ (0.264g, 1mmol) was added as the solid (against a slow stream of nitrogen) and the mixture was again heated to reflux. After 2 minutes (before boiling had started) a faint pink colour was apparent in the reaction mixture. After 8 minutes the solution was scarlet, quickly darkening to deep crimson on continued refluxing. The mixture was refluxed for 18 hours, by which time some dark solid had been deposited at the surface of the reaction mixture. The mixture was left to stand at room temperature, under nitrogen, for 3 days. The product was in two forms; a dark, brick-red powder and a purple/black encrustation on the reaction vessel. These products were analysed separately but were found to give very similar analysis results and infrared spectra. The solid was insoluble in all common solvents at room temperature but was slightly soluble in hot benzene.

Yield 0.275g 42%

Calc. C 44.16% H 4.32% N 17.16%

Found C 43.66% H 4.87% N 15.16%

This compound was obtained in poor yield (c.a. 5%) by reacting $Mo(CO)_6$ with $4,6Me_2 2SPymH$ in benzene.

$\underline{Mo(CO)_4(1Me2OPym)_2}$

1Me2OPym (0.440g, 4mmol) and $Mo(CO)_6$ (0.264g, 1mmol) were refluxed in sodium-dried benzene (20cm^3) under argon for 1 hour, giving a brilliant scarlet precipitate. The solid was filtered from

the hot benzene solution (cooling before filtration gave impure products containing unreacted ligand). The solid was dried on the filter, under a stream of nitrogen and stored, under nitrogen, in the dark at 4°C. (Method V)

Yield 0.257g 60%

Calc. C 39.26% H 2.82% N 13.08%

Found C 38.50% H 2.78% N 12.66%

$\underline{Mo(CO)_4(1,4,6Me_3 2OPym)_2}$

This complex was prepared using method V. The product was again brilliant scarlet but decomposed too rapidly (over a period of about an hour), even under nitrogen, to allow microanalysis.

Yield (assuming $Mo(CO)_4L_2$) 0.257g 57%

$\underline{Mo(CO)_5(1,4,6Me_3 2SPym)}$ This complex was prepared using method V. The product was a crystalline orange solid which decomposed slowly under nitrogen (c.a. 2 days).

Yield 0.228g 58%

Calc. C 36.94% H 2.58% N 7.18%

Found C 35.98% H 2.97% N 8.02%

Reactions with $MoO_2(acac)_2$ followed a general method. 2.2mmol of ligand was dissolved in refluxing methanol ($200cm^3$) under nitrogen. The $MoO_2(acac)_2$ was dissolved in degassed methanol and rapidly transferred to the ligand solution. Refluxing continued for 3 hours or overnight before cooling. The reactions were repeated in the presence of 2,2dmp.

$\underline{(MoO)_2(O,S)(4,6Me_2 2SPym)_2 MeOH}$

The method eventually used to provide crystals suitable for X-ray crystallography was as follows. $4,6Me_2 2SPymH$ (0.617g, 4.4mmol) was finely ground and dissolved in dry degassed methanol ($50cm^3$). $MoO_2(acac)_2$ (0.326g 1mmol) was dissolved in methanol ($40cm^3$) and added immediaitely to the ligand solution. The mixture was refluxed and developed a very deep red colour within 10 minutes. Refluxing was continued for 18 hours, by which time orange crystals were evident in the solution. The mixture was cooled and the crystals were filtered off, washed with cold methanol ($2x5cm^3$) and ether ($5cm^3$), air dried and then vacuum dried at room temperature overnight.

Yield 0.129g 23%

Calc. C 26.95% H 2.61% N 9.67%

Found C 26.94% H 2.97% N 9.60%

5.3.4 Mixed Metal Complex

The mixed-metal complex $(NH_3)_2 Pt(1MeT)_2 Cu(1MeT)_2 Pt(NH_3)_2 SO_4$ was synthesised following the methods of Lippert et al. for the corresponding manganese(II) complex [161], using copper(II) sulphate in place of manganese(II) chloride.

Calc. C 24.54% H 3.43% N 14.31%

Found C 23.75% H 3.33% N 15.44%

CHAPTER 6

APPENDIX - CRYSTALLOGRAPHIC DATA

6.1 Fractional Atomic Coordinates ($X10^4$) For $Pt_2(2SPym)_4I_2$

Atom	x	y	z
Pt1	3187(1)	5635(8)	8582(5)
Pt2	1678(1)	4878(1)	8582(1)
I1	41(1)	4878(1)	8582(1)
I1	4778(1)	6740(2)	8294(1)
S1	3390(3)	6309(5)	9808(3)
S2	2682(3)	5268(5)	7164(3)
S3	1273(3)	5268(5)	7164(3)
S4	2029(3)	2659(5)	8317(3)
N11	2054(9)	4577(14)	9873(8)
N13	2882(10)	5366(17)	11148(8)
N21	1344(8)	6293(14)	8824(8)
N23	1488(9)	9281(17)	8507(10)
N31	2968(8)	5039(14)	7126(8)
N33	2026(10)	4982(16)	5849(9)
N41	3644(8)	3636(14)	8727(8)
N43	3399(10)	1236(16)	8585(10)
C12	2703(12)	5313(19)	10311(11)
C14	2406(14)	4504(20)	11577(11)
C15	1838(12)	3653(20)	11192(10)
C16	1697(11)	3677(21)	10319(12)
C22	1784(11)	7956(17)	8492(10)
C24	818(11)	9549(20)	8864(12)
C25	423(12)	8532(20)	9273(11)
C26	725(12)	7276(22)	9230(12)
C32	2160(11)	5087(17)	6692(10)
C34	2674(14)	4719(23)	5439(13)
C35	3468(12)	4454(23)	5862(12)
C36	3602(12)	4657(20)	6730(11)

Fractional Atomic coordinates ($x10^4$) for $Pt_2(2SPym)_4I_2$ (continued)

Atom	x	y	z
C42	3109(12)	2529(17)	8566(9)
C44	4224(12)	1026(22)	8833(11)
C45	4797(13)	2081(22)	9102(13)
C46	4448(12)	3370(22)	9014(13)
H14	2493(14)	4526(20)	12183(11)
H15	1531(12)	3035(20)	11507(10)
H16	1321(11)	3005(21)	10028(12)
H24	594(11)	10467(20)	8843(12)
H25	-47(12)	8730(20)	9573(11)
H26	467(12)	6564(22)	9523(12)
H34	2587(14)	4714(23)	4832(13)
H35	3918(12)	4137(22)	5567(12)
H36	4158(12)	4518(20)	7041(11)
H44	4437(12)	103(22)	8828(11)
H45	5382(13)	1917(22)	9326(13)
H46	4815(12)	4138(22)	9175(13)

6.2 Fractional Atomic Coordinates ($X10^4$) For $Pt(4,6Me_2 2SPym)_2$

Atom	x	y	z
Pt	0000	0000	0000
S	-1017(2)	1318(3)	182(7)
N1	-1179(8)	- 607(12)	- 231(21)
N3	-2535(8)	261(7)	- 236(27)
C2	-1666(9)	276(8)	- 243(24)
C4	-2896(9)	- 649(12)	- 246(31)
C5	-2454(7)	-1536(9)	- 342(31)
C6	-1583(11)	-1496(9)	- 292(26)
C7	-3877(8)	- 667(12)	- 182(44)
C8	-1015(7)	-2429(8)	- 227(31)
H5	-2749(7)	-2179(9)	- 444(31)
H7A	-3994(8)	- 664(12)	- 54(44)
H7B	-3946(7)	- 989(11)	2270(44)
H7C	-4286(8)	- 973(11)	-2301(44)
H8A	- 749(7)	-2332(8)	-2541(31)
H8B	-1370(7)	-3047(8)	- 520(31)
H8C	- 558(7)	-2495(8)	2050(31)

6.3 Fractional Atomic Coordinates ($X10^4$) For $Mo(2SPym)_4$

Atom	x	y	z
Mo1	2776(1)	5842(1)	-1340(1)
Mo2	2867(1)	-1399(1)	3798(1)
S11	4689(1)	6340(2)	-2152(1)
S12	1846(1)	3563(1)	- 752(1)
S13	3009(1)	6112(1)	- 376(1)
S14	1566(1)	7343(1)	-2086(1)
S21	4394(1)	-1000(1)	2890(1)
S22	3507(1)	-2737(1)	4679(1)
S23	1280(1)	-2073(1)	3111(1)
S24	2186(1)	206(1)	4519(4)
N111	4958(4)	4771(4)	-1283(1)
N113	7070(5)	4620(6)	-1932(2)
N121	2167(4)	4090(4)	-1752(1)
N123	1185(5)	1737(4)	-1440(2)
N131	3521(4)	7933(4)	-1197(1)
N133	4116(5)	8783(5)	- 402(1)
N141	0455(4)	6529(4)	-1145(1)
N143	-1252(5)	7903(5)	-1677(2)
N211	5089(4)	- 551(4)	3784(1)
N213	6980(4)	154(5)	3064(2)
N221	3725(4)	-3615(4)	3779(1)
N223	4375(4)	-5433(4)	4471(1)
N231	685(4)	-2271(4)	4112(1)
N233	-1246(4)	-3248(5)	3691(2)
N241	2051(3)	780(4)	3526(1)
N243	1060(5)	2689(5)	4007(2)
C112	5730(5)	5115(6)	-1770(1)
C114	7681(7)	3686(7)	-1556(3)
C115	7017(6)	3298(7)	-1051(2)
C116	5627(5)	3862(6)	- 918(2)
C122	1692(5)	3008(5)	-1363(2)
C124	1229(7)	1549(7)	-1966(3)
C125	1714(6)	2557(8)	-2380(3)
C126	2192(5)	3842(7)	-2264(2)
C132	3615(5)	7807(5)	- 663(2)
C134	4536(6)	10018(6)	- 705(3)
C135	4475(6)	10277(6)	-1249(2)
C136	3938(5)	9196(5)	-1491(2)
C142	63(5)	7288(5)	-1602(2)
C144	-2273(6)	7718(7)	-1246(2)
C145	-1979(6)	6983(7)	- 758(2)
C146	- 599(5)	6387(6)	- 717(2)
C212	5669(5)	- 376(5)	3257(2)
C214	7801(6)	543(6)	3426(3)
C215	7357(6)	381(6)	3965(2)
C216	5975(5)	- 168(5)	4137(2)

Fractional Atomic coordinates ($x10^4$) for $Mo(2SPym)_4$ (continued)

Atom	x	y	z
C222	3923(4)	-4112(5)	4296(2)
C224	4696(5)	-6298(5)	4101(2)
C225	4576(6)	-5882(6)	3570(2)
C226	4047(5)	-4514(5)	3415(2)
C232	66(5)	-2610(5)	3679(2)
C234	-1960(6)	-3584(7)	4188(3)
C235	-1499(6)	-3281(6)	4645(2)
C236	-0085(6)	-2621(6)	4594(2)
C242	1697(5)	1389(5)	3980(2)
C244	0828(6)	3448(6)	3531(3)
C245	1231(6)	2937(6)	3049(2)
C246	1821(5)	1577(5)	3056(2)
C1	347(25)	10(30)	59(11)
O1	- 423(23)	516(23)	548(8)
O2	- 849(28)	209(27)	- 539(10)
H114	8650(6)	3276(7)	-1651(2)
H115	7505(6)	2644(7)	- 795(2)
H116	5127(5)	3607(6)	- 563(2)
H124	890(7)	647(7)	-2047(3)
H125	1727(6)	2376(8)	-2745(3)
H126	2551(5)	4577(7)	-2550(2)
H134	4901(6)	10771(6)	- 533(2)
H135	4799(6)	11178(6)	-1455(2)
H136	3856(5)	9347(5)	-1870(2)
H144	-3260(6)	8119(7)	-128)(2)
H145	-2735(6)	6890(7)	- 456(2)
H146	- 339(5)	5867(6)	- 382(2)
H214	8760(6)	962(6)	3300(3)
H215	7997(6)	645(6)	4214(2)
H216	5628(5)	- 286(5)	4513(2)
H224	5036(5)	-7268(5)	4212(2)
H225	4851(6)	-6533(6)	3312(2)
H226	3911(5)	-4206(5)	3045(2)
H234	-2893(6)	-4080(6)	4224(3)
H235	-2021(6)	-3509(6)	4989(2)
H236	323(6)	-2412(6)	4910(2)
H244	357(6)	4387(6)	3526(3)
H245	1101(6)	3530(6)	2716(2)
H246	2072(5)	1184(5)	2726(2)

6.4 Fractional Atomic Coordinates ($X10^4$) FOR $(MoO)_2(O,S)(4,6Me_2 2SPym)_2 MeOH$

Atom	x	y	z
Mo1	4420(1)	5284(1)	1665(1)
Mo2	4106(1)	4301(1)	1044(1)
S1	4172(3)	6776(2)	1689(1)
S2	3003(3)	4294(2)	354(1)
S3	2008(3)	5322(2)	1216(1)
N11	6825(9)	5886(4)	1884(2)
N13	7374(10)	7319(5)	1957(2)
N21	6005(9)	3760(4)	620(2)
N23	5739(10)	3659(4)	-76(2)
O1	6053(7)	4585(3)	1391(1)
O11	3635(8)	4836(4)	2069(2)
O2	5728(8)	5515(4)	742(2)
O21	3275(8)	3425(4)	1224(2)
C12	6361(11)	6696(6)	1866(2)
C14	9011(12)	7130(6)	2090(2)
C15	9572(12)	6328(6)	2128(2)
C16	8463(11)	5702(7)	2017(2)
C17	10157(14)	7835(6)	2192(3)
C18	8949(12)	4810(5)	2041(3)
C2	7563(14)	5730(7)	763(3)
C22	5099(11)	3864(5)	277(2)
C24	7371(12)	3316(5)	-87(2)
C25	8318(12)	3196(6)	261(3)
C26	7637(12)	3421(5)	618(3)
C27	8099(14)	3066(7)	-473(3)
C28	8575(14)	3312(7)	1000(3)
H181	9953(12)	4745(5)	2214(3)
H182	9275(12)	4638(5)	1781(3)
H183	7971(12)	4481(5)	2134(3)
H25	9480(12)	2948(6)	249(3)
H15	10732(12)	6208(6)	2234(2)
H281	7853(14)	2994(7)	1177(3)
H282	8887(14)	3824(7)	1122(3)
H283	9644(14)	3012(7)	938(3)
H171	10641(14)	8111(6)	1966(3)
H172	11115(14)	7626(6)	2350(3)
H173	9459(14)	8216(6)	2343(3)
H271	9373(14)	3123(7)	-456(3)
H272	7630(14)	3482(7)	-645(3)
H273	7811(14)	2533(7)	-576(3)
H2	5376(8)	5767(4)	539(2)
H21	7993(58)	5599(53)	1023(11)
H22	7694(56)	6308(15)	719(26)
H23	8222(49)	5425(43)	573(19)

CHAPTER 7

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