CO-ORDINATION CHEMISTRY OF SULFIMIDES

by

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A **Doctoral Thesis** submitted

in partial fulfilment for the award of

Doctor of Philosophy of Loughborough University

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Abstract

Reactions of Ph_2SNH **1** with copper(II) halides in a 2:1 ratio is fast and efficiently generates species of the type *trans*-$Cu(Ph_2SNH)X_2$. A significant aspect of their coordination geometry comes with the observation that two distinct isomers (or allogons) of the chloro complex can be generated and we believe this is the first example of square-planar/pseudo-tetrahedral isomerism in a neutral copper(II) complex. True polymorphism is displayed by these allogons as they can be used to generate each other by crystallisation from the appropriate solvent mixtures. No such isomerism is exhibited by the bromo analogue. Oxo-bridged clusters of the type $[Cu(\mu_4\text{-}O)(\mu\text{-}X)_6(Ph_2SNH)_4]$ (where X = Cl or Br) readily form. The chloro species may be generated by addition of 1.5 equivalents of **1** to $CuCl_2$ in air; the source of the oxo ligand is probably simple water although investigations into the use of degassed water and of dried O_2 as sources provide somewhat confusing results which may hint at a rather more complicated story. The bromo analogue readily forms and indeed can be difficult to avoid.

Homoleptic cations of the type $[M(Ph_2SNH)_4]X_2$ (where M = Cu, Pd, or Pd, X = Cl or Br) readily form when an excess of **1** reacts with the appropriate metal halide complex. More than just the four equivalents of **1** are required for full precipitation and no more than four may be ultimately added to the metal centres. The products exhibit strong, concerted H-bonding from pairs of ligand N-H groups to the counterions suggesting that future investigations into the introduction of N-bonding, bridging anions into the system may well result in the formation of extended structures. Homoleptic $[Co(Ph_2SNH)_6]Cl_2$ also

forms in the reaction of **1** with $CoCl_2$ and again shows significant H-bonding interactions between cation and anion.

Reactions of **1** with $Pt(MeCN)_2Cl_2$ in different nitriles produce a MNCNS ring system in which a new bidentate ligand is formed $[N(H)C(R^1)NSPh_2]$ (where R^1 = Me or Ph). These systems are rare, and we see the new ligand coordinating to the metal centre *via* the sulfur. This is the first example of a sulfimide coordinating through the sulfur.

Other mono-dentate and polysufimide ligands were made. The mono-dentate ligand, $MeS(p\text{-}MeC_6H_4)NTs$ (**18**), prepared coordinated to a copper centre forming *cis*-$Cu(MeS(p\text{-}MeC_6H_4)NTs)_2Cl_2$. Only one isomer was formed unlike **1** reaction the $CuCl_2$, thus showing the properties of the two ligands was different and the coodination seen for **1** was specific. The polysulfimides, $TsNS(Ph)(CH_2)_3S(Ph)NTs$, $1{,}2TsNS(Ph)C_6H_4S(Ph)NTs$, and $1{,}4TsNS(Ph)C_6H_4S(Ph)NTs$, where prepared by the Mann Pope reaction. These sulfimides unfortunately could not coordinate to a metal centre. Attempts to convert the tosyl group ($Ts = SO_2C_6H_5Me$) to a hydrogen using sulfuric acid were unsuccessful.

ACKNOWLEDGEMENTS

I would like to thank foremost my supervisor Dr Paul Kelly for his advice, guidance and above all his patience over the past few years.

I am grateful to the EPSRC, and the Access Fund for financial support when times were hard.

I am also grateful to Dr Alex Slawin for all the crystallography data.

On a personnel note I would like to thank my family and friends, as well as the people I have met in Loughborough who have made my stay here one I will never forget. A big thanks goes out to those friends who kept on encouraging me when things were not going to plan, you know who you are THANKS!!!

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Chapter 1 Introduction to sulfur-nitrogen systems

1.1 Sulfur-nitrides – an overview

A range of binary sulfur nitrides (that is unsubstituted S-N species) are known;[1] as we will see these fall into a variety of structural categories including cages, rings and, in the case of $(SN)_x$, chains. Out of all such compounds, S_4N_4 is undoubtedly the most important; not only was it the first to be discovered[2] but it can act as precursor to many other S-N species. As Fig.1.1 shows it has a cage structure within which a tetrahedron of sulfur atoms is arranged around a square-planer arrangement of nitrogen atoms.

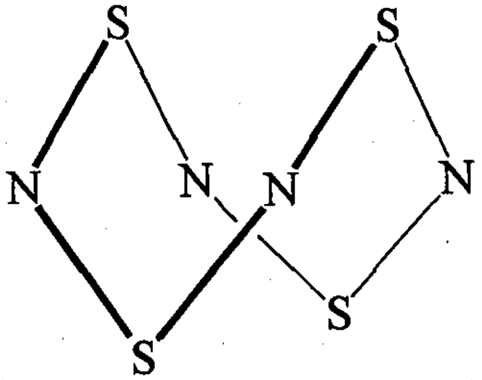


Fig.1.1 *The structure of* S_4N_4

S_4N_4 can be formed simply by reacting ammonia gas with sulfur dichloride in CCl_4 followed by recrystallisation. This is the most convenient synthesis to use in the laboratory, though many other reactions will produce it in varying yields. The complicated interplay between S-N structures is highlighted by the fact that several planar S-N heterocycles (including $[S_3N_2Cl]Cl$ and $[S_4N_3]Cl$) are probably involved in this multi-stage process.

From a structural point of view there are three unusual observations involving the geometrical and electronic structures of S_4N_4 which have interested theoretical chemists, these are:

(i) all the N-S bonds are equivalent (ca 1.62A)

(ii) there is no N-N bonding

(iii) there is a substantial bonding interaction between the transannular sulfurs.

Detailed consideration of the reasons for such observations are still controversial and are beyond the scope of this introduction; perhaps the most pertinent point is the bond distance. This is intermediate between a single (ca 1.7 Å) and double (1.55 Å) S-N bond length indicating that a range of degrees of multiple bonding are possible in S-N systems.

As a reagent S_4N_4 has many good points (including solubility in a range of organic solvents and, as Fig.1.2 and 1.3 show, a broad range of applications) which are only somewhat dampened by its shock-sensitivity. With due care and attention it can be used to form a variety of other S-N systems (Fig.1.2 and 1.3) and, perhaps most crucially to this work, a range of transition metal complexes (Fig.1.6).

As the following two figures show, S_4N_4 has the ability to act as a precursor to many other nitrides. In general, electrophilic reagents attack the nitrogen atoms whereas nucleophilic reactions proceed at the sulfur. According to MO studies this occurs thanks to the fact that the S-N bonds in S_4N_4 are polar, with a charge transfer from sulfur to nitrogen, yielding S^+-N^- bonds. There are three basic types of reactions S_4N_4 undergoes:

(i) Addition reactions (Fig.1.2). Ring retention or ring expansion (e.g. in the formation of the $S_5N_5^+$ and $S_4N_5^-$ ions) occurs.

(ii) Reactions with ring contraction (Fig.1.3). Perhaps the most important of these is the formation of S_2N_2 by thermolysis over silver wool. The latter ring readily polymerises to $(SN)_x$ which was the first example of a metal-free species found to be superconducting (albeit at temperatures well below 1K).

(iii) Reactions with ring cleavage. Although they do not fit into the category of "pure" sulfur nitrides, the unsaturated chains of alternating sulfur and nitrogen atoms which form when organic nucleophiles react with S_4N_4 are of great relevance to this work. A range of chain lengths is known depending upon which organic nucleophile is used. Such chain species are considered in the next section.

1.2 S-N chain systems

A good example of a S-N chain is $Me_3SiN{=}S{=}NSiMe$, perhaps the most important of the sulfur-diimides (its versatility is illustrated by the fact it is one of the very few S-N species commercially available). It finds a source of the $[N{=}S{=}N]^{2-}$ unit in reactions such as the formation of S_5N_6 from $S_4N_4Cl_2$ [3] (in which, as in most cases, the driving force is the formation of Me_3SiCl). Reaction of S_4N_4 with diazo species produces compounds of the formula R-N=S=N-S-N=S=N-R,[4] whereas the reaction of S_4N_4 with aromatic Grignard reagents leads to R-S-N=S=N-S-R.[5]

The range of chain lengths known is extensive, the upper limit (for discrete molecular species as opposed to the infinite chain in $(SN)_x$ coming with species of the type RSNSNSNSNSR.[6] The stability of all long chain S-N

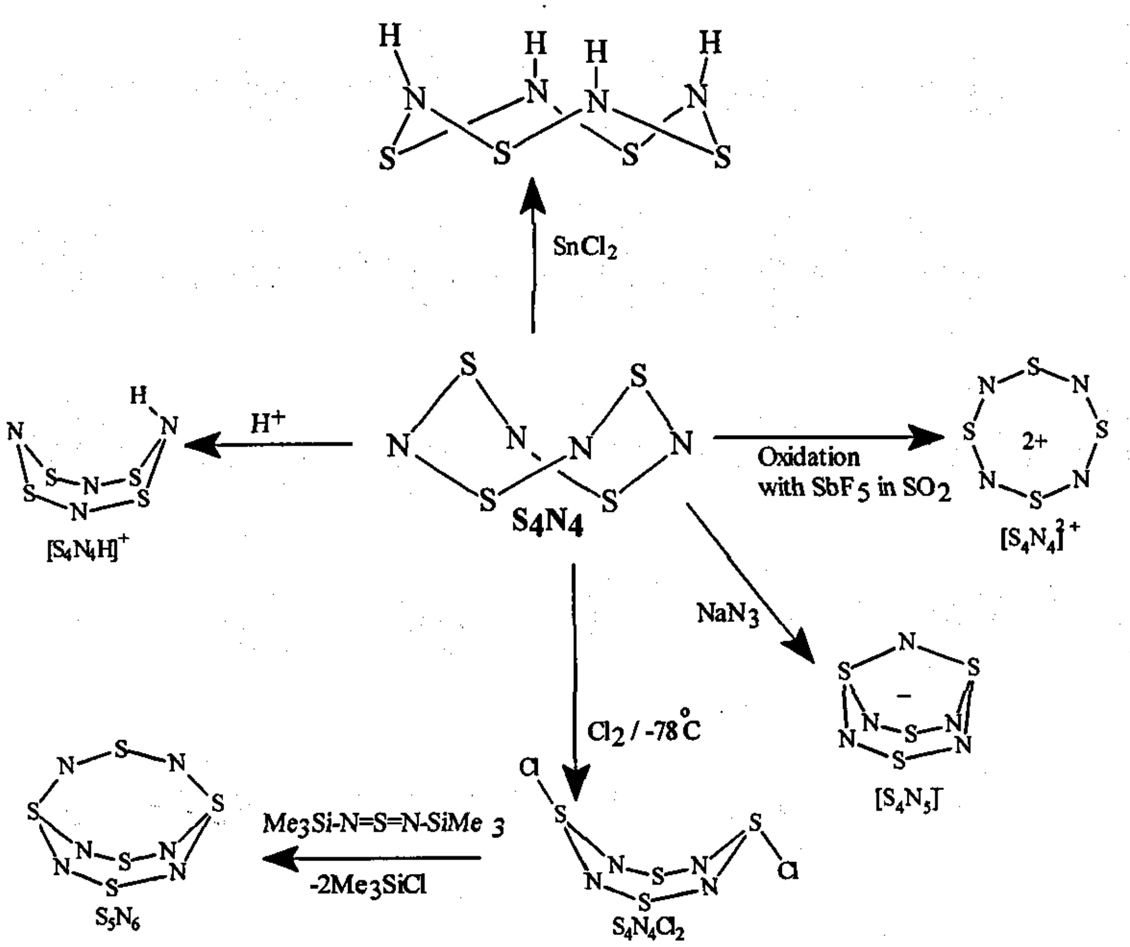


Fig1.2 *Some addition reactions of S_4N_4*

compounds (chain length > 7) seems, according to Zibarev and co-workers, to depend upon the terminal functional groups.[6] They noted that in order to stabilise longer chain lengths, electron withdrawing substituents were required on aromatic terminal groups. For example, a 1:2 ratio reaction of $Me_3SiN_4S_3SiMe_3$ with ArSCl produced ArS_5N_4Ar when Ar = 2-$(NO_2)C_6H_4$. When Ar = Ph, however, the only recovered products were PhS_3N_2Ph and S_4N_4. The stability of very long (ie > 9 atoms) S-N chains is questionable and, for example, reaction of $ArS_4N_4SiMe_3$ (Ar = 2-$(NO_2)C_6H_4$ or 2,4-$(NO_2)_2C_6H_3$) with SCl_2 does not lead to the expected 17 S-N chain compound, but rather to the isolation of the decomposition products ArS_4N_3Ar. In general there are no such problems with disproportionation for short chain S-N compounds.

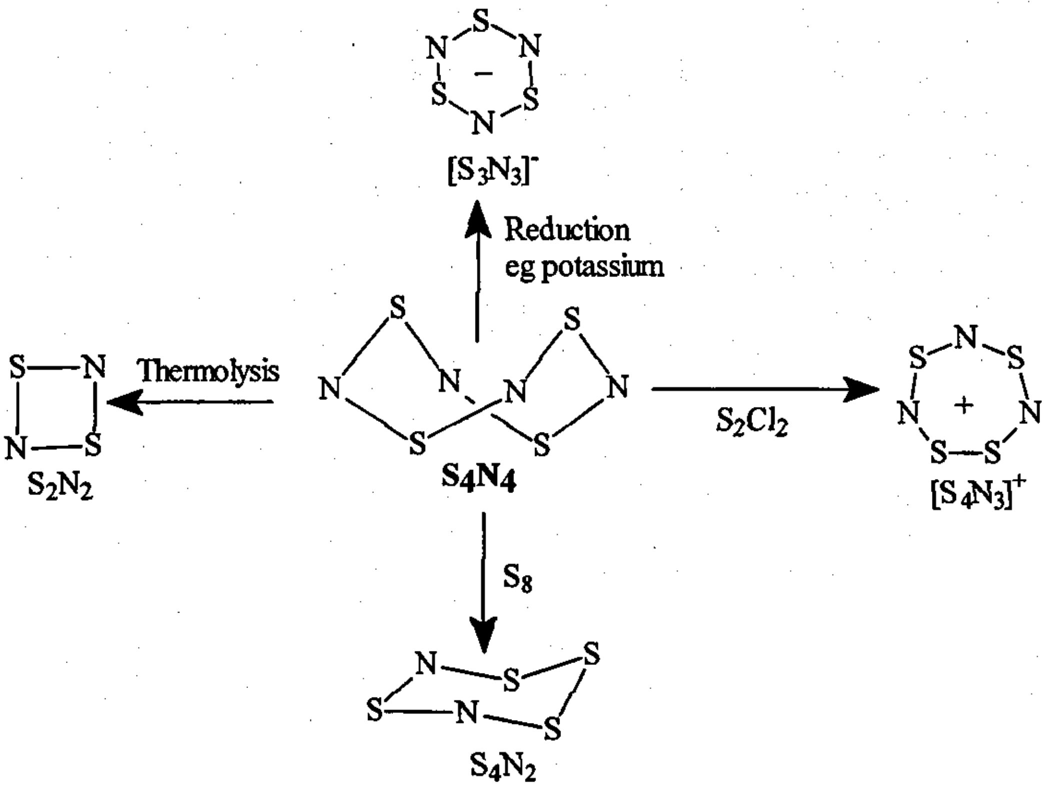


Fig.1.3 *Contraction reactions of S_4N_4*

At the other end of the scale, the shortest S-N chain is of course the two atom S-N unit. This appears in, amongst other systems, the transient $NS^{\cdot}$ radical, the $[NS]^+$ cation, monomeric NSCl and in the systems we are most interested in from the point of view of this work, the sulfimides.

1.3 Single chain S-N systems

1.3.1 SN- thionitrosyls

The neutral thionitrosyl monomer (NS), is a radical with one unpaired electron. It polymerises so readily that it is impossible to isolate it as a monomeric solid or liquid and has only a transient existence in the gas phase,[7] being generated from either the volatilisation of $(SN)_x$ or pyrolysis of S_4N_4. Thionitrosyl cations were first prepared in 1971 by the reaction of NSF with AsF_5 or SbF_5 which forms $[NS][MF_6]$ (M = As or Sb)[8-10] although their application as reagents in the preparation of complexes has not been extensive. However $[NS][PF_6]$ prepared *in situ* form $AgPF_6$ and $(NSCl)_3$ has been used in the synthesis of $[Cr(MeCN)_5(NS)][PF_6]$.[11]

Although there is no *general* synthetic route available yet, a few successful routes to thionitrosyl complexes have been elucidated. These include (a) reaction of nitride complexes with sulfur or sulfur halides, (b) reaction of $(NSCl)_3$ with transition metal complexes, (c) generation of NS^+ salts and their reaction with metal complexes, and (d) elimination of halide from NSCl and NSF metal complexes.

Route (a)

The first thionitrosyl complexes were reported using the reaction of nitride complexes and sulfur in 1974 by Chatt and co-workers[12]

$$MoN(S_2CNR_2)_3 + S_8 \rightarrow Mo(NS)(S_2CNR_2).$$

where R_2 = 2Me, 2Et or $(CH_2)_5$.

The reaction of nitride complexes and sulfur halides were reported in the formation of the rhenium thionitrosyl complex.[13]

$$ReCl_2N(PPh_3)_3 + 0.5S_2Cl_2 \rightarrow ReCl_2(NS)(PPh_3)_3$$

Route (b)

The first reported use of this method was in 1978 by Kolthammer and Legzdins.[14] The use of $(NSCl)_3$ (which is thought to exist as NSCl monomer in solution) is possible thanks to it being a source of NS^+. This reagent has been used extensively as a means of preparing thionitrosyl complexes due to its

$$Na[Cr(CO)_3Cp] + \frac{1}{3}(NSCl)_3 \xrightarrow{thf} Cr(CO)_2Cp(NS)$$

easy preparation.[15]

Route (c)

This route involves preparing the NS^+ salt, which can be done *in situ* from $AgPF_6$ and $(NSCl)_3$ forming $[NS][PF_6]$ which is then reacted with a metal complex. An example of such a reaction is below.[11]

$$\frac{1}{3}(NSCl)_3 + AgPF_6 \rightarrow [NS][PF_6] + Cr(CO)_3(C_6H_6) \xrightarrow{MeCN} [Cr(MeCN)_5(NS)][PF_6].$$

Route (d)

This route has some problems as it is difficult to prepare the required NSF and NSCl compounds. The chloro compounds are usually obtained from $(NSCl)_3$ whilst the fluoro complexes are prepared from NSF monomer. The reactions below illustrate the route for both NSF and NSCl.

$$[Re(CO)_5(NSF)][AsF_6] + AsF_3 \rightarrow [Re(CO)_2(NS)][AsF_6]$$

$$[OsCl_4(NSCl)_2] + AsPh_4Cl \rightarrow (OsCl_4(NS)_2Cl][AsPh_4]$$

There are many thionitrosyl complexes with Cr, Mo, Re, Ru, Os, Co, Rh, Ir, and Pt known.[16-19] Comparison of the spectroscopic properties and the electronic structures of M-NS and M-NO complexes indicates that NS is a better □-donor and π -acceptor ligand than NO.

The geometry for these metal-thionitrosyls complexes has been identified as linear and bent coordinating through the nitrogen. The characteristic stretching vibration for linear M-NS complexes occurs in the range 1150-1370 cm^{-1}, while the terminal bent complexes appear at lower frequencies.

The route for preparing thionitrosyl complexes has to be chosen carefully as the method used to prepare the organometallic complex $Cr(CO)_2Cp(NS)$ as shown above has not been successful for other cyclopentadienyl (Cp) complexes. This is due to the powerfully oxidising NSCl which gives rise to binuclear and chloro complexes.

$Na[W(CO)_3Cp] + (NSCl)_3 \rightarrow [W(CO)_3Cp]_2$ (20%) + $W(CO)_3ClCp$ (10%).

A rare example of a bis(thionitrosyl) complex was obtained by halide abstraction from a chlorothionitrene complex.[20]

$OsCl_4(NSCl)_2 + AsPh_4 \rightarrow [OsCl_4(NS)_2Cl][AsPh_4]$

X-ray crystallography revealed that the M-N-S groups were linear (169.1 and 169.9°) with a loosely bound chlorine atom (S-Cl 2.28Å)

It is possible to desufurate some thionitrosyl complexes and revert them back to their starting nitride complex. One such example[21] involves $Mo(NS)(S_2CNMe_2)_3$ which when treated with tributylphosphine regenerates the starting nitride complex, $Mo(N)(S_2CNMe_2)_3$. The same molybdenum thionitrosyl complex can also by alkylated using triphenylmethyltetrafluoroborate to yield $[Mo(NSCPh_3)(S_2CNMe_2)_3][BF_4]$.

Other S-N compounds can be prepared from the thionitrosyl cation (Fig.1.4).[18] For example, the insertion reactions with S_4N_4 and SCl_2 produce the $S_5N_5^+$ and $ClSNSCl^+$ cations, respectively. Insertion of thionitrosyl cations into the metal-halogen bond of Re(CO)5X (X = Cl, Br) provides a route to thionitrosyl halide complexes. It has also been noted that thionitrosyl salts form thermally unstable, intensely coloured charge-transfer complexes with arenes.[22]

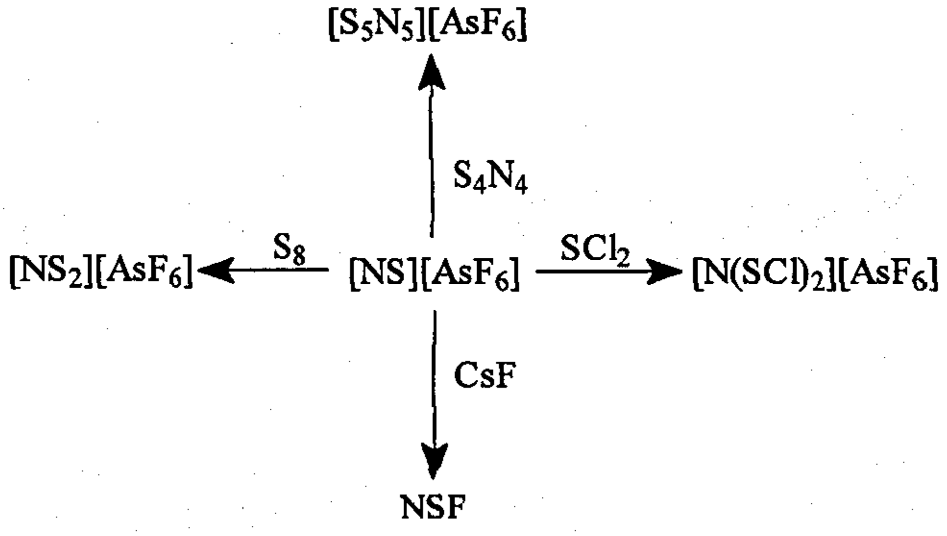


Fig.1.4 *[NS][AsF$_6$] as a precursor to other S-N species*

1.3.2 Thiaryl Halides, NSX$_n$ (X = F, Cl, Br)

NSF and NSF$_3$

These thiazyl halide complexes, as was seen earlier, can be used in the preparation of thionitrosyls complexes (route d). All the thiazyl halides are gases.

Thiazyl fluoride is a moisture sensitive, thermally unstable gas.[23] A few methods are know for the generation of NSF. One method involves the thermal decomposition of FC(O)NSF$_2$ or Hg(NSF$_2$), which contains a unique example of an NSF$_2$ complex.[24] Another is from the reaction of [NS][AsF$_6$] and CsF or from the reaction of (NSCl)$_3$ and KF in tetramethylene sulfone at 80°C. The structure of this thiazyl halide (NSF) has been confirmed as bent.

Thiazyl triflouride is obtained by fluorination of NSF of FC(O)NSF$_2$ with AgF$_2$ forming a pungent colourless gas. The structure of NSF$_3$ is a distorted tetrahedral structure has been confirmed on the basis of spectroscopic data.[23]

To stabilise NSF and NSF_3 they have to be coordination to a transition metal to form stabile compounds. This is usually achieved by displacement of SO_2 using excess ligand.[25-28, 59]

$$[M(CO)_5SO_2][AsF_6] + NSF \rightarrow [M(CO)_5(NSF)][AsF_6]$$

where M = Mn or Re[28]

$$[Re(CO)_5SO_2][AsF_6] + NSF_3 \rightarrow [Re(CO)_5(NSF_3)][AsF_6]$$

$$[M(SO_2)_x][AsF_6]_n + NSF_3 \rightarrow [M(NSF_3)_4][AsF_6]_n$$

where M = Mn, Fe, Co, Ni, or Cu[59]

$$[M(SO_2)_x][AsF_6]_2 + NSF \rightarrow [M(NSF)_6][AsF_6]_2$$

where M = Co or Ni[26]

NSF_3 complexes of silver and rhenium have been reported which use an alternate route.[29-30]

$$AgAsF_6 + NSF_3 \rightarrow [Ag(NSF_3)_2][AsF_6]_2$$

$$Re(CO)_5Br + AgAsF_6 \xrightarrow{NSF_3} [Re(CO)_5(NSF_3)][AsF_6]$$

It has been noticed that the N-S and S-F bond lengths do shorten when NSF_3 forms complexes with metals. There is also an increase in the IR stretches of N-S and S-F when forming complexes compared to the free NSF_3. In $[Mn(NSF_3)_4][AsF_6]_2$ the S-N and S-F bond lengths are 1.365 and 1.506 Å, respectively,[59] while in the free NSF_3 the S-N and S-F bond lengths are 1.416 and 1.552 Å, respectively showing an obvious decrease when forming a complex. There is also an increase in the IR stretching frequencies associated with the N-S and S-F bonds when forming complexes compared to the free NSF_3. In the free NSF_3 the N-S stretch is $1515 cm^{-1}$ and the S-F bonds stretch is

811 and 775cm $^{-1}$, in complexes these increase in frequency to 1575-1650 and *ca* 860 and 825cm^{-1}, respectively. These same trends can be seen in NSF complexes. For example, $[Co(NSF)_6][AsF_6]_2$ has a S-N and S-F bond length of 1.399 and 1.569 Å, respectively. In the free NSF the S-N and S-F bond length are 1.448 and 1.643 Å, respectively with the IR stretches of N-S being 1361cm^{-1} and S-F being 641cm^{-1}. Such values may be compared to those of the metal complex[30] $[Co(NSF)_6][AsF_6]_2$ which has significantly shorter S-N and S-F bond lengths of 1.399 and 1.569 Å respectively.

NSCl

The monomeric NSCl is, as with the other thiazyl halides, a gas - in this case greenish-yellow in colour. It can be prepared by heating the cyclic trimer $(NSCl)_3$ but has to be kept under a vacuum or in an inert gas stream as it trimerizes in the condensed state. It can also be generated in solutions of $(NSCl)_3$ in liquid SO_2 at room temperature or in CCl_4 at 70 °C.[31] Metal-NSCl complexes are known[32], but unlike the fluoro species in which the monomer NSF is stabilised by coordinating to a transition metal these complexes are prepared from $(NSCl)_3$ rather then the monomer NSCl. Typically, these complexes are formed from the reaction of a high oxidation state metal chloride with $(NSCl)_3$ in $POCl_3$ or CCl_4. Using this method a simple addition reaction can be used to make the metal-NSCl complex.[33]

$$NbCl_5 + \frac{1}{3}(NSCl)_3 \rightarrow NbCl_5\bullet(NSCl)$$

It is possible to make NSCl complexes in which one[34] or more chlorides[35] can be dislodged or even contain $POCl_3$.[33]

$$MoCl_5 + \frac{2}{3}(NSCl)_3 \rightarrow MoCl_4(NSCl)$$

$$2\ MCl_6 + \frac{2}{3}(NSCl)_3 \rightarrow [MCl_4(NSCl)]_2 + 2\ Cl_2$$

where M = Mo or W[38]

$$MoCl_5(POCl_3) + \frac{1}{3}(NSCl)_3 \rightarrow MoCl_4(NSCl)(POCl_3)$$

Unfortunately the route used to prepare NSCl complexes is not generic as the $(NSCl)_3$ when reacted with certain metal chlorides gives different products. When iron trichloride[36] is reacted with $(NSCl)_3$ it gives a variety of products depending on the reaction conditions; these include the only known salt of the $[S_4N_4Cl]^+$ cation, $[S_4N_4Cl][FeCl_4]$. An alternate route[37] involves the reaction of $S_3N_2Cl_2$ with $ReCl_5$ to produce $[ReCl_3(NSCl)_2]_2$ or, if the reaction is carried out in $POCl_3$, $[ReCl_3(NSCl)_2POCl_3]$.

The bonding that occurs in these metal-NSCl complexes occurs through the nitrogen coordinating to the metal centre with the NSCl group being bent. Spectroscopic and X-ray structural data indicate M=N=S bonding in the complexes. This is illustrated in the W-N and N-S distances (1.76 and 1.58 Å, respectively) for the tungsten complex $[WCl_4(NSCl)]_2$[38] which indicates M=N=S bonding.

NSBr

There is not that much chemistry known about this monomeric thiazyl halide. It has only been characterised from its IR spectrum. It is generated in the gas phase by the pyrolysis of $[S_4N_3]Br$.

Cyclotrithiazyl trichloride $S_3N_3Cl_3$

Although not specifically a single chain S-N compound its ability in solution to act as monomeric NSCl makes it pertinent to this section.

$S_3N_3Cl_3$ is a pale-yellow crystalline compound, which is moisture-sensitive. It was first obtained from the chlorination of S_4N_4 with chlorine in CCl_4.[39] Later methods involved the chlorination of S_4N_4 with excess refluxing SO_2Cl_2 under SO_2[40] or with excess SO_2Cl_2 under N_2 at room temperature.[41] These methods do produce the required trimer but the involvement of S_4N_4 makes this reactions hazardous and a safer method involves the chlorination of $[S_3N_2Cl]Cl$.[42]

$$3\ S_3N_2Cl_2 + 3\ SO_2Cl_2 \rightarrow 2\ S_3N_3Cl_3 + 3\ SCl_2 + 3SO_2$$

The trimer consists of a six-membered ring in which all three chlorine atoms are in the axial positions forming a chair conformation (**Fig.1.5**). This arrangement is stabilized by the delocalisation of the nitrogen lone pair into an S-Cl σ^* orbital.[43]

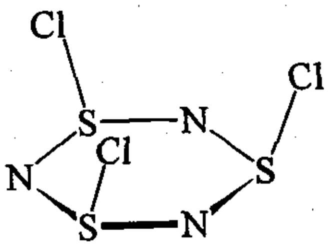


Fig.1.5 *The Structure of $(NSCl)_3$*

Both cyclic and acyclic compounds may be produced from $(NSCl)_3$ indicating its importance as a reagent in S-N chemistry (**Fig.1.6** illustrates this).[44,45] This is due to its ability in solution to dissociate into monomeric

NSCl providing a facile source of the NS^+ cation. Monomeric NSCl, generated from $(NSCl)_3$, undergoes a [2 + 4] cycloaddition reaction with hexafluorobutadiene to give a six-membered ring, but it reacts as a nitrene with fluorinated alkenes to give *N*-(chlorosulfenyl)aziridines.[46] The reactions of $(NSCl)_3$ with sodium alkoxide to give $(NSOR)_3$[47] or with AgF_2 to produce $(NSF)_3$ are two examples of transformations which occur with the six-membered ring staying intact.

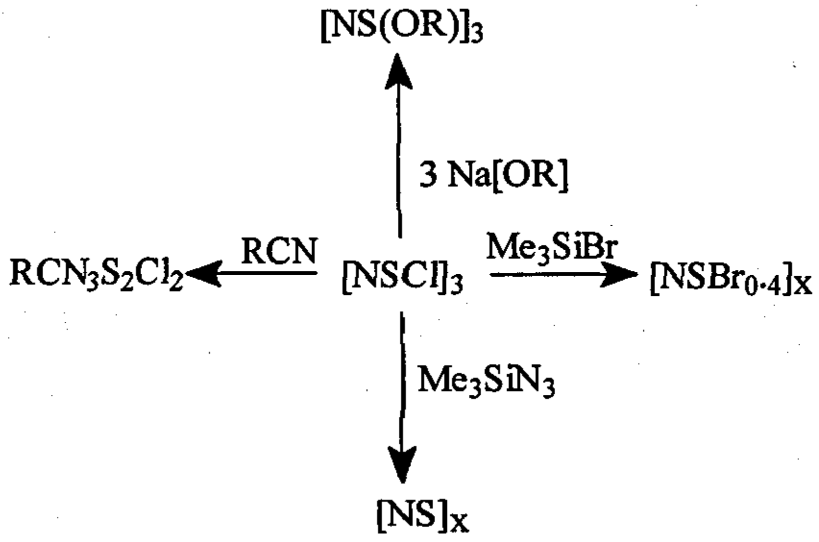


Fig.1.6 *Reactions of (NSCl)₃*

1.3.3 Thionyl imide ion, NSO^-

Thiony imide, HNSO, can be prepared from the reaction of thionyl chloride and ammonia in the gas phase to form a thermally unstable gas that polymerises rapidly.[48] According to IR and microwave spectra it has a planar, *cis* structure. There are only a few transition metal complexes of thionyl imide known.[32]

$$[M(CO)_5SO_2]AsF_6 + (excess)HNSO \xrightarrow{liq.SO2} [M(CO)_5(HNSO)]AsF_6$$

where M = Mn or Re

The reaction of Me_3SiNSO and potassium *t*-butoxide in THF produced potassium thionyl imide, K[NSO]. Using the same method the more soluble $(Me_2N)_3S^+$ salt has been prepared.[49]

$$[(Me_2N)_3S][Me_3SiF_2] + Me_3SiNSO \rightarrow [(Me_2N)_3S][NSO] + 2\ Me_3SiF$$

Metathetical reactions of these salt can be used for the synthesis of both transition metal and main group element thionyl imides, e.g. $Cp_2(TiNSO)_2$ and $Ph_{3-x}As(NSO)_x$ (x = 1, 2), respectively.[50] The bonding occurs *via* the nitrogen in these compounds forming a M-NSO bond.

1.3.4 Thionitrite ion, SNO^-

The thionitrite ion SNO^- is produced when $SSNO^-$ is treated with triphenylphosphine. Not much chemistry is known of this anion, it has a bent structure with a bond angle of ca. 120□ at nitrogen.[51] This is probably due to the stability of this ion as MO calculations, including a correlation energy correction, indicates that the SNO^- ion is less stable than the isomer NSO^- by at least 38 kJ mol^{-1}.[52]

1.3.5 RNSO complexes

There are numerous reported examples of the RNSO ligand coordinating with metals. Examples in which R = aryl seem to be the most common. Group VIII metals form simple complexes with the RNSO ligand.[53-56]

$$Ir(CO)X(PPh_3)_2 + RNSO \rightarrow Ir(CO)X(PPh_3)_2(RNSO)$$

where X = Cl or Br, R = p-$O_2NC_6H_4$

$M(PPh_3)_2L + RNSO \rightarrow M(PPh_3)_2(RNSO)$

where M = Ni, L = C_2H_4 or COD, R = Ph or ^{t}Bu

M = Pt, L = C_2H_4, R = Ph or *p*-MeC_6H_4

M = Pd, L = $2PPh_3$, R = Ph or *p*-MeC_6H_4

The coordination properties of such RNSO complexes vary depending upon the environment in which the reaction has taken place and with the transition metal involved. For example, it has been observed, in $[Pt(PPh_3)_2$(2,4,6-mesitylNSO),[56] that they can act as a bidentate ligand and coordinate via the N=S double bond. In other cases to this ligand coordinates through the sulfur, thus acting as a monodentate ligand eg in the phosphine complex $IrCl(PPh_3)_2(PhNSO)$.[57] As noted earlier, coordination through the nitrogen is seen in the case where R = H, ie HNSO. There is also an example in which coordination occurs through the oxygen, $Pt(OSNH)_2(PPh_3)_2$.[58]

1.4 The sulfimides

This class of two atom chain sulfur-nitrogen compounds can be represented by the general formula $R^1R^2S{=}NR^3$.[60] These are the sulfimides (as named according to IUPAC rules, older literature sometimes refers to them as sulfilimines). They date back to 1917 when Raper reported a crystalline compound forming during the treatment of mustard gas with Chloramine-T.[61] Subsequent work has over the year focussed upon many aspects of their chemistry (though intriguingly, as we will see, very little work has been performed on their affinity for metals).

The relative electronegativities of the atoms involved leads to the prediction that the properties of sulfimides should be intermediate between those of sulfonium ylides and of sulfoxides. They should also be similar in properties to the corresponding sulfoximines but more reactive, just as the sulfonium ylides are more reactive than the corresponding oxo sulfonium ylides. The simplest comparison to make in this area, and the one with perhaps the most importance in terms of the coordination chemistry of the sulfimides, comes with the fact that they are isoelectronic with sulfoxides.

A key contrast between sulfimides and sulfoxides comes from the fact that, while the latter may be derivatised at the sulfur but not, by definition at the oxygen, the former can possess a range of substituents on both the sulfur and the nitrogen. Examples of N-substituents commonly studied include alkyl/aryl groups and halogens; by far the most common, however, is a simple hydrogen (in a so-called *free* sulfimide). By far the most studied free sulfimide is diphenylsulfimide (Ph_2SNH) **1**, a colourless, air stable, organic-soluble material that is actually commercially available.

Diphenylsulfimide can be prepared by a range of methods, principally involving direct amination of Ph_2S. The standard method for this utilises a two step reaction. The first stage involves preparing the N-tosylsulfimide *via* the Mann-Pope reaction; ie reacting diphenysulfide with Chloramine-T to produce the corresponding N-tosylsulfilimine, Ph_2SNTs. This may then be converted to the free sulfimide by treatment with concentrated sulfuric acid. In our experience, however, the latter reaction produces very variable yields and we have found that even recent variations, such as the use of chloramine-B, do not give reproducible results.[62] Later (in the general experimental section) we will report on an improved method.

Ph_2SNH is an important precursor to several types of substituted sulfimide. Figures 1.7 and 1.8 highlight some reactions in which either carbon or heteroatom substituents are added to the compound at the N atom.

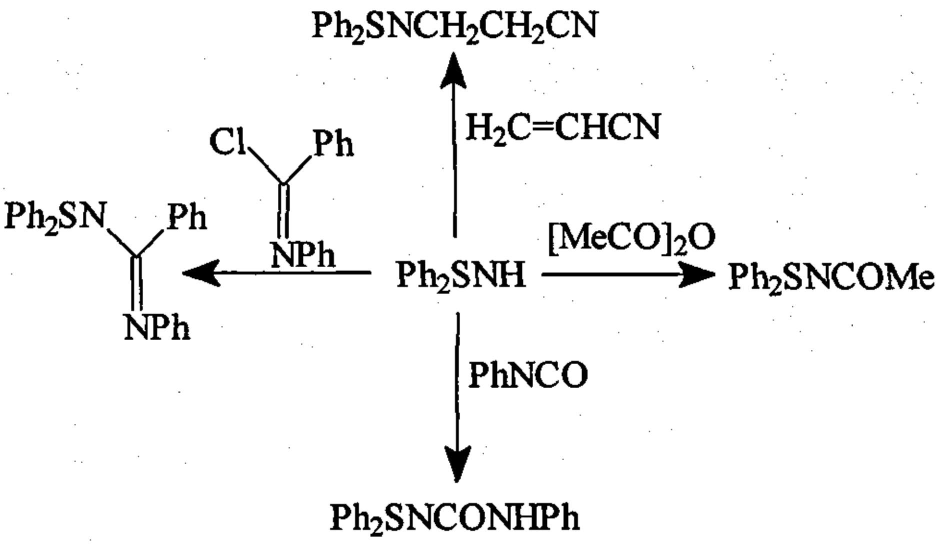


Fig.1.7 *Derivatisation of* Ph_2SNH *with carbon substituents*

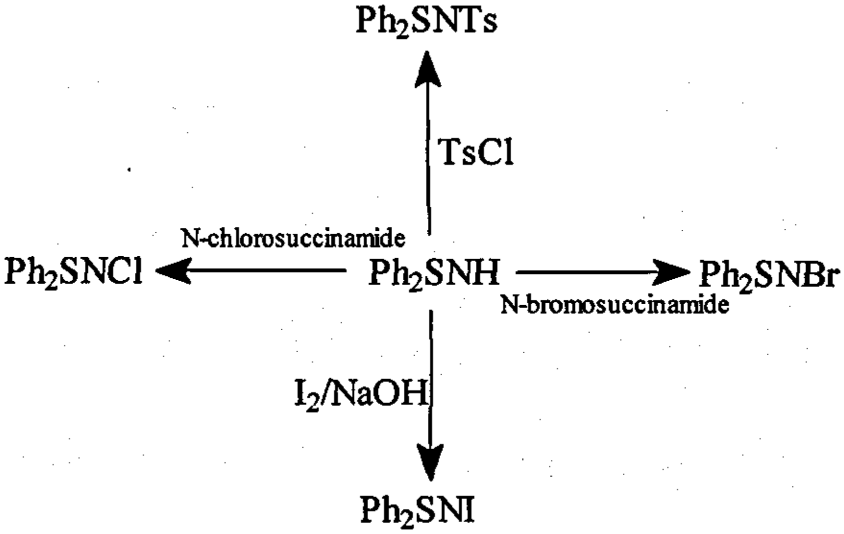


Fig.1.8 *Derivatisation of* Ph_2SNH *with heteroatom substituents*

1.5 Metal S-N complexes

Many examples of metal S-N complexes are now known.[63] They have been generated using a wide range of S-N starting materials and examples containing all the transition metals have been prepared. Such complexes may contain ligands, which are stable as free materials (good examples include adducts of S_2N_2 or NSCl) or which are formally anions which cannot be made as free salts. Many examples of the latter are known; some are shown below in Fig.1.9. The ability of the metal centre to stabilise otherwise unstable fragments is one of the major incentives for work in this area.

Given the extent of such interest in metal complexes it is somewhat surprising to note that very little work has been done on the coordination chemistry of sulfimides. There have been very few reactions involving metal complexes of sulfimides reported. This include the reaction of K_2PtCl_4 with $(CH_3)_2SNC(O)R$ (where R=C_6H_5 or $C_6H_4CH_3$-*p*) (Y) in water gave a stable ylide complex, $PtCl_2(Y)(DMSO)$, in which Y coordinates to the Pt(II) via nitrogen and DMSO via the sulfur to form a *cis*-configuration.[64] Dichloride complexes of palladium(II) and platinum(II) were reacted with ($PhC(O)MSMe_2$ (Y_s) to form $MCl_2(Y_s)(L)$ (M=Pd, Pt; L=PPh_3, PPh_2Me, $PPhMe_2$) compounds.[65] As well as

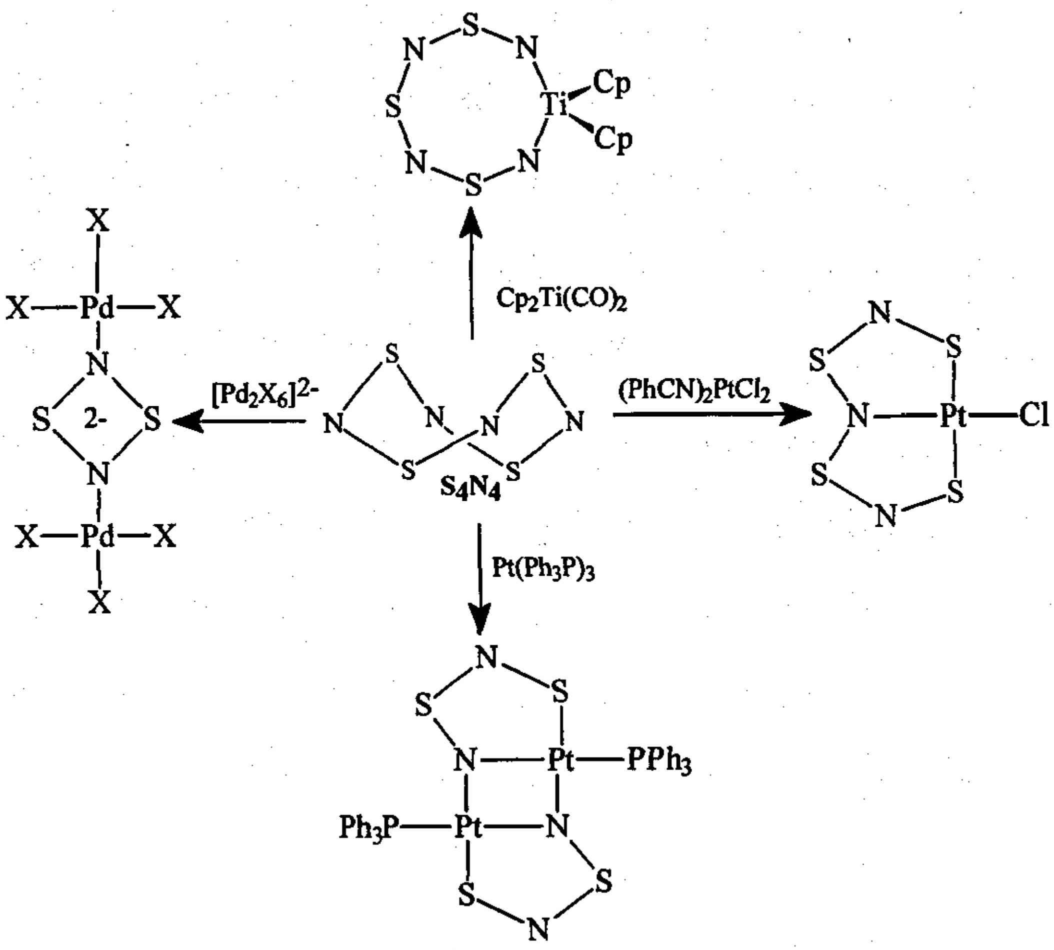


Fig.1.9 *Examples of Metal S-N complexes.*

S,S-dimethyl-N-benzoylsulfimides (Y_s) reactions with palladium(II) and platinum(II) dihalides having produced $MX_2(Y_s)_2$ and $MX_2(Y_s)(L)$ (M = Pd, Pt; X= Cl, Br; L = PPh_3, Me_2SO).[66] Indeed, until we started our work the only fully characterised (ie by X-ray crystallography) complex of Ph_2SNH was the Uranium species $[UCl_2(Ph_2SNH)Cp^*_2]$.[67]

This lack of chemistry is made all the more glaring by the obvious potential that species such as **1** have as ligands – noting, especially, their potential to bind through either the S or the N or potentially even both. In addition their electronic analogy with sulfoxides means that systems wherein sulfoxides bind to metals should also be amenable to sulfimides.

1.6 Metal sulfoxides

Sulfoxides, RR'SO, are isoelectronic to sulfimides and numerous examples of these compounds coordinating to metals are known - contrast the sulfimides for which, until this work, very few metal complexes were known. Though sulfimides have the potential to bond through either the S or the N or potentially even both, as we will see the N-bound coordination mode dominates. In comparison, the sulfoxides can coordinate through either the S or the O atoms in a monodentate fashion. There are rare cases where by two metal atoms have been bridged via the O from the sulfoxide. An example of a sulfoxide demonstrating such versatility is Me_2SO, which can coordinate to metal centres through the S, O, and in the aforementioned bridging manner.[68] Sulfoxides can also act as bidentate ligands bonding through the S, and O bridging two metal atoms. Me_2SO shows this S, O bidentate bridging mode in the product $[Ru_2(\mu\text{-Cl})(\mu\text{-H})(\mu\text{-Me}_2SO)Cl_2(Me_2SO)_4].2CH_2Cl_2$.[69] The structure also consists of the sulfoxide, Me_2SO, bonding to the ruthenium through the sulfur. Looking at the different bonding modes illustrates the diversity of the sulfoxides when bonding to metal centres compared to the limited array of options seen for sulfimides (nitrogen bonding).

1.7 Aims of this work

In view of the aforementioned similarities between sulfimides and sulfoxides, and given the range of coordination chemistry known for the latter, in this work we aimed to start to develop the coordination chemistry of **1**. The latter sulfimide was chosen for the study thanks to its ease of preparation (though as we will see we had to develop a more reliable route than those in the literature) and for the fact that it is a stable, solid material that is easily handled.

The metal systems looked at reflected the results of simple preliminary tests, which showed that reaction with, for example, simple copper halides was quick and easy to perform. However, the precise direction of the study changed as the unexpected properties of some of our first complexes became apparent.

1.8 General experimental conditions.

Unless otherwise noted all reactions were performed under an inert atmosphere using solvents dried and distilled by standard techniques. Microanalysis was performed by the Departmental service as was X-ray crystallography (Pauline King and Dr Alex Slawin respectively). IR spectra were run as KBr discs on a Perkin Elmer PE2000 spectrometer.

The preparation of Ph_2SNH by following published routes exactly proved difficult; after some time and effort we found that a modification of the route of Vlasova *et al* worked best;[62] thus Ph_2SNSO_2Ph (7 g, 0.02 mol) was added in a number of portions to well stirred, degassed 95% H_2SO_4 (25 ml) under a blanket of N_2. The resulting mixture was then heated at 80°C for 15 minutes before being cooled and cautiously poured onto ice (200ml). After warming, the resulting mixture was taken to pH 11 by addition of 5M NaOH; the response of the mixture to this appears to be very variable - on some occasions solid **1** precipitated and was then filtered and recrystallised from Et_2O, on other occasions only a pale orange oil was apparent. In the latter case the entire mixture was extracted into warm Et_2O (typically 2 x 50ml), the solvent reduced in volume and the resulting colourless crystalline mass filtered.

In either case typical yield 1.8 g, 45%. MPt. 69-70°C (lit. 69°C).

Chapter 2 Copper complexes of Ph_2SNH (i): $[CuX_2(Ph_2SNH)_2]$

2.1 General introduction to copper co-ordination chemistry

Copper occurs in a range of oxidation states and the ions readily form complexes yielding an extensive variety of co-ordination compounds.[70] The known oxidation states cover the range 0 to IV, although the chemistry of the two extremes is very limited. The copper (III) oxidation state is more common and though it has only been clearly characterised for 20-30 compounds or complexes, it is extensively invoked as an intermediate oxidation state in mechanistic studies, especially those involving amino acid species. Of the remaining two oxidation states Cu(I) has the less extensive chemistry and readily oxidised to Cu(II). Not only is Cu(II) the most stable of all the states, but it also the most prolific in terms of known complexes and has been crystallographically characterised on numerous occasions.

As the electronic configuration of Cu is (Ar) $4s^2$ $3d^9$ it follows that Cu(II) a d^9 system and this configuration imparts many properties upon its complexes, the most obvious of which is the presence of an unpaired electron. Thus Cu(II) compounds are paramagnetic. The Cu(II) ion is the commonest oxidation state of copper, as Cu(I) is readily oxidised up to copper (II) or may disproportionate into Cu(II) and copper metal, while Cu(III) can only be prepared by strong oxidation of Cu(II). The Cu(II) ion is particularly stable in aqueous solution as the $[Cu(H_2O)_6]^{2+}$cation, from which complexes may frequently be prepared directly by the addition of the appropriate ligand. As we will see in our work, however, the presence of other ligands can impart solubility in a range of common organic solvents.

Like all first-row transition metal(II) cations, Cu(II) readily forms complexes involving the co-ordination numbers four, five, and six, but can also form complexes involving the co-ordination numbers two, seven, eight and nine. In general the relative abundance can be ranked as $6 \approx 5 > 4 >> 7 > 8 >> 9 \approx 2$, with no three co-ordinate structures known.

Unlike the majority of the first row metal ions, the Cu(II) complexes are characterised by a seemingly infinite variety of structural distortions. This has led to a wealth of crystal structure determination to characterise the various regular and distorted stereochemistries of the Cu(II) ion . These distortions are associated with the influence of the Jahn-Teller effect. As a result a regular octahedral geometry is rare for the Cu(II) ion (less than 10 compounds) while a regular tetrahedral geometry is unknown. The majority of six co-ordinate copper (II) complexes involve an elongated tetragonal or rhombic octahedral structure (Fig.2.1), with only a few involving a compressed tetragonal (or rhombic) octahedral structure. The tetrahedral geometry for the copper (II) ion always involves a significant compression along the S_4 symmetry axis. Only the square coplanar geometry is regular for copper (II) ions, but even here sometimes there is a slight tetrahedral distortion, as seen in $[EtNH_3]_2[CuCl_4]$ for example.

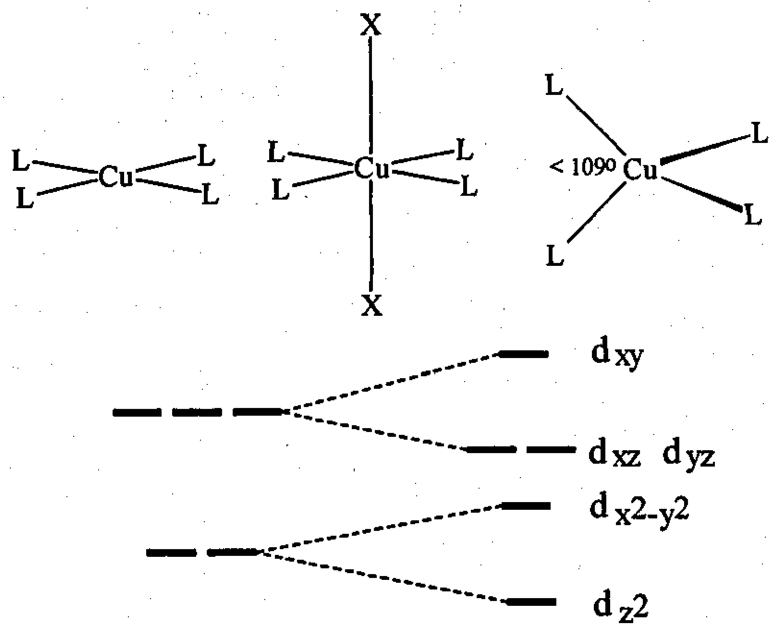


Fig.2.1 *Geometries of Cu(II) complexes (from left, square-planar, elongated tetragonal, pseudo-tetrahedral); change in the energies of d orbitals on distorting tetrahedral geometry.*

The co-ordination chemistry of the Cu(II) ion is dominated by ligands bearing nitrogen and oxygen as donor atoms, followed, in terms of abundance, by chlorine and then sulfur donors; bromide complexes are well characterised, but fluoride analogues are surprisingly limited. Examples containing iodine co-ordinated to Cu(II) only exists in the presence of ligands (particularly nitrogen donors) which stabilise the Cu(II) ion with respect to reduction. The phosphorous atom as a donor is surprisingly uncommon due to an ability to reduce Cu(II) to Cu(I). Equally uncommon are ligand donor atoms involving arsenic, antimony and bismuth, and selenium or tellurium and thus, whereas phosphine ligands are extremely common for most transition metals (e.g. platinum)- they are much rarer for copper.

Nitrogen donors are the commonest ligands to the Cu(II) ion. The most abundant σ donor nitrogen ligand is ammonia, readily forming $[Cu(NH_3)_n]X_2$ systems. The sulfur ligands which form copper-sulfur bonds are limited to thiocarbamate type ligands, as $[Cu(diethylthiocarbamate)_2]$. Due to their reducing properties simple sulfides as ligands to the copper (II) ion are only observed if the oxidation state is stabilized by, generally, nitrogen chelate ligands as with the macrocyclic ligands, as $[Cu_2(p\text{-}XYLpy_2)(OH)](BF_4)_3$.

In most cases complexes show one preferred geometry; thus 4- co-ordinate species may be either planar or pseudo-tetrahderal. An exception to this comes with some salts of $[CuCl_4]^{2-}$. Here, the presence of an appropriate cation can induce a thermochromic effect i.e. the geometry (and hence colour) changes upon heating. An example, which is simple enough to form the basis of a common undergraduate lab experiment, comes with $[Et_2NH_2]_2[CuCl_4]$ which changes (reversibly) from green to yellow at approximately 53°C. Such behaviour has been seen with anionic copper species, but has not been seen for a neutral copper species.

2.2 Aims of this section of the work

In this section our aim is to prepare the first examples of copper complexes of Ph_2SNH. Such studies are motivated by the need to determine which of the potential co-ordination sites of the latter are favoured (ie the S or the N) and to observe the geometry of the resulting species.

2.3 Experimental

[$CuCl_2(Ph_2SNH)_2$] Blue (square planar) form 2a.

Under an atmosphere of dry nitrogen a solution of $CuCl_2$ (25 mg, 0.19 mmol) in degassed acetonitrile (20ml) was prepared. Under the same conditions a solution of **1**(75 mg, 0.38 mmol) in the same degassed solvent (20ml) was prepared. The copper solution was slowly added to the other solution under a blanket of nitrogen giving a green solution which started to precipitate a blue solid after some 15 minutes of stirring. At this point the solution was heated until all the solid had dissolved, then lagged and slowly cooled, first to ambient temperatures then overnight in a freezer, yielding well formed blue crystals of the product.

The same material can also be prepared by the reaction of [$Cu(Ph_2SNH)_4$]Cl_2 with $CuCl_2$; thus under an atmosphere of dry nitrogen solid $CuCl_2$ (15mg, 0.11 mmol) was added to a stirred suspension of $Cu(Ph_2SNH)_4$]Cl_2 (0.1g, 0.11mmol) in degassed MeCN (20ml) which was also prepared under dry nitrogen. This resulted in rapid formation of a green solution which in turn yielded a blue precipitate after 15 minutes stirring. Crystallisation as before yielded blue crystals of the product.

Yield 87 mg (76%).

Micro analysis	%C	%H	%N
Observed value	53.6	3.8	5.1
Calculated value*	53.7	4.1	5.2

* for $C_{24}H_{22}N_2S_2Cl_2Cu$

IR	**ν(N-H) (cm^{-1})**	**ν(S-N) (cm^{-1})**
[CuCl$_2$(Ph$_2$SNH)$_2$] blue	3292	913

[CuCl$_2$(Ph$_2$SNH)$_2$] Green (pseudo-tetrahedral) form 2b.

Under an atmosphere of dry nitrogen a sample of crystalline blue isomer (75 mg) isolated as above was dissolved in degassed CH_2Cl_2 (15 ml) and degassed 60/80 petroleum ether (15 ml) added. The resulting green mixture was treated with just enough degassed CH_2Cl_2 to redissolve the precipitate that had formed and was then allowed to slowly evaporate in an open round bottom flask overnight, during which time fine well formed green needles were produced together with a small crop of the heavier, more three-dimensional crystals of the blue form. The former were decanted from the latter, filtered and dried *in vacuo*.

Yield 55mg (73%).

Micro analysis	**%C**	**%H**	**%N**
Observed value	53.5	4.2	5.2
Calculated value*	53.7	4.1	5.2

* for $C_{24}H_{22}N_2S_2Cl_2Cu$

IR	**ν(N-H) (cm^{-1})**	**ν(S-N) (cm^{-1})**
[CuCl$_2$(Ph$_2$SNH)$_2$] green	3202	918

[$CuBr_2(Ph_2SNH)_2$] 3

Reaction of $CuBr_2$ with **1** on the same molar ratio scale as above does give rise to the desired product; as we will see there are, however, significant problems with contamination with an oxo-cluster by product. A better way to prepare this material involves the use of [$Cu(Ph_2SNH)_4$]Br_2 (see chapter 3). A suspension of [$Cu(Ph_2SNH)_4$]Br_2 (0.1g, 0.097 mmol), prepared as detailed in the next chapter, in degassed MeCN (10ml) under an atmosphere of nitrogen was treated with $CuBr_2$ (22mg, 0.099 mmol) added with vigorous stirring. The solid immediately started to dissolve and the mixture turned green; after stirring for 20 minutes the mixture was heated until all the precipitate had re-dissolved, lagged to promote slow cooling to ambient temperature and then further cooled in a freezer overnight. This yielded a large crop of well-formed dark green crystals. Yield 85 mg (70%)

Micro analysis	**C**	**H**	**N**
Actual value	45.7	3.7	4.8
Calculated value*	46.1	3.5	4.4

* for $C_{24}H_{22}N_2S_2Br_2Cu$

IR	**ν(N-H) (cm^{-1})**	**ν(S-N) (cm^{-1})**
[$CuBr_2(Ph_2SNH)_2$]	3286	888

2.4 Results and discussion

Formation of $[CuCl_2(Ph_2SNH)_2]$ 2

The first reaction of **1** with copper centres to investigated as part of this study was the 2:1 stoichiometry reaction with $CuCl_2$. This reaction system was picked for a number of reasons, the most obvious of which is the fact that it is conceptually simple – we hoped to generate $[CuCl_2(Ph_2SNH)_2]$ by reaction in MeCN. Anhydrous $CuCl_2$ is readily soluble in the latter solvent, presumably generating $[CuCl_2(MeCN)_2]$; thus reaction with **1** should simply be a case of substitution of the nitrile groups. The other reason this simple system was picked came from the fact that preliminary test reactions indicated that an obvious colour change occurs immediately upon mixing the reagents; as we will show, however, this apparent simplicity belies the true nature of the reaction system. Anhydrous $CuCl_2$ was used in order to facilitate its dissolution in MeCN and to reduce the likelihood of oxo-bearing by-products (though as we will see these can form anyway through the reaction conditions); it was generated simply by heating the hydrated material in a hot oven and assumed to be water-free when colour change to dark brown was complete.

Addition of two equivalents of **1** to a solution of anhydrous $CuCl_2$ in MeCN results in immediate formation of a green solution. Within a short while a blue precipitate appears which may be obtained as well-formed crystals by recrystallisation from the same solvent. Although this can be done by filtering off the solid and redissolving in the hot solvent, it is most conveniently done *in situ*. Thus heating the crude mixture results in a green solution; if the vessel is well-lagged in a cotton-wool jacket and allowed to cool very slowly the product may be obtained a well-formed blue crystals.

The IR spectrum of this product **2a** is consistent with the presence of **1** as ligand. The IR of free **1** is shown below; it is pertinent to present it here as it highlights the number of "finger-print" bands in the spectrum, associated with the organic features of the molecule. In the experimental for all our compounds we will tend to mention just the two most obvious bands in the complexes, namely the very broad N-H (3107 cm^{-1} in **1**) and the broad N-S (938 cm^{-1} in **1**) stretches. Obviously these vary somewhat in terms of their precise positions in the complexes; indeed, as we will see this can often tell us very useful information about the complexes in question.

The IR spectrum of this blue product is also shown in Fig.2.2. Comparison of the two immediately reveals that **1** is present as a ligand in this product; of the two aforementioned bands, the N-H stretch is clearly much weaker than in the free ligand while the S-N stretch has moved to 913 cm^{-1}. Microanalysis upon **2a** confirms the formulation as a 2:1 complex while X-ray crystallography adds a couple of pieces of extra information (Fig.2.3) - that the ligands are *trans* to each other and that the copper is in a square-planar geometry.

The bond distances and angles within **2a** are also shown in Fig.2.2. They are discussed in some greater detail later. With the copper in a square planar environment one may have expected to see axial Cu-Cl interations; in fact no such interactions are discernable up to 6Å away from the copper. These are probably precluded by the fact that the two sets of phenyl rings are

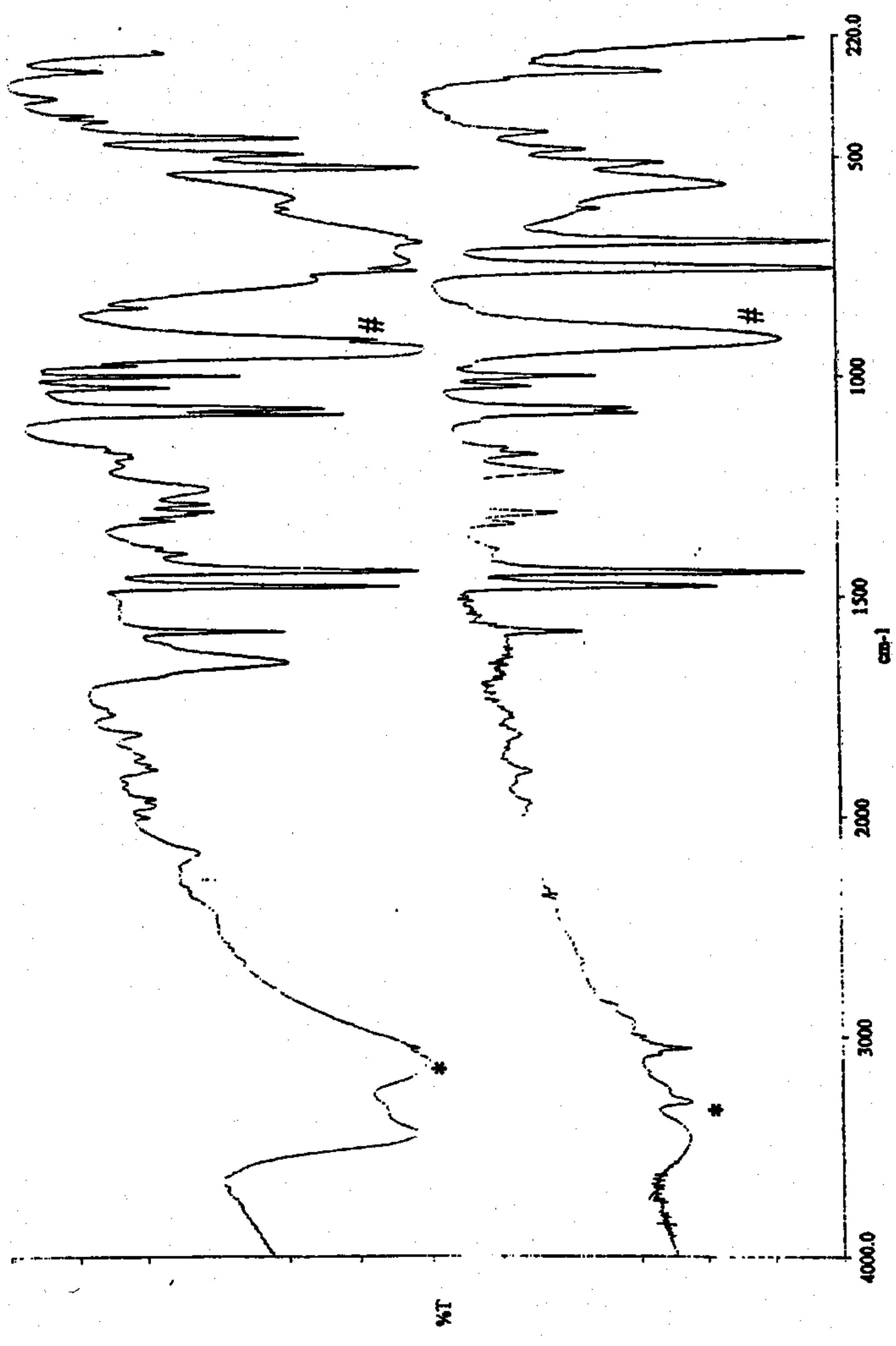


Fig. 2.2 *The IR spectra of* ***1*** *(upper) and of* ***2a****; the bands marked *(ν-N-H) and # (ν-N-S) are the two most commonly used as indicators of the course of reactions involving* ***1*** *as they change significantly upon complexation and between individual complexes.*

arranged roughly perpendicular to the $CuCl_2N_2$ plane, providing a steric barrier to any axial close approaches.

Subsequently, during investigations into the solution properties of **2a** we obtained green crystals, the IR spectrum of which also indicated the presence of **1** as ligand. Our initial assumption was that this new material would prove to be the *cis* isomer of **2a**. In fact X-ray crystallography revealed (Fig.2.3) that this new material also has ligands *trans* to each other; but the key difference comes with geometry at the copper centre. Now the geometry is pseudo-tetrahedral.

The level of distortion in **2b** from planar can be quantified by the N(2)-Cu-N(1) and Cl(1)-Cu-Cl(2) angles of 157.6 and 153.1° respectively (both being *precisely* 180° in **2a**). In other respects, however, there is minimal difference between the two structures; thus the average Cu-N and S-N bond lengths in **2b** (1.926 and 1.596 Å respectively) compare well to those in **2a** (1.911 and 1.582 Å) while the angles at the nitrogens (ie S-N-Cu) are also similar (125.4° in **2b** compared to 129° in **2a**).

The difference in packing arrangements in the two cases manifests itself in their IR spectra. Thus the ν[N-H] stretch in **2b** is seen at 3202 cm^{-1}, which is some 90 cm^{-1} lower than in **2a**, presumably reflecting the fact that the N-H

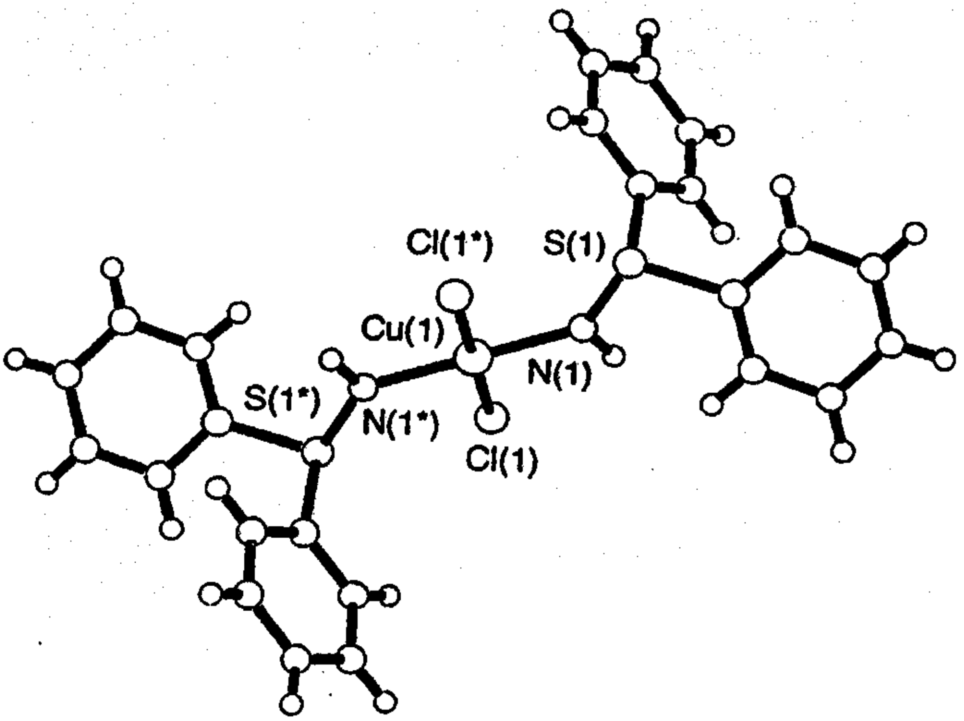


Fig.2.3 The X-Ray crystal structure of **2a**. Selected bond distances (Å) and angles (°): Cu-N(1) 1.911(8), Cu-Cl(1) 2.271(3), N(1)-S(1) 1.582(9); N(1)-Cu-Cl(1) 87.0(3), N(1)-Cu-N(1)* 180.0, Cl(1)-Cu-Cl(1)* 180.0, Cu-N(1)-S(1) 129.0(5).

bond is now free to interact with Cu-Cl bonds of neighbouring molecules (the closest such H...Cl approach being 2.68 Å in **2b** compared to 6.26 Å in **2a**; both have, of course, some degree of *intra*molecular interaction, with H...Cl distances of 2.65 and 2.68 Å for **2a** and **2b** respectively).

This would be appear to be the first example of a neutral Cu(II) system which can exhibit such isomerism. Such an observation makes reproducable isolation of significant amounts of both isomers desirable and we have made some progress in this area. As already noted, simple recrystallisation of the crude material from hot MeCN results in the formation of the blue isomer, which may be isolated as very well-formed, three-dimensional blue crystals if the solution is cooled slowly. Conversely, if the original material is dissolved in CH_2Cl_2, 60/80 petroleum ether added and the mixture allowed to slowly evaporate then the faster loss of CH_2Cl_2 results in crystallisation of **2b** from the mixture as very fine, long needles of the green form. In the latter case a small amount of **2a** sometimes forms, but the difference in size and density of the two types of crystal makes it easy to decant the needles of the green isomer off from their blue counterparts. Although this method does not lend itself to scaling up too far, we have found that it can certainly be used on amounts in the order of 100mg or so, allowing isolation of reasonable amounts **2b.**

If samples of the green isomer of **2b** thus formed are redissolved in a small volume of hot MeCN and the solutions cooled in a freezer, the material crystallises out in the blue form, thus confirming that a true polymorphism is present. This begs the question as to the nature of the driving force behind this unique isomerism; of course many factors will play a part and clearly there must be a relatively small energy difference between the two forms. While the

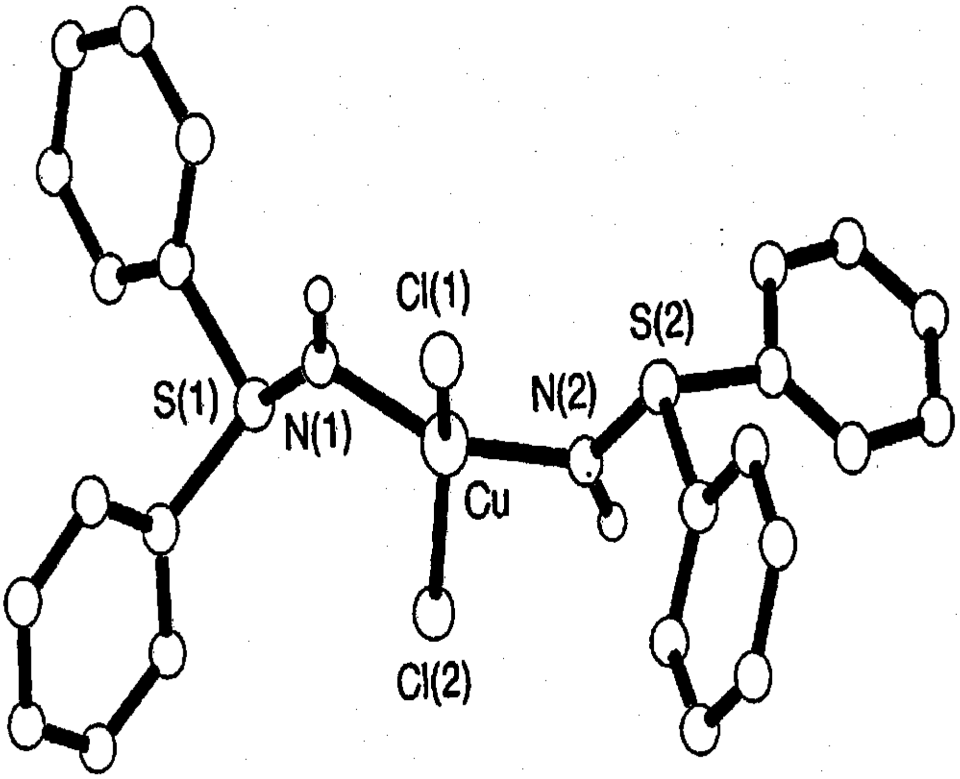


Fig. 2.4 The X-Ray crystal structure of **2b**. Selected bond distances (Å) and angles (°): Cu-N(1) 1.932(8), Cu-N(2) 1.919(8), Cu-Cl(1) 2.280(2), Cu-Cl(2) 2.284(2), N(1)-S(1) 1.607(7), N(2)-S(2) 1.584(7); N(1)-Cu-N(2) 157.6(3), Cl(1)-Cu-Cl(2) 153.1(1), N(1)-Cu-Cl(1) 90.5(2), N(1)-Cu-Cl(2) 96.2(2), N(2)-Cu-Cl(1) 93.8(2), N(2)-Cu-Cl(2) 89.9(2), Cu-N(1)-S(1) 122.9(4), Cu-N(2)-S(2) 125.4(4).

fact that crystallisation from either acetonitrile or petroleum ether yields different forms must impart some information about the interactions of the two isomers with solvent systems, it should be born in mind that when weak solutions of **2** in *any* solvent are allowed to evaporate the residue usually contains both green and blue crystals (in vary variable ratios). One obvious structural feature which could play a significant role in determining the geometry at the metal is the close interaction between the N-H group of the sulfimide unit and the chloride ligand. As we have already mentioned, and as will be seen in due course for homoleptic complexes, significant interaction between coordinated **1** and halide counterions are a feature of ionic complexes. It is therefore possible that *intra*molecular interactions between the N-H and the chloride ligand in neutral **2a** also may be important; indeed, the crystal structures of the isomers of **2a** tend to back this up insofar as the Cu-N-S angle is significantly higher in the planar case (129° cf a mean value of 124.2°). The reaction of $CuBr_2$ with **1** provides us with results which possibly add some weight to this idea.

Formation of $[CuBr_2(Ph_2SNH)_2]$ 3

The copper bromide reaction proceeds in much the same manner as the chloride, giving a green mixture, although in this case an oxo cluster **5** (see below) tends to form as substantial impurity. The latter can be avoided by first forming pure $[Cu(Ph_2SNH)_4]Br_2$ as detailed in the next chapter and then treating this with one equivalent of $CuBr_2$ as in scheme 1. The $[CuBr_2(Ph_2SNH)_2]$ thus formed may be isolated as dark green crystals from MeCN. The results of an X-ray study on these crystals is not formally presented here as the data resulted in a poor solution due to disorder at one of the sulfurs; however, the results are good enough to confirm that the geometry at the metal centre is pseudo-tetrahedral (shown in Fig.2.5; due to the poor nature of the solution the bond distances and angles are not presented), a conclusion that also fits in with the colour of the material. Crucially, we have found no evidence for the formation of any other isomer (ie square-planar) of this material - crystallisation from hot MeCN, from petroleum ether/CH_2Cl_2 or by slow diffusion of Et_2O into CH_2Cl_2 only results in the formation of the green material. Thus it seems that the act of changing from the chloride to bromide ligands mitigates against the formation of a square-planar isomer; at a simplistic level, at least, this would fit in with the idea that an N-H..Cl interaction in **2a** is maybe stabilising the planar arrangement. When the less electronegative bromide ligand is present this interaction is reduced and the planar arrangement is destabilised with respect to the pseudo-tetrahedral. In proposing this model, however, we should clearly add the *caveat* that we have no definitive proof of its veracity; one observation which would add weight to the suggestion would come with the structure of analogues of **2** in which the N-H groups had been replaced with N-R, where R was alkyl or aryl. In such cases there would be minimal interaction between the R group and the chloride. Parallel work to this study has shown that one such substituted sulfimide, $Ph_2SNCH_2CH_2CN$ can coordinate to palladium; reactions with copper centres will be assessed in due course.

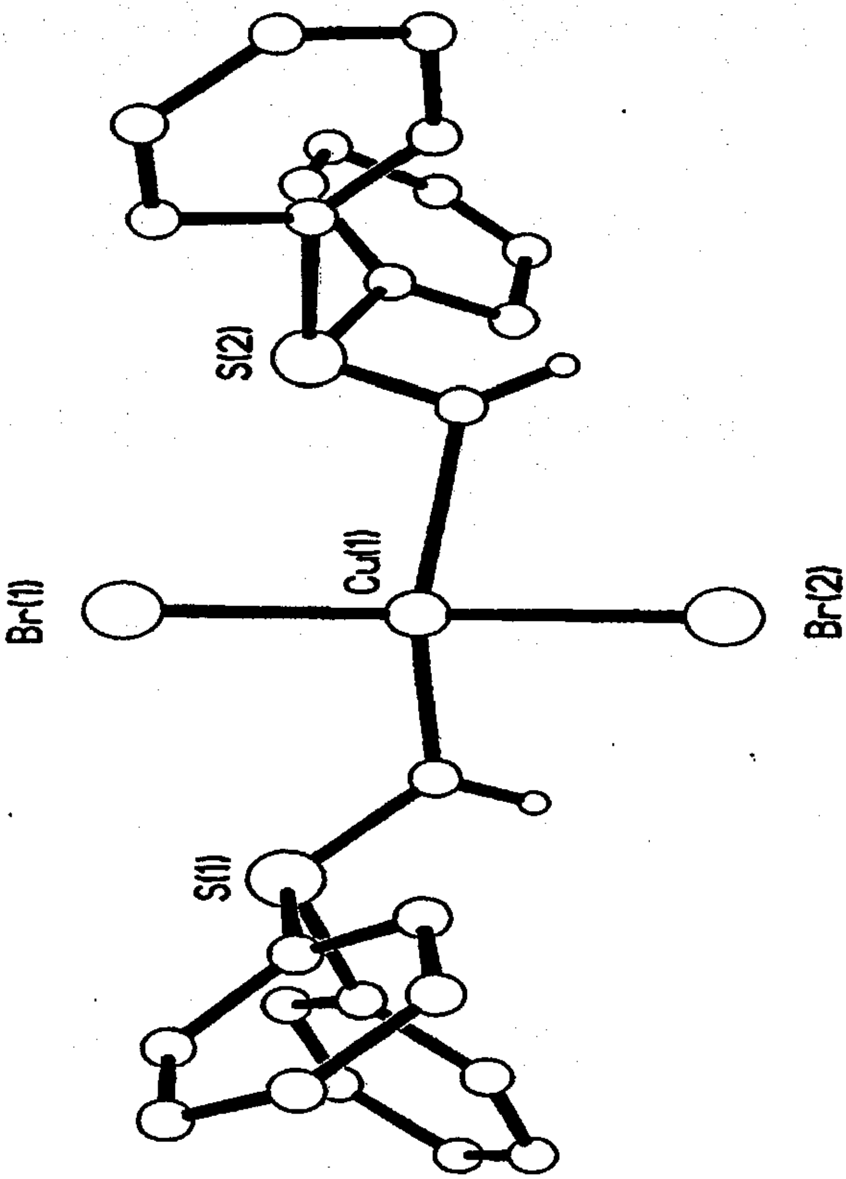


Fig. 2.5 *The X-ray crystal structure of 3 (Bond distances and angles are not presented due to the poor solution. Cell was monoclinic, $a = 21.637(1)$, $b = 12.468(1)$, $c = 18.364(1)$, $\beta = 100.29(1)$. The structure exhibits disorder in one of the ligands resulting in two occupancies for the associated sulfur atom of 70:30%. However, the associated phenyl groups could not be resolved into separate occupancies and were refined in one full weight position. This model worked fairly well and gave unambiguous results for the geometry at the Cu as no significant disorder is noted for either nitrogen).*

2.5 Conclusions

Reaction of **1** with copper (II) halides in a 2:1 ratio is fast and efficiently generates species of the type $Cu(Ph_2SNH)_2X_2$. There is no evidence to suggest that *cis* complexes are formed in this way – only a *trans* arrangement of ligands has been noted. One may envisage steric interactions between the bulky sulfimides mitigating against *cis* formation though as we will see later it is perfectly possible to have homoleptic copper complexes of **1** which by definition therefore do actually exhibit Ph_2SNH ligands *cis* to one another.

A more important aspect of their coordination geometry comes with the observation that two distinct isomers (or allogons) of the chloro complex can be generated and we believe this is the first example of square-planar/pseudo-tetrahedral isomerism in a neutral copper (II) complex. True polymorphism is displayed by these allogons as they can be used to generate each other by crystallisation from the appropriate solvent mixtures.

The fact that no such isomerism is exhibited by the bromo analogue is intriguing and not immediately explicable – it may indicate that intramolecular interactions between the N-H groups and the halogens are important in determining the geometry of the system. As we will see in due course, however, such conclusions are further clouded by the fact that in the right situation it is actually possible to generate the planar $[Cu(Ph_2SNH)_2Br_2]$ unit.

The observation of this allogonism for the chloro complex suggests that investigation of the isomerisation of other complexes of similar ligands would be fruitful. Indeed, unless there is some aspect of the coordination chemistry of **1** that proves to be really unique, it is likely that these results indicate that many other examples of such allogons can be made and indeed may have already been generated unwittingly.

Chapter 3 Copper complexes of Ph_2SNH (ii): oxo-clusters

3.1 Introduction

Oxo cluster compounds of the type $[Cu_4X_6OL_4]$ are well known[71] and consist of a μ_4-O atom surrounded by a tetrahedron of Cu atoms with μ_2-X atoms bridging between the Cu atoms, and with the L completing the distorted trigonal bipyramidal co-ordination around the Cu atoms. Bertrand and Kelley (1966) described the first example of this general class of compound (X=Cl and L= triphenylphosphine). The formation of such compounds often appears relatively favoured as evidenced by the fact that they have been encountered during the recrystallization of other preliminary products. A study of a number of such clusters has revealed an average Cu-O bond distance of 1.90 Å (while the average Cu-Cl bond length for the chloro compounds is 2.417 (30) Å). Water in the reaction system has been identified as the source of the μ_4-oxo atom.

3.2 Aims of this section of the work

Early in our work on simple copper complexes of **1** it became apparent that oxo-cluster species can form in such reaction systems. This chapter aims to fully characterise such products and provide some insight into their formation.

3.3 Experimental

$[Cu_4(\mu_4\text{-}O)(\mu\text{-}Cl)_6(Ph_2SNH)_4]$, **4a**

a) From reaction in undried MeCN in air

A solution of **1** (90 mg, 0.45mmol) in undried MeCN (10 ml) in air was added to a solution of $CuCl_2$ (40mg, 0.3 mmol) in the same volume of the same solvent and the mixture stirred then the reaction vessel sealed and allowed to stand. After one day a mass of brown/orange crystals was apparent; after four days the solution was decanted from this solid which was then washed with a small amount of cold MeCN and dried *in vacuo*.

Yield 48 mg (%Yield 50%)

Micro analysis	**C**	**H**	**N**
Found	44.3	3.5	5.1
Calculated*	44.8	3.4	4.4

* for $C_{48}H_{44}S_4N_4Cu_4Cl_6O$

IR	**ν(N-H) (cm^{-1})**	**ν(S-N) (cm^{-1})**
$[Cu_4(\mu_4\text{-}O)(\mu\text{-}Cl)_6(Ph_2SNH)_4]$	3283 and 3319	947

b) Using water as potential O source

A solution of **1** (90 mg, 0.45mmol) in degassed MeCN (10 ml) in an atmosphere of dry nitrogen was added to a solution of $CuCl_2$ (40mg, 0.3 mmol) in the same volume of the same degassed solvent The mixture was stirred then a small volume of degassed water was added to the reaction vessel and stiired, then allowed to stand. After one day a small amount of brown/orange crystals was apparent; after four days the solution was decanted from this solid which was then washed with a small amount of cold MeCN and dried *in vacuo.*

Yield: 3%

IR data as above

c) Using oxygen as potential O source.

A solution of 1 (90 mg, 0.45mmol) in degassed MeCN (10 ml) in an atmosphere of dry nitrogen was added to a solution of $CuCl_2$ (40mg, 0.3 mmol) in the same volume of the same degassed solvent and the mixture stirred. Then dry oxygen (passed through molecular sieves) was bubbled through the mixture for 5 minutes. The solution was then allowed to stand. After one day a few brown/orange crystals was apparent; after four days the solution was decanted from this solid which was then washed with a small amount of cold MeCN and dried *in vacuo.*

Yield: 7%

IR data as above.

d) Using oxygen and water as potential O source.

A solution of 1 (90 mg, 0.45mmol) in degassed MeCN (10 ml) in an atmosphere of dry nitrogen was added to a solution of $CuCl_2$ (40mg, 0.3 mmol) in the same volume of the same degassed solvent and the mixture stirred. Then dry oxygen (passed through molecular sieves) was bubbled through the mixture for 5 minutes followed by addition of degassed water. The solution was then allowed to stand. After one day a few brown/orange crystals was apparent;

after four days the solution was decanted from this solid which was then washed with a small amount of cold MeCN and dried *in vacuo*.

Yield: 23%

IR data as above.

$[Cu_4(\mu_4\text{-}O)(\mu\text{-}Br)_6(Ph_2SNH)_4]$. ***4b***

A solution of **1** (90 mg, 0.45mmol) in undried MeCN (10 ml) in air was added to a solution of $CuBr_2$ (66mg, 0.3 mmol) in the same volume of the same solvent and the mixture stirred. The dark mixture began to produce a precipitate within 2-3 minutes; after a few hours the latter was filtered from the solution, washed with a small amount of cold MeCN and dried *in vacuo*. Yield 70 mg.(%Yield 61%)

Micro analysis	**C**	**H**	**N**
Found	36.5	2.9	3.6
Calculated	37.1	2.9	3.6

* for $C_{48}H_{44}S_4N_4Cu_4Br_6O$

IR	**ν(N-H) (cm^{-1})**	**ν(S-N) (cm^{-1})**
$[Cu_4(\mu_4\text{-}O)(\mu\text{-}Br)_6(Ph_2SNH)_4]$	3286 and 3319	943

3.4 Results and discussion

Formation of [$Cu_4(\mu_4\text{-}O)(\mu\text{-}Cl)_6(Ph_2SNH)_4$] 4

As we have seen, formation of **2** and **3** can be achieved by reaction of 2 equivalents of **1** with CuX_2 in dry MeCN under a nitrogen atmosphere; if 1.5 equivalents of **1** are employed instead, and the reaction performed in air using undried MeCN, a different product may be isolated.

Thus in the case of the reaction with $CuCl_2$ the solution gradually deposits an orange crystalline material. This is clearly not the same as either isomer of **2**; IR spectroscopy also confirms straight away that not only is this material a new product but also that it is not a simple complex in the manner of **2**.

Although this new product has poor solubility, the crystalline material that forms is fortunately of sufficient quality for analysis by X-ray crystallography. The later technique reveals it to be the cluster compound [$Cu_4(\mu_4\text{-}O)(\mu\text{-}Cl)_6(Ph_2SNH)_4$] **4** (Fig.3.1). The structure of **4** consists of a Cu_4OCl_6 core in which the copper atoms are tetrahedrally displaced about the centre oxygen at an average Cu-O bond length of 1.90Å, a distance which is typical for such clusters. While the average S-N bond distance (1.583Å) within the sulfimide ligands is similar to that of other complexes of **1**, the average angle at the nitrogen (121.9°) is significantly smaller than in any complex of **1** yet prepared (including **6**, *vide infra*). The latter observation may well indicate that there is a weaker H..Cl interaction between the N-H hydrogens and the bridging chlorides in **4** than is found in either the terminal chloride complexes such as **2** or the ionic chlorides such as **6**.

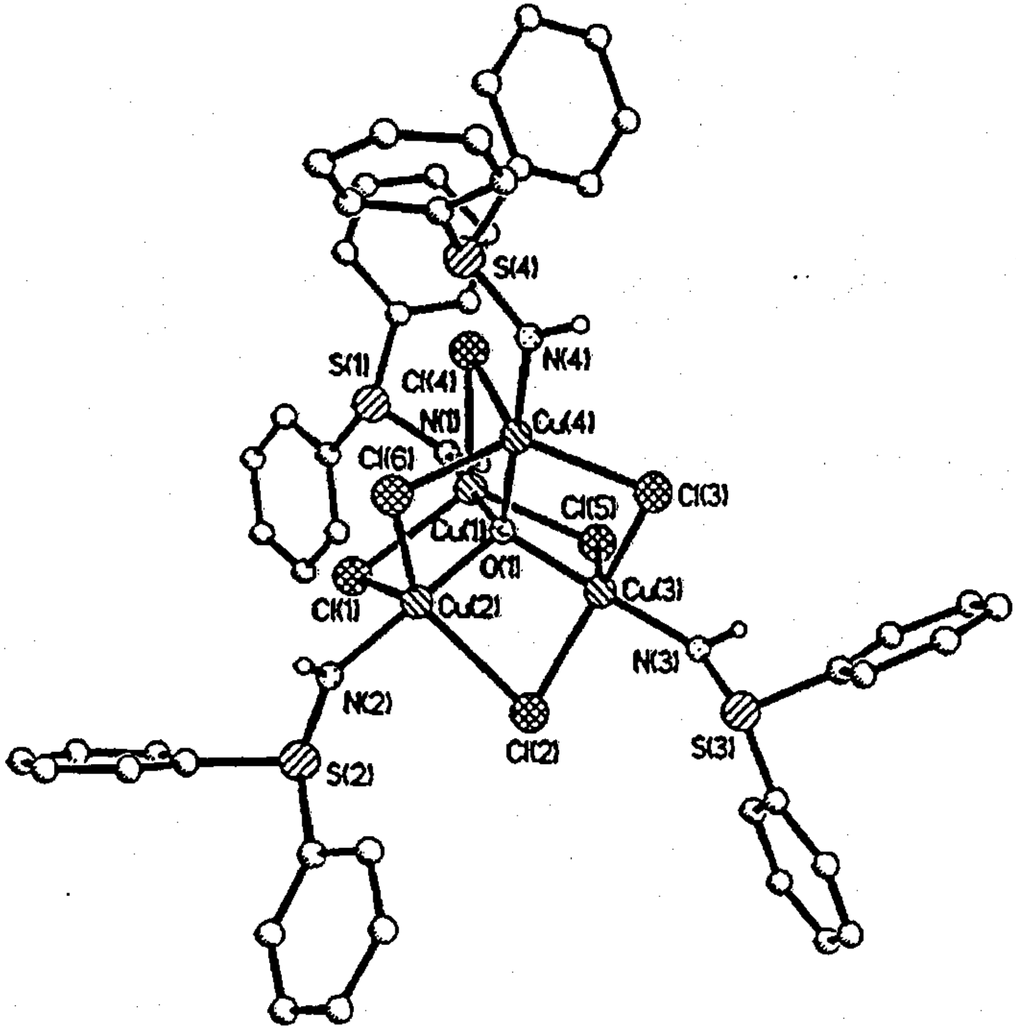


Fig.3.1 Selected bond distances (Å) and angles (°) in **4**:
Cu(1)-O(1) 1.904(4) Cu(1)-Cl(1) 2.444(2) Cu(1)-Cl(5) 2.476(2)
Cu(1)-Cl(4) 2.413(2) Cu(1)-N(1) 1.932(5) N(1)-S(1) 1.586(5)
Cu(2)-O(1) 1.906(4) Cu(2)-Cl(1) 2.458(2) Cu(2)-Cl(2) 2.489(2)
Cu(2)-Cl(6) 2.385(2) Cu(2)-N(2) 1.930(5) N(2)-S(2) 1.576(5)
Cu(3)-O(1) 1.898(4) Cu(3)-Cl(2) 2.410(2) Cu(3)-Cl(3) 2.499(2)
Cu(3)-Cl(5) 2.407(2) Cu(3)-N(3) 1.929(5) N(3)-S(3) 1.584(6)
Cu(4)-O(1) 1.909(4) Cu(4)-Cl(3) 2.372(2) Cu(4)-Cl(4) 2.517(2)
Cu(4)-Cl(6) 2.430(2) Cu(4)-N(4) 1.928(5) N(4)-S(4) 1.586(6)
Cu(1)-O(1)-Cu(2) 110.0(2) Cu(1)-O(1)-Cu(3) 108.9(2)
Cu(1)-O(1)-Cu(4)110.5(2) Cu(1)-N(1)-S(1)122.3(3)
Cu(2)-O(1)-Cu(3)110.8(2) Cu(2)-O(1)-Cu(4)106.7(2)
Cu(2)-N(2)-S(2) 123.2(3) Cu(3)-O(1)-Cu(4) 109.9(2)
Cu(3)-N(3)-S(3) 122.1(3) Cu(4)-N(4)-S(4) 119.8(3)

This brings us to the question of the route for the formation of **4**. As already noted, previous studies have indicated that the oxygen in such clusters comes from water in the system; in the case of **4** results go some way to confirming this though the mechanism is not straightforward. If the reaction is performed in scrupulously dried and degassed MeCN no **4** forms; if dried oxygen is bubbled through, or thoroughly degassed water added to such a solution then a minimal yield of **4** is obtained (ca 7% and 3% respectively).

Interestingly, if **both** degassed water and dried O_2 are added to the original anaerobic solution then a larger yield is obtained (23%); the highest yield of all, 50%, is obtained when the reaction is performed in the presence of water and oxygen from the start. The latter result is not surprising and, by analogy with other systems investigated, probably suggests that initial solutions of $CuCl_2$ in MeCN are in equilibrium with $[Cu_4OCl_6(MeCN)_4]$ making the formation of **4** a simple substitution reaction. Quite why the presence of both O_2 and water would be required for the formation of **4** from the anhydrous starting system is not obvious.

$[Cu_4(\mu_4\text{-}O)(\mu\text{-}Br)_6(Ph_2SNH)_4]$ **5**

The formation of the analogous bromine complex $[Cu_4(\mu_4\text{-}O)(\mu\text{-}Br)_6(Ph_2SNH)_4]$ **5**, which we have characterised by IR and microanalysis, is much more facile than the formation of **4** and indeed is hard to avoid; even traces of water in the system appear to take the reaction mixture through to this product. It is for this reason that we prefer to prepare **3** from **7** rather than directly from **1** plus $CuBr_2$, as the latter method invariably generates significant amounts of **5** contaminant. The similarity in the IR spectra of **4** and **5** suggests that structural differences between the two are probably minimal.

Reaction of **5** with excess **1** results in the breaking up of the cluster structure and formation of the homoleptic $[Cu(Ph_2SNH)_4]^{2+}$ cation; as we will see in the next chapter the latter is best prepared, however, in a more direct manner.

3.5 Conclusions

Oxo-bridged clusters of the type $[Cu_4(\mu_4\text{-}O)(\mu\text{-}X)_6(Ph_2SNH)_4]$ (where X = Cl or Br) readily form. The chloro species may be generated by addition of 1.5 equivalents of **1** to $CuCl_2$ in air; the source of the oxo ligand is probably simply water although investigations into the use of degassed water and of dried O_2 as sources provide somewhat confusing results which may hint at a rather more complicated story. The bromo analogue readily forms and indeed can be difficult to avoid.

Chapter 4 Copper complexes of Ph_2SNH (iii): homoleptic species.

4.1 Introduction

It is not uncommon for Cu(II) to form homoleptic complexes – that is complexes with only one type of ligand present. The most frequently encountered examples are complex anions bearing halide ligands such as $[CuCl_4]^{2-}$. Complexes of larger ligands are known – Millons Salt, for example, contains the $[Cu(NH_3)_4]^{2+}$ ion (together with $[PtCl_4]^{2-}$) – but in fact if we limit consideration to square-planar complexes of *monodentate* ligands then these are rarer than one might imagine. Rarer still are examples in which no axial interactions may be seen – at least at long range.

4.2 Aims of this section of the work

In the light of the ready formation of **2** and **3** we hoped to demonstrate that it is possible to coordinate four Ph_2SNH ligands about a Cu(II) centre. In addition we hoped to determine just what axial interactions may be present in such complexes and to ascertain the copper's ability to accommodate another two ligands in a (distorted) octahedral geometry.

4.3 Experimental

$[Cu(Ph_2SNH)_4]Cl_2$ 6

Under an atmosphere of dry nitrogen a solution of **1** (120 mg, 0.6 mmol) in degassed MeCN(10ml) was treated with solid $CuCl_2$ (20 mg, 0.15 mmol). After vigorous stirring for 20 minutes the mixture consisted of a pale purple solid and a pale green solution. At this point under a blanket of nitrogen a further amount of **1** (10 mg) was added which resulted in an intensification of the purple colour and a concomitant reduction in the colour of the solution. The mixture was then heated until all the solid had dissolved, lagged to promote slow cooling and placed in the refrigerator. Overnight a crop of well-formed purple crystals was obtained; these were filtered and dried *in vacuo*.

Yield 124 mg (%Yield 89%)

Micro analysis	**C**	**H**	**N**
Found	61.2	4.8	5.7
Calculated*	61.4	4.7	6.0

* for $C_{48}H_{44}N_4S_4CuCl_2$

IR	**ν(N-H) (cm^{-1})**	**ν(S-N) (cm^{-1})**
[Cu(Ph_2SNH)$_4$]Cl_2	3081	940

[Cu(Ph_2SNH)$_4$]Br_2, 7

Under an atmosphere of dry nitrogen a solution of **1** (120 mg, 0.6 mmol) in degassed MeCN(10ml) was treated with solid $CuBr_2$ (33 mg, 0.15 mmol). After vigorous stirring for 30 minutes the mixture consisted of a very pale purple solid and a quite intense green solution. At this point under a blanket of nitrogen a further **1** (12 mg, 0.06mmol) was added which resulted in an increase in the amount of precipitate and a reduction in the colour of the solution; addition of further **1** (10 mg, 0.05mmol) under nitrogen completed the precipitation of the intensely purple product and left only a pale green colour to the solution. The mixture was then heated until all the solid had dissolved, lagged to promote slow cooling and placed in the refrigerator. Overnight a crop of well-formed purple crystals was obtained; these were filtered and dried *in vacuo*.

Yield 132 mg (%Yield 87%)

Micro analysis	**C**	**H**	**N**
Found	55.9	4.3	5.4
Calculated*	56.1	4.3	5.5

* for $C_{48}H_{44}N_4S_4CuBr_2$

IR	**ν(N-H) (cm^{-1})**	**ν(S-N) (cm^{-1})**
$[Cu(Ph_2SNH)_4]Br_2$.	3126	936

$\{[Cu(Ph_2SNH)_4][Cu(Ph_2SNH)_2Br_2]Br_2\}$ 8

A solution of 1 (90 mg, 0.45mmol) in MeCN (10ml) was treated with a solution of $CuBr_2$ (33 mg, 0.15 mmol) in MeCN (10 ml) with stirring. The resulting green solution was reduced to dryness *in vacuo* and the residue extracted into CH_2Cl_2 (10 ml). Enough 60/80 petroleum ether was added to just start precipitation of the product; the mixture was then allowed to evaporate slowly during which time green crystals of the product separated and were collected by filtration, washed with petroleum ether and dried *in vacuo*.

Yield 40mg, 33%.

Micro analysis	**C**	**H**	**N**
Found	53.1	4.0	5.3
Calculated value*	52.3	4.0	5.1

* for $C_{76}H_{66}N_6S_6Br_4Cu_2$

IR	**ν(N-H) (cm^{-1})**	**ν(S-N) (cm^{-1})**
{$[Cu(Ph_2SNH)_4][Cu(Ph_2SNH)_2Br_2]Br_2$}	3294 3128	926

The coloured mother-liquor was then allowed to evaporate to dryness; IR showed the presence of both **3** and **7** (the former characterised bands at 3286 (mw, ν N-H) and 888 (s, ν N-S) cm^{-1}.

4.4 Results and discussion

Salts of homoleptic cations of the type $[Cu(Ph_2SNH)_4]^{2+}$ are readily generated by addition of four equivalents of **1** to $CuCl_2$ or $CuBr_2$. In both cases the products can be isolated as purple crystalline material from MeCN. Efficient formation of $[Cu(Ph_2SNH)_4]Cl_2$ **6** and, especially, $[Cu(Ph_2SNH)_4]Br_2$ **7** can only be achieved by addition of a slight excess of **1** (ca 15%) above the precise stoichiometric amount. Thus when exactly four equivalents of **1** are added to $CuBr_2$ the solution retains a quite intense green colour and there is only a pale precipitate; it is only upon addition of the extra **1** that the colour of the solution is discharged and an intensely purple precipitate produced. This presumably indicates that there is appreciable dissociation of the complexes in solution.

The crystal structure of **6** (Fig.4.1) confirms the presence of the four sulfimide ligands in a square-planar arrangement about the copper centre with all the ligands bound by their nitrogen donors. The most interesting aspect of the structure arises from the relative orientations of the four ligands. They arrange themselves in such a way that two pairs of *cis* sulfurs extend on to opposite sides of the CuN_4 plane. An important consequence arising from the resulting orientation of the N-H groups is that each pair can cooperate in significant interactions with the chloride counterion. One result of this strong interaction (average H-Cl distance 2.20Å) is that rather than occupying the expected axial positions (and thus making up an overall octahedral coordination environment via long Cl-Cu bonds) as might be expected, the chlorides actually lie substantially nearer the CuL_4 coordination plane. The side-on view shown in Fig.4.1 highlights this; the Cu-N-Cl angle is 46° indicating just how strong this N-H...Cl interaction is. The strength of the latter is, of course, undoubtedly heightened by the fact that there are two such hydrogen bonds acting cooperatively. In addition, it should be noted that there are no significant long range interactions between the Cu axial position and chlorides from other units; indeed the longest such interaction is as far out as 9.3Å. Four appears to be the maximum number of diphenylsulfimide ligands that copper will accommodate. Thus if either six equivalents of **1** are used in the synthesis from the start, or if solutions of **4** are heated in the presence of excess **1**, **4** is the only isolable product.

One aspect of the IR spectra of **6** and **7**, namely the strength of the N-H stretch bands, proves to be quite different to those of the neutral species **2** and **3**. In the latter compounds such stretches are weak and in fact can be difficult to spot unless a strong sample is used. In contrast the cationic species **6** and **7** exhibit strong, broad bands that are comparable in magnitude to any

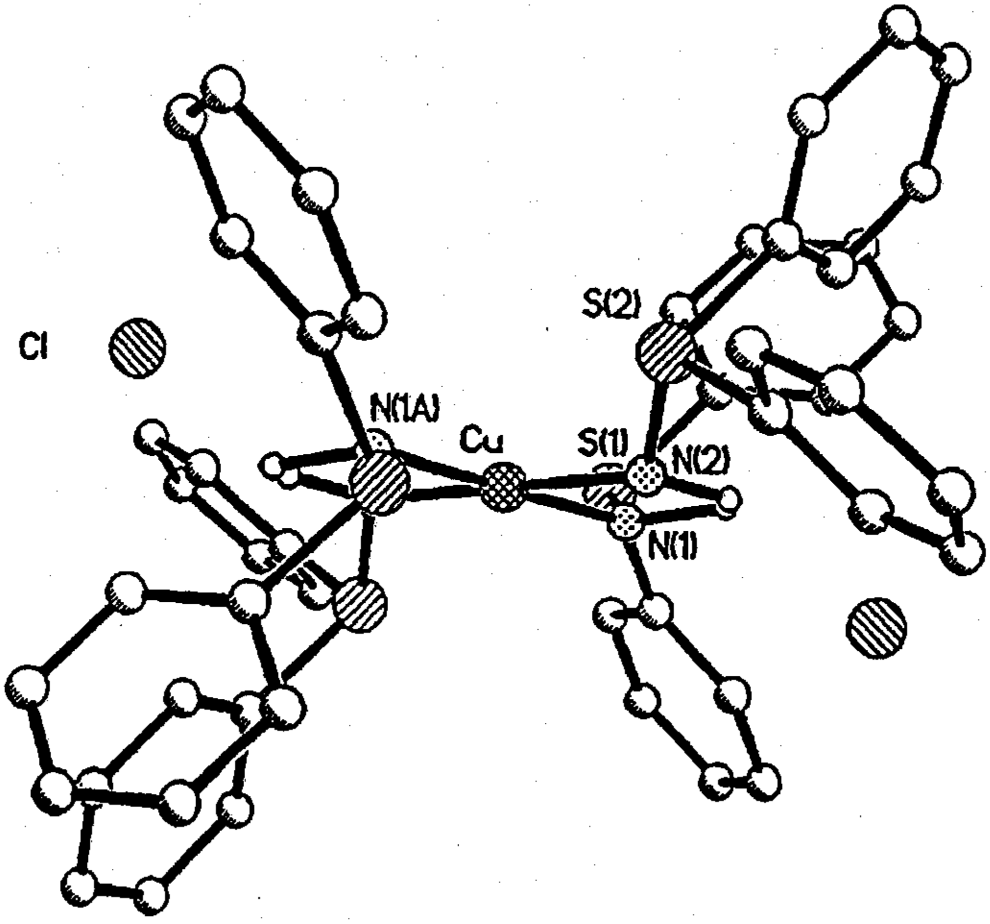


Fig. 4.1 *The X-ray crystal structure of **6***: Selected bond distances (Å) and angles (°):

Cu-N(1) 1.991(4)   Cu-N(2) 1.977(4)   N(1)-S(1) 1.592(4)

N(2)-S(2) 1.591(4)   N(1)-Cu-N(2) 87.7(2)   Cu-N(1)-S(1) 126.3(3)

Cu-N(2)-S(2) 124.2(3)   N(2)-Cu-N(1A) 92.3(2) other ligand bands in the spectra. This difference undoubtedly originates from the strong interactions between the N-H groups and the counterions noted in the crystal structure of **6**.

During investigations into the formation of **7** we noted that in certain circumstances green crystals that appeared to be slightly different in form to those of **3** were generated. We eventually perfected a method of generating this new material in good yield. Thus the reaction of **1** with $CuBr_2$ (molar ratio 3:1) in MeCN results in a green solution. If the solvent is removed, the residue taken into CH_2Cl_2 and treated with 60/80 petroleum ether, slow evaporation to half volume yields a mass of well-formed glistening green crystals of this new product.

X-ray crystallography reveals these to correspond to the formula $[Cu(Ph_2SNH)_4][CuBr_2(Ph_2SNH)_2]Br_2$ **8** (Fig.4.2), that is they contain both the homoleptic cation *and* the neutral *trans*-$CuBr_2(Ph_2SNH)_2$ in the same cell (together with two bromide counterions). The geometry within the cation is much the same as already noted for free $[Cu(Ph_2SNH)_4]Cl_2$, with two pairs of cis sulfurs extending onto opposite sides of the CuN_4 plane. Thus two pairs of cooperative H-bonds hold the bromides into positions that deviate significantly from the expected axial. Of the two copper centres, the more interesting is that of the $CuBr_2(Ph_2SNH)_2$ system. In this case the geometry at the copper is planar, analogous to the blue form of $CuCl_2(Ph_2SNH)_2$. As we have already seen, free $CuBr_2(Ph_2SNH)_2$ has only been noted in a pseudo-tetrahedral form; thus the effect of co-crystallising with the cation has been to radically alter the preferred geometry at the copper centre. This observation again serves to highlight just how sensitive Cu(II) complexes of **1** appear to be to precise

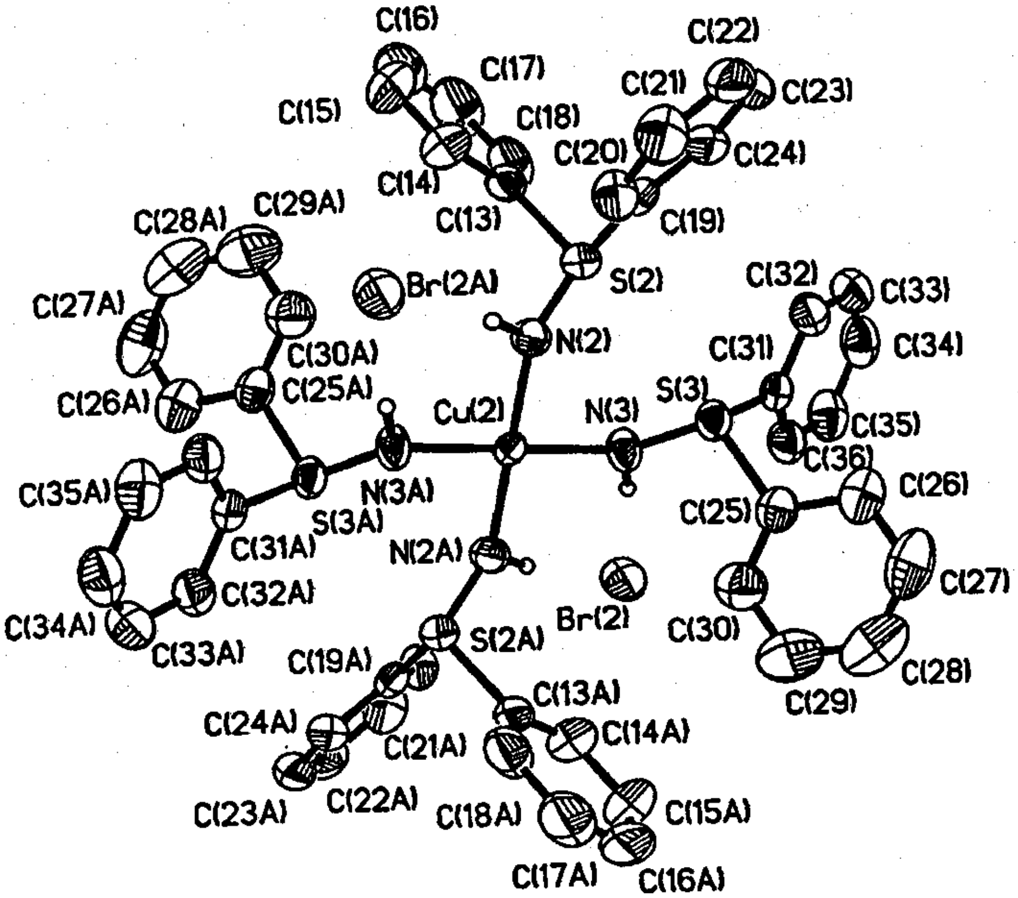


Fig. 4.2a *The X-ray crystal structure of the $[Cu(Ph_2SNH)_4]Br_2$ unit within* **8** *- selected bond distances (Å) and angles (°):*

Cu(2)-N(2) 1.987(3)   Cu(2)-N(3) 1.989(3)

N(2)-S(2) 1.593(3)   N(3)-S(3) 1.596(3)

N(2)-Cu(2)-N(3) 92.75(12)   Cu(2)-N(2)-S(2) 126.9(2)

Cu(2)-N(3)-S(3) 126.2(2)   N(2)-Cu(2)-N(3A) 87.25(13)

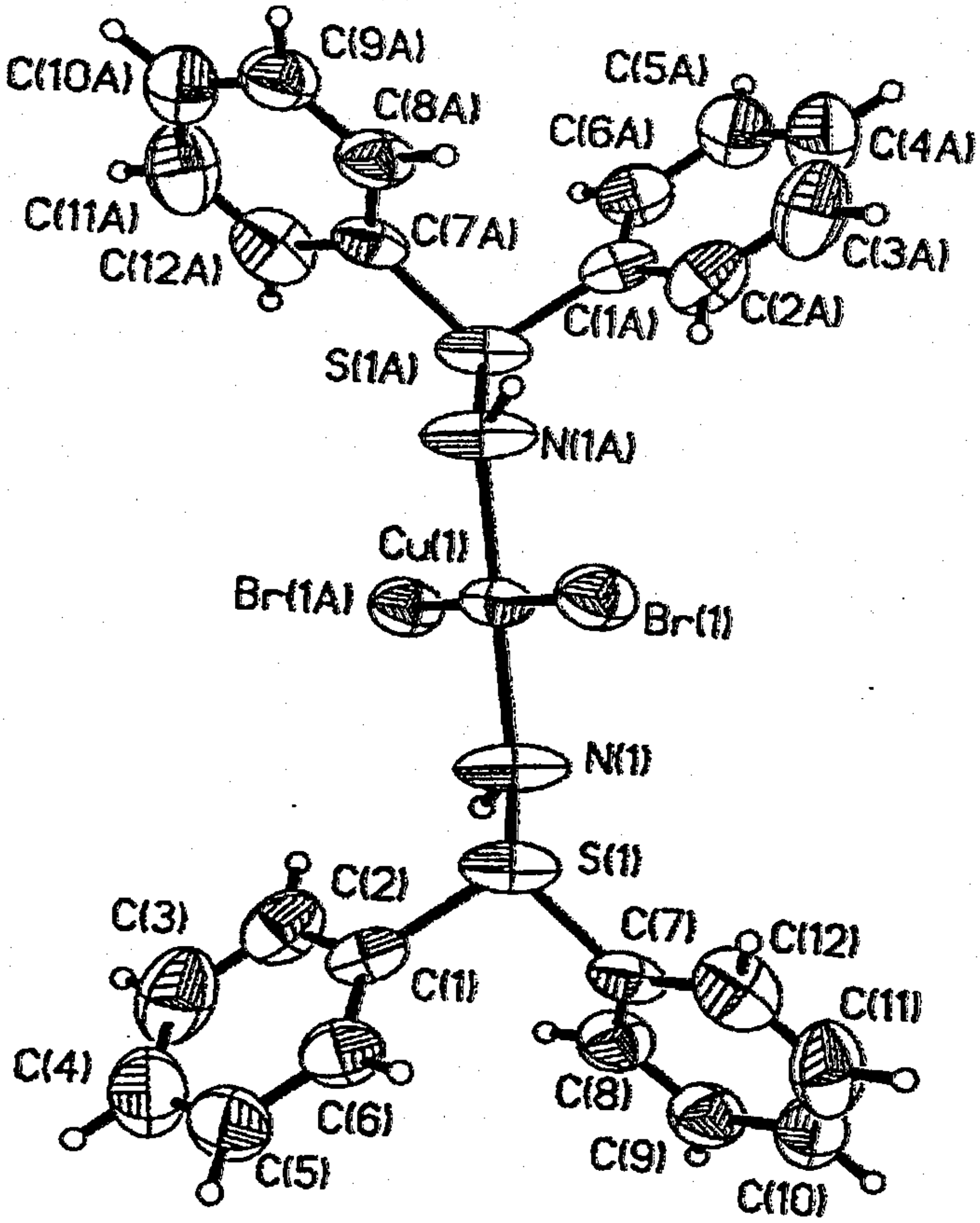


Fig. 4.2b *The X-ray crystal structure of the* $CuBr_2(Ph_2SNH)_2$ *unit within **8** - selected bond distances (Å) and angles (°):*

Cu-N(1) 1.913(4) Cu-Br(1) 2.4672(5) N(1)-S(1) 1.608(4);

N(1)-Cu-Br(1) 92.60(13) N(1)-Cu-N(1A)180.0 Br(1)-Cu-Br(1A) 180.0

Cu-N(1)-S(1) 126.8(2).

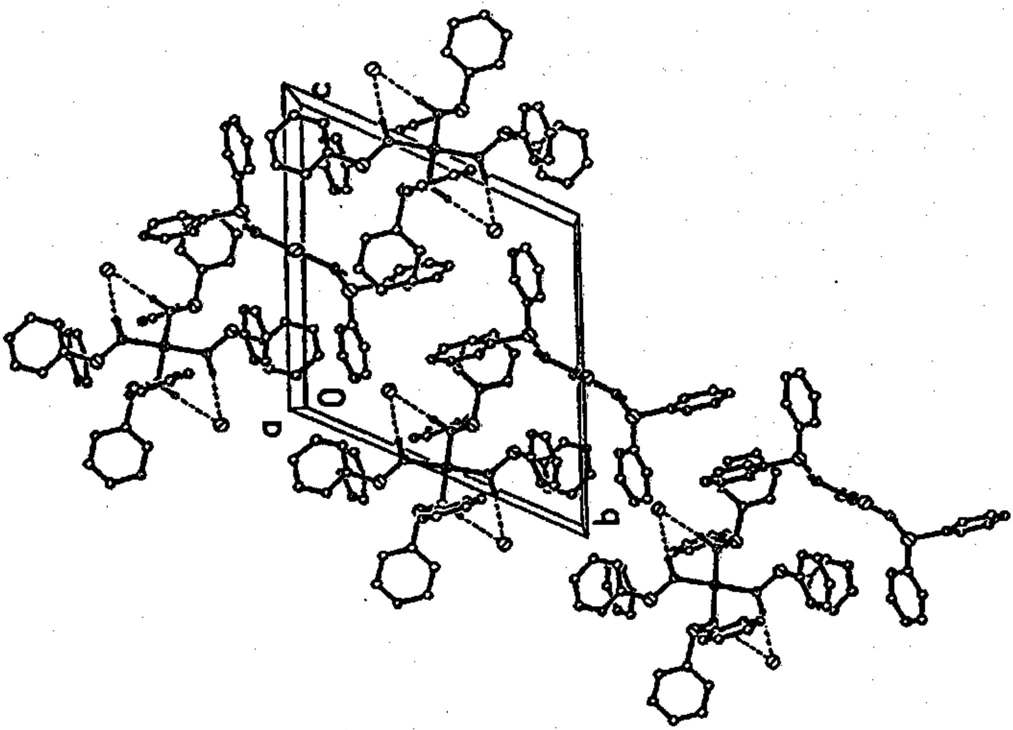


Fig.4.2c: *The packing of the two units in 8.*

crystallisation environments, though it fails to shed much light on the question of just why this should be so. Compound **8** may be characterised by its IR spectrum which distinguishes it from both the free homoleptic cation and **3**. The latter technique also confirms that if the reaction mixtures are reduced to dryness then significant amounts of **3** occur alongside **7** in the crystalline mass. Pure **8** may thus only be obtained by filtration of a green mother-liquor from which not all the copper species have precipitated. It is also interesting that **8** should be light green in colour, given that it contains the $[Cu(Ph_2SNH)_4]^{2+}$ chromophore which is an intense purple colour in its simple salts.

4.5 Conclusions

Homoleptic cations of the type $[Cu(Ph_2SNH)_4]X_2$ readily form when an excess of **1** reacts with copper halides. More than just the four equivalents of **1** are required for full precipitation and no more than four may be ultimately added to the Cu centre. The products exhibit strong, concerted H-bonding from pairs of ligand N-H groups to the counterions suggesting that future investigations into the introduction of N-bonding, bridging anions into the system may well result in the formation of extended structures.

The isolation of **8** from the 3:1 reaction with $CuBr_2$ only serves to highlight the unusual ligand properties of **1**; indeed this is emphasised by the fact that a search of the Cambridge database failed to disclose any other examples of complexes of general formula $[CuL_4][CuX_2L_2]X_2$. These results not only serve to highlight the need for an investigation into complexes of **1** with other transition metals but also suggest that attempts to generate other examples of complexes of this formulation may well prove fruitful.

Chapter 5 formation of a homoleptic cobalt complex of Ph_2SNH

5.1 Introduction - General coordination chemistry of cobalt.

In aqueous solutions the most common oxidation states for cobalt are (II) and (III), although it can be found having oxidation states ranging from –I to +V.[72] As with copper, cobalt complexes are known with a wide range of ligands, which include carbon, silicon, nitrogen, phosphorous, arsenic, oxygen, sulfur, and selenium donors. Typical examples wherein the cobalt has an oxidation state between –1 and +3 include:

Cobalt (-I)	$[Co(CO)_4]^-$
Cobalt (0)	$[Co(PPh_3)_3]$
Cobalt (I)	$[CoH(N_2)(PPh_3)_3]$
Cobalt (II)	$[CoCl_2]$
Cobalt (III)	$[Co(H)_3(PPh_3)_3]$

Due to the electronic configuration of Co^{2+} ion, $3d^7$, it is possible in the octahedral fields that it can form either high spin $t_{2g}^5e_g^2$ or low spin $t_{2g}^6e_g^1$ complexes. The latter complexes are uncommon due to the rather high value of the ligand field splitting parameters ($Dq>1500cm^{-1}$) needed to cause spin pairing with Co(II). This only occurs with the strongest field ligands. Only high spin tetrahedral complexes exist with the $e^4t_2^3$ configuration. It is rare for Co(II) to form square planar complexes, although one example of such a compound is the bis(maleonitriledithiolate) anion $[Co(MNT)_2]^{2-}$. Up to now only low spin compounds have been seen.

5.2 Aims of this section

In view of the great affinity **1** shows towards copper centres we aimed to look at similar reactions with the simple cobalt halide $CoCl_2$. In particular we aimed to assess the ability of cobalt to coordinate to six such ligands; as noted above this should be far more feasible for this metal system than for copper.

5.3 Experimental

[Co(Ph$_2$SNH)$_6$]Cl$_2$ **9**

A solution of anhydrous $CoCl_2$ (25mg, 0.19 mmol) in degassed MeCN (20 ml) was treated with a solution of **1** (232mg, 1.15mmol) in the same solvent (20 ml) added over a period of a minute, under an atmosphere of dry nitrogen. The resulting blue solution was stirred for an hour during which time a pink precipitate appeared. The mixture was then heated until the latter redissolved, lagged to promote slow cooling and placed in the refrigerator. Overnight a large crop of well-formed pink crystals was obtained; these were filtered and dried *in vacuo*.

Yield 160mg (65%)

Micro analysis	**C**	**H**	**N**
Found	64.4	5.2	6.0
Calculated value*	64.7	5.0	6.3

* for $C_{76}H_{66}N_6S_6Cl_2Co$

IR	**ν(N-H) (cm^{-1})**	**ν(S-N) (cm^{-1})**
$[Co(Ph_2SNH)_6]Cl_2$	3156	956

5.4 Results and discussion

Despite the relative bulk of **1**, containing as it does the two phenyl groups, we find that it is indeed possible to coordinate six such ligands on to a cobalt atom. When the 6:1 reaction is performed in acetonitrile a mixture of blue solution and pink solid is obtained. If this is reheated and allowed to cool slowly, well formed, air stable crystals of the product can be isolated and X-ray crystallography confirms its formulation as $[Co(Ph_2SNH)_6]Cl_2$ **2** (Fig.5.1).

The structure exhibits a regular octahedral geometry, with Co-N bonds of some 2.14 Å in length. Within the ligands themselves the bonding arrangement appears to be much as expected, with, for example, a S-N distance of 1.57Å. A more interesting effect is seen, however, when we consider the relative orientation of the ligands. The positioning of the twelve phenyl rings is presumably dictated by the need for minimising steric interactions, though another important aspect of this arrangement comes with the relative disposition of the six N-H groups. This is perhaps best seen in a space filling diagram (Fig.5.2) which reveals that the N-H groups form into two pairs of three directed on opposite faces of the coordination octahedron. Each set of three in effect forms a hydrogen-bonding pocket within which the chloride counterion sits. The cooperative effect of the three directed hydrogen bonds undoubtedly means that the chloride is tightly bound within this "pocket" (the N-Cl length, for example, is 3.39Å). As a consequence of this interaction we see significant attraction of the three nitrogens towards the chloride, resulting in N-Co-N angles within each trio of 84.8° rather than the 90° of a pure octahedral geometry.

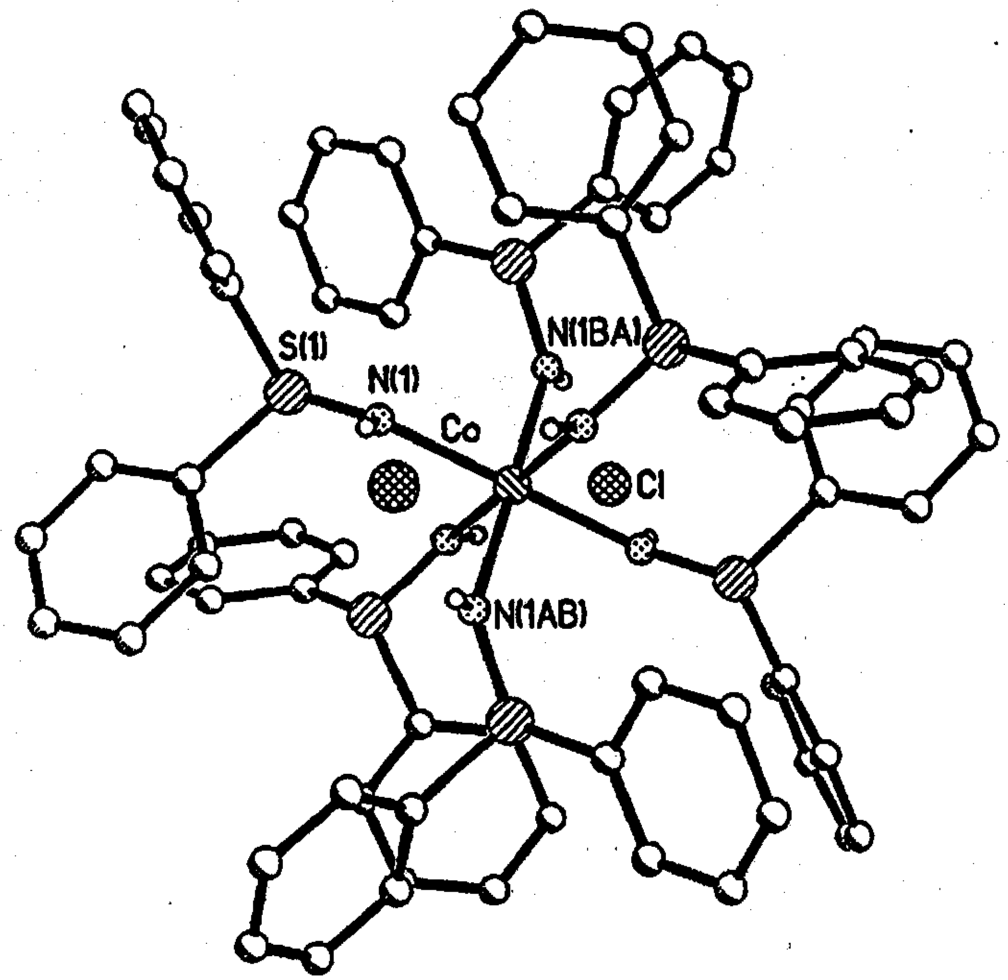


Fig.5.1 *The X-ray crystal structure of [Co($Ph_2SNH)_6]Cl_2$; bond distances and angles:*

Co-N(1) 2.142(3) N(1)-S(1) 1.571(3)

Co-N(1)-S(1) 128.0(2) N(1)-Co-N(1BA) 95.2

N(1)-Co-N(1AB) 84.8.

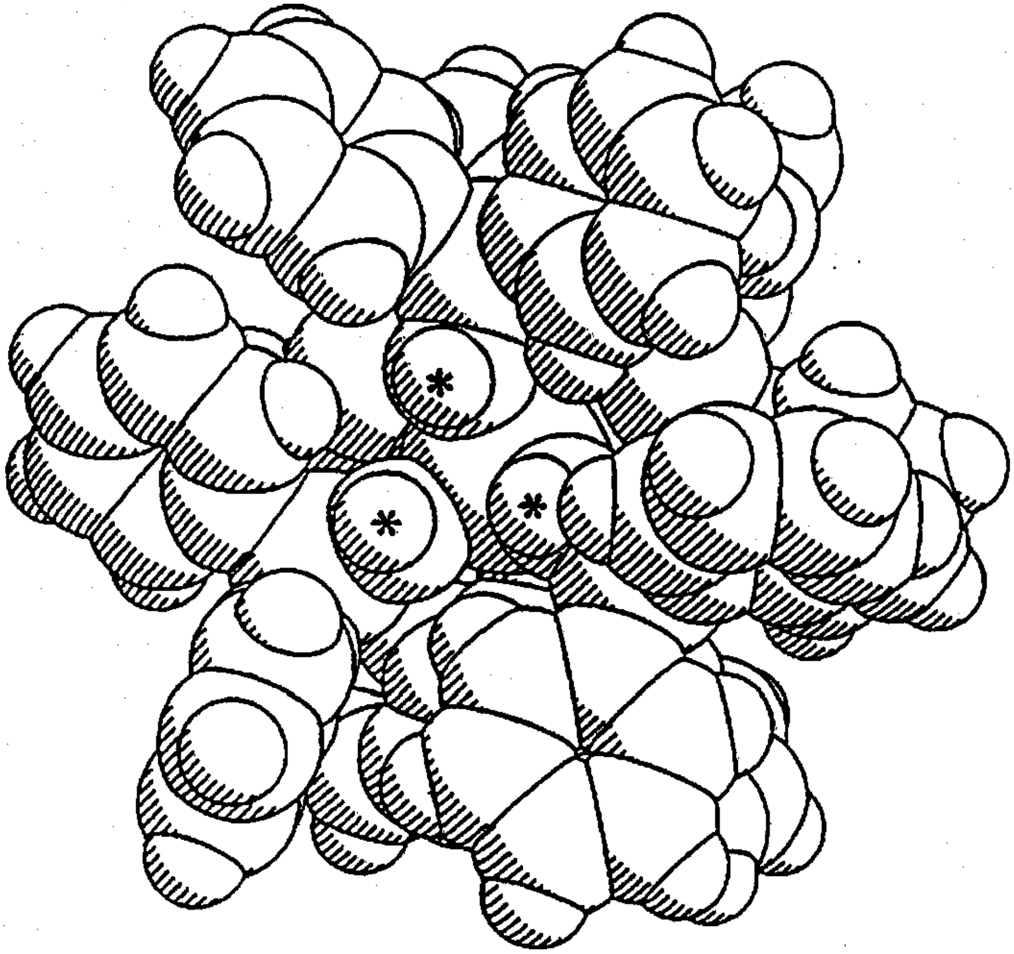


***Fig.5.2** Representation of the structure of the $[Co(Ph_2SNH)_6]^{2+}$ cation as a space filling diagram, emphasising the hydrogen bonded pocket containing the three cooperative N-H units (marked*)*

As noted above the presence of such ordering of the phenyl ligands is rather surprising and is presumably indicative of their desire to be associated with significant H-bonding. This is of course consistent with the results for the homoleptic copper cations from the last chapter but in this case is even more dramatic. This cooperative hydrogen bonding effect raises the intriguing possibility that the cationic unit of **9** could be used as the basis for assembling extended H-bonded structures. This does not happen in **9** of course due to the presence of the monoanionic chlorides - in other words, there is no sharing of counterions between adjacent cations. But given the strong H-bonding effects on either face of the cations (and, for that matter, the complete blocking of interactions in other directions brought about by the presence of the mass of phenyl units exemplified by Fig.5.2) it is possible that a hydrogen-bonding dianion could be introduced into the system that would then bridge the cations.

The use of H-bonding interactions to assemble extended architectures has been much studied both within organic and metal-bearing systems; interest in the latter stems from the potential of such systems to exhibit a variety of optical, magnetic and electrical properties.[73] Some good examples of the kind of arrays that may be generated in this way comes with the work of Mingos *et al* who showed recently that introduction of terephthalate ($[1,4\text{-}C_6H_4(CO_2)_2]^{2-}$) and fumarate ($[O_2CC(H)C(H)CO_2]^{2-}$) into nickel systems capable of forming double H-bonds from cation to anion results in the formation of extended tape/sheet structures.[74] If these were introduced into salts with $[Co(Ph_2SNH)_6]^{2+}$ or indeed the homoleptic copper cations from the last chapter in this case it would be intriguing to see how the CO_2^- units would align relative to the three N-H bonds on each face of the metal coordination centre. In both cases the overall structures should arrange as shown in Fig.5.3.

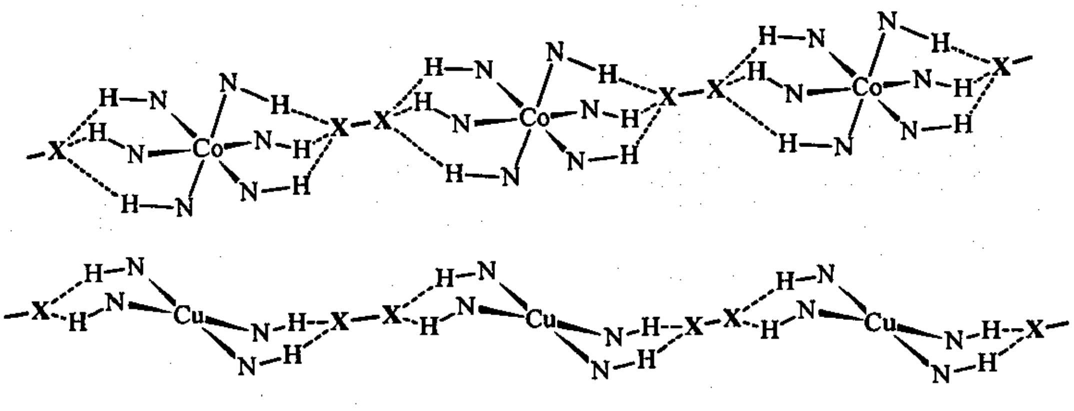


Fig.5.3 Examples of potential extended structures based upon hydrogen bonding from our homoleptic cations. Note that for the sake of clarity only the nitrogens and hydrogens of the sulfimide ligands have been shown; X-X represents a hydrogen bonding spacer anion.

The fact that solutions of **9** in warm MeCN are blue presumably suggests the presence of extensive dissociation. As noted in the introduction blue is the classic colour of four-coordinate tetrahedral Co(II) species; we have not attempted to isolate complexes with less than the six ligands, however. Indeed, even solutions containing less than the full amount of **1** required for 6:1 stoichiometry tend to deposit **9** in some yield. Again this is consistent with the presence of solution equilibria between a variety of structures.

Another important aspect of the reaction between **1** and $CoCl_2$ stems from its efficiency. The reactivity is easily demonstrated in two ways. Firstly, if an aqueous solution of $CoCl_2$ is layered above a CH_2Cl_2 solution of **1** it only takes the briefest shake of the reaction flask to transfer the colour from the water layer to the organic phase. In other words the formation of **9** is extremely quick and efficient. This can also be shown by the fact that addition of solid **1** to an aqueous cobalt solution result in the solid starting to take on a blue colour. In other words formation of a complex is immediate; so much so in fact that if a small "column" is made by packing a mixture of **1** and celite into a glass pipette (above a glass wool plug) and aqueous cobalt solution passed through it, the colour is discharged during the passage down the column. At the same time the **1**/celite mixture takes on a blue colour. It is not impossible that future work could utilise this, especially as it is quite likely that small variations in the R groups on the sulfimide may well change metal affinities, raising the possibility of the development of metal specific extraction systems.

5.5 Conclusions

This brief look at the cobalt chemistry of **1** demonstrates that high coordination homoleptic complexes of the sulfimides are isolable, even with the presence of the sterically demanding phenyl groups. This bodes well for the potential extension of sulfimide coordination chemistry to other transition metals, while the presence of interactive cooperative hydrogen bonding paves the way for the construction of interesting self assembled extended networks within such systems.

Chapter 6 Palladium and Platinum complexes of Ph_2SNH

6.1 Introduction – General co-ordination chemistry of Pd and Pt

It has been previously shown that we can coordinate **1** to copper and cobalt forming complexes with these transition metals. The following chapter will look at the prospect of **1** reacting with platinum and palladium compounds and if so would they react differently then previously observed with copper and cobalt.

Palladium has the ground state electronic configuration $[Kr]4d^{10}$ and belongs to Group 10. There are similarities between the chemistry of Pd and Pt but generally Pd is more reactive. Palladium can form six oxidation states; thus, although its chemistry is dominated by the oxidation state II (the most stable for the element), palladium can also be found in oxidation states 0, I, IV, and there are several examples of Pd^{III} compounds known. There is also the unstable Pd^{V} complex $[PdF_6]^-$ which has been reported but very little studied. Due to the increased stability of the d valence orbitals in Pd there is a reluctance to form high oxidation states and this trend is seen through the late transition metals. Palladium(0) (d^{10}) forms $[PdL_n]$ complexes with phosphines, arsines, phosphites, cyanide, isocyanides and alkenes. The coordination geometry is tetrahedral if the coordination number is four, trigonal if the coordination number is three, and linear if the coordination number is two. Pd^0 complexes are also important catalysts for transformations in organic synthesis.[75] All Pd^1 compounds so far characterized have Pd-Pd or Pd-M bonds. The anticipated paramagnetic behaviour of the d^9 configuration is not observed due to the unpaired electrons being involved in the formation of a metal-metal bond (example of such a compound is $[Pd_2(CNMe)_6](PF_6)_2$.[76] A considerable palladium(II) coordination chemistry is found for S-, N-, P-, and As- donor ligands as well as halogens. Different stoichiometry is available for Pd^{II} complexes and this can be represented by $[PdX_nL_{4-n}]^{2-n}$. An example of this is $PdCl_2(PhCN)_2$.[77] The stereochemistry of Pd^{II} is almost exclusively square planar as this is energetically the most favourable considering the splitting of the d-orbitals in crystal fields of different symmetry, and therefore are diamagnetic, although there are a few exceptions to this behaviour. Conductimetric and electronic spectral measurements provide evidence for a five-coordinated species of the type $[PdXL_4]X$ in solution for L = *N,N'*-disubstituted thio- and selenoureas.[78] Palladium(IV) complexes are usually six coordinated and octahedral.

Platinum compounds are among the most important chemotherapeutic agents for treating cancer, cisplatin (*cis* – $[Pt(NH_3)_2Cl_2]$ is an important antitumor drug.[79] Platinum and compounds of platinum are used in a wide variety of catalytic applications as in removing NO_x from power generator, internal combustion, and gas turbine engine effluents.[80] Platinum can be found in a range of different oxidation states (Pt^0, Pt^I, Pt^{II}, Pt^{III}, Pt^{IV}, and Pt^{VI}), with the commonest being Pt^0, Pt^{II}, and Pt^{IV}. Complexes of Pt^0 can form different geometries depending upon the coordination number. For four coordinate the geometry is tetrahedral or pseudo-tetrahedral, planar three-coordinate, or linear two-coordinate. The tetrahedral tetrakis(phosphine) complexes are the most important Pt^0 complexes. Pt^I complexes form species with Pt-Pt bonds, similar complexes are formed with Pd^I. An example is the reaction of $PtCl_4^{2-}$ with dppm.[81] Pt^{II}, d^8, is the most stable oxidation state and is almost always 16-

electron and square planar forming *cis* and *trans* isomers. As seen for Pd^{II} there are a lot of ligands that Pt^{II} can form complexes with, including a host of S-, N-, aryl-, alkyl- and halogen donor species. An example of such a compound is *trans* and *cis*$[PtCl_2(NH_3)_2]$ both of which bond to DNA, the cis form finding use as an antitumor drug.[79] There are few complexes of Pt^{III} and the first mononuclear Pt^{III} complex to be isolated was $(Bu_4N)[Pt(C_6Cl_5)_4]$.[82] Pt^{IV} compounds are usually octahedral complexes and are much more common than the Pd^{IV} complexes such a complex is the Pt^{IV} bis(hydroxyl) species $Pt(OH)_2Cl_2(NH_3)_2$.[83]

Platinum has a natural isotope, ^{195}Pt (in 33.7% abundance), with a nuclear spin of a half that is amenable to study by NMR spectroscopy, this is in contrast to palladium. The magnitude of nuclear spin coupling between ^{195}Pt and other nuclei, particularly $J_{Pt\text{-}H}$, $J_{Pt\text{-}C}$, or $J_{Pt\text{-}P}$ coupling, as observed in the NMR spectra of the appropriate nucleus, has been used as an important structural parameter for organoplatinum compounds.[84]

6.2 Aims of this section of the work

In this section of the work we aimed to form a range of simple platinum and palladium complexes of **1**. This would allow us to contrast the effect of the metal present both in terms of geometries at the metal centre (which should be much more restrictive than for copper, for example, and in terms of hydrogen-bonding effects.

6.3 Experimental

[Bu_4N][$PdCl_3(Ph_2SNH)$] 10.

Under an atmosphere of dry nitrogen a solution of [NBu_4]$_2$[Pd_2Cl_6] (67mg, 0.07mmol) in degassed CH_2Cl_2 (20ml) was treated with a solution of 1 (30mg, 0.15mmol) in the same volume of CH_2Cl_2. A clear red/orange solution formed. The volume was reduced *in vacuo*. Slow diffusion of diethylether yielded a mass of a well formed red/orange crystals of the product.

Yield: 38mg (36%)

Micro analysis	**%C**	**%H**	**%N**
Found	50.50	7.16	3.50
Calculated*	51.22	7.22	4.27

* for $C_{28}H_{43}N_2SPdCl_3$

IR	**ν(N-H) (cm^{-1})**	**ν(S-N)(cm^{-1})**
[Bu_4N][$PdCl_3(Ph_2SNH)$]	3193	944

[$Pd(Ph_2SNH)_4$]Br_2 11.

Under an atmosphere of dry nitrogen a solution of [PPh_4]$_2$[Pd_2Br_6] (78mg, 0.06 mmol) in degassed CH_2Cl_2 (20 ml) was treated with solid 1 (100mg, 0.5 mmol) and the mixture stirred. After all the solid had dissolved the colour of the mixture lightened to yellow-orange. The mixture was left overnight during which time an orange crystalline material was deposited. This was filtered, washed with CH_2Cl_2 and dried *in vacuo*.

Yield: 72mg (61%)

Micro analysis	**%C**	**%H**	**%N**
Found	53.9	4.0	5.0
Calculated*	53.8	4.1	5.2

*for $C_{48}H_{44}Br_2PdN_4S_4$.

IR	**ν(N-H) (cm^{-1})**	**ν(S-N)(cm^{-1})**
$[Pd(Ph_2SNH)_4]Br_2$	3114	955

$[Pd(Ph_2SNH)_4]Cl_2$ 12.

Under an atmosphere of dry nitrogen a solution of $[PPh_4]_2[Pd_2Cl_6]$ (67mg, 0.06mmol) in degassed CH_2Cl_2 (20ml) was treated with solid 1 (100mg, 0.50mmol) and the mixture stirred. After the solid had dissolved the colour of the mixture was orange. The mixture was left overnight during which time orange/yellow crystalline material was deposited. This was filtered, washed with CH_2Cl_2 and dried *in vacuo*.

Yield: 43mg (73%)

Micro analysis	%C	%H	%N
Found	57.31	4.37	5.80
Calculated*	58.63	4.48	5.70

*for $C_{48}H_{44}Cl_2PdN_4S_4$.

IR	ν(N-H) (cm^{-1})	ν(S-N)(cm^{-1})
$[Pd(Ph_2SNH)_4]Cl_2$	3079.3	959.5

$[Pd(Ph_2SNH)_4][PF_6]_2$ **13.**

Under an atmosphere of dry nitrogen a solution of $PdCl_2$ (25 mg, 0.14 mmol) in degassed MeCN (20ml) was treated with solid **1** (114 mg, 0.57 mmol) and the mixture stirred then treated with $TlPF_6$ (99mg, 0.28mmol), added as a solid. The mixture was stirred overnight and then filtered through celite; after removal of the solvent *in vacuo* the residue was crystallised by slow diffusion of ether into a CH_2Cl_2 solution. This yielded the product as orange/yellow crystalline material.

Yield: 127mg (76%)

Micro analysis	%C	%H	%N
Found	46.47	3.64	4.46
Calculated*	47.98	3.69	4.66

*for $C_{48}H_{44}P_2F_{12}PdN_4S_4$.

IR	ν(N-H) (cm^{-1})	ν(S-N)(cm^{-1})
$[Pd(Ph_2SNH)_4]Br_2$	3062.2	832.6

[PtCl(Ph$_2$SNH)(PMe$_2$Ph)$_2$][BF$_4$] **14.**

Under an atmosphere of dry nitrogen a solution of [PtCl$_2$(PMe$_2$Ph)$_2$] (50mg, 0.09mmol) in degassed CH$_2$Cl$_2$ (10ml) was treated with a solution of **1** (23mg, 0.11mmol) in the same volume of CH$_2$Cl$_2$. After 1 hour the colourless solution was treated with solid [NH$_4$][BF$_4$] (10mg, 0.1 mmol). The mixture was left stirring overnight then filtered and the volume reduced *in vacuo*. Slow diffusion of diethylether yielded a mass of well-formed colourless crystals of the product. ^{31}P NMR of solutions before crystallisation showed an effectively quantitative yield of the product: AX spectrum, δ_A – 12.7 ppm $^1J(^{31}P - ^{165}Pt)$ 3651 Hz; δ_B -20.0 ppm $^1J(^{31}P - ^{165}Pt)$ 3651 Hz.

Micro analysis	**%C**	**%H**	**%N**
Found	41.6	1.4	4.1
Calculated*	42.3	1.8	4.2

*for $C_{28}H_{33}BClF_4NP_2PtS$.

IR	**v(N-H) (cm^{-1})**	**v(S-N)(cm^{-1})**
[PtCl(Ph$_2$SNH)(PMe$_2$Ph)$_2$][BF$_4$]	3057.4	835.8

[Pt(Ph$_2$SNH)$_4$]Cl$_2$ **15.**

Under an atmosphere of dry nitrogen a solution of [PPh$_4$]$_2$[PtCl$_4$] (100mg, 0.01mmol) in degassed CH$_2$Cl$_2$ (20ml) was treated with solid **1** (100mg, 0.5 mmol). The mixture was stirred and left to stand overnight in which time a small crop of pale yellow crystals appeared. The mixture was subsequently allowed to stand for a week during which time the amount of crystalline material increased. At this point the solution was decanted from the crystals. The crystals were washed with CH_2Cl_2 and dried *in vacuo*.

Yield: 83mg (79%)

Micro analysis	**%C**	**%H**	**%N**
Found	53.2	3.9	4.7
Calculated*	53.8	4.1	5.2

*for $C_{48}H_{44}N_4S_4PtCl_2$.

IR	**ν(N-H) (cm^{-1})**	**ν(S-N)(cm^{-1})**
[Pt(Ph_2SNH)$_4$$Cl_2$	3056	842.8

[Pt(Ph_2SNH)(Ph_2SNC(Me)NH)Cl]Cl.MeCN **16**.

Under an atmosphere of dry nitrogen a solution of $PtCl_2$ (61mg, 0.18mmol) in MeCN (20ml) was generated by heating the mixture with stirring. This was then treated with a solution of **1** (71mg, 0.35mmol) in the same solvent (5ml) added slowly with stirring. The yellow solution precipitated a yellow solid within 10 minutes of completion of addition. The mixture was left stirring for 30 minutes after which time the solid was filtered and washed with cold MeCN (10ml) and then Et_2O (10ml) and dried *in vacuo* to give a pale yellow product. The solid was recrystallised from hot MeCN to give well formed yellow crystalline product.

Yield 60mg (48%)

Micro analysis	**%C**	**%H**	**%N**
Found	44.5	3.9	7.6
Calculated*	44.8	3.8	7.5

*for $C_{28}H_{28}N_4S_2PtCl_2$.

[Pt(Ph$_2$SNH)(Ph$_2$SNC(Ph)NH)Cl]Cl.PhCN **17.**

Under an atmosphere of dry nitrogen a solution of $PtCl_2$ (61mg, 0.18mmol) in hot PhCN (20ml) was generated by heating the mixture with stirring. This was then treated with a solution of **1** (71mg, 0.35mmol) in the same solvent (5ml) added slowly and stirred. The yellow solution precipitated a yellow solid within 10 minutes of completion of addition. The mixture was left stirring for 30 minutes after which time the solid was filtered and washed with cold MeCN (10ml) and then Et_2O (10ml) and dried *in vacuo* to give a pale yellow product. The solid was recrystallised from hot MeCN to give well formed yellow crystalline product.

Yield 83mg (53%)

Micro analysis	**%C**	**%H**	**%N**
Found	51.16	3.65	6.24
Calculated*	54.38	3.81	6.67

*for $C_{38}H_{32}N_4S_2PtCl_2$.

[Pt(Ph$_2$SNH)(Ph$_2$SNC(C$_2$H$_5$)NH)Cl]Cl **18.**

This was prepared in an analogous manner to the previous two complexes using the same amount of **1** and MeCH$_2$CN as solvent.

Yield 71mg (%Yield 55%)

Micro analysis	**%C**	**%H**	**%N**
Found	44.55	3.94	6.13
Calculated*	44.81	3.76	5.81

*for $C_{27}H_{27}N_3S_2PtCl_2$.

6.4 Results and discussion

The first reaction involving a palladium centre looked at was the reaction of the chloro-bridged species $[Bu_4N]_2[Pd_2Cl_6]$ with **1** in a 1:2 stoichiometry. This bridged starting material was chosen as it has proved to be a very effective reagent for the formation of a range of palladium S-N complexes thanks to its ability to act as a source of the coordinatively unsaturated $[PdCl_3]^-$ unit *via* breakage of the weak halide bridges present. The reaction proceeds quite readily giving a crystalline product whose IR spectrum shows typical bands associated with the N-H (3193cm^{-1}) and S-N stretches (944cm^{-1}) of co-ordinated **1.** The presence of the latter is confirmed by X-ray crystallography **(Fig.6.1)** which reveals that the product is the expected N-bound sulfimide complex *[Bu$_4$N][PdCl$_3$(Ph$_2$SNH)]* **10.**

The crystal structure of **10** confirms the presence of one sulfimide ligand in a square planar arrangement about the palladium centre with the ligand bonded through the nitrogen donor and the chlorides occupying the three other sites. Within this arrangement Pd(1)-N(1) and N(1)-S(1) bond distances of 2.00(3) and 1.55(4)Å respectively are seen while the average Pd-Cl bond distance is 2.29Å. The former values are similar to those in the copper sulfimide complexes mentioned in previous chapters while the halide bond lengths are entirely typical for such a Pd^{II} complex.. The level of distortion from a perfectly square planar structure can be obtained from looking at the bond angles of N(1)-Pd-Cl(2) and Cl(3)-Pd-N(1) being 176.5(13) and 175.1(7)° respectively. These result show that the structure is slightly distorted if it had been perfect the angles would have both been precisely 180°.

The fact that salts of $[Pd_2X_6]^{2-}$ are very reactive towards simple SN compounds has already been alluded to; in contrast, simple platinum complexes of the type *cis*-$[PtCl_2(PR_3)_2]$ prove very useful reagents but only with an appropriate driving force. By way of illustration of the different reactivties of the two, S_4N_4 reacts almost instantaneously with the Pd species even at ambient temperatures. In contrast it will only react with the platinum phosphine species at elevated temperatures (which proves inherently dangerous given the explosive nature of the nitride at > 100°C). Thus we initially expected **1** would be relatively inert towards *cis*-$[PtCl_2(PMe_2Ph)_2]$; in fact it proved to unexpectedly reactive. Thus ^{31}P nmr revealed that a mixture of **1** and *cis*-$PtCl_2(PMe_2Ph)_2$ in CH_2Cl_2 at ambient temperatures contained both the platinum starting material and a complex identified by an AX pattern. Even when the relative amounts of the reagents were altered both these features of the spectrum remained, albeit in varying ratios.

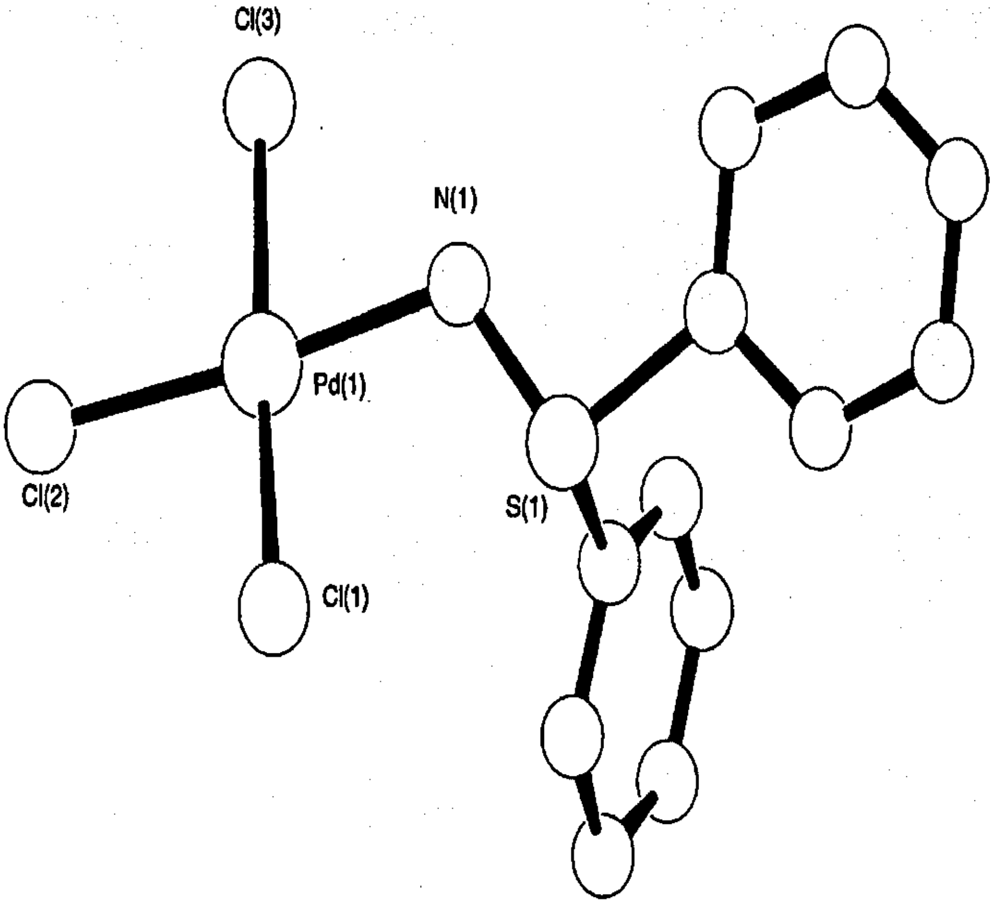


Fig.6.1 *The X-ray crystal structure of 10. Selected bond distances (Å) and angles (°)*:

Pd(1)-Cl(1) 2.312(14)
Pd(1)-Cl(2) 2.283(13)
Pd(1)-Cl(3) 2.286(13)
Pd(1)-N(1) 2.00(3)
N(1)-Pd(1)-Cl(2) 91.2(13)
N(1)-Pd(1)-Cl(2) 176.5(13)
Cl(2)-Pd(1)-Cl(1) 91.6(5)
Cl(3)-Pd(1)-Cl(1) 175.1(7)

In an attempt to remove all the *cis*- $PtCl_2(PMe_2Ph)_2$ from the system a large excess of **1** was added but in fact this did not successfully remove all of it. This observation suggested the presence of equilibrium between **1**, *cis*-$PtCl_2(PMe_2Ph)_2$ and a new coordination complex. To identify the new coordination complex it was decided to remove the free chloride from the system. This was achieved by treating the mixture with $[NH_4][PF_6]$ which resulted in the complete conversion of the platinum starting material through to the product. Unfortunately when the salt was precipitated by the addition of ether it did not crystallise well *via* slow diffusion forming an oil. The anion was changed to $[BF_4]^-$, by treating the mixture with $[NH_4][BF_4]$. In this case the slow diffusion with ether lead to colourless crystals of the product, which have been characterised as *cis*-$[PtCl(Ph_2SNH)(PMe_2Ph)_2][BF_4]$, **14**, by a combination of NMR, IR and micro-analysis. The fact that an AX pattern is observed in the ^{31}P NMR spectrum rules out a trans structure. The ^{195}Pt-^{31}P coupling constants of the phosphorus atoms are consistent with P *trans* to Cl and to N. A comparison of the value for P *trans* to N(H) in the $[S_2N_2H]^-$ complex $[Pt(S_2N_2H)(PMe_2Ph)_2]^+$ (3240Hz) with that of the above compound (3141Hz) seems to confirm that the ligand is N-bound. The value for P trans to S for the aforementioned case is significantly different (2595Hz).[85] With this information it would seem that the sulfimide has coordinated through the nitrogen atom and X-ray crystallography goes some way towards confirming this.

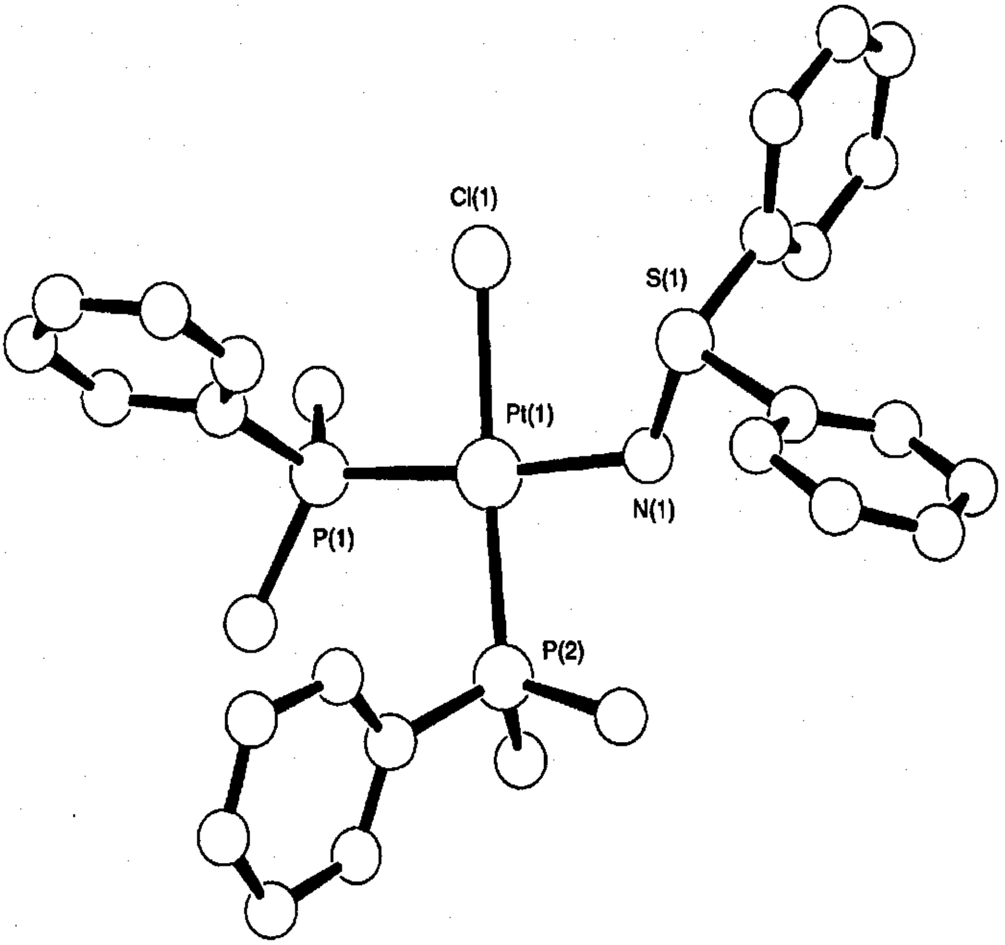


Fig.6.2.*The X-ray crystal structure of* ***14****. Selected bond distances (Å) and angles (°)*:

Pt(1)-Cl(1) 2.363(9)	Pt(1)-(N1) 2.04(2)
Pt(1)-P(1) 2.234(8)	Pt(1)-P(2) 2.256(8)
Cl(1)-Pt(1)-P(2) 175.8(3)	P(1)-Pt(1)-N(1) 173.6(7)
P(1)-Pt(1)-P(2) 97.8(3)	P(2)-Pt(1)-N(1) 88.1(6)

The X-ray structure of this compound can be found in **Fig.6.2**; the connectivity of the molecule can thus be confirmed, though it must be noted that the X-ray data is not of sufficient quality for publication due to the high value of the residuals (R = 0.089, and Rw = 0.099). There were problems brought about by the small size and poor quality of the crystals and by disorder within the anions. The Pt-N-S bond angle in the compound is 121° with Pt(1)-N(1) and N(1)-S(1) bond length being 2.04(2) and 1.64(2)Å, respectively.

To find out what kind of equilibrium was present in the reaction of **1** and $[PtCl_2(PMe_2Ph)_2]$ a solution of **14** in CH_2Cl_2 was treated with one equivalent of $[^nBu_4N]Cl$. ^{31}P NMR revealed that the mixture contained both **1** and **14.** From this information it was concluded that the initial reaction of **1** with $[PtCl_2(PMe_2Ph)_2]$ must proceed *via* the kind of equilibrium shown in **Fig.6.3**. The only way the reaction can be pushed to completion is through the

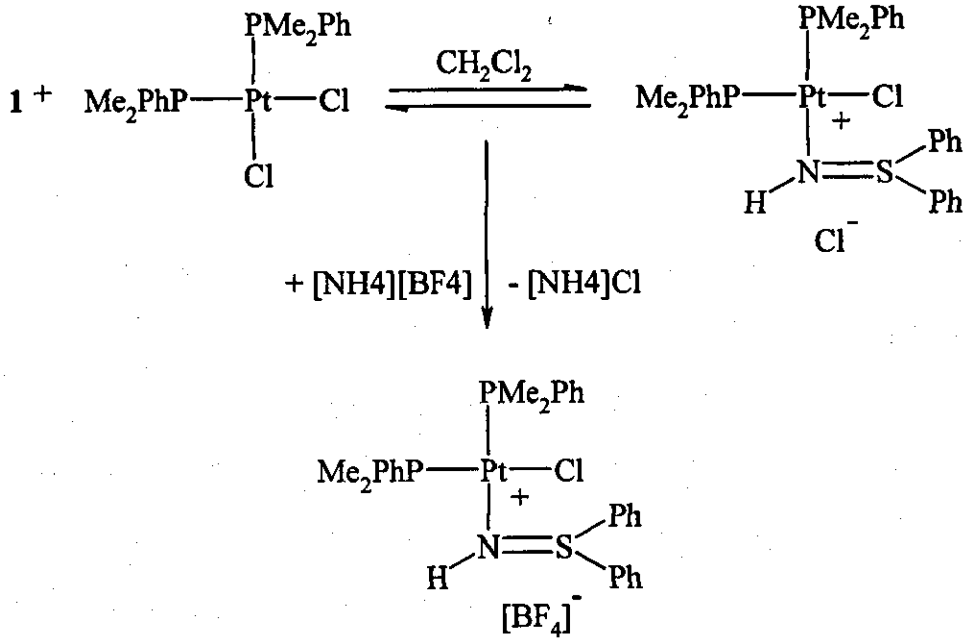


Fig.6.3. *The equilibrium present in solutions of 1 and $PtCl_2(PMe_2Ph)_2$ and the formation of 14.*

removal of the free chloride as $[NH_4]Cl$.

Attempts were made to coordinate a second molecule of **1** to **14**, unfortunately this proved futile. This could be due to steric problems playing a part in restricting the formation of the aforementioned complex. Although, we will show below it is possible to form homoleptic sulfimide complexes of platinum and palladium so this would make the steric problems explanation unlikely. The formation of the *trans* isomer of **14** proved unsuccessful. There is a technique used to generate the *trans* isomer of $[PtCl_2(PMe_2Ph)_2]$ from the *cis,* which involves heating in toluene.[86] This proved futile and there has been no evidence to suggest that the *trans* isomer can be formed. This could be due to the steric effects of the bulky **1** ligand again. As in the *trans* isomer **1** would interact with both the phosphines while in the *cis* arrangement **1** can only interact with one of the phosphines making the *cis* isomer more favourable as we have seen.

So far we have only looked at the addition of one unit of **1** to platinum and palladium complexes to see if it could coordinate to these transition metals. We will now look at complexes in which we generate homoleptic platinum and palladium complexes of **1**. The reaction of $[PPh_4]_2[PtCl_4]$ with **1** produces such a homoleptic platinum complex. The process occurs because the presence of the phosphonium cation solublises the $[PtCl_4]^{2-}$ anion in CH_2Cl_2. The addition of four equivalents of **1** results in the formation of $[Pt(Ph_2SNH)_4]Cl_2$ **(15)** as a well-formed pale yellow crystalline product. The reaction is slow and it takes a few days for the crystals to form. The product has been characterised by micro-analysis and IR spectroscopy. There are similarities between the spectrum and that of the copper analogue $[Cu(Ph_2SNH)_4]Cl_2$ mentioned earlier. It shows a very strong and broad N-H stretch at 3056cm^{-1} (3081cm^{-1} for the Cu analogue) and a strong S-N stretch at 934cm^{-1} (which comes at 940cm^{-1} in the copper case). When **1** present within a cationic complex we have noticed that the N-H stretch is very strong and there is thus H-bonding to the anion; in neutral species it can often be hard to detect. In this case it does suggest that we have **1** present as a cation. The structure was confirmed by X-ray crystallography, which can be seen in **Fig.6.4**. The expected square-planar arrangement is confirmed as is the fact that the ligands are all N-bound. If we compare the S-N bond distance within the ligands with the structure of $[Cu(Ph_2SNH)_4]Cl_2$ we can see that they a almost identical though the average bond angle of the nitrogens is less (122.6° cf 125.3°) in $[Pt(Ph_2SNH)_4]Cl_2$. Another similarity with the Cu complex is the arrangement of the ligands themselves. The two pairs of *cis* sulfurs extend on to opposite sides of the MN_4 plane. This allows each pair of N-H groups to cooperate in H-bonding to a chloride. Therefore the overall average H-Cl bond distance is only 2.25Å, with N-H-Cl angles of 168°. This seems to be a feature of complexes of **1** as we saw earlier such cooperative H-bonding with the cobalt compound. As with the cobalt compound it could lead to the formation of extended structures due to the possibility of the insertion of appropriate bridging H-bonding anions such as fumarate or terepthalate into the system that could then link the cations into extended arrays.

Moving on to homoleptic palladium complexes involving **1**, reaction of either $[PPh_4]_2[Pd_2Br_6]$ or $[PPh_4]_2[Pd_2Cl_6]$ with four equivalents of **1** in CH_2Cl_2 respectively results in complete substitution of the halides. In both cases the

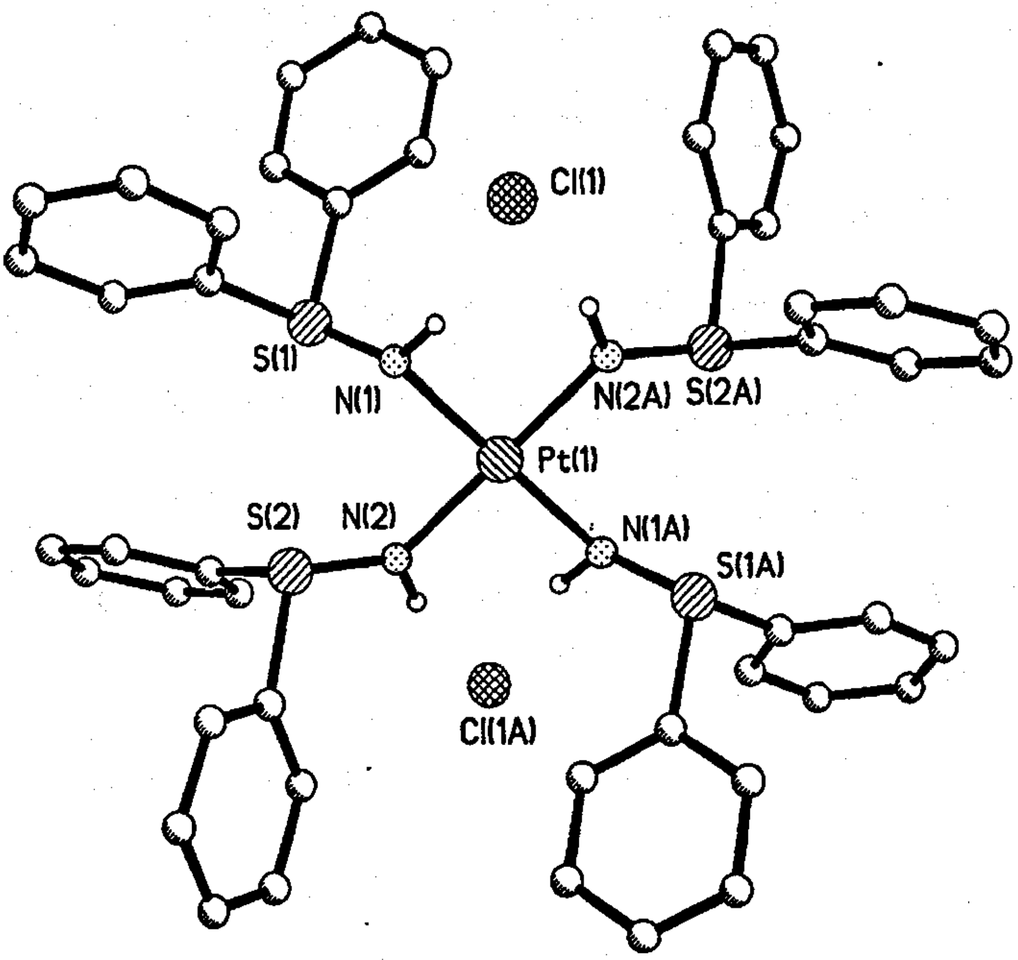


Fig.6.4. *The X-ray crystal structure of 15. Selected bond distances (Å) and angles (°):*

Pt(1)-N(1) 2.042(5)	Pt(1)-N(2) 2.041(5)
N(1)-S(1) 1.589(5)	N(2)-S(2) 1.580(5)
N(1)-Pt(1)-N(2) 92.2(2)	N(1)-Pt(1)-(N2A) 87.8(2)
Pt(1)-N(1)-S(1) 120.6(3)	Pt(1)-N(2)-S(2) 124.6(3)

solutions where left overnight. In this time the bromide reaction produced yield of orange crystalline yield of $[Pd(Ph_2SNH)_4]Br_2$ **11** while the chloride reaction produced a yellow/orange crystalline mass of $[Pd(Ph_2SNH)_4]Cl_2$ **12**. Both these products have been characterised by micro-analysis and IR. These compounds are very similar to their platinum and copper analogues of these homoleptic compounds. The IR shows a very strong broad N-H stretch seen at 3114 cm^{-1} for **11** and 3079 cm^{-1} for **12** compared to 3081, 3126 and 3056cm^{-1} for $[Cu(Ph_2SNH)_4]Cl_2$, $[Cu(Ph_2SNH)_4]Br_2$ and $[Pt(Ph_2SNH)_4]Cl_2$ respectively. Due to the strong degree of H-bonding between cation and anion the strength and width of this N-H band is distinctive to ionic complexes of **1**. If we look at the S-N stretch of these compounds we see that they are also very similar; 950cm^{-1} for **11** and 959 cm^{-1} for **12** compared to 940, 936 and 934cm^{-1} for $[Cu(Ph_2SNH)_4]Cl_2$, $[Cu(Ph_2SNH)_4]Br_2$ and $[Pt(Ph_2SNH)_4]Cl_2$ respectively. From this information it seems that **1** can also form homoleptic palladium complexes.

We decided to change the anion from a halide to another anion to observe what, if any, effect it would have on the structure of these compounds. With this in mind we reacted **1** with palladium chloride and $TlPF_6$ (molar ratio 4:1:2) to displace the chloride anions and replace them with PF_6 anions to give $[Pd(Ph_2SNH)_4[PF_6]_2$ **13**. Micro-analysis and IR seem to suggest we have formed the right compound. The IR shows a very similar strong and broad N-H stretch at 3062 cm^{-1}, compared to 3079 cm^{-1} for $[Pd(Ph_2SNH)_4]Cl_2$ and a S-N stretch of 832 cm^{-1}. The structure was confirmed as $[Pd(Ph_2SNH)_4[PF_6]_2$**(13)** by X-ray crystallography (Fig.6.5a).

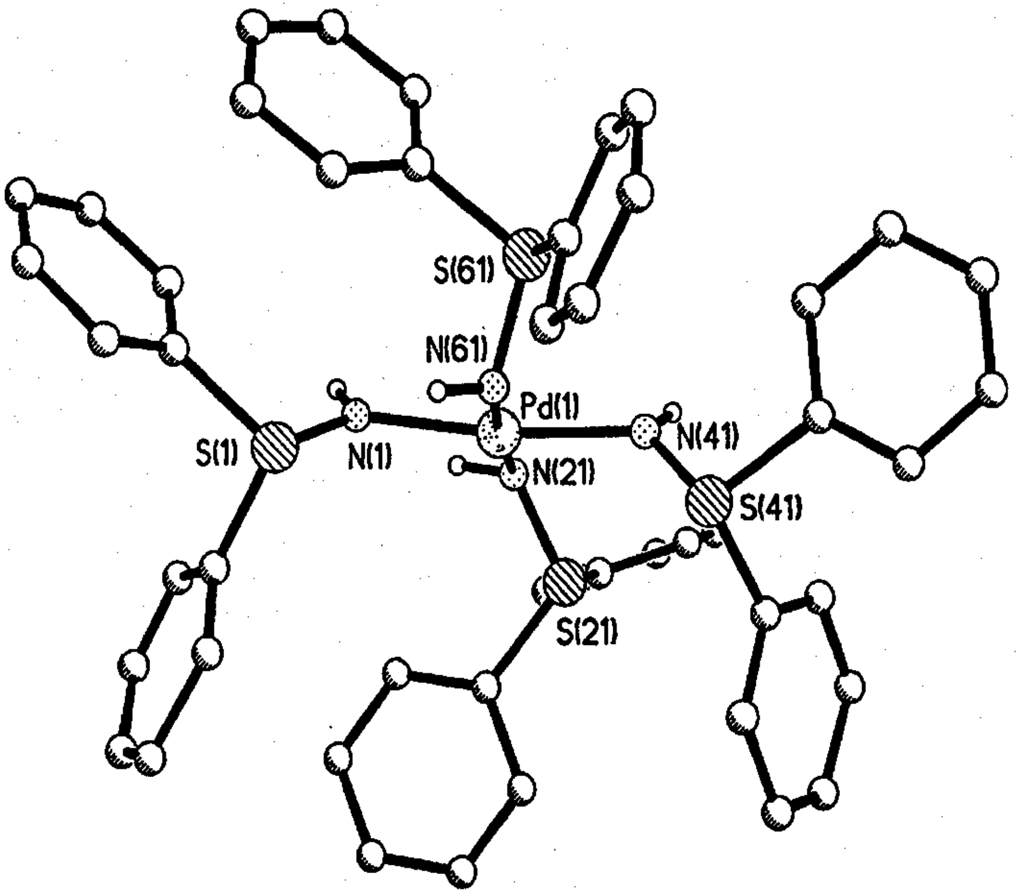


Fig.6.5a. *The X-ray crystal structure of 13. Selected bond distances (Å) and angles (°):*

Pd(1)-N(1) 2.0403(5)	Pd(1)-N(21) 2.014(6)
Pd(1)-N(41) 2.009(6)	Pd(1)-N(61) 2.040(5)
N(41)-Pd(1)-N(21) 88.4(2)	N(41)-Pd(1)-N(61) 87.6(3)
N(21)-Pd(1)-N(61) 175.9(3)	N(41)-Pd(1)-N(1) 171.0(2)

Within the crystal structure of the cation we see an unexpected orientation of the ligands. In contrast to all aforementioned homoleptic cases, where we see a symmetrical "2 up, 2 down" arrangement of the sulfur atom, in this case what is best described as "1 up, 3 down" arrangement of the sulfur atoms is found - as Fig.6.5b illustrates more clearly. The average Pd-N and S-N bond lengths are 2.03 and 1.60Å respectively. The bond lengths of the ligand pointing down are similar to the other bond lengths of the other ligands. The distortion from perfectly square planar (180°) can be quantified by the bond angles of N(41)-Pd(1)-N(1) and N(61)-Pd(1)-N(21), which are 171.0 and 175.9° respectively.

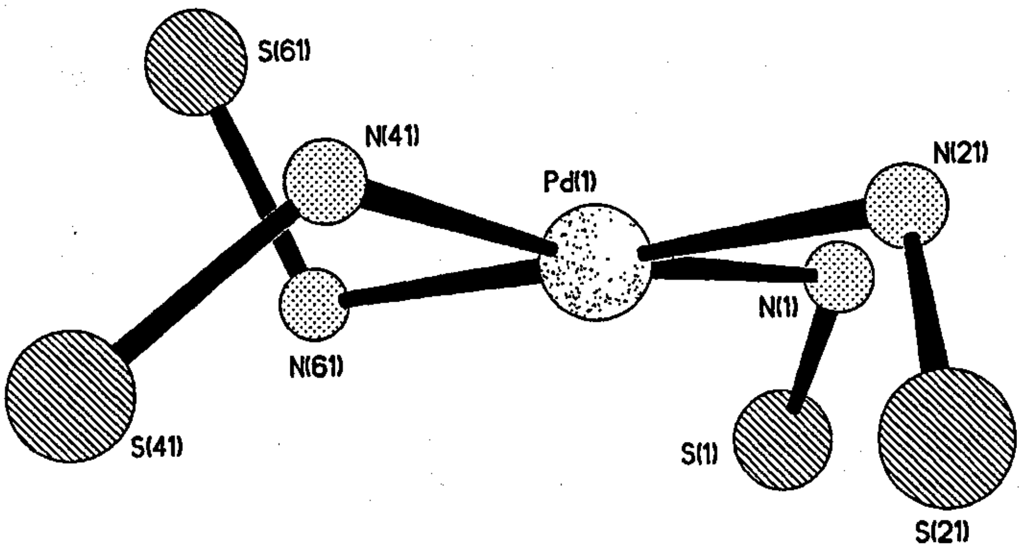


Fig.6.5b *"1 up, 3 down" ligand arrangement in **13**.*

The reactions of **1** so far with copper, cobalt, platinum and palladium compounds have seen the ligand coordinate to the metals through the nitrogen. This trend is still observed here although **1** is involved in the preparation of a new bi-dentate ligand, which bonds through the sulfur as well as the nitrogen.

This occurred in the reaction of **1** with $Pt(MeCN)_2Cl_2$ in a stoichiometric 2:1 reaction in acetonitrile. We had assumed this reaction would simply involve displacement of the nitrile groups by the Ph_2SNH ligands - indeed this is a very common stategy for the effective utilisation of the co-ordinatively unsaturated (but solublised) $PtCl_2$ unit.. In this case the reaction produces a crystalline material, which we initially assumed was $[Pt(Ph_2SNH)_2Cl_2]$. When an IR was carried out on the product we found that we had, to our surprise, a very strong broad N-H peak at 3071cm^{-1}. This was unexpected as this was usual associated with cationic sulfimide complexes and not only that there were extra bands not normally associated with the Ph_2SNH ligand at 1540, 1249, and 807 cm^{-1}. As this information was not consistent with our assumed product we investigated the complex by X-ray crystallography (Fig.6.6.).

The results showed that we had formed the platinum complex $[Pt(Ph_2SNH)(Ph_2SNC(Me)NH)Cl]Cl.MeCN$ **16.** The structure reveals two of the four coordination sites on the platinum contain the expected ligands (N-bound **1** and a chloride). The other two sites are occupied by nitrogen and sulfur atoms of a chelating $[Ph_2SNC(Me)N(H)]$ ligand thus forming a MNCNS metallocycle. During the reaction one of the sulfimide units has added to an acetonitrile and completed the metallocycle by binding to the platinum through a sulfur. If we look at the S-N distances in the metallocycle(1.625 Å) and compare them to the sulfimide ligand (1.618 Å) we can see that they are practically the same indicating that this may be best represented as a double bond. Due to the fact that one of the two C-N bonds, N(14)-C(13), is significantly shorter than the other (1.302 cf 1.358 Å) indicating a higher bond

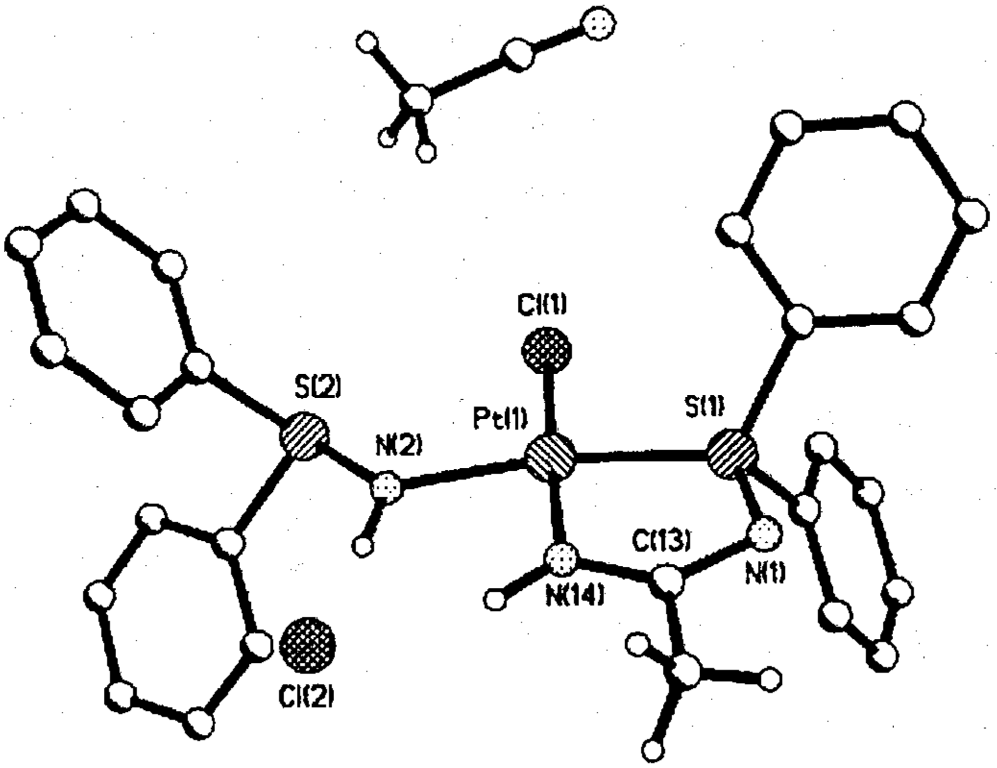


Fig.6.6 *The X-ray crystal structure of 16. Selected bond distances (Å) and angles (°)*:

Pt(1)-S(1) 2.1876(12)	S(1)-N(1) 1.625(4)
N(1)-C(13) 1.358(6)	C(13)-N(14) 1.302(6)
N(14)-Pt(1) 1.989(4)	Pt(1)-Cl(1) 2.3191(14)
Pt(1)-N(2) 2.012(4)	N(2)-S(2) 1.618(4)
Pt(1)-S(1)-N(1) 106.7(2)	S(1)-N(1)-C(13) 110.8(3)
C(13)-N(14)-Pt(1) 119.1(3)	N(2)-Pt(1)-S(1) 167.56(14)
N(2)-Pt(1)-Cl(1) 94.36(14)	Cl(1)-Pt(1)-S(1) 97.84(5)
N(2)-Pt(1)-N(14) 87.8(2)	Pt(1)-N(2)-S(2) 127.5(3)

order we can estimate the bonding within the neutral ligand to N(H)=C(Me)N=SPh_2. As we have seen with the bonding in **1** this does represent a simplification of what is happening. The coordinated unreacted sulfimide unit's bond distances and angles are not significantly different from those noted in other complexes of **1**. There is significant H-bonding interaction between the two N-H bonds and the free chloride as we have seen before for complexes of **1**. The average of the two H···Cl distances being 2.26 Å). This could have some bearing on the significant deviation of the N(2)-Pt-S(1) angle from linear (167.6°). The unexpectedly strong N-H band observed in the IR spectrum can now be associated to the hydrogen bonding that occurs in the structure. The other bands maybe assigned to C-N stretches and deformations. ^{1}H and ^{13}C NMR data also confirms the structure. The ^{13}C NMR for example shows the CH_3-C carbons at δ 19.0 and 183.6 respectively. The most important thing about this structure compared to anything else we have made is that it is the first example of a sulfimide unit bonding through the sulfur atom as opposed to the nitrogen.

This reaction has a number of aspects that are worth mentioning. The first is that we can make the product by reacting $Pt(MeCN)_2Cl_2$ in CH_2Cl_2. With this route we can clearly see that the coordinated MeCN ligands must be reacting as we no longer have the excess of the ligand in the form of the solvent. Furthermore, in the absence of the metal centre **1** does not react with MeCN. We proved this by making a solution of **1** with MeCN at both ambient temperature, and reflux temperature and stirring it for one hour. The solid we got back had an identical IR spectrum to the starting material. It seems that the choice of metal is also important as we have seen no such reactions with copper, cobalt, or any analogous reactions using $Pd(MeCN)_2Cl_2$ or $[Pd(MeCN)_4[BF_4]_2$. The reaction thus seems specific to Pt, at least amongst the aforementioned metals. The next question we have to look at is the reaction mechanism. The first stage in the reaction could involve the coordination of one **1** ligand followed by reaction with the remaining coordinated MeCN. This would suggest that coordinating **1** to the metal is activating the sulfimide towards attack by MeCN which seems less likely if we look at the earlier reaction of **1** with $[PPh_4]_2[PtCl_4]$ in CH_2Cl_2 which produced $[Pt(Ph_2SNH)_4]Cl_2$, **15**. If the idea was correct it would suggest that **15** would be prone to react with MeCN as well. In fact when we dissolve it in boiling MeCN and, after precipitation by cooling we see no change in its IR spectrum. There is also an unreacted sulfimide ligand attached to **16**. Another possible mechanism for the reaction could involve nucleophilic addition of the sulfimide to the nitrilic carbon followed by proton transfer and coordination of the sulfur via loss of the remaining MeCN. Theoretically this is a straight forward route, a slight problem being that it would require the sulfimide/acetonitrile addition to be faster or more efficient than simple substitution. If we look at earlier reactions involving platinum it seems this idea could be substantiated in that it appears to be less effective (or at least slower) at binding **1** then lighter metals. For example the conversion of $[Pd_2Cl_6]^{2-}$ to $[Pd(Ph_2SNH)_4]Cl_2$ takes place in a matter of minutes, while $[Pt(Ph_2SNH)_4]Cl_2$ only forms from $[PPh_4]_2[PtCl_4]$ over the course of a few days. Also as we looked at earlier (Fig.6.3) the $[Pt(PMe_2Ph)_2(Ph_2SNH)Cl]^+$ cation forms a solution equilibrium with $Pt(PMe_2Ph)_2Cl_2$ upon addition of Cl^-. For these reason it would seem that the second of the two reactions mechanisms is favourable. Nucleophilic addition

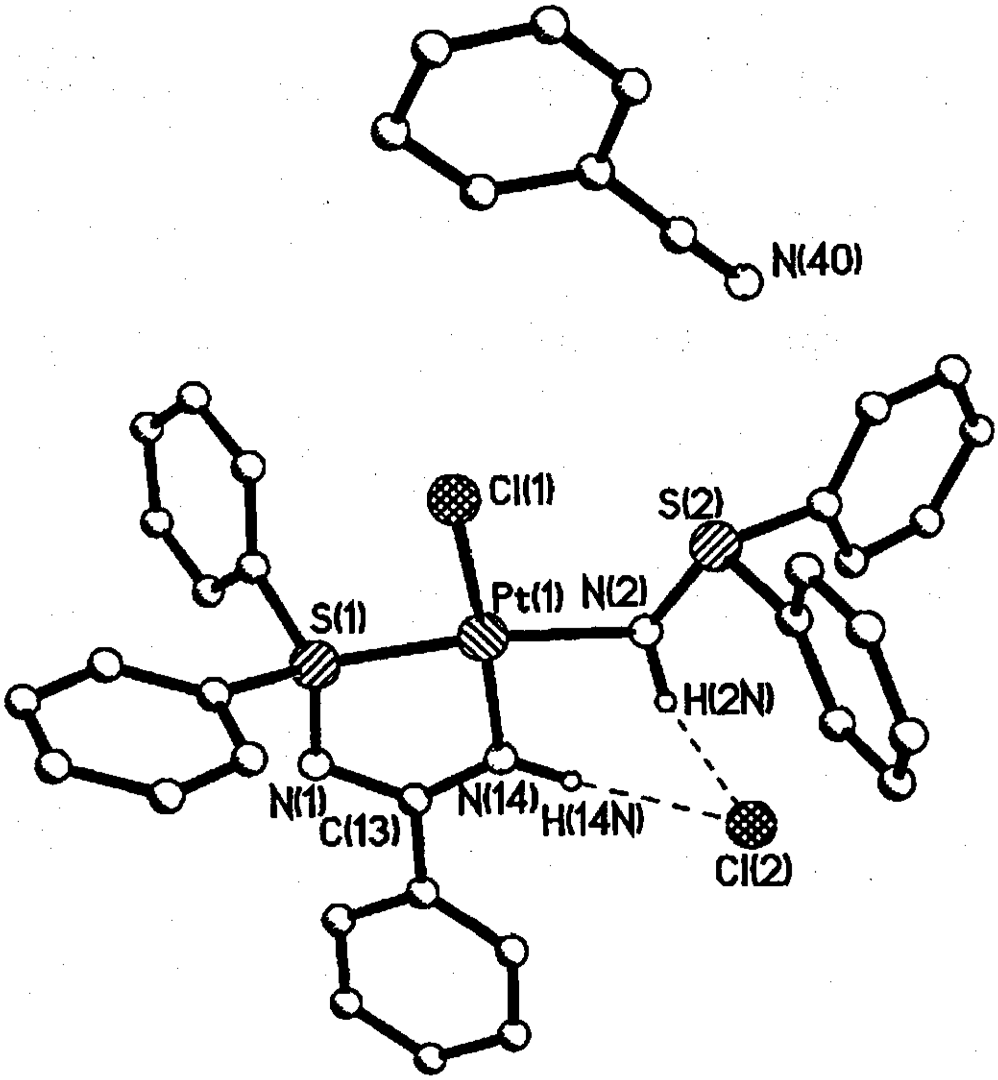


Fig.6.7. *The X-ray crystal structure of 17. Selected bond distances (Å) and angles (°):*

Pt(1)-S(1) 2.1871(16)	S(1)-N(1) 1.608(5)
N(1)-C(13) 1.355(7)	C(13)-N(14) 1.325(7)
N(14)-Pt(1) 1.999(5)	Pt(1)-Cl(1) 2.3176(18)
Pt(1)-N(2) 2.022(5)	N(2)-S(2) 1.600(6)
Pt(1)-S(1)-N(1) 107.16(19)	S(1)-N(1)-C(13) 111.6(4)
C(13)-N(14)-Pt(1) 118.4(4)	N(2)-Pt(1)-S(1) 168.51(17)
N(2)-Pt(1)-Cl(1) 93.23(17)	Cl(1)-Pt(1)-S(1) 98.17(6)
N(2)-Pt(1)-N(14) 88.9(2)	Pt(1)-N(2)-S(2) 125.8(3)

to coordinated nitriles is well documented and confirms this theory. We have shown through micro-analysis and low resolution Fast Atom Bombardment (LSIMS) that other nitriles such as propionitrile and benzonitrile can also follow this reaction mechanism. Above (Fig.6.7) is a crystal structure of the benzonitrile reaction product (**17**). The structure obtained also shows a benzonitrile of solvation as was also seen with **16.** The new bi-dentate ligand in this reaction is [$Ph_2SNC(Ph)N(H)$]. A comparison of the bond distances (A) and angles (°) around the MNCNS cyclic system (**16** and **17**) show that the structures are very similar (values can be seen under the appropriate X-ray crystal structure Fig.6.6 and Fig.6.7). Unlike the MeCN analogue we cannot statistically differentiate between the CN bonds lengths.

The transition metal based MNCNS cyclic system formed in these reactions is very rare. In fact there seems to be only one other example of such a unit characterised by X-ray crystallography, [$Pt\{PhSNC(MeC_6H_4)NNC(MeC_6H_4)NSPh\}(PPh_3)$][87], here though it is part of a tridentate ligand system (the X-ray structure of recently formed [$Pt\{N(H)C(Ph)N(H)S\}(dppe)$]$^+$ was not reported, though the species does indeed contain the cyclic PtNCNS unit[88]). A search of the Cambridge Structural Database[89] actually only found one other structure of the type cyclo-XNCNS in which X=O[90] excluding where X=S (the very well known and much studied dithiadiazolyls).

6.5 Conclusion

Platinum and palladium complexes of **1,** as seen for copper and cobalt, have shown that **1** can coordinate to metal centres quite efficiently. Although the option to bind *via* sulfur is there, it prefers to coordinate through the nitrogen.

The formation of **10** gave us a complex of **1**, which was anionic. The N-H stretch of this complex was different from the characteristic observed for previous complexes of **1** (ionic and neutral). This observation allows us in the future to be able to identify the type of complex **1** is involved in.

The platinum and palladium homoleptic complexes, as was seen for copper and cobalt, exhibit strong H-bonding from pairs of ligand N-H groups to the counterions suggesting that future investigations into the introduction of N-bonding, bridging anions into the system may well result in the formation of extended structures.

The novel reaction of **1** with $Pt(MeCN)_2Cl_2$ and different nitriles form a group of complexes with a very rare structural system (MNSNS ring). As well as forming new bidentate ligands in the process. These new bidentate ligands are the first example of a sulfimide coordinating through the sulfur. If these new neutral ligands prove labile we could have found an efficient route to new imine-substituted systems.

Chapter 7 Monodentate and polydentate sulfimide ligands

7.1 Introduction

Sulfimides are a group of compounds of the general formula $R^1R^2SNR^3$ in which R^1 and R^2 are carbon substituents. They can be grouped into two groups, those that are N-unsubstituted and N-substituted sulfimides.

The N-unsubstituted sulfimides can be prepared by direct amination of the appropriate sulfide. O-mesitylenesulfonyl hydroxylamine is the best reagent for the process,[91,92] but hydroxylamine-O-sulfonic acid[93,94] and chloroamine[93] can also be used.

$$R^1R^2S + NH_2X \xrightarrow{base} R^1R^2S\text{-}NH$$

Where $X = OSO_2Mes, OSO_2H, Cl$

These N-unsubstituted sulfimides can also be prepared from the reaction of *N*-tosylsulfimides with concentrated sulfuric acid at room

$$R^1R^2S\text{-}NTs \xrightarrow{H2SO4} R^1R^2SNH_2\text{-}OTs \xrightarrow{NaOH} R^1R^2S\text{-}NH$$

temperature.[94] The reaction of *S,S*-diarylsulfur dichlorides with ammonia[95] can be used to prepare *S,S*-diarylsulfimides this method is much less efficient then the previous two.

$$Ar_2SCl_2 + 3NH_3 \rightarrow Ar_2S\text{-}NH + 2NH_4Cl$$

The N-substituted sulfimides are important precursor to several types of sulfimides. This can be observed in the alkylation or acylation of these

$$R^1R^2S\text{-}NH + R^3X \text{ or } R^3C(O)X \rightarrow R^1R^2S\text{-}NR^3 \text{ or } NC(O)R^3$$

sulfimides. They can also be prepared directly. The addition of Chloramine-T to an appropriate sulfide produces N-substituted sulfimides in the correct conditions.

$$R^1R^2S + \text{Chloramine-T} \rightarrow R^1R^2S\text{-NTs.}$$

7.2 Aims of this section of the work

In view of the excellent ligand properties of **1** the aim of this section of the work was to attempt to extend this area of chemistry by preparing other monodentate and polydentate sulfimides; these would have the potential to be even more effective ligands (thanks to having multiple binding sites). Interestingly the whole idea of generating polysulfimides starting from polysulfides appears to have been overlooked - irrespective of any consideration of their potential as ligands - and so attempts to prepare such species actually constitute advances in our general knowledge of sulfimide chemistry *per se.*

7.3 Experimental

MeS(p-MeC$_6$H$_4$)NTs. ***18***

Under an atmosphere of dry nitrogen a solution of Chloramine-T (340mg, 1.494 mmol) in degassed MeCN (10mls) was treated with methyl-p-tolyl sulfide, $CH_3S(C_6H_4)CH_3$, (0.21mls, 1.494 mmol). After vigorous stirring and refluxing for 6 hours the mixture consisted of a pale white solid and a colourless solution. At this point the solvent was removed to leave the pale white solid. The pale white solid was then washed with a small amount of degassed deionised water. The solution was left stirring for an hour. The solution was then filtered and the white solid was dried *in vacuo.*

Yield: 223mg(49%)

Micro analysis	**%C**	**%H**	**%N**
Found	55.59	5.31	4.74
Calculated*	58.60	5.57	4.56

*for $C_{15}H_{17}NO_2S_2$

IR	**ν(S-O) (cm^{-1})**	**ν(S-N)(cm^{-1})**
MeS(p-MeC$_6$H$_4$)NTs	1277 and 1139	935

Cu[MeS(p-MeC$_6$H$_4$)NTs]$_2$Cl$_2$. **19**

A solution of **18** (90mg, 0.27mmol) in degassed MeCN (10ml) in an atmosphere of dry nitrogen was added to a solution of $CuCl_2$ (18mg, 0.13mmol) in the same volume of the same solvent and the mixture stirred. The dark mixture was left overnight. In the morning the solvent was removed and the green solid was redissolved in degassed MeCN(10ml) and layered with ether. After a number of days a few yellow/green crystals were apparent, after a week the solution was decanted from this solid which was then washed with a small amount of cold MeCN and dried *in vacuo.*

Yield: 47mg (23%)

Micro analysis	**%C**	**%H**	**%N**
Found	46.76	4.39	3.61
Calculated*	48.09	4.57	3.74

*for $C_{30}H_{34}N_2O_4S_4CuCl_2$

IR	**ν(S-O) (cm^{-1})**	**ν(S-N) (cm^{-1})**
$Cu[MeS(p\text{-}MeC_6H_4)NTs]_2Cl_2$	1286 and 1142	931

$TsNS(Ph)(CH_2)_3S(Ph)NTs$. ***20***

Under an atmosphere of dry nitrogen a solution of Chloroamine-T (1.230g, 5.40mmols) in degassed MeCN(50mls) was treated with $(PhS)_2(CH_2)_3$ (550mg, 2.11mmols). After vigorous stirring and refluxing for a day the solvent was removed to leave a white solid. The pale white solid was then washed with small amounts of degassed deionised water, then with degassed ether twice. The solution was then filtered and the white crystalline material was dried *in vacuo*.

Yield:843mg (67%)

Micro analysis	**%C**	**%H**	**%N**
Found	55.05	4.82	5.00
Calculated*	58.17	5.05	4.68

*for $C_{29}H_{30}N_2O_4S_4$

IR	ν(S-O) (cm^{-1})	ν(S-N) (cm^{-1})
TsNS(Ph)(CH$_2$)$_3$S(Ph)NTs	1280 and 1140	962

1,2 TsNS(Ph)C$_6$H$_4$S(Ph)NTs. **22**

Stage 1: Preparation of 1,2 PhSC$_6$H$_4$SPh **21**

Under an atmosphere of dry nitrogen a solution of PhSH (15g, 136mmols) in degassed DMSO (100ml) was treated with ground up KOH(7.6 g, 136mmols). The solution was heated until all the KOH had dissolved. The mixture was then treated with a solution of 1,2 dibromobenzene (16 g, 68mmols) in DMSO (100ml). After the mixture was refluxed for 24 hours a white precipitate had formed. This was filtered, washed with ether and dried *in vacuo*.

Yield: 14.52g (78%)

m/z (M=PhSPhSPh): 218 $[M - Ph]^+$, 185 $[M - SPh]^+$, 109 $[M - PhSPh]^+$, 77 $[M - SPhSPh]^+$.

Stage 2:Addition of Chloramine-T

Under an atmosphere of dry nitrogen a solution of Chloramine-T (4.540g, 20mmols) in degassed MeOH(20mls) was treated with a solution of **21** (1.860g, 5mmols) in the same solvent. To this mixture an acetic acid solution (1ml acetic acid in 5ml MeOH) was added drop wise. After refluxing at 50°C for 3 hours the solution was poured onto a cold, dilute NaOH solution.

A white precipitate had formed which was filtered and washed with water. The water layer was extracted with $CHCl_3$, the organic layer was washed with water and dried over $MgSO_4$. The solvent was removed and the residue was washed with ether. The crude product was recrystallised from acetone/hexane solution (1:1). The white crystals were filtered and dried *in vacuo*.

Yield:1.070g (32%)

m/z (FAB) (M = [TsNS{Ph}C_6H_4S{Ph}NTs]): 633 $[M + H]^+$, 464 $[M - NTs]^+$, 310 $[M - NTsSO_2C_6H_4Me]^+$, 295 $[M - 2NTs]^+$.

Micro analysis	**%C**	**%H**	**%N**
Found	60.73	4.35	4.43
Calculated*	60.27	4.66	3.88

*for $C_{32}H_{28}S_4O_4N_2$.

IR	**ν(S-O) (cm^{-1})**	**ν(S-N) (cm^{-1})**
1,2 TsNS(Ph)C_6H_4S(Ph)NTs	1282 and 1142	952

1,4 TsNS(Ph)C_6H_4S(Ph)NTs. ***24***

Stage 1: Preparation of 1,4 PhSC_6H_4SPh **23**

Under an atmosphere of dry nitrogen a solution of PhSH (15g, 0.136 mol) in degassed DMSO (100ml) was treated with ground up KOH(7.6 g, 0.136 mol). The solution was heated until all the KOH had dissolved. The mixture was then treated with a solution of 1,4 dibromobenzene (16 g, 0.068

mol) in DMSO(100ml). After the mixture was refluxed for 24 hours a white precipitate had formed. This was filtered, washed with ether and dried *in vacuo*.

Yield 14.3 g (76%)

m/z (M=PhSPhSPh): 218 $[M - Ph]^+$, 185 $[M - SPh]^+$, 109 $[M - PhSPh]^+$, 77 $[M - SPhSPh]^+$.

Stage 2:Addition of Chloramine-T

Under an atmosphere of dry nitrogen a solution of Chloramine-T (5.120 g, 0.022 mol) in degassed MeOH(40mls) was treated with a solution of **23** (3.720 g, 0.013 mol) in the same solvent. To this mixture an acetic acid solution(2ml acetic acid in 10ml MeOH) was added drop wise. After refluxing at 50°C for 36 hours the solution was poured onto a cold, dilute NaOH solution. A white solid formed which was filtered and washed with ether. The white solid was recrystallised from acetone/hexane solution (1:1). The white crystals were filtered and dried *in vacuo*.

Yield:3.560g (52%)

m/z (FAB) (M = $[TsNS\{Ph\}C_6H_4S\{Ph\}NTs]$): 633 $[M + H]^+$, 464 $[M - NTs]^+$, 310 $[M - NTsSO_2C_6H_4Me]^+$, 295 $[M - 2NTs]^+$.

Micro analysis	**%C**	**%H**	**%N**
Found	56.63	4.51	3.37
Calculated*	60.27	4.66	3.88

*for C32H28S4O4N2.

IR	**ν(S-O) (cm^{-1})**	**ν(S-N) (cm^{-1})**
1,4 TsNS(Ph)C_6H_4S(Ph)NTs	1283 and 1144	963

1,4 PhSC_6H_4S(Ph)NTs **25**

Under an atmosphere of dry nitrogen a solution of Chloramine-T (9.080g, 40mmols) in degassed MeCN(100ml) was treated with solid **23** (3.720g, 10mmol).After refluxing at 50°C for 3 days under nitrogen a white precipitate had formed it was collected and washed with water. The water layer was extracted with $CHCl_3$, the organic layer was washed with water and dried over $MgSO_4$. The solvent was removed and the residue was washed with ether. The crude product was recrystallised from acetone/hexane solution(1:1). The white crystals were filtered and dried *in vacuo*.

Yield:3.560g (52%)

m/z (FAB) (M = PhSPhS{Ph}NTs): 464 $[M + H]^+$, 310 $[M - SO_2C_6H_4Me]^+$, 294 $[M - NTs]^+$.

Structure confirmed by X-ray crystallography .

Attempted conversion of tosyl group to hydrogen.

A sample of white crystalline solid **22** or **24** (0.43g) was dissolved in 1ml of sulfuric acid (98%) at room temperature. The solution was then poured onto ice and made alkaline with dilute NaOH. The mixture was extracted with $CHCl_3$ and dried over $MgSO_4$. After the solvent was removed a yellow oil was obtained in both cases although sometimes a white solid precipitated out on the addition of NaOH and was collected.

6.4 Results and discussion

The first reaction we looked at in our aim to prepare other sulfimides was the reaction of $MeSC_6H_4Me$ with Chloramine-T in a 1:1 stoichiometric reaction in dry MeCN to hopefully produce the monodentate sulfimide $MeS(NTs)C_6H_4Me$. A white solid was produced as was expected - most sulfimides are white solids. The IR spectrum of the product showed the characteristic bands that would be associated with a tosylate group (S-O stretches at 1277 and 1139, and S-N stretch at $935cm^{-1}$). Micro-analysis and the IR spectrum seemed to suggest we had formed **18**. Two equivalents of **18** were reacted with $CuCl_2$ in dry MeCN under an atmosphere of nitrogen. The aim of this experiment was to ascertain whether it is possible to coordinate two **18** ligands to a copper centre in the same way were achieved with **1**. It was also of interest to see if the same kind of isomerism witnessed earlier with copper complexes of **1** would be present with this sulfimide (**18**).

The reaction is substantially slower than the analogous reaction of **1**, ultimately generating a yellow/green crystalline material. Interpreting the IR spectrum of the product revealed S-O and S-N stretches at 1286, 1142, and $931cm^{-1}$, respectively. These stretches are characteristic for the tosylate group. From the IR spectrum and micro-analysis it would suggest that we had formed **19**. The structure was confirmed by X-ray crystallography (Fig.7.1.).

The structure shows that we had formed a tetrahedral complex with the ligands *cis* to each other. The level of distortion from planar can be quantified by the Cl(1)-Cu-N(1) and Cl(2)-Cu-N(3) angles of 142.7 and 138.4° respectively. These values show a slightly more distorted structure than

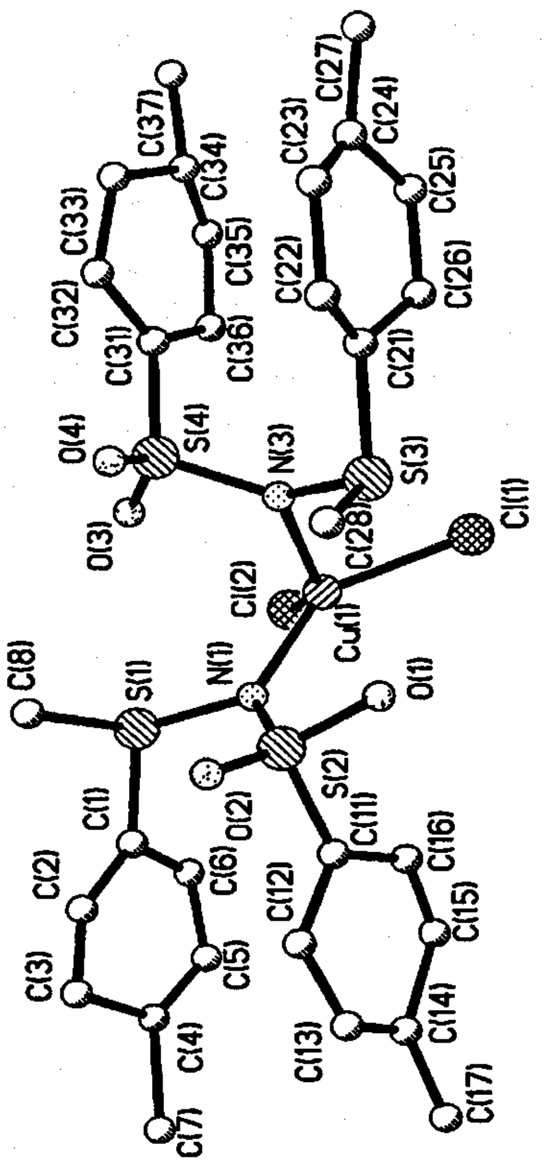


Fig.7.1. *The X-ray crystal structure of 19. Selected bond distances (Å) and angles (°):*

Cu(1)-N(1) 1.88(1) Cu(1)-N(3) 2.205(8)

Cu(1)-Cl(1) 2.198(5) Cu(1)-Cl(2) 2.177(5)

Cl(1)-Cu(1)-N(1) 142.7(5) Cl(2)-Cu(1)-N(3) 138.4(3)

Cl(1)-Cu(1)-Cl(2) 98.9(1) N(1)-Cu(1)-N(3) 97.9(3) observed with **1** reaction with $CuCl_2$ as it formed a planar complex **2a** (both180°) and the level of distortion for **2b** was157.6 and 153.1°. If we compare other structural features of the compounds such as the average Cu-N and S-N bond lengths in **19** (2.043 and 1.650A respectively) with that of **2a** (1.911 and 1.582 A) and **2b** (1.926 and 1.596 A respectively) we can see that both bond lengths are longer in **19**. Additionally if we compare the average angles at the nitrogens (i.e. S-N-Cu) we see that they are smaller (119.4° in **19**, compared to 129 and 125.4° in **2a** and **2b** respectively). The orientation of the ligands(**18**) in the structure **19** is to position them in such a way as they can interact with other molecules of **19** and take part in H-bonding. These results show the differences between the two ligands (**1** and **18**) coordinating to $CuCl_2$ and that the isomerism seen in **2a** and **2b** is due to the coordination properties of **1** and not sulfimides as a group, proving that the peculiar bonding seen for **1** is specific to this ligand and not a property of all sulfimides.

Unlike the reactions of 2 equivalents of **1** with $CuCl_2$ in which 2 isomers (**2a** and 2b) are formed the reaction of 2 equivalents of **18** only produces one isomer (**19**). This could be due to the steric effects of the tosylate group only allowing the ligand (**18**) to bond to the copper in such a manner. This could be true as further attempts to bond four **18** ligands to the copper centre proved futile. It seems that changing the R groups on the sulfur and nitrogen do change the behaviour of the sulfimide. It seems that the coordination properties seen earlier for **1** are not observed with other sulfimides and as such are specific to **1**.

Reaction of $PhS(CH_2)_3SPh$ with 2 equivalents of Chloramine-T generates a white crystalline material. The intended target of this reaction was of course the *bis*-sulfimide $TsNS(Ph)(CH_2)_3S(Ph)NTs$(**20**) and in fact this formulation is supported by the IR spectrum of the product (S-O stretches at 1280 and 1140, and an S-N stretch at $962cm^{-1}$) and by X-ray crystallography (Fig.7.2.). The latter technique reveals that the reaction does indeed generate the aforementioned polysulfimide ligand, confirming the coordination of the N-tosylate groups to both of the sulfur atoms [S(16) and S(2)]. The structure shows the tosylated sulfimide units to be in effect *trans* to each other, a position presumably dictated by the steric interactions between them. In such an arrangement the material clearly could not act as a bidentate ligand, although it is plausible that this structure is not necessarily rigidly maintained in solution. The overall effect of this stereochemistry is to make the distance between the two nitrogen atoms, N(1)-N(16), just over 9Å.

In an attempt to coordinate **20** to a metal centre it was reacted with $CuCl_2$, $CoCl_2$, $[PPh_4]_2[PtCl_4]$, and $[Pd_2Cl_6][PPh_4]_2$. Solutions were made of each of the metal compounds, in each case forming a coloured solution (blue solution for copper and cobalt, and a red solution for platinum and palladium). When **20** was added to each solution there was no change in the colour of the metal solution, although this didn't mean that no reaction had proceeded. Also no product was seen to precipitate out of solution. In an attempt to grow crystals the solutions were put on for slow diffusion with ether. White crystalline material did form but unfortunately when it was analysised by IR they showed only the properties of the original polysulfimide ligand with no coordination to any metal centre observed. This could be due to the distance

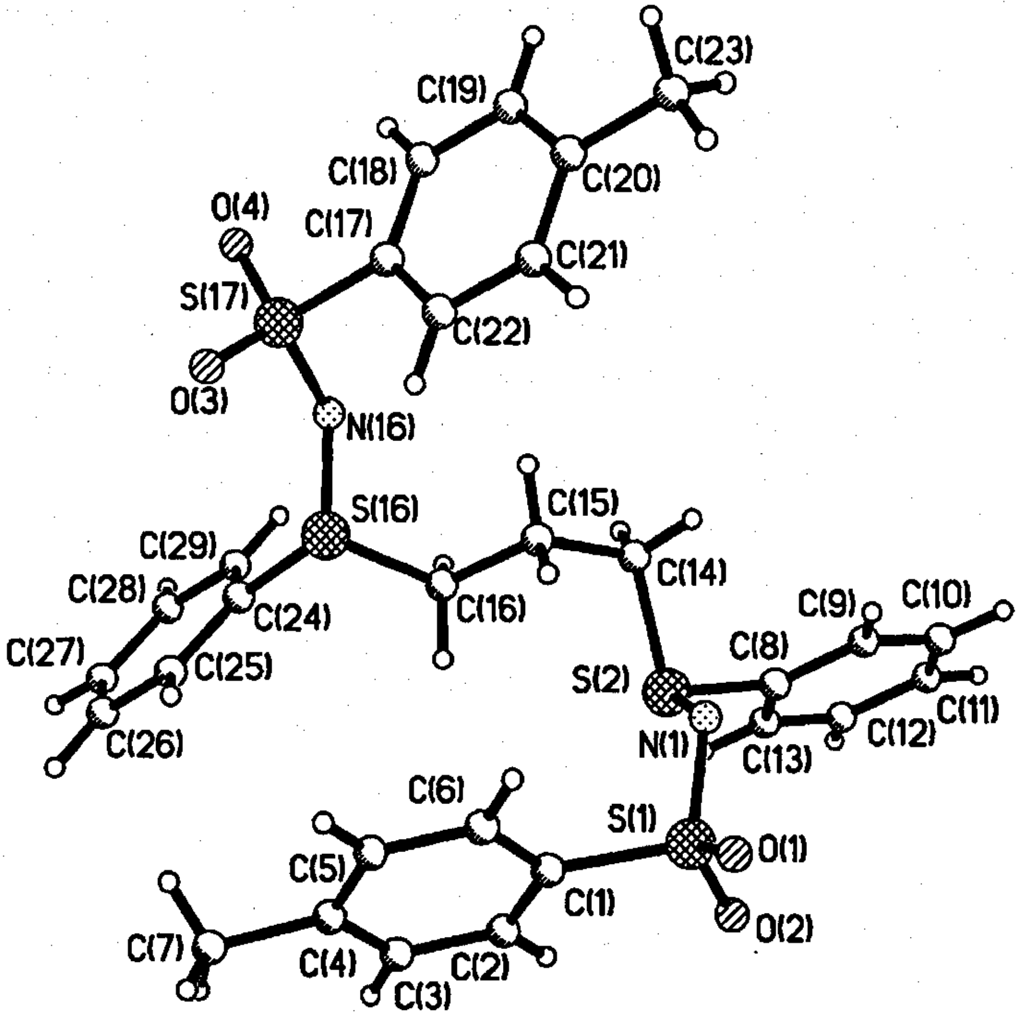


Fig.7.2. *The X-ray crystal structure of* ***20****. Selected bond distances (Å) and angles (°):*

N(16)-S(16) 1.631(4)	S(16)-C(16) 1.798(4)
C(16)-C(15) 1.529(6)	C(15)-C(14) 1.521(6)
C(14)- S(2) 1.801(4)	S(2)-N(1) 1.623(4)
S(17)-N(16)-S(16) 115.0(2)	N(16)-S(16)-C(16) 100.7(2)
S(16)-C(16)-C(15) 110.3(3)	C(16)-C(15)-C(14) 111.4(4)
C(15)-C(14)-S(2) 110.9(3)	C(14)-S(2)-N(1) 98.7(2)
S(2)-N(1)-S(1) 114.4(2)	

between the nitrogens being too great to coordinate to a metal centre in a bidentate manner. It could also be due to the bulky groups that are attached or close to the nitrogens causing steric problems not allowing any coordination to a metal centre to occur; we also have to consider the basicity of the nitrogen atoms in this case. Given that it has been shown that Ph_2SNH acts as a much stronger base than Ph_2SNTs it follows that the electronic effects of the presence of the tosyl groups in such potential ligands does decrease their affinity for metal centres (on this point it is worth noting that the rate of formation of **19** is far slower than the rate of formation of analogous copper complexes of Ph_2SNH).

Another *bis*-sulfimide targeted came in the form of 1,2 TsNS(Ph)PhS(Ph)NTs. In order to prepare this we had to first prepare the bis-sulfide1,2 PhSPhSPh, which is actually not commercially available. A method in the literature showed how to produce these bis(phenylthio)benzenes[96] from the reaction of KOH, and PhSH, mixed in DMA with the addition of 1,2 dibromobenzene and then finally water. Unfortunately the literature work is not specific about the time of reaction and a number of attempts were required to take the reaction through to completion. It turns out that the initial mixture in DMA has to be heated to reflux for approximately one week in order to take the reaction to completion. Work up by addition of water at this stage produces the desired product. The next stage involved a variation on the traditional Mann-Pope reaction in which sulfides are reacted with Chloramine-T to produce the corresponding sulfimide.[97] In our case it involved reacting 2 equivalents of Chloramine T with **21** and refluxing the mixture. A white crystalline solid was produced and a sample was sent for analysis by mass spectrometry. The results showed that we had formed a mixture of both the mono substituted compound 1,2 PhSPhS(Ph)NTs (peak observed at 464) as well as the desired 1,2 TsNS(Ph)PhS(Ph)NTs (peak observed at 633). In an effort to increase the amount of the disubstituted material we increased the amount of Chloramine T with **21** and proceeded as before. A white crystalline solid was produced and a sample of it was sent for analysis by mass spectrometry; the results showed we had produced the required product, 1,2 TsNS(Ph)PhS(Ph)NTs (**22**). A comparison of the IR spectra of **21** and **22** (Fig.7.3.) showed we had coordinated a tosylate group to **21** as there were peaks at 1282, 1142, and 952cm^{-1} in the spectrum of **21** but not in **22** which are characteristics of the tosylate group (S-O and N-S stretches respectively).

A sample of the white crystalline material was sent for a FAB and the results showed that there was a peak present at the same molecular weight of **22** suggesting we had our product. The FAB spectrum of **22** shows a fragmentation pattern (which is also observed for **24**). The pattern involves the initial loss of NTs from the molecule (peak observed at 464). A peak then follows this at 310 representing the loss of $NTsSO_2C_6H_4Me$ from **22**. A peak is observed at 294 representing the loss of 2NTs from **22**. The peak at 294 is the same molecular weight as the bis-sulfide **21** (in the case of **24** it represents the bis-sulfide **23**). With this and the results of the micro-analysis and the IR it seems to suggest that we had made the desired product **22**.

As a comparison to 1,2 TsNS(Ph)PhS(Ph)NTs polysulfimide ligand the preparation 1,4 TsNS(Ph)PhS(Ph)NTs was attempted to compare the reactions of the two polysulfimide systems. An analogous reaction was attempted, this time using 1,4 dibromobenzene. The reaction produced a white solid, which we

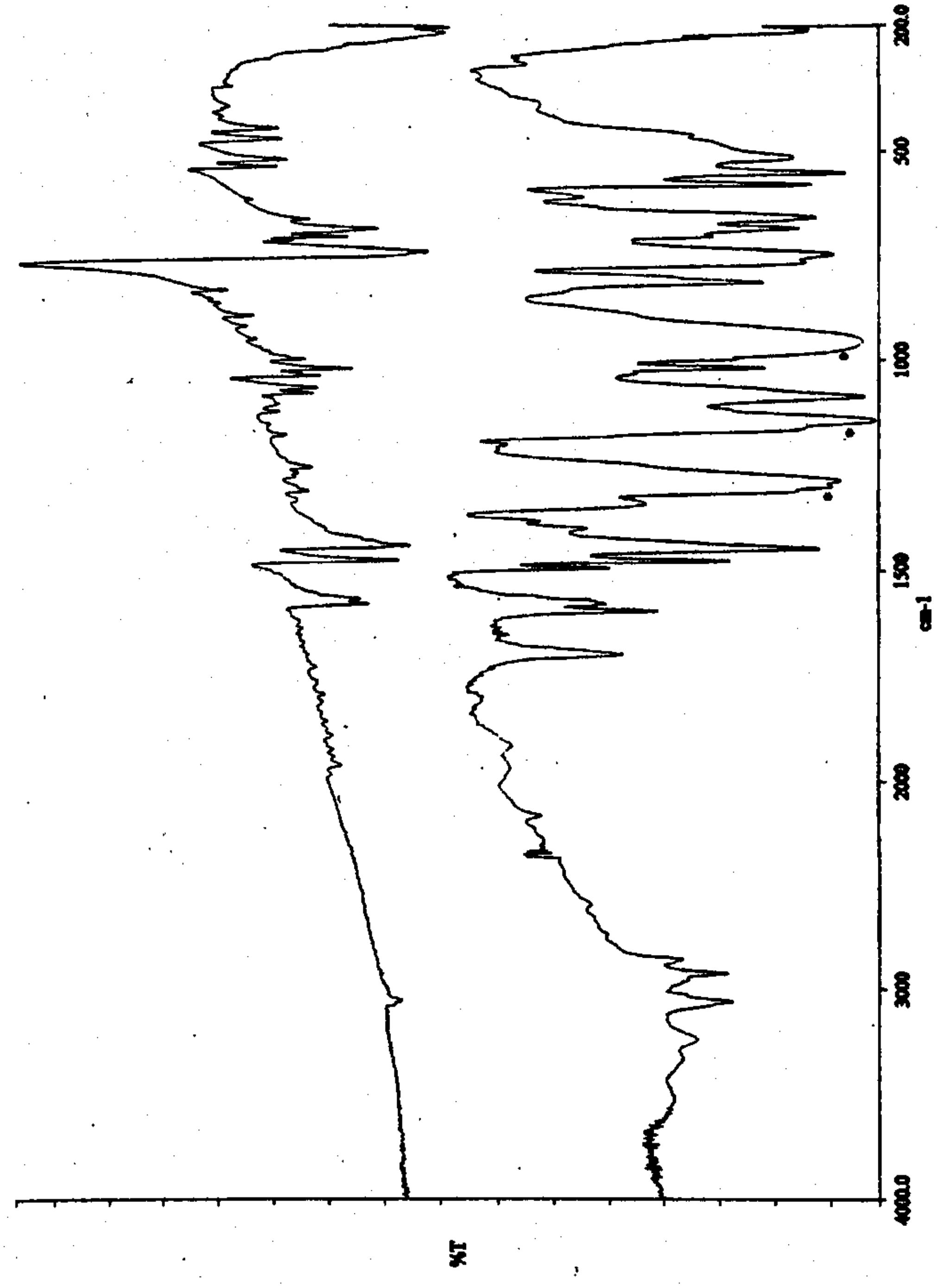
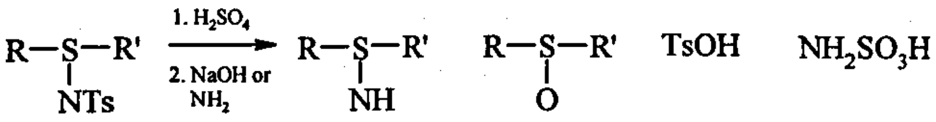


Fig.7.3. *Comparison of the IR spectra of 21 and 22. The main peaks associated with the tosylate group in complex 22 labelled (*).*

hoped was 1,4 PhSPhSPh, **23**. Mass spectrometry was carried out on the product, the results showed we had produced **23** (peak observed at 294 with 100% intensity). Having learned from preparing **22** we used an excess of Chloramine-T for the next stage. This resulted in a white crystalline product from which a sample was analysed by FAB. The results revealed a peak present at the same molecular weight of **24** implying we had made the desired polysulfimide ligand. The same fragmentation pattern as **22** could be observed in the FAB for **24**. Comparison of the IR spectra of **23** and **24** again confirmed characteristic peaks of the tosylate group present in the IR spectrum of **24** but not in **23**, S-O stretch 1283 and 1144cm^{-1}, and an S-N stretch at 964cm^{-1}. With the FAB, micro-analysis, and IR it was fair to assume that we had formed the required product **24**.

Now we had more polysulfiimide ligands (**22**, and **24**) the next stage was to treat them with metal centres to try to produce complexes of these polysulfimide ligands. Reactions were tried with $CuCl_2$, $CoCl_2$, $[PPh_4]_2[PtCl_4]$, and $[PPh_4]_2[Pd_2Cl_6]$. Visually there was no change in the colour of the appropriate metal solution although this didn't mean that no reaction had taken place. In each case no product precipitated out of solution. In an attempt to grow crystals the solutions were put on for slow diffusion with ether. White crystalline material did form but unfortunately when they were analysised by IR they showed only the properties of the original polysulfimide ligand in each case with no coordination to any metal centre observed. This could be due to the tosyl groups attached to the polysulfimides lowering the reactivity of the sulfimides when attached to the nitrogen. We can't over look the steric effects of the tosyl group, which must play some part in the failure to bond to metal centres.

To overcome this problem we attempted to convert the tosyl group on the polysulfimide ligands to hydrogen. The literature described a method in which the tosyl group on a sulfimide could be replaced with hydrogen by dissolving the ligand in sulfuric acid and then treating it with NaOH[98]. The reaction sequence below shows what can and should occur.



$$\text{R}-\underset{\text{NTs}}{\underset{|}{\text{S}}}-\text{R}' \xrightarrow[\text{2. NaOH or } NH_2]{\text{1. } H_2SO_4} \text{R}-\underset{\text{NH}}{\underset{|}{\text{S}}}-\text{R}' \quad \text{R}-\underset{\text{O}}{\underset{|}{\text{S}}}-\text{R}' \quad \text{TsOH} \quad NH_2SO_3H$$

Fig.7.4. *Expected products from the reaction of N-p-Tolysulfimides with con. Sulfuric acid.*

The reaction had been tried with various sulfimides showing the process did work for mono-tosylated sulfimides.[98]

The reaction was attempted with the polysulfimide ligands **22** and **24.** In each case a known mass of the polysulfimide ligand was dissolved in sulfuric acid (98%) and then poured onto some ice. This was then made alkaline with dilute NaOH. The mixture was then extracted with $CHCl_3$ and dried over $MgSO_4$. The solvent was then removed to leave yellow oil in each case although sometimes a white solid was produced on the addition of the dilute NaOH and collected. The white solid formed was sent for FAB and the predicted molecular mass of our converted tosyl compound was not seen in both cases. The spectrum shows a molecular weight peak at 327 with an adjacent peak of 325.9, which could indicate the loss of hydrogen. The next peak was at 309.9, with small adjacent peaks, which is a loss of 16 coincidentally also the molecular weight for oxygen and NH_2. There is another loss of 16 (peak at 293.9, with small adjacent peaks), again could represent a loss of oxygen or NH_2. The peak at 293.9, again with small adjacent peaks, could well be PhSPhSPh coincidently the starting sulfide **24**.

There are different molecules, which can fit the above profile. The compounds which have a molecular weight of between 325-328 include the following compounds: $PhS(NH_2)PhS(OH)Ph$, $PhS(NH_2)PhS(O)Ph$, PhS(O)PhS(OH)Ph, PhS(O)PhS(O)Ph, $PhS(NH_2)PhS(NH_2)Ph$, $PhS(NH)PhS(NH_2)Ph$, PhS(NH)PhS(O)Ph, PhS(NH)PhS(NH)Ph. All of which can undergo the aforementioned profile with some undergoing the loss of a hydrogen while others may not involve the initial lose of hydrogen in the profile.

The fragmentation pattern for the PhSPhSPh molecule is observed with the loss of Ph to leave PhSPhS (peak observed at 217). Followed by the loss of a sulfur (peak observed at 185 to leave PhSPh) and then the loss of another sulfur (peak observed at 152) leaving PhPh.

The data is inconclusive as to what is being produced, as there could be a mixture of products. The only thing that can be said for definite is that the tosylate groups has been displaced and replaced by NH, NH_2, O, or an O-H group. The PhSPhSPh skeleton can be seen in the spectra it is just a case of what has coordinated to the sulfurs. Due to oxygen, NH, NH_2 and OH having almost the same molecular weight it is hard to distinguish what is happening in the spectra.

The oils and the white solid produced in this reaction were analysised by IR. The IR spectra of the oils showed that we had not formed the required compound as we would have seen characteristic strong S-N bands which are usually observed around 930-960cm^{-1} for free sulfimides as well as an N-H stretch at around 3120cm^{-1} which were not seen. It would seem that the S-N bond has been broken as there is no peak in the region associated with an S-N bond. This suggests that the tosylate group has been displaced. If we had produced a sulfoxide the IR would have shown characteristically strong IR bands at 1020-1040 (S-O) which none of the oils possessed.

The IR of the white solids showed that we had not formed the required compound as we would have seen characteristic strong S-N bonds which are usually observed around 930-960 cm^{-1} for free sulfimides as well as an N-H stretch at around 3120cm^{-1}. The IR of the solids produced in these reactions does not show these characteristics. It would seem that reaction with sulfuric acid generates something else. We can see from the IR information that the S-N bond has been broken as there is no peak present on the IR spectra at the predicted frequency. From what we looked at earlier it could be that we have formed a sulfoxide. The characteristic IR bands are at 1020-1040 (S-O). The IR of both the solids had a strong IR band around 3400cm^{-1} and an IR band seen at 1060 could represent an N-H and S-O band respectively. Due to the lack of reproducibility of this reaction when the reaction was carried out again we could see a strong band at 3400cm^{-1} but also a band at 963cm^{-1} showing that we could have a combination of the starting compound **24,** the sulfoxide, or the desired product. The band at 963cm^{-1} could be the S-N band of S-N-H with the tosyl displaced with the expected peak at 3100cm^{-1} for the N-H peak being eclipsed by a broad N-H band of a by-product.

The attempted conversion of the tosyl group in **22** and **24** produced oil and a white solid showing a lack of reproducibility. Some reaction condition must be associated to this fact. It has been noted that different reaction times are required for the conversion of the tosyl group to a hydrogen.[98] this could account for the different products we formed when converting **22** and **24**.

The only methods found in the literature involved the conversion of sulfimides with a single tosylate group on, not two as our products possess. It could be that we had prepared a mixture of the corresponding sulfimide(NH), sulfoxide or a hybrid compound as the exact method needs some tampering to form the desired product exclusively. There are cases in which this conversion process has led to some sulfimides, undergoing this method, producing only the sulfoxide.[98] it could be that we are preparing the sulfoxide by hydrolysis of the free sulfimide when the sulfuric acid solution was poured onto the ice-water. This problem has been seen for *N-p*-tosyl dialkyl or akyl aryl sulfimides. To avoid this problem the sulfuric acid solutions could be added to cold ethyl ether, which we tried but it still gave an IR spectrum indicative of a mixture of products. It has been noted that by and large dialkyl or alkyl aryl free sulfimides can be unstable and they decompose to their corresponding sulfides and ammonia, it could be that the products we are making are unstable. There is a reaction involving aryl methyl *N-p*-tosylsulfimide that under both acidic and alkaline conditions undergoes hydrolysis to form the corresponding sulfoxides[99] this could be happening in our case. We could be seeing any of these outcomes as no one has looked at converting a bi-tosylated compound before and any of the observations seen for mono tosylated compounds could quite easily be associated to these compounds.

As the attempt to convert the tosyl group to a hydrogen seemed to have failed and that the polysulfimide ligands unfortunately did not co-ordinate to any metal centres we decided to try to add only one equivalent of Chloramine-T to **23**. We did this in order to see if we could coordinate the resulting mono-sulfimide species to a metal centre and thus show that the polysulfimides **20, 22,** and **24** were not forming metal complexes due to the presence of the two tosylate groups. The reaction was the same as for the preparation of **24** except we used one equivalents of Chloramine-T initially. It was observed that if the reaction is carried out in methanol we only form the mono substituted compound (**25**) and not **24** (in fact even an excess of the Chloramine in this solvent appears to still favour mono-sulfimide formation). A white crystalline solid was obtained from the reaction and a sample and FAB mass spectrometry revealed a peak at the molecular weight of 1,4 $PhSC_6H_4S(Ph)NTs$(**25**). The identity of this product was confirmed by X-ray crystallography (Fig 7.5.). The structure showed that we had coordinated a tosylate group to one of the sulfurs [S (2)]. With this hybrid species we had presumed that there would be the clear possibility of metal coordination through the sulfide group (S1) augmented by interactions to the sulfimide nitrogen. Unfortunately reactions of **25** with metal centres proved, as seen with the previous polysulfimide ligands earlier, fruitless only producing the initial ligand on crystallisation.

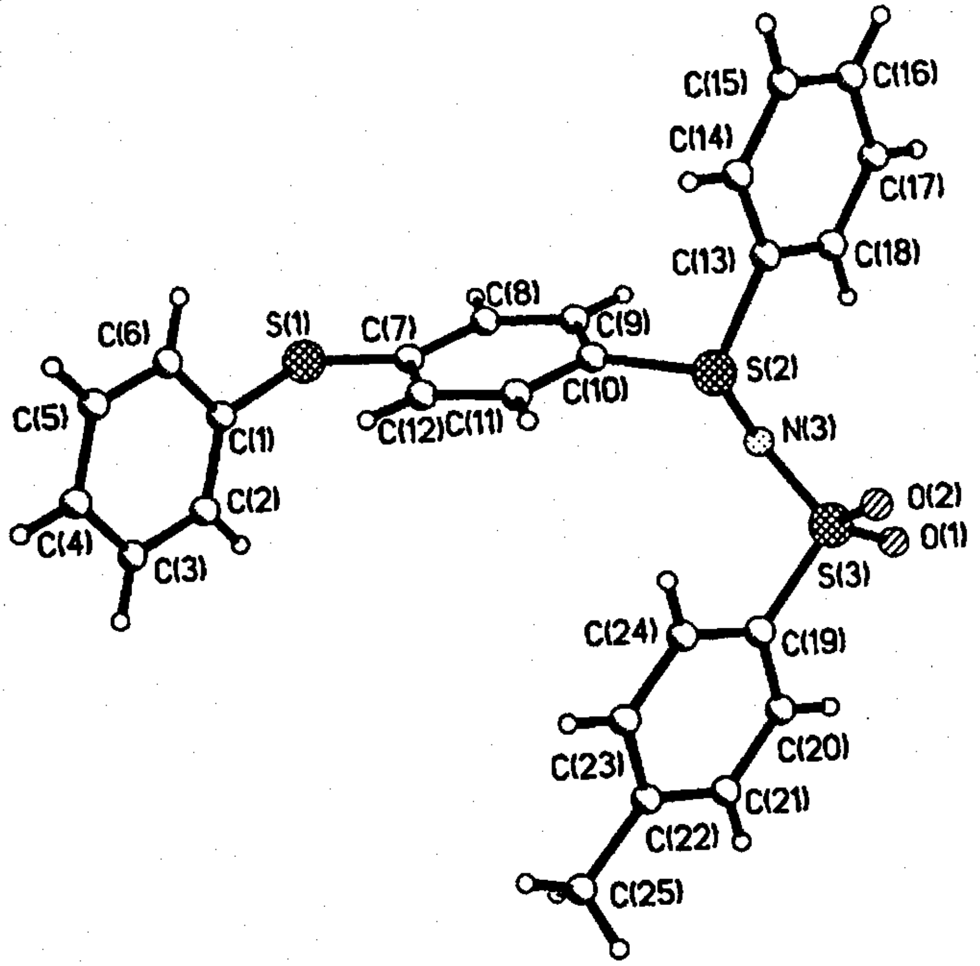


Fig.7.5. *The X-ray crystal structure of 25. Selected bond distances (Å) and angles (°):*

S(2)-N(3) 1.6299(18)	N(3)-S(3) 1.6126(18)
S(1)-C(1) 1.779(2)	S(1)-C(7) 1.768(2)
S(2)-C(10) 1.781(2)	S(2)-C(13) 1.797(2)
C(1)-S(1)-C(7) 103.89(10)	C(10)-S(2)-C(13) 102.12(10)
C(10)-S(2)-N(3) 102.72(10)	S(2)-N(3)-S(3) 113.83(11)

7.5 Conclusions.

The formation of the monodentate sulfimide, **18**, showed that we could prepare other sulfimides and compare the chemistry of these with **1**. The reaction of **18** with copper chloride proved we could co-ordinate ligands with the tosyl group on the sulfimide, though the reaction is much slower than that of Ph_2SNH. Unlike the latter's reaction with copper chloride, **18** appears to only generate one product with the ligands in a *cis* arrangement. The ligands orientated themselves in such a way to form H-bonding with other molecules of **19**.

The formation of the polysulfimide ligands **(20, 22,** and **24)** showed that we could readily produce such potential bidentate ligands. Unfortunately, these ligands would not coordinate to metal centres. This could be due to the steric effects of the tosylate groups attached to the sulfurs restricting any possible coordination to a metal centre, or to electronic effects induced by the tosylates (or, of course, a combination of the two effects). Even when there was only one tosylate group attached to the bis(thiophenyl)benzene**(23)** no coordination with a metal centre was observed.

Conversion of the tosyl group to hydrogen proved fraught for these polysulfimide ligands **(22** and **24)**. It would seem that the reaction forms a mixture of products in which the tosylate group has been removed from the ligands **(22** and **24)** but what has displaced them is unclear. The main candidates are N-H, $N-H_2$, S-O, or S-OH. The products could involve a hybrid with two of the four options forming a product. More work is needed to be carried out to perfect the method for the conversion of polysulfimide compounds containing two tosylate groups The reaction time could be the problem as it has been observed that different sulfimides require a different amounts of time for the reaction to proceed successfully.[98] These polysulfimide ligands (**22 and 24**) have two tosyl groups attached and the literature found only dealt with the conversion of mono tosyl compounds. This could explain why the process didn't work as expected because nobody has tried to convert such tosyl compounds before and as such no one can predict what the outcome will be. Further work needs to be carried out to solve the problem.

Chapter 8 Final conclusion and future work

8.1 Final Conclusion

In conclusion we have shown that diphenysulfilimine, **1**, is an efficient ligand at coordinating to metal centres. Before this study was undertaken there had only been one reported characterised structure of **1** which was the uranium species $[UCl_2(Ph_2SNH)Cp^*_2]$.[11] We now know that **1** is an efficient coordination ligand which forms some rare and specific complexes not seen before this study (square-planar/pseudo-tetrahedral isomerism in a neutral copper(II) complex). It was also observed that the homoleptic complexes which **1** formed with copper, cobalt, platinum, and palladium displayed strong, concerted H-bonding from pairs of ligand N-H groups to the counter ions suggesting that the introduction of N-bonding, bridging anions into the system may well result in the formation of extended structures. The ligand (**1**) was seen to coordinate to the metal centres via the nitrogen in all cases. The ligand can also be used to prepare other bi-dentate sulfimide ligands which can coordinate *via* the nitrogen to form the rare MNSNS ring systems when reacted with $Pt(MeCN)_2Cl_2$ and the appropriate nitrile. This system could lead to a variety of new bi-dentate sulfimide ligands if the were labile.

We have found that complexes involving **1** can be identified by their characteristic IR spectrum. This is due to all complexes involving **1** having an N-H stretch around $3100cm^{-1}$ and a S-N stretch around $930cm^{-1}$. Cationic complexes of **1** exhibit strong, broad bands for the N-H stretch. Anionic complexes exhibit strong, narrow bands for the N-H stretch. While neutral complexes of 1 exhibit weak N-H stretches. These characteristics were seen with all the metal complexes of 1 we tested.

We showed that we could make mono-dentate and polysulfimide ligands successful and even get the mono-dentate ligand to form a metal complex. The removal of the tosyl group proved a problem as the polysulfimide ligands would not coordinate to a metal centre with the tosyl group attached. The conversion method needs a bit of tweaking to sort out the problems.

Overall, we have increased the knowledge of sulfimide chemistry in particular the sulfimide chemistry of diphenylsulfilimine.

8.2 Future work

The reactions of 1 with $Pt(MeCN)_2Cl_2$ and the appropriate nitrile formed new bi-dentate sulfimide ligands. We have shown that if a different nitrile is used we can form a different bi-dentate sulfimide ligand. Future work could look at using a variety of different nitriles to form different bi-dentate sulfimide ligands. Once these new ligands are formed a procedure could be found to remove the ligands from the metal. This would mean that you would have the new ligands as free material and a new range of bi-dentate sulfimide ligands to study.

The homoleptic complexes of 1 exhibit strong hydrogen bonding suggesting that future investigations into the introduction of bridging anions into the system may result in the formation of extended structures. If instead of the anion being chloride if it was a bit more complicated like fumarate it could bridge metal centres forming these extended structures. In fact the first steps towards this are underway. It has been shown that you can put fumarate and terepthalate in as anions and they do in fact link the $[Cu(Ph_2SNH)_4]^{2+}$ centres by hydrogen bonding.

We have shown that Ph_2SNH, **1**, is a good efficient ligand at coordinating to metal centres and forming new ligands. It should be possible to derivatise on the N (ie put general R groups on and R may itself be coordinating) or to have other groups apart from phenyls in the system. The conversion of the tosyl group to hydrogens on the polysulfimides can also be looked at. Work is underway where by some polysulfimide systems have been made which have coordinated to metals. Below is an example of one of the products.

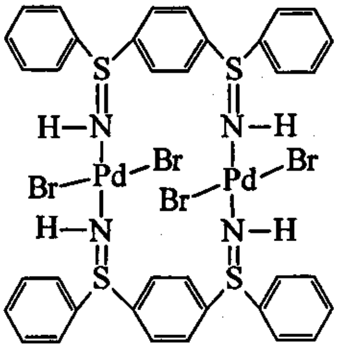


Fig 8.1 *Polysulfimide coordinated to metal centres.*

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Publications resulting from this work

1) P.F.Kelly, A.M.Z.Slawin and K.W.Waring, "Preparation and crystal structures of two forms of *trans*-$[CuCl_2\{N(H)SPh_2\}_2]$; an unusual example of square planar / pseudo-tetrahedral isomerism in a neutral copper (II) complex"., *J.Chem.Soc.,Dalton Trans.*, 1997, pp 2853-2854.

2) P.F.Kelly, A.M.Z.Slawin and K.W.Waring, "The preparation and X-ray crystal structure of $[Co(Ph_2SNH)_6]Cl_2$, a homoleptic sulfimide complex exhibiting cooperative, directed hydrogen bonds between cations and anions", *Inorg,Chem.Commun.,* 1, 1998, pp 249-250.

3) P.F.Kelly, S-M. Man, A.M.Z.Slawin and K.W.Waring, "The preparation of a range of copper complexes of diphenylsulfimide", *Polyhedron,* 1999, **18**, pp 3173-3179.

4) P.F.Kelly, A.M.Z.Slawin, K.W.Waring and S.Wilson , "Further Investigations into the Isomerism of Cu(II) Complexes of Diphenylsulfimide; the Preparation and X-Ray Crystal Structure of $\{[Cu(Ph_2SNH)_4][CuBr_2(Ph_2SNH)_2]Br_2\}$, the First Example of a $\{[CuL_4][CuX_2L_2]X_2\}$ Structure", *Inorg.Chim.Acta,* submitted.

Appendix: Xray data

	2a	**2b**
Colour, habit	Blue block	Green needle
Formula	$C_{24}H_{22}Cl_2CuN_2S_2$	$C_{24}H_{22}Cl_2CuN_2S_2$
M	537.02	537.02
Crystal system	Monoclinic	Monoclinic
Space group	*C2/c*	$P2_1/a$
a (Å)	17.038(2),	11.443(5).
b (Å)	8.928(5),	16.114(4),
c (Å)	16.234(2)	14.267(2)
β	97.53(7)	109.62(3)
U (Å^3)	2448(1)	2478(2)
Z	4	4
Data Used	866	1748
μ (Cu-Kα) (mm^{-1})	4.99	4.93
R (R')	0.058 (0.050)	0.053 (0.048)

Crystal data and structure refinement for 4a

Identification code	kwpk15
Empirical formula	$C_{52}H_{50}Cl_6Cu_4N_6OS_4$
Formula weight	1370.08
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	I2/a
Unit cell dimensions	a = 24.2378(3) Å alpha = 90°
	b = 28.9490(3) Å beta = 94.7800(10)°
	c = 17.640 Å gamma = 90°
Volume, Z	12334.0(2) $Å^3$, 8
Density (calculated)	1.476 Mg/m^3
Absorption coefficient	1.796 mm^{-1}
F(000)	5552
Crystal size	.01 x .03 x .2 mm
θ range for data collection	1.10 to 23.32°
Limiting indices	$-21 \le h \le 26$, $-32 \le k \le 32$, $-19 \le l \le 19$
Reflections collected	26828
Independent reflections	8892 (R_{int} = 0.0571)
Absorption correction	SADABS
Max. and min. transmission	1.000000 and 0.698307
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	8842 / 4 / 692
Goodness-of-fit on F^2	1.043
Final R indices [$I>2\sigma(I)$]	R1 = 0.0512, wR2 = 0.1182
R indices (all data)	R1 = 0.0956, wR2 = 0.1715
Extinction coefficient	0.00025(4)
Largest diff. peak and hole	0.715 and -0.318 $eÅ^{-3}$

A. Crystal Data

Empirical Formula	$C_{48}H_{44}N_4S_4CuCl_2$
Formula Weight	939.59
Crystal Color, Habit	purple, prism
Crystal Dimensions	0.20 X 0.20 X 0.20 mm
Crystal System	monoclinic
Lattice Type	Primitive
No. of Reflections Used for Unit Cell Determination (2θ range)	25 (70.4 - 74.9°)
Omega Scan Peak Width at Half-height	0.29°
Lattice Parameters	$a = 14.960(2)Å$ $b = 10.372(1)Å$ $c = 15.185(2)Å$ $\beta = 105.663(8)°$ $V = 2268.7(4)Å^3$
Space Group	$P2_1/n$ (#14)
Z value	2
D_{calc}	1.375 g/cm^3
F_{000}	974.00
μ(CuKα)	37.78 cm^{-1}

B. Intensity Measurements

Diffractometer	Rigaku AFC7S

Radiation	CuKα ($\lambda = 1.54178$ Å) graphite monochromated
Attenuator	Ni foil (factor = 9.42)
Take-off Angle	6.0°
Detector Aperture	9.0 mm horizontal 13.0 mm vertical
Crystal to Detector Distance	400 mm
Voltage, Current	0kV, 0mA
Temperature	20.0°C
Scan Type	ω
Scan Rate	16.0°/min (in ω) (up to 4 scans)
Scan Width	$(0.84 + 0.35 \tan\theta)°$
$2\theta_{max}$	120.2°
No. of Reflections Measured	Total: 3757 Unique: 3604 ($R_{int} = 0.349$)
Corrections	Lorentz-polarization Absorption (trans. factors: 0.4488 - 1.0000) Decay (0.03% increase) Secondary Extinction (coefficient: 8.24860e-07)

C. Structure Solution and Refinement

Structure Solution	Direct Methods (SIR92)
Refinement	Full-matrix least-squares
Function Minimized	$\Sigma w(\lvert Fo\rvert - \lvert Fc\rvert)^2$
Least Squares Weights	$w = \frac{1}{\sigma^2(Fo)} = [\sigma_c^2(Fo) + \frac{p^2}{4}Fo^2]^{-1}$
p-factor	0.0030
Anomalous Dispersion	All non-hydrogen atoms
No. Observations ($I>3.00\sigma(I)$)	2421
No. Variables	269

Reflection/Parameter Ratio	9.00
Residuals: R; Rw	0.062 ; 0.057
Goodness of Fit Indicator	3.39
Max Shift/Error in Final Cycle	0.02
Maximum peak in Final Diff. Map	0.86 $e^-/\text{Å}^3$
Minimum peak in Final Diff. Map	-0.60 $e^-/\text{Å}^3$

Crystal data and structure refinement for 8

Identification code	kwpk7
Empirical formula	$C_{72}H_{66}Br_4Cu_2N_6S_6$
Formula weight	1654.39
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	a = 9.47820(10) Å alpha = 114.9930(10)
	b = 14.159 Å beta = 93.1930(10)°
	c = 14.7618(2) Å gamma = 97.60°
Volume, Z	1765.99(3) Å^3, 1
Density (calculated)	1.556 Mg/m^3
Absorption coefficient	3.088 mm^{-1}
F(000)	834
Crystal size	.03 x .10 x .24 mm
θ range for data collection	1.53 to 23.27°
Limiting indices	$-10 \le h \le 10$, $-15 \le k \le 15$, $-11 \le l \le 16$
Reflections collected	7699
Independent reflections	5013 (R_{int} = 0.0196)
Absorption correction	Sadabs
Max. and min. transmission	1.000000 and 0.788658
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4963 / 3 / 422
Goodness-of-fit on F^2	0.919
Final R indices [$I>2\sigma(I)$]	R1 = 0.0337, wR2 = 0.0735
R indices (all data)	R1 = 0.0596, wR2 = 0.0927
Extinction coefficient	0.0011(4)
Largest diff. peak and hole	0.343 and -0.485 eÅ^{-3}

Crystal data and structure refinement for 9

Identification code	kwpk4	
Empirical formula	$C_{72}H_{66}Cl_2CoN_6S_6$	
Formula weight	1337.50	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Cubic	
Space group	$Pa\bar{3}$	
Unit cell dimensions	a = 19.1373(3) Å	alpha = 90°
	b = 19.1373(3) Å	beta = 90°
	c = 19.1373(3) Å	gamma = 90°
Volume, Z	7008.8(2) $Å^3$, 4	
Density (calculated)	1.268 Mg/m^3	
Absorption coefficient	0.545 mm^{-1}	
F(000)	2788	
Crystal size	.15 x .2 x .25 mm	
θ range for data collection	1.84 to 24.06°	
Limiting indices	$-14 \le h \le 21$, $-20 \le k \le 21$, $-21 \le l \le 2$	
Reflections collected	28117	
Independent reflections	1753 (R_{int} = 0.3111)	
Absorption correction	Semi-empirical from psi-scans	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	1751 / 0 / 137	
Goodness-of-fit on F^2	1.111	
Final R indices [$I>2\sigma(I)$]	R1 = 0.0527, wR2 = 0.1036	
R indices (all data)	R1 = 0.0807, wR2 = 0.1197	
Extinction coefficient	0.0012(3)	
Largest diff. peak and hole	0.507 and -0.744 $eÅ^{-3}$	

Table 1. Crystal data and structure refinement for structure **10**.

Identification code	rypk1	
Empirical formula	C36 H31 Cl3 N P Pd S	
Formula weight	753.40	
Temperature	293(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	P2(1)	
Unit cell dimensions	a = 13.150(9) Å	α= 90°.
	b = 17.231(9) Å	β= 90.62(5)°.
	c = 14.820(9) Å	γ = 90°.
Volume	3358(4) Å^3	
Z	4	
Density (calculated)	1.490 Mg/m^3	
Absorption coefficient	7.886 mm^{-1}	
F(000)	1528	
Crystal size	.12 x .12 x .03 mm^3	
Theta range for data collection	2.98 to 60.04°.	
Index ranges	0<=h<=13, 0<=k<=19, -16<=l<=16	
Reflections collected	4734	
Independent reflections	4481 [R(int) = 0.2454]	
Completeness to theta = 60.04°	86.2 %	
Absorption correction	Difabs	
Max. and min. transmission	1.00000 and .36	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4481 / 1 / 272	
Goodness-of-fit on F^2	0.971	
Final R indices [I>2sigma(I)]	R1 = 0.1135, wR2 = 0.2767	
R indices (all data)	R1 = 0.3065, wR2 = 0.3919	
Absolute structure parameter	0.00	
Extinction coefficient	0.0001(2)	
Largest diff. peak and hole	1.588 and -0.943 e.Å^{-3}	

Table 1. Crystal data and structure refinement for 13

Identification code	kwpk23
Empirical formula	$C_{49}H_{45.50}F_{12}N_{4.50}P_2PdS_4$
Formula weight	1221.98
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
Unit cell dimensions	a = 13.6496(2) Å alpha = 90°
	b = 19.856 Å beta = 90°
	c = 40.1359(5) Å gamma = 90°
Volume, Z	10877.7(2) $Å^3$, 8
Density (calculated)	1.492 Mg/m^3
Absorption coefficient	0.633 mm^{-1}
F(000)	4952
Crystal size	0.09 x 0.09 x 0.11 mm
θ range for data collection	1.01 to 28.31°
Limiting indices	$-18 \le h \le 13$, $-24 \le k \le 25$, $-53 \le l \le 53$
Reflections collected	68641
Independent reflections	25592 (R_{int} = 0.0615)
Absorption correction	Sadabs
Max. and min. transmission	1.000000 and 0.775723
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	25530 / 8 / 1314
Goodness-of-fit on F^2	0.977
Final R indices [$I>2\sigma(I)$]	R1 = 0.0669, wR2 = 0.1463
R indices (all data)	R1 = 0.1491, wR2 = 0.2035
Absolute structure parameter	-0.02(3)
Extinction coefficient	0.00000(4)
Largest diff. peak and hole	1.352 and -0.533 $eÅ^{-3}$

A. Crystal Data

Empirical Formula	$C_{28}H_{33}NSClPtP_2BF_4$
Formula Weight	794.93
Crystal Color, Habit	clear, block
Crystal Dimensions	0.03 X 0.03 X 0.10 mm
Crystal System	triclinic
Lattice Type	Primitive
No. of Reflections Used for Unit Cell Determination (2θ range)	20 (41.0 - 47.6°)
Omega Scan Peak Width at Half-height	0.12°
Lattice Parameters	$a = 15.724(5) Å$ $b = 17.407(6) Å$ $c = 14.64(1) Å$ $\alpha = 112.31(3)°$ $\beta = 108.79(4)°$ $\gamma = 90.86(3)°$ $V = 3466(3) Å^3$
Space Group	$P\bar{1}$ (#2)
Z value	4
D_{calc}	1.523 g/cm^3
F_{000}	1560.00
$\mu(CuK\alpha)$	97.65 cm^{-1}

B. Intensity Measurements

Diffractometer	Rigaku AFC7S
Radiation	CuKα ($\lambda = 1.54178$ Å) graphite monochromated
Attenuator	Ni foil (factor = 9.42)
Take-off Angle	6.0°
Detector Aperture	9.0 mm horizontal 13.0 mm vertical
Crystal to Detector Distance	400 mm
Temperature	20.0°C
Scan Type	ω
Scan Rate	16.0°/min (in ω) (up to 4 scans)
Scan Width	$(0.84 + 0.35 \tan \theta)°$
$2\theta_{max}$	120.3°
No. of Reflections Measured	Total: 10775 Unique: 10335 ($R_{int} = 0.207$)
Corrections	Lorentz-polarization Absorption (trans. factors: 0.4252 - 1.0000) Decay (14.54% decline)

C. Structure Solution and Refinement

Structure Solution	Direct Methods (SHELXS86)
Refinement	Full-matrix least-squares
Function Minimized	$\Sigma w(\lvert Fo\rvert - \lvert Fc\rvert)^2$
Least Squares Weights	$\frac{1}{\sigma^2(Fo)} = \frac{4Fo^2}{\sigma^2(Fo^2)}$
p-factor	0.0130
Anomalous Dispersion	All non-hydrogen atoms
No. Observations ($I>3.00\sigma(I)$)	3946
No. Variables	374
Reflection/Parameter Ratio	10.55

Residuals: R; Rw	0.089 ; 0.099
Goodness of Fit Indicator	3.50
Max Shift/Error in Final Cycle	3.45
Maximum peak in Final Diff. Map	1.74 $e^-/\AA^3$
Minimum peak in Final Diff. Map	-1.93 $e^-/\AA^3$

Crystal data and structure refinement for **15**

Colour	Yellow crystals
Formula	$C_{48}H_{44}Cl_2PtN_4S_4$
M	1071.102
Data collected	11178
Data used	3293 (R_{int}=0.1197)
Corrections	Lorentz-polarization
	Empirical absorption
Max. and min. transmission	1.000 and 0.842
Structure solution	Direct methods
Refinement method	Full-matrix least squares on F^2
Final R indices [$I>2\sigma(I)$]	$R1 = 0.0376$, $wR_2 = 0.0494$
Maximum peak in Final Diff. Map	0.991 $e^-/Å^{-3}$
Minimum peak in Final Diff. Map	-1.068 $e^-/Å^{-3}$

Crystal data and structure refinement for **16**

Colour, habit	yellow crystals
Formula	$C_{28}H_{28}Cl_2N_4PtS_2$
M	750.65
Crystal system	Monoclinic
Space group	$P2_1/n,a$
a (Å)	13.223(1)
b (Å)	10.941(1)
c (Å)	20.912(1)
β (°)	100.302(1)
U (Å^3)	2976.5(1)
Z	4
T (K)	293
Data Collected	12830
μ (Mo-Kα) (mm^{-1})	5.11
λ (Å)	0.71073
F (000)	1472
Final R indices [I>2□(I)]	$R_1 = 0.0268$, $wR_2 = 0.0486$
Independent reflections	4267
Observed reflections	4217

Table 1. Crystal data and structure refinement for 17

Identification code	kwpk26	
Empirical formula	C36.25 H30.75 Cl2 N3.75 Pt S2	
Formula weight	849.01	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 18.1378(5) Å	α= 90°.
	b = 8.6601(2) Å	β= 92.4480(10)°.
	c = 23.0492(4) Å	γ = 90°.
Volume	3617.15(14) Å^3	
Z	4	
Density (calculated)	1.559 Mg/m^3	
Absorption coefficient	4.172 mm^{-1}	
F(000)	1674	
Crystal size	.01 x .1 x .1 mm^3	
Theta range for data collection	2.05 to 23.25°.	
Index ranges	-20<=h<=19, -9<=k<=8, -25<=l<=24	
Reflections collected	15369	
Independent reflections	5143 [R(int) = 0.0575]	
Completeness to theta = 23.25°	98.9 %	
Absorption correction	SADABS	
Max. and min. transmission	1.00000 and 0.678321	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5143 / 2 / 433	
Goodness-of-fit on F^2	0.954	
Final R indices [I>2sigma(I)]	R1 = 0.0363, wR2 = 0.0622	
R indices (all data)	R1 = 0.0633, wR2 = 0.0684	
Extinction coefficient	0.00000(6)	
Largest diff. peak and hole	1.026 and -0.755 e.Å^{-3}	

A. Crystal Data

Empirical Formula	$C_{30}H_{34}N_2S_4Cl_2CuO_4$
Formula Weight	749.30
Crystal Color, Habit	yellow/grecube, cube
Crystal Dimensions	0.10 X 0.10 X 0.10 mm
Crystal System	monoclinic
Lattice Type	Primitive
No. of Reflections Used for Unit Cell Determination (2θ range)	25 (72.3 - 74.5°)
Omega Scan Peak Width at Half-height	0.26°
Lattice Parameters	$a = 14.627(4)Å$ $b = 12.159(2)$ Å $c = 19.540(2)$ Å $\beta = 108.15(1)°$ $V = 3302(1)$ Å^3
Space Group	$P2_1/a$ (#14)
Z value	4
D_{calc}	1.507 g/cm^3
F_{000}	1548.00
μ(CuKα)	50.99 cm^{-1}

B. Intensity Measurements

Diffractometer	Rigaku AFC7S

Radiation	CuKα ($\lambda = 1.54178$ Å) graphite monochromated
Attenuator	Ni foil (factor = 9.42)
Take-off Angle	6.0°
Detector Aperture	9.0 mm horizontal 13.0 mm vertical
Crystal to Detector Distance	400 mm
Voltage, Current	0kV, 0mA
Temperature	20.0°C
Scan Type	ω
Scan Rate	16.0°/min (in ω) (up to 4 scans)
Scan Width	$(1.05 + 0.35 \tan \theta)^\circ$
$2\theta_{max}$	120.2°
No. of Reflections Measured	Total: 5408 Unique: 5184 ($R_{int} = 0.065$)
Corrections	Lorentz-polarization Absorption (trans. factors: 0.8196 - 1.0000) Decay (1.17% decline) Secondary Extinction (coefficient: 1.45934e-07)

C. Structure Solution and Refinement

Structure Solution	Direct Methods (SIR92)
Refinement	Full-matrix least-squares
Function Minimized	$\Sigma w(\lvert Fo\rvert - \lvert Fc\rvert)^2$
Least Squares Weights	$w = \frac{1}{\sigma^2(Fo)} = [\sigma_c^2(Fo) + \frac{p^2}{4}Fo^2]^{-1}$
p-factor	0.0040
Anomalous Dispersion	All non-hydrogen atoms
No. Observations ($I>4.00\sigma(I)$)	2039
No. Variables	364

Reflection/Parameter Ratio	5.60
Residuals: R; Rw	0.072 ; 0.072
Goodness of Fit Indicator	5.47
Max Shift/Error in Final Cycle	0.70
Maximum peak in Final Diff. Map	0.83 $e^-/\AA^3$
Minimum peak in Final Diff. Map	-0.60 $e^-/\AA^3$

A. Crystal Data

Empirical Formula	$C_{29}H_{30}N_2O_4S_4$
Formula Weight	598.81
Crystal Color, Habit	colourlessplate, plate
Crystal Dimensions	0.10 X 0.04 X 0.10 mm
Crystal System	triclinic
Lattice Type	Primitive
No. of Reflections Used for Unit Cell Determination (2θ range)	25 (70.6 - 74.9°)
Omega Scan Peak Width at Half-height	0.27°
Lattice Parameters	$a = 12.751(2) \mathring{A}$ $b = 12.754(3) \mathring{A}$ $c = 10.137(4) \mathring{A}$ $\alpha = 107.60(2)^\circ$ $\beta = 102.78(2)^\circ$ $\gamma = 69.64(1)^\circ$ $V = 1460.7(7) \mathring{A}^3$
Space Group	$P\bar{1}$ (#2)
Z value	2
D_{calc}	1.361 g/cm^3
F_{000}	628.00
$\mu(CuK\alpha)$	32.40 cm^{-1}

B. Intensity Measurements

Diffractometer	Rigaku AFC7S
Radiation	CuKα ($\lambda = 1.54178$ Å) graphite monochromated
Attenuator	Ni foil (factor = 9.42)
Take-off Angle	6.0°
Detector Aperture	9.0 mm horizontal 13.0 mm vertical
Crystal to Detector Distance	400 mm
Voltage, Current	0kV, 0mA
Temperature	20.0°C
Scan Type	ω
Scan Rate	16.0°/min (in ω) (up to 4 scans)
Scan Width	$(1.00 + 0.35 \tan\theta)°$
$2\theta_{max}$	120.1°
No. of Reflections Measured	Total: 4577 Unique: 4348 ($R_{int} = 0.070$)
Corrections	Lorentz-polarization Absorption (trans. factors: 0.8919 - 1.0000) Decay (1.42% decline) Secondary Extinction (coefficient: 2.71232e-06)

C. Structure Solution and Refinement

Structure Solution	Direct Methods (SIR92)
Refinement	Full-matrix least-squares
Function Minimized	$\Sigma w(\lvert Fo\rvert - \lvert Fc\rvert)^2$
Least Squares Weights	$w = \frac{1}{\sigma^2(Fo)} = [\sigma_c^2(Fo) + \frac{p^2}{4}Fo^2]^{-1}$
p-factor	0.0020
Anomalous Dispersion	All non-hydrogen atoms
No. Observations ($I>3.00\sigma(I)$)	3111

No. Variables	353
Reflection/Parameter Ratio	8.81
Residuals: R; Rw	0.049 ; 0.043
Goodness of Fit Indicator	3.03
Max Shift/Error in Final Cycle	0.01
Maximum peak in Final Diff. Map	0.25 $e^-/\AA^3$
Minimum peak in Final Diff. Map	-0.57 $e^-/\AA^3$

Table 1. Crystal data and structure refinement for 25

Identification code	pkal1	
Empirical formula	C25 H21 N O2 S3	
Formula weight	463.61	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 12.2542(2) Å	α= 90°.
	b = 15.0392(3) Å	β= 91.3550(10)°.
	c = 12.40380(10) Å	γ = 90°.
Volume	2285.30(6) Å^3	
Z	4	
Density (calculated)	1.347 Mg/m^3	
Absorption coefficient	0.347 mm^{-1}	
F(000)	968	
Crystal size	.2 x .2 x .06 mm^3	
Theta range for data collection	1.66 to 23.26°.	
Index ranges	-13<=h<=12, -16<=k<=10, -13<=l<=12	
Reflections collected	9740	
Independent reflections	3233 [R(int) = 0.0215]	
Completeness to theta = 23.26°	98.4 %	
Absorption correction	Sadabs	
Max. and min. transmission	1.000000 and 0.813648	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3233 / 0 / 281	
Goodness-of-fit on F^2	0.910	
Final R indices [I>2sigma(I)]	R1 = 0.0311, wR2 = 0.0776	
R indices (all data)	R1 = 0.0418, wR2 = 0.0843	
Extinction coefficient	0.0010(5)	
Largest diff. peak and hole	0.273 and -0.204 e.Å^{-3}	