Investigations in liquid ammonia chemistry

Acknowledgements

I would like to dedicate this work to the memory of my mother, who sadly passed away five weeks after I started my research.

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Abstract

Reaction of $PtCl_2(PR_3)_2$ with a solution of $SOCl_2$ in $NH_3(l)$ is known to yield compounds of the type $Pt(NSO)_2(PR_3)_2$. Reaction of $Pt\ Cl_2\ (PR_3)_2$ with a solution of SO_2 in $NH_3(l)$ is known to yield compounds of the type $Pt\ (SO_2(NH)_2(PR_3)_2$. The initial part of this work was to try and expand this field of synthetic chemistry, and investigate whether metal dichlorides would be amenable starting material for the production of metal bis-thionylimide compounds via a liquid ammonia route, as opposed to more traditional wet chemical methods. This was largely unsuccessful, with the exception of the production of $Hg(NSO)_2$, which was verified by i.r. and Raman spectroscopy and mass spectroscopy.

Reaction of $PtCl_2\ (PR_3)_2$ with $SeOCl_2$ in $NH_3(l)$ was also tried, in an attempt to produce a selenium analogue of the thionyl imide compounds. This was not successful.

Much Raman spectroscopic work was undertaken to try and expand upon the data previously published by authors such as Chivers and Lelieur, with respect to the species present in solutions of S, $SOCl_2$, SO_2Cl_2, S/Se and mixtures thereof in liquid ammonia. We were unfortunately unable to improve upon previously published work.

Contents

1. Introduction

1.1. Sulfur-Nitrogen (S-N) Chemistry

Sulfur-nitrogen chemistry has been a focus of attention for many years, the oldest known S-N compound being tetrasulfur-tetranitride (S_4N_4), which was initially discovered in 1895 [1],[2]. S-N compounds fall into three main categories; rings, chains and cages [3]; the planar rings being of greatest interest to theoreticians due to their pseudo aromatic character.

Complexes containing transition metals and S-N ligands, for example $MoCl_5$, S_4N_4 and $TiCl_4$, S_4N_4 have been known since the early part of the twentieth century [4]. Little progress in the characterisation of these compounds was made until the advent of X-Ray crystallography and since the 1970's there has been a considerable increase in interest in the chemistry of sulfur-nitrogen systems. Complexes between binary sulfur nitrides such as SN, S_2N_2 and S_4N_4 and metals may be thought of as Lewis acid-Lewis base adducts in which the ligand bonds to the metal via a nitrogen atom. Conversely sulphur imides, e.g.S_4N_4H exhibit attachment to the metal via a sulfur atom. The other main classes of S-N compounds are thiazyl halides (e.g. NSCl), sulfur nitrogen oxides (e.g. thionylimide anion, NSO^-) and cyclometallathiazines [4].

A great deal of interest has been placed in S-N compounds due to the conductivity and super-conductivity of S-N polymers and also because of their potential for use in non-linear optics[5].

Sulfur-nitrides have been studied for a long time. Many examples of this class of compound are known: they are categorised into two main types of structure:-

a) Cages (e.g. S_sN_6, $S_4N_5^-$)

b) Planar Rings (e.g.$S_3N_3^-$, $S_4N_3^+$) – these are of interest due to their pseudo aromaticity.

The compound generally considered as the most important is the cage-structured S_4N_4 (tetrasulfur tetranitride), which is the oldest and was first discovered in 1835.
4 Nitrogen atoms are planar, Sulfurs are arranged tetrahedrally around them.
This is most easily prepared by passing $NH_3(g)$ through a solution of SO_2 in CCl_4, the crude product is recrystallised from toluene forming orange crystals[6].

The precise electronic structure of the S_4N_4 molecule has been the subject of considerable debate for many years. Numerous semi-empirical and ab-initio M.O. calculations of varying levels of sophistication have been conducted. From these studies three main points arise which are broadly in agreement[7]:

The S-N bonds are polar, there is considerable bonding interaction between the transanular sulfurs and there is very little or no N-N bonding. Bonding between the transanular sulfurs is accepted because it arises from M.O. calculations and from the observed S-S distance of 2.58Å, which is less than the Van der Waals radii of sulfur. The N-S bonds are all equivalent, (1.62Å) which implies a certain degree of multiple bonding[8].

S_4N_4 is explosive; this is clearly a major disadvantage to its use as a synthetic reagent. It does, however, have the considerable advanges that it is inexpensive and easy to prepare, and it is non-toxic and soluble in many organic solvents. Due to its explosive

nature, care must be taken to avoid exposing it to either friction or extreme heat, most especially in it's pure form[9].

The importance of S_4N_4 as a synthetic reagent arises from its ability to behave as a precursor to numerous sulfur-nitrides via two types of reaction. One involves the retention of the initial eight atom structure, commonly combined with the addition of sulfur and/or nitrogen atoms to this structure. The other involves the molecule fragmenting into smaller ring structures. Examples of this type of reaction are shown in fig.1 below.

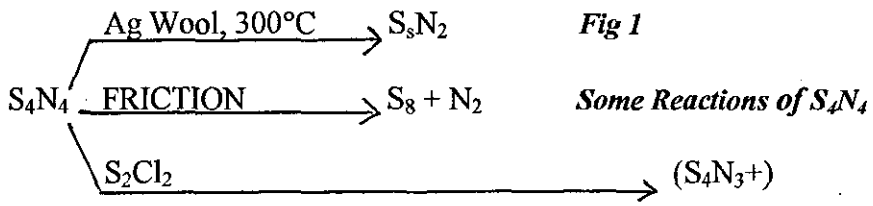


Fig 1

Some Reactions of S_4N_4

S_2N_2 has the ability to polymerise to an anisotropic metallic conductor and low temperature semi-conductor (SN_x)[10].

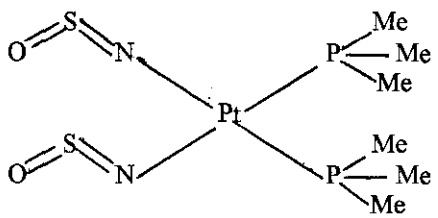
1.2 Liquid Ammonia Chemistry

The synthesis of mettalla-sulfur-nitrogen complexes presents the opportunity to stabilise S-N species which are otherwise unknown. It has been found that reacting $S(SNO)_2$ or $SOCl_2$ with cis-$MCl_2(PR_3)_2$, (where M = Pd^2 +, Pt^2 +, PR_3 = PMe_2Ph, PEt_3, PPh_2Me, dppe) yields complexes of the type $M(NSO)_2(PR_3)_2$. The cis co-ordination of the NSO^- ligands has been confirmed by x-ray crystallography and this technique also shows a local non-crystallographic C_2 symmetry for the molecule. This observation has proved difficult to reconcile with the somewhat complicated i.r. spectra of such

complexes [11,12,13]. The products were isolated in 60% yield. The reactions proceed according to equation 1 below.

$$PtCl_2(PR_3)_2 + S(NSO)_2 \longrightarrow Pt(NSO)_2(PR_3)_2 + SCl_2 \qquad \textbf{Equation 1}$$

The x-ray crystal structure of $Pt(NSO)_2(PMe_3)_2$ is shown in diagram 1 below [12].



Crystallographic data suggests a more ionic structure for M-NSO$^-$ as compared to R-NSO (R= organic group) with little or no $p\pi$- $d\pi$ overlap between the nitrogen and the metal centres [12].

Complexes of the type $M(S_2N_2H)_2$, $M(S_2N_2H_2)_2$ and $M(S_2N_2)_2$($M=Ni^{2+}$) have been synthesised by reaction of MCl_2 with $[S_4N_3]Cl$ in liquid NH_3. This reaction is not mechanistically understood, nor is it readily extended to other systems. If Palladium was used, an extra complex $Pd_2[S_3N_3]_2(S_3N_2)$ is produced, while if $M=Pt^{2+}$ the yields were found to be poor. Equation 2 below is the general equation for the reaction [12].

$$MCl_2 + S_4N_4 \longrightarrow \begin{cases} M(S_2N_2H_2)_2 \\ M(S_2N_2H)_2 \\ M(S_2N_2)_2 \end{cases} \qquad \textbf{Equation 2}$$

Mixed S-N/Phosphine complexes have been prepared by similar routes, but using metal-bis-phosphine dichlorides rather than metal dichlorides. Initially $[S_3N_3]Cl$ was reacted with $PtCl_2(PR_3)_2$ in liquid ammonia giving good yields of $Pt(S_2N_2)(PR_3)_2$, as described by Equation 3 below.

Equation 3

$$2[S_4N_3]Cl + 8NH_3 + 2PtCl_2(PR_3)_2 \longrightarrow Pt(S_2N_2)(PR_3)_2 + S_4N_4 + 6NH_4Cl$$

The reaction was also found to proceed well with Me_2SnCl_2 to give $[Me_2Sn(S_2N_2)]_2$ and with $NiCl_2$ or $[Ni(NH_3)_6]Cl_2$ to give $Ni(S_2N_2H)_2$. Further studies revealed SCl_2 also provides an appropriate source of sulfur for the preparation of $Pt(S_2N_2)(PR_3)_2$ in liquid NH_3 as shown in Equation 4.[14]

$$SCl_2 + 8NH_3 + PtCl_2(PR_3)_2 \longrightarrow Pt(S_2N_2)(PR_3)_2 + 6NH_4Cl \qquad \textbf{Equation 4}$$

These reactions may be extended to incorporate the synthesis of complexes containing $Se_2N_2^{2-}$, for example $Pt(Se_2N_2)(PMe_2Ph)_2$.[11,12,15] Although in the case of this particular compound it is necessary to heat the liquid NH_3 solution containing the reagents (Se_4N_4 and $PtCl_2(PMe_2Ph)_2$) to 70°C in a pressure tube. [15]

$Pd(L-L`)(S_2N_2H)$ and $Pt(S_2N_2)(PR_3)_2$ complexes have been synthesised by the reaction of $[S_4N_3]Cl$ with $PdCl_2Pd(L-L`)$ (where L – L` = monoionic C – N bidentate ligand) or $PtCl_2(PR_3)_2$ in liquid NH_3 [11,16] . These two compounds were found by X-ray crystallography to have square planar geometry. Woolins *et al* [16] also used ^{14}N nmr spectroscopy to reveal that the NH_3 solution of $[S_4N_3]Cl$ and $[S_3N_2Cl]Cl$ used in their preparation contained the $S_3N_3^-$ anion, whilst solutions of S_4N_4 contain $S_3N_3^-$ and

$S_4N_5^-$.[16] It was found that the thionitrosone complex could be readily prepared by protonating the metal-bound nitrogen of $Pt(S_2N_2)(PR_3)_2$ complexes using HBF_4 or HCl as shown in Equation 5.

$$Pt(S_2N_2)(PR_3)_2 + HX \longrightarrow [Pt(S_2N_2H)(PR_3)_2]X \qquad \textbf{Equation 5}$$

The reaction of sulphamide or SO_2Cl_2 with $PtCl_2(PR_3)_2$ (PR_3 = PMe_2Ph, $PMePh_2$, PPh_3, PEt_3, or ½ dppe) in liquid ammonia has also been studied and found to yield $Pt[(HN)_2SO_2](PR_3)_2$, which has the structure shown in Diagram 2.

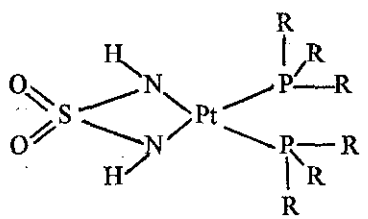


Diagram 2. Structure of $Pt[(HN)_2SO_2](PR_3)_2$

The $[O_2S(NH)_2]_2^-$ ligand is isoelectronic with SO_4^{2-}.

The reaction of $SOCl_2$ with $[TiCl_2(C_5H_5)_2]$ or $[PtCl_2(PR_3)_2]$ has been found to yield $[Ti(NSO)_2(C_5H_5)_2]$ and $[Pt(NSO)_2(PR_3)_2]$ respectively with ca. 60% yield [13] and the compound $S_4N_4O_2$ has been found to react with $[MCl_2(PR_3)_2]$ to yield $[Pt\{S_2N_3(SO_2NH_2)\}(PR_3)_2]$ (M = Pt,PR_3 = PMe_2Ph, PEt_3, PPr_3^n or PBu_3^n, M = Pd, PR_3 = ½ dppe) in 40% yield. The reaction of $S_4N_4O_2$ with NH_3 (l) produces $S_3N_3^-$ (which decomposes to $S_2N_2^{2-}$) and the concentration of $S_3N_3^-$ increases with time, which leads to the production of the complexes $[Pt(S_2N_2)(PPh_3)_3]$ and $[Pt(S_2N_2)(dppe)]$ as the

solutions warm up. This is because the starting materials for these two products have only low solubility in NH_3 at -78°C, but as the temperature rises they become more soluble and the production of the $S_2N_2^{2-}$ complexes is favoured because of the increasing time period[13].

Very few examples of complexes of Platinum containing di-imido ligands are known. These ligands are isoelectronic with di-thiolenes and may be of interest, from the point of view of preparing stacking compounds. On the basis of this, Woollins *et al* reacted *o*-$(NH_2)_2C_6H_3$-4-NO_2 with $PtCl_2(PR_2)_2$ in liquid NH_3, producing $Pt\{(NH_2)C_6H_3$-$NO_2\}(PR_3)_2$ (PR = PEt_3, PMe_2Ph, PPh_2Me or ½ dppe) in 80% yield. The complexes were characterised by ^1H and ^{31}P nmr, UV-vis, mass spectrometry, micro-analyses, and for PR_3 = PMe_2Ph, by X-ray crystallography with the anticipated square-planar geometry at Pt. The products were sensitive to hydrolysis and weak acids, showing a gradual deterioration to the free ligand and $PtCl_2(PR_3)_2$ in dichloromethane solutions.[17]

Recently, Selenium-Nitrogen compounds have become the focus of much attention. The reaction of $[Se_2N_2S]_2Cl_2$ with *cis*-$[PtCl_2(PR_3)_2]$ in liquid NH_3 was shown to produce $[Pt(SeSN_2)(PR_3)_2]$ in 70% yield. This compound may also be produced by heating a mixture of $[S_4N_3]$Cl-$SeCl_4$ (or Se_2Cl_2) with $PtCl_2(PR_3)_2$ in liquid NH_3. It has been hypothesised that in the $[S_4N_3]$Cl-$SeCl_4$ reactions the initial step is the formation of an anion such as $S_3N_3^-$ which may undergo nitrogen exchange with those of liquid NH_3. The anion is in equilibrium with short chained species such as N_2S^{2-} and S_2N^-, *which may then react to form mixed Se-S-N anions and cations, which then* subsequently react to form compounds such as $[Pt(SeSN_2)(PEt_3)_2]$. It is interesting to

note that with the $SeSN_2^{2-}$ ligand the only product observed is the one bound by the Se. The reaction of $SeCl_4$ with $[PtCl_2(PR_3)_2]$ (PR_3 as previously mentioned) produces $[Pt(Se_2N_2)(PR_3)_3]$ in yields varying between 24 – 74%. [18]

The complex $NH_4[S_4N_5)]$ was produced as water-soluble yellow crystals from reaction of thionyl chloride with liquid NH_3 and subsequent hydrolysis of the products. The i.r. and mass spectra of the products suggested an unusual cage structure for the $S_4N_5O^-$ anion, Steudel *et al* carried out a single crystal X-ray structure of $NH_4[S_4N_5O]$. This revealed that two neighbouring ions, NH_4^+ and $S_4N_5O^-$ are joined by an O-H hydrogen bridge and are placed upon a common mirror plane. The NH_4^+ ion is bonded to a further two anions by two N-H hydrogen bridges. Just one of the four H atoms of the NH_4^+ ion is not involved in hydrogen bridging, and the cation is not therefore, tetrahedral in structure, but is strongly deformed with three different N-H nuclear separations.[19]

Synthetic Liquid Ammonia Chemistry

Liquid ammonia has significant advantages as a solvent for reactions of a range of S-N and Sulfur halides; they are:- (i) it is commercially available at relatively low cost and in a very highly pure state, (ii) inorganic metal salts and starting materials are readily dissolved in it, and (iii) it may also act as a source of N atoms in the final molecule.[14]

The earliest example of a reaction in liquid ammonia was the synthesis of $Pb(NH_3)(S_2N_2)$ in 1904, as reported by Ruff and Geisel [20]. The reaction involved reacting PbI_2 with S_4N_4 in $NH_3(l)$, as shown in equation 6. below, and indicated that dissolution of S_4N_4 on liquid ammonia might act as a source of S-N anions. The

structure of $Pb(S_2N_2)(PCl_5)$ was established by Wein in 1966 using simple crystal X-Ray studies. [3]

$$PbI_2 + S_4N_4 \xrightarrow{Liq.NH_3} Pb(NH_3)(S_2N_2) \qquad \textbf{Equation 6.}$$

The majority of S-N species are also known to dissolve in liquid ammonia, yielding reactive solutions therein. Early work by Woollins *et al* [4] showed that $[S_4N_3]Cl$ and $[S_3N_2Cl]Cl$ were highly efficient sources of the $S_2N_2^{2-}$ anion. The species involved in these solutions were generally found to be a combination of $S_3N_3^-$ and / or $S_4N_5^-$. [5] It was subsequently found that SCl_2 provides an appropriate source of sulfur for the synthesis of compounds of the type $Pd(S_2N_2)(PPh_3)_2$, and the use of a preformed S-N compound for these reactions was unnecessary. As illustrated in equations 7 and 8 below.

$$2(S_4N_3)Cl + 8NH_3 + 2PtCl_2(PR_3)_2 \rightarrow Pt(S_2N_2)(PR_3)_2 + S_4N_4 + 6NH_4^+ \qquad \textbf{Equn.7.}$$

$$2\,SCl_2 + 8NH_3 + PtCl_2(PR_3)_2 \rightarrow \quad Pt(S_2N_2)(PR_3)_2 + 6NH_4Cl \qquad \textbf{Equn.8.}$$

Addition of $PtCl_2(PR_3)_2$ to solutions containing these anions yields products of the type $Pt(S_2N_2)(PR_3)_2$. [5] Earlier work had shown that salts such as (a) $Na[S_3N_3]$ or (b) $Na[S_4N_5]$ react in a not dissimilar way, as illustrated in equation 9 below. [12] However, neither of these starting materials is satisfactory as (a) is explosive in its own right, and (b) is obtained from the highly explosive S_4N_4. [14]

$$2\,Na(S_3N_3) + PtCl_2(PR_3)_2 \rightarrow Pt(S_2N_2)(PR_3)_2 + S_4N_4 \qquad \textbf{Equation .9.}$$

Platinum dichloro-bis-phosphines are particularly efficaceous reagents in entraining the species formed in $NH_3(l)$. In this class of reaction, the capabilities of $NH_3(l)$ to act as the lone source of nitrogen, this is of importance since it facilitates the generation, in situ, of useful anions, from starting materials such as sulfur dichloride and thionyl chloride (SCl_2 and $SOCl_2$). The reaction of $SOCl_2$ with $NH_3(l)$ produces the thionylimide anion (NSO^-), which will react with species such as $PtCl_2(PR_3)_2$ to yield complexes of the type $Pt(NSO)_2(PR_3)_2$, [13] as illustrated in equations 10 and 11. Typically reactions involve dissolving 1m mol of the appropriate S-N species or S/Se species in 15ml $NH_3(l)$ followed by 1m mol of $PtCl_2(PR_3)_2$, stirring at -78°C and gradually warming to room temperature, during which time the ammonia evaporates off, the resulting solid is then extracted with an appropriate organic solvent such as CH_2Cl_2 to yield the metal complex. [1]

$$SOCl_2 + NH_3(\ell) \rightarrow NSO^- + S_4N_4 + NH_4^+ \qquad \textbf{Equation .10.}$$

$$PtCl_2(PR_3)_2 + 2NSO^- \rightarrow Pt(NSO)_2(PR_3)_2 + 2Cl^- \qquad \textbf{Equation.11.}$$

The species $Pt(NSO)_2(PR_3)_2$ are readily extracted from the reaction residue in CH_2Cl_2 after removal of $NH_3(l)$.

Similarly , SO_2Cl_2 (sulfuryl chloride) is known to react with $NH_3(l)$ to produce the sulfamide anion ($SO_2(NH)^-_2$), which will subsequently react with the above-mentioned $PtCl_2(PR_3)_2$ to produce complexes of the type $Pt(SO_2(NH)_2)(PR_3)_2$.

Many anions that are stabilised by co-ordination are otherwise not known. Numerous metalla-sulfur-nitrogen complexes with ligands from monodentate thionitrosyl NS, through tridentate $S_2N_2^{2-}$, S_3N^-, $S_3N_2^{2-}$ to tridentate $S_4N_3^-$ and $S_4N_4^{2-}$ have been

previously documented. Most of the previously reported syntheses entail reactions of sulfur-nitrogen halides or S_4N_4, such reactions frequently proceed in good yield, but are seldom mechanistically explicable. A fundamental problem with using S_4N_4 as a starting material is its explosive nature which clearly makes it somewhat unsuitable as a starting material unless stringent safety precautions are complied with. [1]

Complexes of the type $[Pt(S_2N_2H)(PR_3)_2]X$ (X = Halide) are particularly interesting because they form stacking structures in the solid state.

Metalla-sulfur-nitrogen compounds are of interest because the metal centres stabilise S-N anions which are otherwise unknown. Most synthetic routes involve a number of steps, frequently including isolating one or more S-N precursors. Woollins *et al* [13] developed simple one-pot synthetic routes to various metalla-chalcogen-nitrogen complexes that depend neither on the separation of any S-N or S-N-O starting materials or any special handling requirements. They were also able to apply the approach to the synthesis of the first examples of complexes incorporating the bidentate $[O_2S(NH\}_2]^{2-}$ or $Se_2N_2^{2}$ ligands as illustrated in equations 12 and 13 below.

$SO_2(NH_2)_2 + 2NH_3(\ell) + PtCl_2(PR_3)_2 \rightarrow Pt[(HN)_2SO_2](PR_3)_2 + NH_4Cl$ **Equation.12.**

$2\ SeCl_4 + 8NH_3(\ell) + PtCl_2(PR_3)_2 \rightarrow Pt(Se_2N_2)(PR_3)_2 + 6NH_4Cl + 2Cl_2$ **Equation.13.**

The sulfur halide or organic halide (between 1 – 2 mmol.) is carefully added to $NH_3(l)$ at -78°C and stirred for 30 minutes, after which $PtCl_2(PR_3)_2$ is added and the reaction is then allowed to warm to ambient temperature, with the NH_3 being blown-off under a stream of nitrogen. The final products were acquired by recrystallisation from CH_2Cl_2

/ petroleum ether, with yields ranging from 50 – 75%. The molecule $Pt[(HN)_2SO_2](PPh_2Me)_2$ was found by X-Ray analysis to have the anticipated square planar geometry, with Pt-P and Pt-N bond lengths typical for Pt^{II}. The PtN_2S ring was found to be essentially planar (max. deviation 0.3Å), the oxygen atoms lying equidistant above and below the plane. Both S and N atoms are pyramidal.

The reaction of $SO_2(NH)_2$ or SO_2Cl_2 with $[PtCl_2(PR_3)_2]$ in $NH_3(l)$ gives $[Pt\{SO_2(NH)_2\}(PR_3)_2]$ (where PR_3 = PMe_2Ph, $PMePh_2$, PPh_3, PEt_3 or ½ $Ph_2PCH_2CH_2PPh_2$) in yield of ca 70% isolated.

When $SOCl_2$ was reacted in $NH_3(\ell)$ with $[TiCl_2(C_5H_5)_2]$ or $[PtCl_2(PR_3)_2]$ it gave products of the type $[Ti(NSO)_2(C_5H_5)_2]$ and $[Pt(NSO)_2(PR_3)_2]$ respectively in ca 60% yield.$S_4N_4O_2$ was found to react with $[MCl_2(PR_3)_2]$ in liquid ammonia to give $[M\{S_2N_3\}(PR_3)_2]$ (where M = Pt, PR_3 = PMe_2Ph, $PMePh_2$, PEt_3, PPr_3 or PBu_3; M = Pd, PR_3 = ½ $Ph_2PCH_2CH_2PPh_2$) in 40% yield.

Reaction of $S(NSO)_2$ in liquid ammonia has also been shown as a synthetic route to complexes of the type $Pt(NSO)_2(PR_3)_2$. The ^{14}N nmr spectra of solutions of $S(NSO)_2$ and $SOCl_2$ in $NH_3(l)$ show the same peak associated with the NSO^- ion (500ppm). This indicated that $SOCl_2$ might be used instead of $S(NSO)_2$ in synthesising [Pt $(NSO)_2$] complexes.Manipulations are all carried out in an inert nitrogen atmosphere and all solvents dried prior to use.Reaction of SO_2Cl_2 or $SO_2(NH_2)_2$ with $[PtCl_2(PR_3)_2]$ in $NH_3(l)$ gives $[Pt\{SO_2(NH)_2\}(PR_3)_2]$ as shown in equation 14.

$$SO_2(NH_2)_2 + [PtCl_2(PR_3)_2] + 2NH_3 \rightarrow 2NH_4Cl + [Pt\{SO_2(NH)_2\}(PR_3)_2]$$

Equation.14.

The sulfuryl chloride acts as an insitu source of $SO_2(NH_2)_2$, see equation 15.

$SO_2Cl_2 + NH_3 \longrightarrow NH4Cl + SO_2(NH_2)_2$ **Equation .15.**

The reaction proceeds cleanly with isolated yield of ca 80%.

Compounds of the type $[Pt\{SO_2(NH)_2\}(PR_3)_2]$ are isoelectronic with the well-known sulphate complex $[Pt(SO_4)(PR_3)_2]$. Reacting $N_2[NHSO_2\ C_6H_4Me]$ or NH_2SO_2Ph with $PtCl_2(PR_3)_2$ was found to give $[Pt(NHSO_2R`\}_2(PR_3)_2]$ (R` = Ph or $C_6H_5Me\}$ in yield. *(ca 38 – 40%) and the* ^{31}P *nmr shifts were found to be similar to those of the products* of type $Pt\{SO_2(NH\}_2\}(PR_3)_2$. This is to be expected since both sets of species are nitrogen donors on a Pt (II) centre with effectively the same co-ordinated groups $((NH)_2SO_2$ and $(NHSO_2R)_2)$[13].

Woollins *et al* [22] have reported on ^{14}N nmr investigations into the nature of the interaction between $NH_3(l)$ and $[S_3N_2Cl]$ (1), $[S_4N_3]$ Cl (2) and S_4N_4 (3).

$NH_3(l)$ solutions of (1) or (2) have a ^{14}N nmr Spectrum consisting of signals due to liquid ammonia plus a further resonance at 147ppm. When (3) is dissolved in $NH_3(l)$ the spectrum is composed of a large peak at 147ppm and two smaller peaks at 51 and 137ppm as well as a series of weaker signals at higher chemical shifts. The major species in the solutions were unequivocally identified as $S_3N_3^-$ and $S_4N_5^-$ by comparison of the ^{15}N chemical shifts reported for these ions in solution in $CHCl_3$. (S 143.4 and 138.7, 53.3ppm respectively) and $[PPh_4][S_3N_3]$ in CH_2Cl_2 (S 146ppm). It is

thought likely that the weak signals are due to $S_2N_2^{2-}$, S_4N^- and S_3N^-, which are present at low concentration in equilibrium with the $S_3N_3^-$ anion.

Spectral acquisition was straightforward and facilitated measurements on solutions of (2) and (3) at various time intervals and temperatures; freshly prepared solutions that were not warmed beyond -40°C contained $S_3N_3^-$ alone, and warming to room temperature in 10°C increments (spectra rec. every 10min, req. ca 5 min. acquisition time) and standing for 24 hours, no significant change was observed. From the nmr data, equilibrium of the type shown on equations 16 and 17 below were proposed.

$$S_3N_3Cl + NH_3 \rightleftharpoons S_3N_3^- + 3H^+ + Cl^- \qquad \textbf{Equation .16.}$$

$$7S_4N_3^+ + 6NH_3 \rightleftharpoons 9S_3N_3^- + H_2S + 16H^+ \qquad \textbf{Equation.17.}$$

No change in the amounts of $S_4N_5^-$ and $S_3N_3^-$ was detected with time.

Dissolution of $[S_3N_2]Cl$ or $[S_4N_3]Cl$ in $NH_3(\ell)$ at -78°C caused the formation of a purple-red solution [13]. When these solutions were treated with $[PtCl_2(PR_3)_2]$ or L'(L-L')$PdCl_2$Pd(L-L')] (L- L' = C-N ligand) yields $[Pt(S_2N_2\}(PR_3)_2]$ and $[Pd(S_2N_2H)$(L-L')] respectively, and in certain cases complexes containing the S_3N^- ligand were also obtained. The reaction of S_8-NH_3(l) solutions with $[PtCl_2(PR_3)_2]$ was found to yield $[PtS_4(PR_3)_2]$.

When simple S_8 or simple S-N species are dissolved in NH_3(l) a complex set of equilibria are involved. It is believed that when sulfur is dissolved in liquid ammonia the following ions are formed:- S_7N^-, S_4N^-, S_3N^-, S_6^{2-}, and S_4^{2-}, which upon work up yield sulfur imides such as S_7NH and $S_6(NH)_2$. Dissolution of S_4N_4 or $(NSCl)_3$ in NH_3(l) have been found to yield $[NH_4][S_4N_5]$ after work up; and it was reported by

Goehring in 1957 that upon evaporation of NH_3 solution $[S_4N_3]Cl$ yields an explosive brown solid.

It has been found that if $NH_3(l)$ solutions of $[S_3N_2Cl]Cl$ are evaporated to dryness and extracted into THF, then a reactive intermediate suitable for the preparation of compounds of the type $[Pt(S_2N_2)(PR_3)_2]$ is formed. In addition to this type of compound, $Pb(S_2N_2\}\ NH_3$ has been prepared from $Pb(NO_3)_2$ and S_4N_4 in $NH_3(l)$ and $[(H_3N)\text{-}HgSN_2]_2$ has also been synthesised from reaction of S_4N_4 with HgI_2 with $NH_3(g)$ in chloroform.

In the preparation of compounds such as $[M(S_2N_2)(PR_3)_2]$ from reactions on $NH_3(l)$, $[S_4N_3]Cl$ (0.037g, 0.15mml) was added to $5cm^3$ $NH_3(l)$ at -78°C and the appropriate $[MCl_2(PR_3)_2]$ complex was added and the mixture stirred for 30 minutes at -78°C. (M = Pt, Pd). Subsequently the reaction mixture was allowed to warm to room temperature and the ammonia blown-off under a stream of nitrogen. The resulting brown solid (for Pt complex) was extracted with $CHCl_3$, filtered through celite and purified by preparative t.l.c. on silica using CH_2Cl_2 as eluent. 0.07mml S_4N_4 and 0.11mml of complex were typically separated. The Pd complexes were a red-brown coloured solid. They were prepared by a similar procedure [13].

Equation 18. below partially represents the reaction that occurs between $[S_4N_3]Cl$ or $[MCl_2(PR_3)_2]$ in liquid ammonia [13].

$$[[S_4N_3]Cl + NH_3(\ell) + [MCl_2(PR_3)_2] \rightarrow [M(S_2N_2)(PR_3)_2] + S_4N_4$$

Equation.18.

A considerable amount of S_4N_4 is formed, but the amount isolated doesn't correspond to a simple stoichiometric reaction. It is not thought that S_4N_4 is an intermediate in these reactions since if S_4N_4 in $NH_3(l)$ is treated with $[MCl_2(PR_3)_2]$ under similar reaction conditions to those above, some $[M(S_2N_2)(PR_3)_2]$ is formed, but the reaction is much slower. If, however, S_4N_4 is permitted to react at -33°C (bpt. of NH_3} for two hours prior to adding cis-$[PtCl_2(PR_3)_2]$ then $[Pt(S_2N_2)(PR_3)_2]$ is formed quantitatively according to ^{31}P nmr spectroscopy. This suggests that there is a slow reaction between $NH_3(l)$ and S_4N_4 and ^{14}N nmr studies of the $NH_3(\ell)$ solution infer that the reactive species in the solution is $S_3N_3^-$ [13].

The ease of reaction 18 led to the extension of its use to the synthesis of mixed-ligand Palladium complexes containing S-N ligands by use of dimeric chloro-bridged [(L-L')$PdCl_2$Pd(L-L')] complexes as starting materials. The major difference between the products obtained from phosphine complexes and the organometallic palladium complexes is that the latter contains the protonated $S_2N_2H^-$ ligand rather than $S_2N_2^{2-}$ [13].

Woollins *et al* [23] reported the synthesis of $[Pt(PMe_2R)_2(\mu\text{ - }NH_2)_2\ Pt(PR_3)_2]\ (BF_4)_2$ from the reaction of liquid ammonia solutions and $[S_3N_2NH_2]BF_4$ with metal centres of the type $PtCl_2(PR_3)_2$. Further investigations did, however, lead to the conclusion that $[Pt(PMe_2Ph)_2(\mu\text{ - }NH_2)_2\ Pt(PMe_2Ph)_2]\ (BF_4)_2$ was in fact produced from the reaction between $PtCl_2(PR_3)_2$ and $NH_3(l)$. $[S_3N_2NH_2]BF_4$ was produced by reaction between $PtCl_2(PR_3)_2$ with a slight excess of sodium in liquid ammonia prior to the addition of the platinum salt. Compounds with phosphine groups PMe_3, PMe_2Ph, $PMePh_2$, PEt_3

and ½ $Ph_2PCH_2CH_2PPH_2$ with Pt metal centres and with M = Pd with PR_3 = ½ $Ph_2PCH_2CH_2PPH_2$ were isolated in greater than 80% yield [21].

In a typical reaction HBF_4 . $2Et_2O$ (0.11 mml) was added dropwise, with caution, to $5cm^3$ $NH_3(l)$. At -78°C, followed by 0.13 mml Na, generating a dark blue solution. Subsequently 0.08 mml $MCl_2(PR_3)_2$ was added and the resulting brown-blue suspension stirred at -78°C for half an hour. The reaction was then allowed to warm to room temperature and the ammonia evaporated under nitrogen, yielding a white solid which was extracted with $5cm^3$ CH_2Cl_2, removal of which in vaccuo yielded $[M(PR_3)_2(\mu - NH_2)_2M(PR_3)_2] (BF_4)_2$ (0.03mml, 80%). Very few binuclear amido-bridged Pt complexes have been reported. It was reported in 1967 that the reaction of *cis*-$PtCl_2(PPh_3)_2$ with hydrazine crystals yields crystals that are a mixture of $[(Ph_3P)_2 Pt(NNH)_2Pt(PPh_3)_2]^{2+}$ and $[(Ph_3P)_2Pt(NH_2)_2Pt(PPh_3)_2]^{2+}$. The reaction between $PtCl_2$ dppm (dppm =$Ph_2P(CH_2)_2PPh_2$), NaOH and $NH_3(l)$ was found to yield an uncharged NH_2 – bridged species $[(Ph_2Me)P(Ph_2PO)Pt(NH_2)_2Pt(PCO)Ph_2)(PMe_2Ph_2)]$ [23].

It was concluded that producing $[M(PR_3)_2(\mu - NH_2)_2M(PR_3)_2] (BF_4)_2$ **(a)** is very pH dependent; since adding BHF_4 to $NH_3(l)$ and titrating with Na until there was a slight excess of Na followed by $PtCl_2(PR_3)_2$ produced **(a)** in high yield, whereas direct addition of $NaBF_4$ in $NH_3(\ell)$ were unsuccessful. The reaction is illustrated by equation 19 below:-

2 *cis*-$PtCl_2(PR_3)_2$ + Na NH_2(trace) + 2Na BF_4 $\underline{NH_3(l)...}$ $[(R_3P)_2Pt(NH_2)_2Pt(PR_3)_2] (BF_4)_2$

Equation .19.

The location of protons on bridging N atoms in the crystal structure confirmed that the cation is a bis-amido bridged species. There was found to be no H-bonding interaction between the amido groups and the BF_4^- counterions.

Di-imido ligands are isoelectronic with dithiolene and hence are of interest with respect to the possible synthesis of starting compounds. Reacting 0 - $(NH_2)_2C_6H_3$ - 4 - NO_2 with $PtCl_2(PR_3)_2$ in $NH_3(l)$ was found to yield bis-imido complexes of the type $Pt\{(NH)_2C_6H_3NO_2\}(PR_3)_2$ (where PR_3 = PEt_3, PMe_2Ph, PPh_2Me, ½ dppe) (ca 80% isolated). [14] The products of the reaction between p-nitro - o - phenylenediamine with *cis* – $PtCl_2(PR_3)_2$ contain the doubly deprotonated dianion $[p - O_2NC_6H_3(NH]_2]^{2-}$ as a ligand in simple platinum (II) complexes. The products were characterised by ^{31}P and ^1H nmr, IR, UV – Vis, mass spectrometry, microanalyses, and in the instance where PR_3 = PMe_2Ph, by X-Ray crystallography [24].

The reaction typically involved dissolving 4 – nitro – o – phenylmediamine (0.16mmol.) in $NH_3(\ell)$ at -78°C, producing a red solution, to which $PtCl_2(PR_3)_2$ (0.1mml) was added. This slurry was subsequently stirred for 30 minutes at -78°C and the ammonia was then allowed to evaporate under a blanket of nitrogen as the solution slowly warmed to room temperature, yielding a black-purple solid. This was purified by extraction with CH_2Cl_2 followed by filtration through a celite/glass wool plug and passage down a Biobead (SX – 8) column with CH_2Cl_2 as eluent. The product, $Pt\{(NH)_2C_6H_3NO_2\}(PR_3)_2$ was obtained from the eluted purple band after solvent was removed in vacuo. Crystals suitable for X-ray analysis were obtained by slow diffusion of hexane into a CH_2Cl_2 solution of $Pt\{(NH)_2C_6H_3NO_2\}$ $(PMe_2Ph)_2$ [24].

If a solution of 4 - nitro – 0 – phenylene diamine (1) in liquid ammonia is reacted with $PtCl_2(PR_3)_2$, the following (equn. 20) occurs:-

$$O_2NC_6H_3(NH_2)_2 + PtCl_2(PR_3)_2 \xrightarrow{NH_3(l)} Pt\{(NH)_2C_6H_3NO_2\}(PR_3)_2 + 2\ NH_4Cl$$

Equation.20.

It is likely that in the course of the reaction (1) is deprotonated by ammonia to form an anionic species. This is suggested by the fact that the colour of the solution changes, however, Woollins *et al* could present no strong evidence for this. It is presumed that a singly charged anion is produced which forms a hitherto unobserved intermediate which eliminates HCl to yield the product. [24]

The metal chalcogenides ME (M = Ca, Sr, Ba, En, Yb, Ni, Zn, Cd, Hg, Sn or Pb; E = S, Se or Te) were produced by reaction of the aforementioned chalcogenides and elemental metals in liquid ammonia in pressure vessel at room temperature.

Ag_2E and solid solutions of mixed-metal chalcogenides MxMyEz ($x+y = 1$, $z = 1$ or 2) and metal-mixed chalcogenides MSxSey. The products were characterised by FTIR, Raman spectroscopy, scanning electron microscopy (SEM), electron microscopy. X-Ray photoelectron spectoscopy, elemental analysis and magnetic susceptibility studies.

Amorphous and crystalline binary metal chalcogenides were found to be produced by the reaction of some elemental metals with sulfur-selenium or tellurium – ammonia solutions at room temperature and elevated pressure (ca 7 atmospheres). How facile the reaction is depends upon the metal but is most greatly favoured by late-transition

and main-group metals. The reactions proceed by direct combination of the elements, using a liquid in which the elements need not be soluble. The products formed were found to be highly pure. Crystallinity was induced in the X-Ray amorphous materials by heating at 250 - 300°C for two hours, whilst this did not generally alter the composition of the products. It was also possible to produce a variety of ternary solid solutions, with respect to both mixed-metal and mixed-chalcogenide materials [25].

Caesium ozonide was used by Korber and Jansen [26] to initiate an anion exchange reaction in anhydrous liquid ammonia, yielding for the first time solutions of LiO_3 and NaO_3. It was not, however, possible to precipitate any solid LiO_3 or NaO_3. When the solvent was removed, the ozonide anion oxidises the ammonia, and results in the precipitation of LiOH and NaOH respectively. This is markedly different from the behaviour of solutions of HO_3, RbO_3 and CsO_3. The existence of the Li and Na ozonides in solution was proved by complexing the cations and yielding solid $(Li[2.1.1]O_3$ on $(Na[2,2,2])_3$; crystallographic analysis of these ionic solids revealed that they contain the V-shaped O_3^- anion.

Jensdottir and Klar [27] have reported the use of liquid ammonia as a solvent for cobalamins in the preparation of anhydrous ammin – and cyanocobalamin and in the synthesis of alkynylcobalamins. The only previously prepared example of an alkynylcobalamin was ethynylcobalamin, was synthesised using bromoethyne as a source of the ligand. Reactions with cobalamins are usually performed in aqueous solutions, in which alkynyl anions cannot be handled. Liquid ammonia is, however, a very good solvent for these anions, and since $NH_3(l)$ is not dissimilar to water, it would

be expected to be a suitable solvent for cobalamins. Cobalamins were found to dissolve readily in $NH_3(l)$ and it was also found that by repeatedly condensing and evaporating the ammonia, water of crystallisation could either be completely removed or considerably removed from the compounds.

If aquacobalamin ($[Cbl - CH_2] + Cl^{\cdot}. 17H_2O$) was subjected to these reaction conditions, it was found that as well as the solvate water being removed, the axial aqua ligand was also substituted by ammonia, producing ammincobalamin ($[Cbl - NH_3]^+ Cl^- .½ NH_3.H_2O$). The partially anhydrous ammincobalamin was found to be very suitable for the synthesis of alkynylcobalamins. The axial ligand in ammincobalamin (NH_3) and in alkynylcobalamins (H_2O) are both good leaving groups, but they are however different in their acidity. Water, unlike ammonia, protonates alkynyl anions. The known [28, 29] ethynyl and previously unknown phenylethynylcobalamin were synthesised in liquid ammonia from ammincobalamin and the respective alkynyl anions by a simple displacement reaction.

The nitrito-nitro linkage isomerisation reaction of pentammine cobalt (IV) in $NH_3(l)$ is known to proceed via a wholly intramolecular conjugate-base mechanism. [30] The reaction is entirely retentive and Balt *et al* [30] found that the penta-ammine (nitro) cobalt (IV) complex was the only species detectable by proton nmr after completion of the reaction. It was recently reported by Jackson *et al* [31] that the isomerisation reaction is subject to base catalysis, via a conjugate bare mechanism, with the actual isomerisation being intramolecular in nature. The reaction in liquid ammonia was expected to proceed by the same mechanism, and evidence to support this came from the identification of the end product of the reaction, which was found to be wholly

penta-ammine (nitro) cobalt (IV), having the same structure as the starting material. The presence of the linkage isomer was monitored during the reaction by UV spectroscopy at 325nm and 520nm. The activation parameters of the rate determining step gave further evidence to support this. The bond to the NO_2^- ligand is still considerably present in the transition state, this is implied due to the intramolecular retentive mechanism of the reaction. The reaction may be represented by the equations 21, 22, and 23below.

$$[Co(NH_3)_5(ONO)][ClO_4]_2 + NH_3 \rightleftharpoons^{K1} [CO(NH_3)_4(NH_2)(ONO)]ClO_4 + NH_4ClO_4$$

Equation.21.

$$[Co(NH_3)_4(NH_2)(ONO)]ClO_4 \rightleftharpoons^{K2} [Co(NH_3)_4(NH_2)(NO_2)]ClO_4$$

Equation.22.

$$[Co(NH_3)_5(NO_2)][ClO_4]_2 + NH_3 \rightleftharpoons^{K3} [Co(NH_3)_5(NO_2)]ClO_4 + NH_4ClO_4$$

Equation.23.

The substantial presence of the NO_2^- ligand in the transition state is seen in the entropy of activation for K_2 (29 JK^{-1} mol^{-1}). If this value is compared to that of, for example, the ammoniation reaction of the penta-ammine (nitrate) cobalt (III) complex (139 $JK^{-1}mol^{-1}$), the absence of the increase in entropy because of the loss of the leaving group in the former reaction is profoundly obvious.

Iron (II) thiocyanate is known to dissolve in $NH_3(l)$, forming the ammines $Fe(NCS)_2 \cdot 8NH_3$, $Fe(NCS)_2 \cdot 7NH_3$ and $Fe(NCS)_3 \cdot 5NH_3$, which subsequently evolve ammonia at room temperature and from the diammine $Fe(NCS)_2(NH_3)_2$ which is tetragonal in structure and has thiocyanate bridges. Iron (II) bromide also dissolves in liquid ammonia, but with only partial ammonolysis. When iron (II) bromide or these

compounds are reduced with potassium or caesium in ammonia solutions of appropriate alkali metal cyanides, cyanometallates are produced. These reactions were investigated by Nicholls *et al* [32]. The only product they were able to isolate in the pure state was $Cs_4Fe(CN)_4$, and found that in an ammonia solution of ammonium cyanide it is oxidised to $Cs_4[Fe(CN)_6]$.

Although the range of metal carbonyl chemistry is considerable, the only compounds containing transition metals in the zero oxidation state that are bonded to the cyanide ion have been prepared from solutions of alkali metals in liquid ammonia. Potassium tetracyanonickellate ($K_4Ni(CN)_4$) was the first of these to be isolated, and was isolated by Eastes and Burgess [33] in 1942, and many other cyanometallates (O) containing transition elements have subsequently been synthesized, for example $K_4Ti(CN)_4$ [34] and $K_2V(CN)_2 \cdot O.SNH_3$ [35]. Low oxidation state cyanides have now also been isolated for all of the first row transition elements with the exception of iron and copper.

Iron (II) thiocyanates in $NH_3(l)$ at -36°C yields a brown solution. The dissolution of $Fe(NCS)_2 \cdot 8NH_3(s)$ in $NH_3(l)$ involves the dissolutions shown in equations (24) and (25) below:-

$$Fe(NCS)_2 \cdot 8NH_3(s) \rightleftharpoons Fe(NCS)_2 \cdot 7NH_3(s) + NH_3(g)$$

Equation.24.

$$Fe(NCS)_2 \cdot 7NH_3(s) \rightleftharpoons Fe(NCS)_2 \cdot 5NH_3(s) + 2NH_3(g)$$

Equation.25.

The enthalpies of the dissolutions were calculated to be 34.9 and 85.9 $kJmol^{-1}$, using the varit Holt Isochore equation. Heats of dissociation such as these indicate that the molecules of ammonia which are evolved are held by weak ion-dipole type forces. The stable phase is $Fe(NCS)_2 \cdot 5NH_3$ at -36°C, but when warmed to room temperature a further three ammonia molecules are lost, yielding $Fe(NCS)_2 \cdot 2NH_3$, which, from measurement of its magnetic moment (5.1BM) is known to contain high-spin Fe(II).

Nicholls *et al* [32] also attempted to isolate an iron (O) cyanide complex, initially trying to reduce potassium hexacyanoferrate (II). It was previously reported by Watt [36] in 1950, that the reduction of potassium hexacyanoferrate (III) with potassium in $NH_3(l)$ only proceeds as far as the hexacyanoferrate (II). Nicholls *et al* were able to confirm that no reaction of hexacyanoferrate (II) by potassium occurs at temperatures of up to -40°C. Iron (III) bromide was found to react rapidly with potassium cyanide and potassium in $NH_3(l)$ even at -78°C, with vigorous evolution of hydrogen and the formation of a dark coloured precipitate in the yellow solution. A black, pyrophoric powder was obtained after filtration and washing, but it was not possible, however, despite performing numerous experiments with varying K:KCN:$FeBr_3$ ratios, to derive a consistent stoichiometric formula. But, in each instance, analytical data showed that only K, Fe, C and N were present, with up to 1%H. The average stoichiometry was approximately $K_2Fe(CN)_2$. The solids were found to be ferromagnetic, with the electronic spectra only showing rising absorption between 9000 and 30,000 cm^{-1} and hence no d-d bands were observed. This shows that a low oxidation state iron-cyanide complex is produced in this reaction.

The effervescence in the reaction most likely arises initially from the reaction of NH_4Br (product of the ammonolysis of $FeBr_3$) with K, but the on-going discolouration of the solution must take place by catalysis by one of the products. It is likely that the catalyst is either iron metal and/or iron nitride, both of which are known reduction products of iron (II) bromide with potassium in $NH_3(l)$. The identity of the catalyst is inferred due to the ferromagnetism. If iron (II) bromide or iron (II) thiocyanate were used as the starting material then $K_{1.5}Fe(CN)_{1.5}$ was obtained; this shows that the ammonolysis of iron (II) bromide was not solely responsible for the vigorous effervescence and non-integral stoichiometry of the product.

Reacting iron (II) or (III) bromide or iron (II) thiocyanate with caesium in the presence of an excess of caesium cyanide in $NH_3(l)$ yields $CsFe(CN)_4$, which is grey-green in colour, this is sensitive to air and moisture, but is not pyrophoric, which suggests that the pyrophoricity of the black products may be due to the presence of finely divided iron [32].

Much of the studied liquid NH_3 chemistry has involved spectroscopic investigations rather than synthetic work.

The use of ^{14}N nmr as a mechanistic tool in S-N chemistry has been illustrated for reactions in liquid NH_3 by Woollins *et al,* [37] who recorded the ^{14}N nmr spectra of various S-N heterocycles and metalla-S-N complexes, and correlated the observed chemical shifts to bonding type. The chemical shift was found to be considerably affected by the degree of saturation, for example, singly bonded species were observed at δ 0 ppm, whilst triply-bonded NSF was observed at δ 576 ppm. Formal N=S double bonds, such as those found in di-imides RNSNR and isolectronic RNSO systems produce signals at δ 250-400 ppm. Pseudo-aromatic planar species such as S_3N_3 were observed to give chemical shifts intermediate between singly and doubly bonded species. For complexes of the type $M(S_2N_2)$ and $M(S_2N_2H)_2$ both nitrogens were observed and easily distinguished, the line width being considerably larger than for the free di-imides.[37]

$S_3N_3^-$ was seen to be in equilibrium with the other S-N species in reactions which incorporate solvent N atoms. In ^{15}N labelled compounds the initial exchange between ^{14}N-^{15}N is very rapid in the case of $[S_4N_4]Cl$, and it has been suggested that two processes account for the loss of ^{15}N from the heterocycle; the rapid formation of $S_3N_3^-$ and then it's subsequent involvement in further equilibria which result in further exchange of N atoms.[37]

^{14}N and ^{15}N nmr have been used in various studies by Chivers *et al* [38, 39, 40, 41]., the techniques that were used in the characterisation of the S_7N^- anion[38, 39] and $S_2N_2H^-$ anion[38, 40] in solutions of liquid NH_3. The S_7N^- anion showed a resonance at δ -324

ppm[38, 39], whilst the $S_2N_2H^-$ anion had two resonances at +7 and –149ppm. The two anions were shown to be thermally unstable with respect to $SSNSS^-$ (which was also found to be the main nitrogen containing constituent in S-N solutions) and $S_3N_3^-$[38, 40, 41]. The formation of $S_2N_2H^-$ was found to proceed *via*-sequential formation of S_7N^-, S_4N^- and S_3N^- to $S_2N_2H^-$, which subsequently decomposes to $S_2N_3^-$ (δ -230ppm).[40, 41] This was the first spectroscopic characterisation of the thermally unstable $S_2N_2H^-$ anion[40]. Multinuclear nmr has shown that introducing ^{15}N into systems such as $Pt(S_2N_2)(PR_3)_2$ can provide useful information about the ^{15}N-^{31}P interactions present in such complexes. The preparation of these compounds is achieved by the use of starting materials such as $S_4{}^{15}N_4$ and $[S_4{}^{15}N_3]Cl$. It is more difficult however, to extend this technique to complexes of $(SSeN_2)^{2-}$ and $(Se_2N_2)^{2-}$. This form was produced in 33% ^{15}N abundance by reacting mixtures of $SeCl_4$ and $[S_4{}^{15}N_4]Cl$ with $PtCl_2(PMe_2Ph)_2$ in liquid NH_3. The ^{15}N-^{31}P complexes of such compounds are apparently unaffected by the nature of the halogen atoms present, as shown in Table 1 below. [42]

Table 1: Comparison of 15N – 31P coupling constant with compounds of the type $Pt(E2{}^{15}N_2)(PMe_2Ph)_2$[1-E(1) = E(2) = S; 2-(1) = S. E(2) =Se; 3-E(1) =(E2) =Se].

Compound	**(1)**	**(2)**	**(3)**
P(1) – N(1)	24	24	22
P(1) – N(2)	12	12	8
P(2) – N(1)	5	6	3
P(2) – N(2)	-	-	5

Raman spectroscopy and UV –vis spectrophotometry was used by Lelieur *et al* in several investigations[43] The solubilisation of sulphur in liquid NH_3 in the equilibrium state of the solutions was monitored over a period of time using UV-vis spectophotometry, and at temperatures of –35 and –15°C. The S_7N^- ion was not evident during solubilisation. The S_3N^- ion (precursor to S_4N^-) was seen to go through a maximum concentration. It was noted that adding NH_4Cl to liquid NH_3 solutions

inhibits the first steps of solubilisation, whilst the opposite effect was observed if an alkali amide was added. At least 50% of the solubilised sulphur was found to be in a neutral state, proposed to be S_2NH_3 rather than S_8.[43, 44, 45]

Lithium and Ammonium polysulphides in liquid NH_3 solutions have also been studied, using Raman spectroscopy and UV-vis spectrophotometry. the liquid NH_3 solutions were prepared by reducing S-NH_3 solutions with H_2S or hydrazine monohydrochloride. The radical anion was always observed with S_6^{2-} for n>1 (where n = no. S atoms in polysulphides). S_4^{2-} was also seen to exist in solution, and found to disproportionate. Disproportionation of polysulphides is systematically higher for NH_4S_n solutions, where n is less than or equal to 4, than for solutions of lithium polysulphides (Li_2S_n). This is because in the presence of NH_4^+, HS^- is the most reduced species, and S_2^- is the most reduced in the presence of Li^+. [43, 44, 45]

Raman spectroscopy was used by Chivers and Lau[46], to identify S_4N^- and S_3N^- ions in blue solutions of sulphur in liquid NH_3. The species S_3^-, S_3N^- and S_4N^- are known to exhibit Resonance Raman (RR) spectra. A medium intensity band at 710 cm^{-1} and a weak band at 592 cm^{-1} in the spectrum (corresponding to symmetric SNS and SS stretching vibrations respectively) were assigned to S_4N^- anion. For more concentrated solutions the intensity of these bands relative to S_3^- dramatically increases. No evidence was found for the existence for the S_3N^- ion in sulphur/ammonia solutions, but it did however, appear that S_3N^- is formed in ammonia solutions of S_4N_4. It was proposed that S_4N^- is formed by $H_2NS_8^-$ losing H_2S to give S_7N^- which rearranges to give S_4N^-.[34]

Lelieur et al [43] have reported the use of Raman and UV-visible spectrophotometry in characterising and identifying lithium polysulphides in liquid ammonia solutions. The least reduced polysulphide was found to be S_6^{2-}, and this was in equilibrium with the radical S_3^{*-}. S_6^{2-} disproportionates weakly, this was shown through observing S_4^{n-}. The equilibrium between S_6^{2-} and S_3^{*-} was seen to be very dependant upon the temperature. The observation of the S_3^{*-} radical revealed that it disproportionates with S_4^{2-}, thus confirming the existence of S_4^{2-} in solution. The equilibrium constant for the disproportion of S_4^{2-} was approximately 10^{-4}M, this was estimated from the absorbance of $S^*_3^-$.

Understanding of solutions of sulphur in liquid ammonia was considerably advanced from the synthesis of S_4N^- [47], the identification of $S^*_3^-$ [48, 49] and from studying the equilibrium between S^*_3- and S_6^{2-} in various media [50, 51, 52]. The slow dissolution of sulphur in NH_3(l) is now acknowledged as being a redox disproportionation process [53, 45], and these solutions have been observed as being photosensitive [11-13 paper]. Solutions of alkali metals in liquid ammonia are known to decompose yielding alkali amides, and that the decomposition is catalysed by traces of impurities in solution. When alkali metal solutions in NH_3(l) are used in the synthesis of alkali polysulphides this decomposition must be minimised since it causes an error in the stoichiometry of the product and purifies the solution.

Solutions of lithium polysulphides in NH_3(l) are considered as being sulphur-ammonia solutions which are reduced by a lithium-ammonia solution. Sulphur is solubilized in NH_3(l) by a redox disproportionition, an oxidised species in the solution being S_4N^- and a reduced species being S_6^{2-}, which exists in equilibrium with the S_3^{*-} radical

anion. which is readily identified by its Raman lines at 535 and 232 cm^{-1}, and its absorption band at 610nm. This equilibrium is known to be temperature dependant.

The authors [43, 44, 45] propose that the solubilisation of sulphur in $NH_3(l)$ may be described by equations 26 and 27 below

$$10S + 4NH_3 \longrightarrow S_4N^- + S_6^{2-} + 3NH_4^+ \qquad \text{Eqn.26.}$$

$$S_6^{2-} \longleftrightarrow 2S_3^{*-} \qquad \text{Eqn.27.}$$

Raman spectroscopic measurements in resource conditions at low temperatures (-40°C) have shown the presence of a small amount of S_3N^-, so eqns. .26 and 27. do not completely describe solutions of this type. However, the chemical reduction of an S-NH_3 solution by Li should cause the disappearance of these oxidised species.

The authors identified S_6^{2-} (in equilibrium with S_3^{*-}), S_4^{2-}, S_2^{2-} and S^{2-} in liquid ammonia, and they concluded that the S_6^{2-} and S_4^{2-} polysulphides are highly soluble, whilst S_2^{2-} and S^{2-} are not. S_6^{2-} and S_4^{2-} are both disproportionated, and the existence of polysulphides less reduced than S_6^{2-} is unlikely, and the existence of S_5^{2-} is questionable and that of S_3^{2-} is also unlikely. The only radical found in the solutions is S_3^{*-} [43, 44, 45].

Gardiner et al [21] have reported their observations from a Raman and ^1H nmr study of liquid NH_3 and liquid ND_3 solutions of $[BF_4]^-$ (tetrafluoroborate), $[ClO_4]^-$ (perchlorate) and PF_6 salts. Interactions between ammonia and carbons were observed to be dominant, but no evidence of anion-cation or anion-solvent interactions was found;

thus indicating a similarity of behaviours for these anions in aqueous and ammonia media.

The Raman spectra of concentrated electrolyte solutions in liquid ammonia show the presence of solvent separated ion-pairs [55] and contact ion pairs [56] in respect of the latter example, the complex formation between $[CN]^-$ and $[SCN]^-$ with Ag^+ has been investigated [57]. As a general rule, studies such as these parallel those with analogous aqueous systems, frequently with very similar results.

It has been possible to identify three types of electrolyte :

i. electrolytes in which both the anion and cation interact significantly with the solvent (ammonia) molecules. In dilute solution the ions will be strongly solvated, whilst in concentrated solutions there exist solvent separated ion-pair and contact ion-pair formation, therefore the Raman spectra of the ammonia in these instances show effects due to both the cation and the anion. Typical electrolytes of this sort are Li^I and AgSCN.

ii. Electrolytes where only the interaction of the anion with the solvent is significant. The electrolytes in this group are only sparingly soluble, but increasing concentration would result in anion-solvated contact ion-pairs and the Raman spectrum of the solvent would be heavily anion dependant. R_4NI and KSCN are typical electrolytes of this type.

iii. Electrolytes where the cation interaction with ammonia is dominant. In this instance concentration will induce the formation of cation solvated contact ion-pairs, and the Raman spectrum will be largely cation dependant.

The non-interacting ions in categories (ii) and (iii) are not considered as being free ions, but rather as very weakly solvent interacting ions.

The authors found that raising the concentration of $[BF_4]^-$, $[ClO_4]^-$ and $[PF_6]^-$ salts in liquid NH_3 and ND_3 caused no change in the anion vibrations, but does, however, cause the following changes in the spectra of NH_3 and ND_3, which are primarily due to the interaction between cation and solvent.

a) ammonia vibrations all increase in frequency, with υ2 being the most obvious

b) the intensity of the lower frequency component of the υ1 / 2υ4 Fermi resonance doublet decreases and the intensity of υ3 increases.

c) whilst the peak height decreases, the half band width of υ2 increases.

The ^1H nmr shifts (relative to benzene as an internal standard) were measured for pure $NH_3(l)$ and a range of $LiBF_4$ / $NH_3(l)$ solutions. It was observed that as the concentration of $LiBF_4$ was increased, the shift upfield from benzene decreased, thus amounting to an overall shift downfield as the concentration of electrolyte is increased.

The observed changes in the N-H stretching region of the spectrum are consistent with the break-down of the hydrogen-bonded structure of $NH_3(l)$and are characteristic of other $NH_3(l)$ / electrolyte solutions [58, 59, 56] The increase in the frequency of the NH_3 and ND_3 vibrations is due to interactions between metal ions and $NH_3(l)$ [58, 55, 56]. The

increase in the υ2 band intensity observed in concentrated solutions of salts containing polarisable anions like I^- and $[SCN]^-$ is due to the formation of solvent separated ion pairs. However, in the solutions studied by the authors, there was no overall increase in the intensity of υ2, only a broadening of the band along with a decrease in its height, thus indicating that there is little interaction between the cations and anions; this was also supported by the fact that there were no changes in the anion spectrum as a function of concentration.

The ^1H nmr shifts for NH_3 in the $NH_3(l)$ / $LiBF_4$ solutions indicate that as the electrolyte concentration is increased the protons become more deshielded.

If the H-bonded structure of $NH_3(l)$ merely broke up, then the NH_3 protons would be more greatly shielded, and their nmr shifts would, therefore, be anticipated to more upfield relative to benzene. But, if the protons were deshielded, for example by the M^+ ..... NH_3 interaction, then the proton shifts would move downfield, as was actually observed. It must be concluded, therefore, that the M^+ .....NH_3 interaction is the dominant effect.

It would seem, therefore, that the dissolution of $[BF_4]^-$, $[ClO_4]^-$ and $[PF_6]^-$ salts in $NH_3(l)$ produces solutions where the H-bonded structure is broken up and replaced by M^+ .... NH_3 interactions, whilst the anions remain relatively non-interacting.

Lelieur et al [43, 44, 45] have used UV-vis spectrophotometry and Raman spectroscopy to identify ammonium polysulphides ($(NH_4)_2S_n$) in ammonia solutions. They prepared the polysulphide solutions by reduction of sulphur-ammonia solutions with H_2S or

hydrazine monohydrochloride. For n>1, the $S_3^{\cdot-}$ radical anion was always observed in equilibrium with S_6^{2-}. S_4^{2-} was found to be present in solution, and it was found to be disproportionated. The authors compared the results of this study to those investigating lithium polysulphides in liquid ammonia. They found that for n>4, the disproportionation of polysulphides is systematically greater for ammonium polysulphide solutions than for lithium polysulphide solutions. This is because in the presence of ammonium ions, HS^- is the most reduced species, whilst in the presence of Li+ S^{2-} is the most reduced species.

It has been shown that the solubilisation of sulphur in liquid ammonia occurs with a redox disproportionation process. The authors, like Chivers and Lau [59] observed the reduced species S_3^- and the oxidized species S_4N^- in sulphur-ammonia solutions. S_3^- is known to be in equilibrium with S_6^{2-} [45] which led Lelieur et al to propose the following equations (eqn.28,29.) for the solubilisation of sulphur in ammonia.

$$10S + 4NH_3 \rightarrow S_4N^- + S_6^{2-} + 3NH_4^+ \qquad \text{Eqn.28.}$$

with

$$S_6^{2-} \leftrightarrow 2S^{3-} \qquad \text{Eqn.29.}$$

The solutions were subsequently observed by resonance Raman spectroscopy at temperatures below -40°C, when another oxidised form of sulphur is present in these solutions; that species being S_3N^-. From this it is clear that equations .28. and .29. do not entirely describe sulphur-ammonia solutions. It was suspected that the acidity of the solution could modify the disproportionation of polysulphides. To investigate this, solutions of Li_2S_n and $(NH_4)_2S_n$ were studied.

$(NH_4)_2S_n$ - NH_3 solutions were prepared with well defined values of the stoichiometry, n, and the concentration. Absorption and Raman spectra of these solutions were

recorded versus temperature for various values of n and the concentration. The identity of polysulphides in solution was based upon some species that are considered as being well known, particularly the $S_3^{\cdot-}$ radical anion, which had been previously identified in solution and is characterised by an absorption band at 610nm, and an intense Raman line at 535 cm^{-1} which corresponds to a symmetrical stretching vibration ($\upsilon 1$), and a smaller line at 232 cm^{-1}. S_4N^- is characterised by Raman lines at 570, 590, 710 and 898 cm^{-1}, as identified by Chivers et al . It was also found that S_4N^- is photosensitive in $NH_3(l)$.

The possible disproportionation of polysulphides in $NH_3(l)$ makes their study more difficult. Disproportionation of a given polysulphide produces a more reduced and a less reduced form of sulphur. For Lithium polysulphide solutions in $NH_3(l)$, S_4^{2-} and S_6^{2-} are partly disproportionated. The acidic characters of the ammonium polysulphide solution influences the disproportionation.

Ammonium polysulphide solutions in $NH_3(l)$ were prepared by reducing sulphur-ammonia studies with hydrogen sulphide, as described by equation 30 below.

$$nS + H_2S + xNH_3 \rightarrow (NH_4)_2\,Sn{+}1 + (x\text{-}2)\,NH_3 \quad \text{Eqn .30.}$$

It was also found that hydrazine monohydrochloride could be used to reduce sulphur-ammonia solutions, and ammonium polysulphides were subsequently prepared in $NH_3(l)$ as shown in equation .31 . below.

$$nS + 2N_2H_4Cl{+}xNH_3 \rightarrow (NH_4)\,Sn + N_2 + 2NH_4Cl{+}(x - z)\,NH_3 \quad \text{Eqn .31 .}$$

For solutions of $(NH_4)_2S_2$; $(NH_4)_2S_4$ and $(NH_4)_2S_{10}$ the absorption band at 610nm was found to decrease as the temperature was lowered, thus providing evidence of the $S_3^{\cdot-}$ radical. Further evidence was provided by the fact that as the temperature was reduced, absorption band between 400 and 450nm simultaneously increased with the decrease in the band at 610nm. Solutions with n>6 have to be viewed as solutions of sulphur and ammonium hexasulphide in $NH_3(l)$. This is confirmed by the presence of an absorption band (at 200K) for S_4N^- at 580nm.

S_4^{2-} was found to exist in ammonium polysulphide solutions, and has an intense Raman line at 437cm^{-1}, this is also an indication of the presence of S_6^{2-} in solution. A line observed at 535cm^{-1} was attributed to $S_3^{\cdot-}$, even at 200K under Raman spectroscopy, it is thought that this is because the temperature of the solution at the laser's point of impact the temperature of the solution is likely to be higher than 200K. It was found the intensity of this line is independent of the concentration and stoichiometry of the solution. This indicates that the observation of $S_3^{\cdot-}$ at 200K is actually due to a small concentration of this species, being observed under resonance conditions.

S_4^{2-} was evidenced in solution using Raman spectroscopy by lines at 647.1 and 514.5nm. The Raman and absorption spectra of $(NH_4)_2S_4$ solutions show the presence of $S_3^{\cdot-}$, proving the disproportionation of S_4^{2-}. It was also found that the Raman spectra of this solution was independent of concentration. A line at 400cm^{-1} was attributed to S_6^{2-}, and an intense line at 437cm^{-1} to S_4^{2-} [43, 44, 45].

Dissolution of sulphur in liquid ammonia yields highly coloured solutions. At the turn of the century the characterisation of these solutions was misdirected when

tetrasulphur tetranitride (S_4N_4) was identified after silver iodide was added to the solution and the ammonia evaporated.

Lelieur et al [43, 44, 45] have written that the dissolution of sulphur in $NH_3(l)$ is a redox process, mainly producing the oxidized species S_4N^-, and the reduced species S_6^{2-}, which exists in equilibrium with the $S_3^{\cdot-}$ radical anion. It is thought that the species present in liquid ammonia solutions of sulphur are pH dependant.

A considerable step in the understanding of sulphur-ammonia solutions was made when Chivers and Lau identified S_4N^- and $S_3^{\cdot-}$ by Raman Spectroscopy on S-$NH_3(l)$ solutions. Lelieur et al went on to show that such solutions are photosensitive, and this affects both absorption and Raman spectra. With resonance Raman conditions S_3N^- a sulphur amide more oxidized than S_4N^- was identified, albeit at a much smaller concentration than that of S_4N^-. Absorption spectra of these solutions illustrate the equilibrium between $S_3^{\cdot-}$ and S_6^{2-}. The fact that S-NH_3 solutions are sensitive to light and traces of reducing agents are important if satisfactory absorption spectra are to be obtained. In dilute solutions at room temperature, absorption bands were observed at 595 and 460nm, whilst at 200K they were observed at 580, 460 and 290nm, with a shoulder at ca 330nm.

It was observed that the absorption spectrum is dependant upon concentration. At room temperature three absorption bands were observed at 580, 420 and 300nm, and the intensities of the visible absorption bands have a greater difference for more dilute solutions. The absorbance at 580nm was always observed to be larger than that at ca 420nm. Nelson and Lagowski [60, 61] observed the opposite trend, and it is thought that this is due to the photosensitive nature of the solutions, since this causes a decrease in the main visible absorption band or is a consequence of a partial reduction of the

solution by impurities. The second visible absorption band was concentration dependant, shifting from 460nm for dilute solutions to 420nm for solutions in the 10^{-1} - 10^{-2} mol.dm^{-3} concentration range.

As the temperature was reduced from room temperature to 200K, the absorbances were observed to decrease in the long wavelength part of the visible absorption band, whilst the absorbance of the other bands in the visible and UV regions was found to increase. This is attributed to the dimerization of $S_3^{\cdot-}$ to S_6^{2-} with falling temperature. The apparent increase of absorbance of the 580nm line has been correlated to the corresponding increase in density of the ammonia with falling temperature. (NB: The authors presumed that the density of the solution and its thermal variations were identical to that of pure liquid ammonia). It would, therefore, seem that the absorbance of the main band at 580nm doesn't vary with temperature, and this means that the equilibria which S_4N^- might be involved in are not significantly influenced by the temperature of the solution. The relative contribution of $S_3^{\cdot-}$ to the main visible absorption band at room temperature was larger for very dilute solutions, in which the dissociation of S_6^{2-} into $S_3^{\cdot-}$ is great.

The Raman spectra of S-NH_3 solutions are dependant upon concentration since the more dilute solutions are photosensitive under the laser conditions used. For solutions of concentration greater than 0.5 mol.dm^{-3} the intensity of the Raman lines were observed to remain constant with time. The Raman spectra for a given excitation line were observed to be independent of concentration up to saturation (ca 5 mol.dm^{-3}) at room temperature. Therefore, the lines due to S_4N^- and S_6^{2-} are concentration independent. However, the line due to $S_3^{\cdot-}$ at 535 cm^{-1} was observed to decrease in intensity with increasing concentration for a given temperature and excitation line.

This is due to the temperature dependence of the equilibrium between S_6^{2-} and $S_3^{\cdot-}$. The radical anion is well known to dimerize as the temperature falls.

The spin-lattice relaxation times and Knight shifts of ^7Li in $NH_3(l)$ and methylamine have been investigated by Nakamura et al [62] , with particular interest being placed upon the transition from localised to itinerant electron states in the respective systems. The Korringa relaxation rate was found to be noticeably enhanced in the Lithium-methylamine solutions, and less pronounced in Lithium-ammonia solutions. The difference was seemingly linked to the structural homogeneity of the different solutions.

Solutions of metals in ammonia exhibit drastic changes in various properties with changes in the concentration of the metal. Very dilute solutions contain paramagnetic solvated electrons and solvated metal ions; and concentrated solutions which show characteristics of liquid metals containing almost free electrons.

NMR studies yielded useful information about the state of the dissolved metals through the Knight shifts and relaxation rates of the various nuclei in these solutions. The nmr of the Lithium-methylamine solutions was also useful for investigation into the role of the host solvent by comparison with the results in metal-ammonia solutions.

The electron spin densities at the lithium nuclei were found to be almost the same in both systems (deduced from Knight shift data). The value of $(1(\psi(Li)|^2)$ in the metallic region is around 0.5% of the corresponding value for the free lithium atom. Larger Knight shifts in the Lithium-methylamine system are due largely to the greater paramagnetic susceptibility or less pronounced spin-pairing in $Li\text{-}CH_3NH_2$.

The relaxation rate due to electron-nuclear contact interaction decreased with rising metal concentration in the non-metallic region of both systems. This is reflected in the shortening of the correlation time of the contact interaction with increasing mobility of localised electrons.

The relaxation rate of ^{7}Li was observed to increase above 8MPM in the Li-NH_3 system and was found to be an apparent one which is due to the decreasing skin-depth in the metallic region.

The Korringa relaxation rate was observed to be greatly enhanced in the metallic and transition regions of the Lithium-methylamine system. This enhancement was much smaller in the corresponding regions of the lithium - NH_3(l) system. This difference was attributed to the partial delocallisation of the electronic wave functions in advance of the bulk metallisation in Li-NH_3 due to a more pronounced concentration fluctuation in the transition region of the system.

Gruwel has carried out a nuclear magnetic relaxation study on the rotational dynamics of nitrate and thiocyanate ions in liquid ammonia. For both anions D_1 was found to be greater than that observed in aqueous solution. The nitrate ion's rotational anisotropy was found to be temperature dependant (over the range 233 - 303K). The spin rotation mechanism was found to dominate the 13C relaxation of the thiocyanate ion. The overall dynamics of both ions was found to be less restricted in liquid ammonia than in aqueous solution.

The nitrate and thiocyanate ions both show, at room temperature, an approximate doubling of D_1 in $NH_3(l)$. The author attributes this to a weakening of the hydrogen-bond network in liquid ammonia as compared to water. The reorientation of the NO_3^- ion was found to still be anisotropic in $NH_3(l)$ as well as in water, but the rotational anisotropy of this ion in $NH_3(l)$ was greater than that obtained in H_2O. This was also correlated to a change in the H-bonding of the solvent. Because of the low H-bond donor capacity of ammonia, the dynamics of both NO_3^- and SCN^- is less hindered in this solvent. The low H-bonding donor capacity of NH_3 weakens the H-bond network.

Ion-pairing interactions have been reported to be of less importance in $NH_3(l)$ than water, and of greater importance for the nitrate ion than for the thiocyante ion. No large change in the ion-pairing interactions was observed for the ammonia/thiocyanate system over the temperature range studied. For the NO_3^- ion, however, ion pairing interactions are likely to be more important at lower temperatures both in liquid ammonia and water.

The activation energies for the DI reorientation of the NO_3^- ion in $NH_3(l)$ were found to exhibit a similar ratio to that observed in water [63].

Chivers et al [64, 65] have carried out ^{14}N and ^{15}N nmr characterisation of the S_7N^- ion in sulphur ammonia solutions. Both the cyclic sulphur imide, S_7NH and the thermally unstable S_7N^-ion were characterised by ^{14}N and ^{15}N nmr spectroscopy. The existence of S_7N^-, S_4N^- and small amounts S_3N^- in sulphur-ammonia solutions were demonstrated by ^{14}N nmr spectroscopy.

The existence of the S_7N^- ion was inferred from alkylation studies. It is known to decompose at temperatures above -50°C, yielding S_4N^- and sulphur. Chivers et al proposed the initial formation of S_7N^- to explain the production of S_4N^- in sulphur-ammonia solutions (SAS). Schindewolf and Prestel subsequently estimated by UV - vis spectrometry 36 ± 4% of dissolved sulphur in ammonia is present in the form of S_7N^- [66]. Lelieur et al, however, could find no evidence for S_7N^- in SAS by either UV-vis or Raman spectroscopy. By ^{14}N and ^{15}N nmr spectroscopy the S_7N^- anion was found to exhibit a resonance at -364ppm, and this anion was also found to be the major nitrogen containing species present in sulphur-ammonia solutions at 25°C.

As mentioned above, the S_7N^- anion exhibits a broad resonance at -364ppm, but no ^1J (^{14}N - ^1H) coupling was observed because of the ≈ 700Hz line width. S_4N^- exhibited a resonance at +106ppm (by comparison to $\delta(^{14}N)$ = +106ppm for $(Ph_3P)_2N^+S_4N^-$ in MeCN), after one day at 25°C the concentrations of S_7N^- and S_4N^- were observed to be approximately equal.

The formation of S-N anions in $NH_3(l)$ has been demonstrated using both Raman and UV-vis spectroscopy. The ^{14}N nmr of a deep blue solution of S_7NH in $NH_3(l)$ in equilibrium at 25°C was found to exhibit a major resonance at +107ppm due to S_4N^- and a weak resonance at -324ppm for S_7N^- (compared with -331ppm for S_7NH in $NH_3(l)$). The production of the S-N anions in $NH_3(l)$ was also monitored using ^{14}N nmr spectroscopy. After 2 hours resonances at -323 and +109 ppm due to S_7N^- and S_4N^- were observed, plus a much weaker resonance at +231ppm was also seen, this was attributed to S_3N^- (by comparison with $(Ph_3P)_2N^+S_3N^-$ in MeCN, for which $\delta^{14}N$ =

+ 235ppm). S_7N^- was found to constitute 80% of the nitrogen containing species, with this value rising to 88% after 5 days.

Chivers et al [64, 65] also used ^{14}N and ^{15}N nmr spectroscopy to show that deprotonation of S_7NH by potassium amide in $NH_3(l)$ occurs via the stepwise formation of S_7N^-, S_4N^- and S_3N^- to yield $S_2N_2H^-$, which then decomposes to form $S_3N_3^-$. The $S_2N_2H^-$ ion was also produced by treating $S_4N_4H_4$ with two molar equivalents of potassium amide in $NH_3(l)$, this resulted in S_4N^- being partially converted to S_3N^- ($\delta^{14}N$ + 230ppm) and $S_3N_3^-$ ($\delta^{14}N$ - 230ppm). Adding a third molar equivalent of KNH_2 resulted in two further resonances at +7ppm and -149ppm, which correspond to no known sulphur-nitrogen species, but they are associated with the same species as they increase and decrease together. The resonance at 149ppm was observed as a doublet, suggesting that one of the nitrogen atoms is attached to a proton. The resonances were attributed to the inequivalent nitrogen atoms of $S_2N_2H^-$ as illustrated in Fig.1. below.

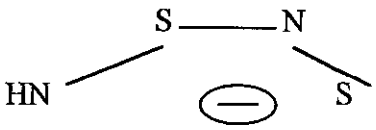


Fig.1. The $S_2N_2H^-$ anion.

The co-ordinated $S_2N_2H^-$ ligand is known to exhibit ^{14}N nmr resonances at ca. -20 and -150ppm. After several days as 25°C the two resonances associated with $S_2N_2H^-$ decreased in intensity whilst the signal due to $S_3N_3^-$ at -230ppm increased concomitantly [64, 65].

EXPERIMENTAL SECTION

PART A - SYNTHETIC WORK

i) Attempted Synthesis of Metal-bis thionylimide compounds.

The purpose of this study was to investigate whether compounds of the type $M(NSO)_2$ (M=Metal, NSO^- = thionylimide) could be synthesised by a reaction previously used to produce complexes of the type $Pt(NSO)_2(PR_3)_2$; (R = Organic group such as e.g. Me, Et, C_6H_5).

Experimental.

A typical reaction procedure was as follows:

$NH_3(l)$ was obtained by condensing $NH_3(g)$ into a Schlenk tube at -78°C (dry ice/acetone cold bath) under $N_2(g)$. To this was added a slight excess of $SOCl_2$ (slightly greater than 2:1 molar ratio of $SOCl_2$: MCl_2). The resulting solution was stirred for ten minutes to facilitate production of the NSO^- ion. The metal dichloride (0.5g) was then added to the solution, an oil bubbler placed in the neck of the Schlenk tube and the $N_2(g)$ supply turned off. The solution was stirred for a further 45 minutes and then left to warm up slowly (ca 12 hours). Residual $NH_3(g)$ was removed in vaccuo (ca 2 hours) and the product recovered by heating to 30°C in THF for 30 minutes in a water bath. The solution was then filtered through a celite/glass wool plug and the solvent removed in vaccuo. Characterisation of the product was attempted by, initially, i.r. spectroscopy and secondly by mass spectrometry where appropriate (i.e. where i.r. indicated that the desired product had been synthesised).

Results

The following reactions were attempted.

Starting Material	**Product**
$HgCl_2$	$Hg(NSO)_2$
$NiCl_2$	$Ni(NH_3)_6$
$CuCl_2$	$CuCl_2$
$PbCl_2$	$PbCl_2$
$SnCl_2$	$SnCl_2$
$RuCl_3$	$RuCl_3$

See also i.r. and mass spectrum on following page.

Fig.2. Infra-red Spectrum of $Hg(NSO)_2$

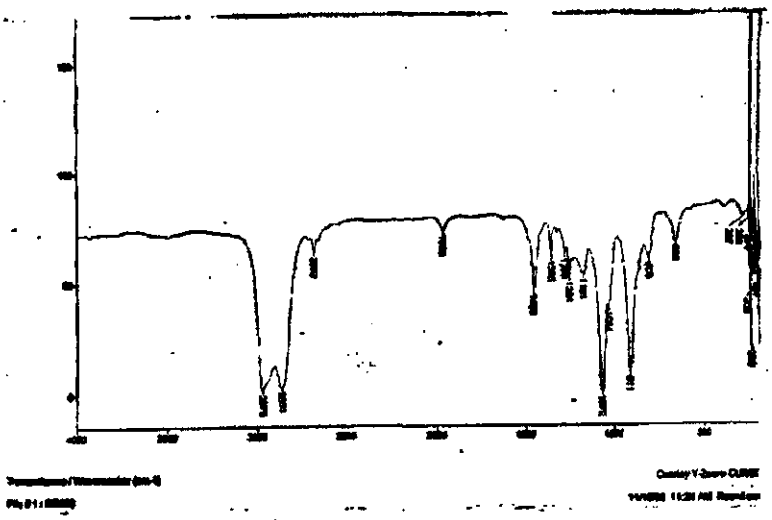
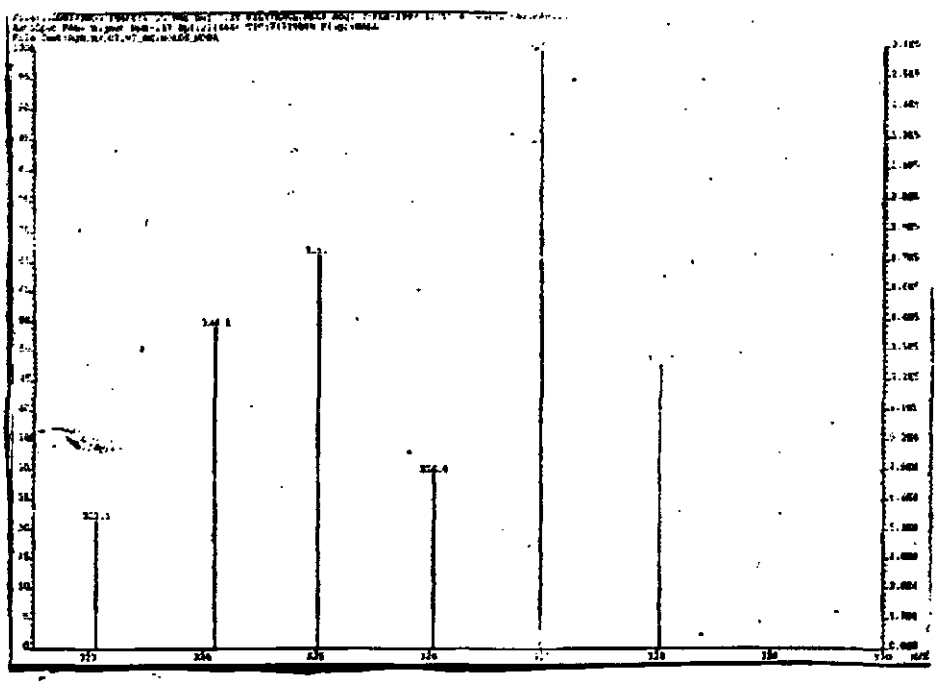


Fig.3. Mass Spectrum of $Hg(NSO)_2$



Discussion

The reaction scheme is illustrated in equations .32. and .33. below.

Equation .32 . $SOCl_2$ (l) + NH_3(l) → NH_4Cl + NSO^-

Equation .33 . $2NSO^- + MCl_2 \rightarrow M(NSO)_2 + 2Cl^-$

(NB: Little is known about the overall stoichiometry of these reactions).

The only reaction where the desired product was produced was that using $HgCl_2$ as the starting material. This was characterised by bands characteristic of the NSO^- ion in the i.r. spectrum at 1261 cm^{-1} (vs) and 1070cm^{-1}(s). EI mass spectrometry gave a spectrum identical to that which was theoretically predicted. It was not possible to obtain a Raman spectrum of the product due to its oily nature. The i.r. and mass spectra of the product are shown in figures 2 and 3.

It is thought that for the attempted syntheses where no reaction occurred, that the reaction conditions were simply too cold for the metal salts to dissolve, and therefore, subsequently react.

ii) Reaction of $SeOCl_2$ and $PtCl_2(PPh_3)_2$

Method

$5cm^3$ $NH_3(l)$ was collected under $N_2(g)$ in a Young's tube (dry ice/acetone cold bath). To this was added $PtCl2(PPh_3)2$ (142mg, 0.18mmol), with stirring. The mixture was then cooled to -196°C (liquid N_2 bath). Subsequently $SeOCl_2$ ($0.25cm^3$) was added dropwise, and the tube was sealed and allowed to warm to room temperature with stirring. The mixture was then stirred for a further 24 hours, after which the tube was re-cooled to -78°C and the $NH_3(l)$ allowed to evaporate under a stream of $N_2(g)$ and any residual $NH_3(g)$ was removed in vaccuo (ca 2 hours). The remaining pink/red solid was extracted in CH_2Cl_2 and filtered through a celite/glass wool plug. The solvent was removed in vaccuo and ^{31}P nmr spectrum of the product was taken in $CDCl_3$ (degassed and dried).

Results

An uncharacterisable product was obtained.

iii) Attempted Syntheses of $(PR_3)_x M(NSO)_y$

A typical reaction is detailed below.

$10cm^3$ $NH_3(l)$ was collected under $N_2(g)$ in a Schlenk tube (dry ice/acetone cold bath) to this was added a slight excess of $SOCl_2$ (NB: for starting materials of the type $(PR_3)_xMCl$ just over 1 equivalent $SOCl_2$ was used; and for starting materials of the type $(PR_3)_x MCl_2$ slightly greater than 2 equivalents of $SOCl_2$ was used) slowly with stirring. The solution was stirred for a further ten minutes to allow production of the NSO^- ion. Subsequently $(PR_3)_x MCl_y$ was added to the solution (typically 1×10^{-4} mmol) with stirring. An oil bubbler was then placed in the neck of the Schlenk tube, the $N_2(g)$ supply was turned off, the solution stirred for a further hour and then left to warm up over night. Residual $NH_3(g)$ was removed in vaccuo (ca 2hours). The product was extracted in CH_2Cl_2, filtered through a celite/glass wool plug and the solvent removed in vaccuo. The product was then dissolved in $CDCl_3$(dried, degassed) and a ^{31}P nmr spectrum taken. Where appropriate and possible i.r. and Raman spectra of the product were also recorded.

The attempted syntheses are detailed in table .2. below.

Table.2. Attempted Syntheses of $(PR_3)_xM(NSO)_y$.

Starting Material	Product	Reaction?
$PtCl_2$ $(PMePh_2)_2$	$Pt(NSO)_2(PMePh_2)_2$	Y*
$PtCl_2$ dppe	$Pt(NSO)_2$ dppe	Y*
PtCl2 dppm	$Pt(NSO)_2$ dppm	Y*
$PtCl_2$ dppa	$Pt(NSO)_2$ dppa	Y*
$NiCl_2$ dppm	$Pt(NSO)_2$ dppm	Y
$NiCl_2$ dppe	$Ni(NSO)_2$ dppe	Y
$TiCl_2$ Cp_2	$Ti(NSO)_2$ Cl_2	Y*
SnCl Me_3	Uncharacterisable	
$PdCl_2$ dppe	$Pd(NSO)_2$ dppe	Y*
$HgCl_2(PPh_3)_2$	$HgCl_2(P$ $Ph_3)_2$	N
$(Ph_3P)AuBr$	$(Ph_3P)AuBr$	N
$RhCl(PPh_3)$	$RhCl(PPh_3)$	N
$PtCl_2COD$	$PtCl_2COD$	N
K_2PtCl_4	K_2PtCl_4	N
$PtCl_2$ $(NH_3)_2$	$PtCl_2$ $(NH_3)_2$	N
$RuHCl(CO)(PPh_3)_3$	$RuHCl(CO)(PPh_3)_3$	N
$RuCl_2(PPh_3)_3$	$RuCl_2(PPh_3)_3$	N
$RhCl(CO)(PPh_3)_2$	$RhCl(CO)(PPh_3)_2$	N
$(Ph_3P)AuCl$	$(Ph_3P)AuCl$	N
PhHgCl	PhHgCl	N
$TeCl_4$	$TeCl_4$	N

Results and Discussion

All "Reaction?" marked Y* denote that the compound had previously been synthesised, but the reactions were carried out to gain a feel for the chemistry. Products were characterised by comparing i.r., Raman and ^{31}P nmr data to those previously published by Woollins et al.

For instances where no reaction occurred, it is concluded that the reaction conditions were simply too cold either for the starting material to dissolve, or, if they did dissolve, it was too cold for any reaction to occur.

iv) Attempted Synthesis of $Pb(S_2N_2)$

Dithiazene compounds have previously been synthesised from $(PR_3)_2MCl_2$ starting materials. This was an attempt to investigate whether they could be synthesised from a metal dichloride starting material.

$10cm^3$ $NH_3(l)$ was collected in a Schlenk tube under N_2 (dry ice/acetone cold bath), and to this was added $[S_4N_3]Cl$ 10.296g, 1.438×10^{-3}mol). The mixture was stirred for ten minutes and $PbCl_2$ (0.4g, 1.438×10^{-3}mol) was added. An oil bubbler was placed in the neck of the Schlenk and the $N_2(g)$ supply turned off. The mixture was stirred for 2 hours and then allowed to warm up over night. Residual $NH_3(g)$ was removed in vaccuo (ca 2hours), the product was extracted into CH_2Cl_2, filtered through a celite/glass wool plug and the solvent removed in vaccuo, i.r. and Raman spectra of the product were recorded.

Results and Discussion

The product was uncharacterisable.

The expected reaction scheme would have been :-

$2[S_4N_3]Cl + 8NH_3 + 2MCl_2 \rightarrow 2M(S_2N_2) + S_4N_4 + 6NH_4Cl.$

v) Attempted Synthesis of [PPN][NSO]

(PPN = bis-(triphenyl phosphine) iminium nitrite)

$10cm^3$ $NH_3(l)$ was collected under N_2 in a Schlenk tube (dry ice/acetone cold bath) to this was added $SOCl_2$ ($0.05cm^3$, 6.82×10^{-4}mol) and the mixture was stirred for ten minutes. To this was added [PPN]]NO_2] (200mg, 3.42×10^{-4}mol), with stirring. An oil bubbler was placed in the neck of the Schlenk tube and the $N_2(g)$ supply turned off. The mixture was stirred for a further hour and then left to warm up over night. Residual $NH_3(g)$ was removed in vaccuo (ca 2 hours) and the product was then extracted into CH_2Cl_2 and filtered through a celite/glass wool plug, and the solvent removed in vaccuo. ^{31}P nmr and i.r. spectra of the product were recorded.

Results

^{31}P nmr/ppm.	Product.	21.071 (764.31Hz)
	[PPN][NO_2]	21.193 (768.71Hz)
15/cm^{-1}	Product	1255, 1115, 1023, 1014
	[PPN][NO_2]	1244, 1115, 1025, 997

Discussion

By comparison of the ^{31}Pnmr and i.r. data for the product and starting material, it is concluded that no reaction occurred; it is surmised that this is because the conditions were too cold to facilitate any reaction occurring.

(**NB**: The same reaction was attempted with [PPN]Cl, and again no reaction occurred, as evidenced from comparison of i.r. and ^{31}P nmr spectra of the starting material and the product. It is, once more, considered that this is due to the low temperature conditions of the reaction).

vi) Attempted Synthesis of $Pt(SO_2(NH)_2)(PR_3)_2$ complexes.

A typical reaction is described below:-

SO_2Cl_2 (equivalent of starting complex) was added to $10cm^3$ $NH_3(l)$ in a Schlenk tube under $N_2(g)$ (dry ice/acetone cold bath) and the mixture stirred for 10 minutes. To this was added $PtCl_2(PR_3)_2$, (100mg), an oil bubbler was then placed in the neck of the Schlenk and the $N_2(g)$ supply turned off. The solution was stirred and left to warm up overnight. Residual $NH_3(g)$ was removed in vaccuo (ca 2 hours), the product extracted into CH_2Cl_2, filtered through a celite/glass wool plug and the solvent removed in vaccuo. ^{31}P nmr, i.r. and Raman spectra of the products were taken and compared to those of the starting materials.

Results

Starting Material	**Product**
$PtCl_2$ dppe	$PtCl_2$ dppe
$PtCl_2(PEt_3)_2$	$PtCl_2(PEt_3)_2$
$PtCl_2(PMe_3)_2$	$PtCl_2(PMe_3)_2$
$PtCl_2(PMePh_2)_2$	$PtCl_2(PMePh_2)_2$
$PtCl_2(PMe_2Ph)_2$	$PtCl_2(PMe_2Ph)_2$
$PtCl_2(PPh_3)_2$	$PtCl_2(PPh_3)_2$

Discussion

It is concluded that the reaction conditions were too cold to facilitate the production of compounds of the type $Pt(SO_2(NH)_2)(PR_3)_2$.

vii) Attempted Synthesis of $Pt(PMe_2Ph)_2$ ($SO_2(NH(CH_2Ph)_2)$).

Method

To $30cm^3$ CH_2Cl_2 was added $1cm^3$ benzylamine and 0.5ml SO_2Cl_2, to generate the $[SO_2(NR_2)]_2^-$ ion. At this point the solution was white. Upon addition of $Pt(Me_2Ph)_2Cl_2$ (1.84×10^{-4}mol), and the solution immediately turned a bright yellow colour. The solution was stirred for a further five minutes and the CH_2Cl_2 was removed on a rotary evaporator. The product was washed with MeOH to remove any salts that may have been present. The product was washed with 3 x $10cm^3$ portions of MeOH and dried at the pump. ^{31}Pnmr spectra and a crystallographic structure of the product were taken.

Results

^{31}Pnmr data

8/ppm: -33.87(Pt), -4.638(P), 24.710(Pt)
^{1}J Pt-P = 2129.07 Hz

X-Ray crystallography showed this to be $PtCl_4(PMe_2Ph)_2$.

Discussion

The reaction was not successful. The platinum centre reacted more readily with the free Cl^- ions present in the solution than with the di-alkyl amine that is formed in the initial reaction (whether this has a merely transient existence or not we can only speculate). In order to make the reaction work successfully it would be necessary to include some sort of chloride abstractor in the reaction mixture and hence prevent Cl^- reacting with the $PtCl_2(PMe_2Ph)_2$.

viii) Reflux of $Pt(NSO)_2(PMe_2Ph)_2$ with Sulphur

Method

To toluene ($100cm^3$) was added $Pt(NSO)_2(PMe_2Ph)_2$ (15mg, 2.89×10^{-5}mol) and sulphur (2mg, 7.23×10^{-6}mol). The mixture was heated under reflux for 48 hours and then the solvent was removed in vaccuo. A ^{31}Pnmr spectrum of the product was recorded.

Results

The product was very oily and uncharacterisable.

ix) Synthesis of the Pt Cyclohexene dppe

(i) $PtCl_2$ dppe (50 mg, 7.31×10^{-5} mol) was dissolved in thoroughly degassed (freeze – thaw method) THF, and (ii) 3.65×10^{-4} moles (=3.07×10^{-2}g, =0.038 cm^3) cyclohexene (used in excess) dissolved in THF and the mixture thoroughly degassed (freeze – thaw method). (ii) was then added to (i) and the resulting solution stirred under N_2 for 90 minutes. 42 mg $NaBH_4$ were then added and the solution stirred for a further 10 minutes. 15 cm^3 of degassed, deionised water were then added to destroy any unreacted $NaBH_4$. The THF was then removed under vacuum, causing precipitation of a yellow solid, and the water was removed using a filter stick. Any remaining water was removed by gentle heating under vacuum. The solid was dissolved in freeze – thaw degassed and dried THF/d^6 acetone and ^1H and ^{13}C nmr of the product recorded.

Results.

<u>^1H and ^{13}C nmr Data.</u>

^1H:

δ / ppm	Multiplicity	Assignment
04084	Doublet. ^1J = 3.42 Hz	Alkane Protons
2.0769	Unresolvable Multiplet	Alkane Protons
3.9257	Unresolvanle Multiplet	Alkane Protons

^{13}C:

δ / ppm	Multiplicity	Assignment
5.5564	Singlet	Alkane C
30.5520	Singlet	Alkane C
72.3612	Singlet	Alkane C

Discussion

^1H and ^{13}C nmr spectra, it is clear that the target compound has not been produced. 4C signals and 5 H signals would be expected to be observed. However, 3 signals were observed in both the ^1H and ^{13}C spectra, and it may, therefore be concluded that the target compound was not produced.

x) Thermolysis of $Pt(NSO)_2$ dppm

An attempt to produce a bi-Pt-centred compound.

a.) 20 mg $Pt(NSO)_2$ dppm were refluxed in toluene, under N_2 (g) for 72 hours. The solvent was then removed in vaccuo and a ^{31}P nmr of the product recorded.

b.) The experiment was repeated, using the same amount of $Pt(NSO)_2$ dppm, this time refluxing in THF for 2 hours, and a subsequent experiment for 4 hours; based upon the principal that a 72 hour reflux in toluene may have been too extreme conditions. ^{31}P nmr of the product was then recorded.

Results

^{31}P nmr. Peaks were observed in the following positions.

Experiment	δ / ppm
a:	35.62, 5.91, -45.144 (Spectrum very noisy)
b:	35.867 (only discernible peak) (Spectrum very noisy)

Discussion

If the experiment had been successful, a singlet due to the phosphorus atoms should be observed, along with two Platinum satellites. This is clearly not the case. Further work will be required to try and produce a bi-Pt-centred compound, using different reaction conditions.

xi) Hydrolysis of $Pt(NSO)_2$ dppm

$Pt(NSO)_2$ dppm (20 mg, 2.84×10^{-5} mol) were dissolved in $CDCl_3$ ($1cm^3$) and 0.04 cm^3 of thoroughly degassed water was added. ^{31}P nmr spectra were taken after 1 hour, 24 hours and 48 hours. The spectra were very noisy and it was not possible to distinguish any specific peaks. The experiment was repeated twice more to confirm that the spectra from the first attempt were not anomalous. The same results were observed as for the first attempt.

The experiment was also tried using the same quantity of $Pt(NSO)_2$ dppm, but rather than adding water to the solution directly, it was left exposed to the air to allow moisture into the system. The results were the same as above.

Discussion

Since no data could be obtained to monitor any change in the Pt compound, it is possible that the presence of the water in the system may have destroyed the Pt compound, or that the $Pt(NSO)_2$ dppm may, in fact have decomposed due to the presence of other impurities in the solvent.

xii) Preparation of $Ni(S_2N_2PPh_2)_2$

$Ni(S_2N_2H_2)_2$ (50 mg, 2.04×10^{-4} mol) was dissolved in 100 cm^3 THF (dry – from still) to this was added $ClPPh_2$ (90 mg ≡ 0.07 cm^3) and the solution stirred under N_2 and very gentle reflux for 2 hours. The solution became a raspberry-reddish colour within 15 minutes. Every 10 minutes a small amount of solvent was removed in vaccuo in order to remove the HC1 that is a by-product of the reaction. ^{31}P nmr of the product was recorded.

Results

^{31}P *nmr.* Peaks were observed in the following positions:-
δ / ppm: *29.6880, 30.0036, 30.2517, 32.9158, 54.3555, 55.9501, 81.0130,* 81.2637, 81.4513.

Discussion.

From the ^{31}P nmr it is clear that this compound will require further purification (possibly by Prep TLC) before it can be fully characterised.

xiii) Reaction of $Ni(S_2N_2PPh_2)_2$ and $PtCl_2$ COD

$Ni(S_2N_2PPh_2)_2$ (164 mg, 2.67×10^{-4} mol) and $PtCl_2$ COD (100mg, 2.67×10^{-4} mol) were dissolved in THF (100 cm^3, dry from still) and heated under gentle reflux for 2 hours under N_2. Upon cooling a small amount of undissolved solid was observed to be present in the solution, and therefore, the mixture was heated more vigorously for a further 48 hours. At the end of this period it was observed that the solution had changed colour from raspberry-red to pale brown. The solvent removed in vaccuo and a ^{31}P nmr spectra of the product recorded.

Results

Yield = 0.105 g.

^{31}P nmr. Peaks were observed in the following positions:-
δ / ppm: 29.5923, 30.0170m, 30.2643, 32.9006, 33.7360, 55.9961, 81.0132,81.25944, 81.4683.

It was not possible to calculate the percentage yield of this product since from the nmr data it is very impure, and it is therefore difficult to say what its structure will be to calculate it's relative formula mass.

Discussion

As has already been stated the nmr data shows that the product is impure, and therefore, it will require further purification before it can be fully characterised. It is worth noting however, that the chemical shifts observed in the ^{31}P nmr spectrum are very similar to those of the $Ni(S_2N_2PPh_2)_2$ product. This may well indicate that a considerable amount of the starting material is present amongst the product.

xiv) Reflux of $Pt(NSO)_2$ dppe with Na_2S

$Pt(NSO)_2$ dppe (50 mg, 6.97×10^{-5} mol) and Na_2S (43 mg, 5.51×10^{-4} mol, 8 equivalents) were refluxed with stirring under nitrogen for 2 hours. The solution was

then allowed to cool and the solvent removed in vaccuo. A ^{31}P nmr spectrum of the product was taken.

Result

The ^{31}P nmr spectrum showed a singlet (no Pt satellites) at δ +45.35 ppm.

Discussion

The chemical shift observed in the ^{31}P nmr spectrum of the product is the same as that for dppe S_2. This, combined with the absence of Pt satellites in the spectrum shows that the di-phosphine ligand has been displaced from $Pt(NSO)_2$ dppe, and oxidised. It is possible that the reaction conditions used were too severe (i.e.too high a temperature), and it may be worth repeating the experiment in a lower boiling solvent such as THF.

xv) Attempted preparation of $SSNO^-$ anion and co-ordination to $PtCl_2$ dppe

a) [PPN][NO_2]/S_8 Method

[PPN][NO_2] (1g, 1.065 x 10^{-4} mol) and S_8 (1.75g, 6.84 x 10^{-3} mol were dissolved in 75 cm^3 of acetone which had been dried for a minimum of 24 hours over a molecular sieve and thoroughly degassed. The resulting solution was refluxed overnight. According to the literature, the resulting solution should have been a bright orange colour, yet despite trying the experiment eight times this was the case only twice.

25 cm^3 (assume homogenous therefore contains 3.01 x 10^{-3} mol $SSNO^-$) of this solution was added to Pt Cl_2 dppe (100 mg, 1.51 x 10^{-4} mol) via a canular, and the resulting solution stirred overnight under N_2 (g). The solvent was then removed in vaccuo and a ^{31}P nmr spectrum of the product taken.

Results

^{31}P nmr spectrum. A resonance at δ21.1933 ppm with no Pt satellites.

Discussion

Since no Pt satellites were observed in the ^{31}P nmr spectrum of the product, it was concluded that the di-phosphine ligand had been displaced from the starting material, and, therefore the target compound had not been produced. No further characterisation of the compound was attempted.

b) KNO_2/S_8 Method

The reaction was also tried using KNO_2 rather than [PPN][NO_2]. KNO_2 (145 mg, 1,71 x 10^{-3} mol) was refluxed with S_8 (1.75g, 6.84 x 10^{-3} mol), under the same conditions outlined previously. The resulting solution was bright orange in colour. This was transferred to a Schlenk containing $PtCl_2$ dppe ().568g, 8.53 x 10^{-4} mol) and the

resulting solution stirred under N_2 (g) overnight. The solvent was then removed in vaccuo and a ^{31}P nmr spectrum of the crude material taken.

Results

^{31}P nmr spectrum. A resonance was observed at δ41.203 ppm, with no Pt satellites.

Discussion

The absence of Pt satellites in the product indicates that the dppe ligand had been displaced from the starting material, and, therefore the target compound had not been synthesised. Because of this no further characterisation of the product was attempted.

c) [PPN]{NO_2]/Na_2S Method

The reaction was carried out under the same conditions outlined previously, but with Na_2S being used instead of S_8 as a source of sulphur, the principle being that the S_2^- ion may react more readily with [PPN][NO_2] to produce $SSNO^-$ ion.

[PPN][NO_2])1g. 1.065×10^{-4} mol) and Na_2S (1.16333g, 1.37×10^{-2} mol) were used. To the resulting solution, $PtCl_2$ dppe (1.102g, 1.66×10^{-3} mol) and 1 drop of dbu)diazabicyclaundec-7-ene) ere added and the solution was stirred under N_2 for 2 hours. A ^{31}P nmr spectrum of the crude product was recorded.

Result

^{31}P nmr. Resonances were observed at:-

δ 29.6074, 40.2855, and 47.7477 ppm.

No Pt Satellites were observed.

Discussion

Since no Pt satellites were observed in the ^{31}P nmr of the product, it is evident that the dppe ligand had been displaced from the starting material, and the target compound had not been produced. No further characterisation of the product was attempted.

xvi Preparation of SNO^- ion

According to the literature [2], this may be generated by reacting $SSNO^-$ with 1 equivalent of triphenylphosphine. 37.5 cm^3 of "$SSNO^-$" solution (assume homogenous and therefore contains 1.7×10^{-3} mol $SSNO^-$) were transferred by canular into a Schlenk flask containing $PtCl_2$ dppe (0.564 g, 8.5×10^{-4} mol), and the solution stirred under N_2 overnight. The solvent was then removed in vaccuo and ^{31}P nmr of the crude product taken.

Results

^{31}P nmr. A signal was observed at δ 21.193 ppm, but no Pt satellites were present.

Discussion

Since no Pt satellites were observed in the ^{31}P nmr, it is evident that the dppe ligand had been displaced from the starting material. therefore the target compound had not been produced and no further characterisation of the product was attempted.

xvii) Synthesis of $dppeS_2$

N.B. This was synthesised to facilitate a comparison of its ^{31}P nmr shift with the products of both the $SSNO^-$ reactions and the reflux of $Pt(NSO)_2$ dppe with S_8 and Na_2S.

dppe (100 mg, 2.39 x 10^{-4} mol) was refluxed with 2 equivalents of S_8 (0.123 g, 4.78 x 10^{-4} mol) for 1 hour under nitrogen in toluene. The solvent was then removed in vaccuo and its ^{31}P nmr spectrum recorded.

Results

^{31}P nmr: δ dppeS_2 = 45.3512 ppm (singlet).

xviii) Liquid Chromatography on S_x from $NH_3(l)$ / S solution.

The purpose of this experiment was to investigate whether the structure of sulphur was changed (as compared to its naturally occurring form) after dissolution in ammonia, and the subsequent evaporation of the ammonia.

Experimental

500mg S was dissolved in $10cm^3$ $NH_3(l)$ and was left to stir and warm up overnight. Residual $NH_3(g)$ was removed in vaccuo (ca 2 hours). The product dissolved in MeOH and washed through a silica plug in a filter funnel to remove any ionic species that would damage an LC column. Absorbance maxima were ascertained prior to running a chromatograph by taking the UV spectrum of a solution of the product against a CH_2Cl_2 blank. Subsequently absorbance maxima for S in CH_2Cl_2 were measured in the same way to enable comparison of the chromatograph for the product with that of the starting material.

1mg of the product was dissolved in $10cm^3$ 60/80 petrol, and the chromatograph run using HPLC grade MeOH as the mobile phase. The column was C-18 reversed-phase. 10µl of the sample solution was injected onto the column and a flow rate of $1cm^3$ /ml was used.

The procedure was also carried out using S.

Results

	Starting Material			**Product**		
Wavelength /nm	300.4	301.6	304.0	300.4	301.6	304.0
Time	5 min 34 sec	5 min 42 sec	5 min 40 sec	5 min 34 sec	5 min 42 sec	5 min 40 sec

Discussion

By comparison of the HPLC traces of the starting material and product, it is clear the sulphur reverts to its original structure upon evaporation of NH_3 from the solution.

SECTION B

SPECTROSCOPIC WORK

Experimental

ixx) Raman Spectroscopy on Liquid Ammonia Solutions (Overview)

The remit for this particular part of this project was to try and expand upon earlier work by Chivers et al. [66]

Systems using $NH_3(l)$ as the solvent, but with various other components added to them (e.g. Sulphur, $SOCl_2$, SO_2Cl_2, S_4N_3Cl, Se, $SeOCl_2$ and Se/S) were investigated using Raman spectroscopy, to both ascertain the species present in the solutions, and also if their concentration (inferred as a function of the relative intensity of signal for a given species) varies with time.

Method (General)

Measurements were made using a Perkin-Elmer System 2000 FT-IR/Raman spectrometer. All solutions were prepared using standard Schlenk line techniques and the solutions were protected from light in between measurements by wrapping the Raman cells in aluminium foil. (**NB:** liquid ammonia solutions containing sulphur are known to undergo photo-induced degradation).

The experiments were carried out in specially constructed cells as illustrated in fig.2. below :

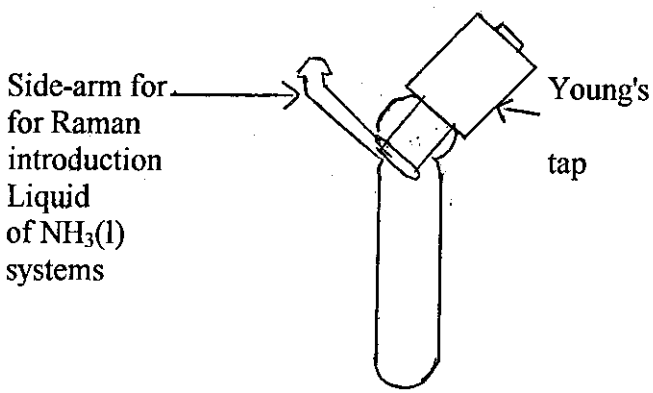


Fig.2. Cell used
spectroscopy on
Ammonia

Ammonia was collected under $N_2(g)$ in oven-dried Schlenk tubes and was condensed by standing the Schlenk tubes in a dry-ice/acetone cold bath at -78°C. The Raman cells were also cooled in a dry-ice/acetone prior to the introduction of $3cm^3$ of ammonia.

In all experiments a blank Raman spectrum of $NH_3(l)$ was subtracted from the spectrum of the sample solution to enable a clearer view of the species present in the solution to be obtained.

xx) Raman Spectroscopy on $NH_3(l)$ / S system.

Three cells (distinguished by a dot numbering system) were set up as detailed in Table 3 below.

Table 3

Cell#	Volume of $NH_3(l)/cm^3$	Amount of S /g
1	3	0.109
2	3	0.218
3	3	0.327

Initially the cells were allowed to warm for 4 hours prior to any measurements being taken, this was to prevent condensation on the outside of the cells affecting the passage of light through the cells. The intensity of the signals was normalised as a percentage against the largest peak in the spectrum, this was to allow for variations in the absorbance of the solution from one measurement to another.

The laser power was optimised in order to achieve the best spectrum (i.e. best signal: noise ratio) in a previous experiment. Each spectrum was the average of 20 scans of the solution.

A further experiment on this system was carried out over the initial 17 minute time period from adding the liquid ammonia to the sulphur. The purpose of the investigation was to ascertain the species present as the sulphur dissolved in the $NH_3(l)$. This time period was used as it was already known from the previous experiment that the sulphur would be completely dissolved in the ammonia by this time.

Vial #	Time/min	Species Present and Wavenumber / cm^{-1}	
1	1	S	475(s), 441(w), 249(w), 220(s), 180(w)
	5	S	475(s), 440(w), 249(w), 220(s), 188(w)
	9	S_4N^-	712(s), S_3N^-/S_2^- 573(w), S 474 (m/s), 441(w), S_4^-403(w), S 248(m/w), 220(s), 187(w)
	13	S_4N^-	712(s), S_3N^-/S_2^- 573(m), S 474 (m/s), 441(w), S_4^-403(w), S 248(w), 220(s), 187(w)
	17	S_4N^-	712(s), S_3N^-/S_2^- 573(m), S_4^-514(m/w), S_2^{2-} 461(m), S_4^-404(m), S 248(m), 226(m), 181(m)
2	1	S	475(s), 220(s)
	5	S	475(s), 440(w), 249(w), 220(s), 180(w)
	9	S_4N^-	712(m), S_3N^-/S_2^- 573(w), S 474(m/s), 441(w), 403(w), 248(w), 220(s), 182(w)
	13	S_4N^-	712(m), 594(w), S_3N^-/S_2^-573(m), S_4^{2-} 481(m), S_3^{2-}462(m/s), S_4^-404(m/s), S248(w), 224(w/m), 182(w/m)
	17	S_4N^-	712(s), 593(w/m), S_3N-/S_2^- 573(m), S482(m), 461(m/s), S/S_4^- 404(m), S249(m), 225(m), 181(m)
3	1	S	475(s), 441(w/m), 249(w/m), 220(s), 188(w)
	5	S_4N^-	712(v,w), S475(s), 440(w/m), 249(w/m), 220(s), 188(w)
	9	S_4N^-	712(m/w), S_3N^-/S_2^- 573(w), S474(s), 440(m/w), 248 (m/w), 220(s), 188(w)
	13	S_4N^-	712(m/s), 593(m), S_3N^-/S_2^-573(m), S_4^-511(m/w), S_3^{2-}462(m), S_4^-/S404(m) S250(m/w) , 224(m/w), 181(m/w)
	17	S_4N^-	712(s), 594(m/w), S_3N^-/S_2^-573(m), S_4^{2-}481(m), S_3^{2-}462(m), S_4^-/S404(m), S248(w), 225(w), 181(w)

Table .4. S/NH_3(l) Raman.

Discussion

As can be seen from the tabulated data, over the initial 17 minutes of the experiment S, S_4N^-, S_3N^- / S_2^-, S_4^- are observed from the Raman spectra to be in solution; the only species present over the first 5 minutes being S itself. As the solution warmed up and the sulphur became more soluble in the ammonia more species were observed in the solutions, as the ammonia and sulphur reacted with each other. (**NB:** these reactions are known to be reversible, since upon evaporation of ammonia, only sulphur remains, see previous section on HPLC of the residue from a sulphur/ammonia solution).

After this initial time period the only discernible species in solution were S_4N^- (~ $709cm^{-1}$),

S(~ $449cm^{-1}$), S_3N^- / S_2^- (~$587cm^{-1}$) and S_4^- (~$400cm^{-1}$). This did not alter over the 170 hour period of the experiment. The approximate quantity of each species present expressed as a percentage, remained approximately constant over the period of the experiment. This confirms the earlier findings of Chivers et al [66] who also postulated that the species present are involved in a highly complex series of equilibrium which even as yet require further investigation to understood.

xxi) Raman Spectroscopy on S / $SOCl_2$ / NH_3(l) solutions.

Method

The solutions detailed in table .4. below were set up. Liquid ammonia was collected as previously described, to which was added 1cm^3 $SOCl_2$, the mixture was then stirred for 10 minutes prior to transferring a 3cm^3 alginate to each Raman cell. (NB: the reaction between $SOCl_2$ and NH_3(l) is known to be generate the thionylomide ion, NSO^- [1]).

Table .5.

Cell#	Amount of S /g
1	0.109
2	0.218
3	0.327

A Raman laser power of 250mW was used, and 20 scans were taken for each spectrum. A blank spectrum of NH_3(l) was subtracted from the spectrum of each sample solution.

Results

See Table .6. for results.

Table .6. $NH_3(l)/SOCl_2$/ S Raman

Cell #	Wavenumber /cm^{-1}	Time/Lb							
		1	24	48	72	120	144	168	192
		Intensity/%							
1	712	100	100	100	100	100	100	100	100
	591	19.40	19.37	18.71	18.75	17.50	18.35	17.95	18.01
	572	30.0	30.0	30.32	28.13	29.38	28.48	28.21	27.95
	511	8.75	6.25	5.48	3.75	4.38	3.16	3.21	2.48
	461	38.75	29.37	27.74	24.38	23.75	18.98	16.66	14.91
	403	33.13	24.38	20.65	18.13	16.88	13.92	13.46	11.80
	246	27.5	15.63	14.84	12.50	15.63	11.39	12.18	9.32
	226	32.5	20.63	20.65	18.75	23.13	19.62	19.23	17.39
	179	28.13	14.38	13.55	11.88	17.50	11.39	12.18	9.94
2	712	100	100	100	100	100	100	100	100
	591	18.13	18.00	18.13	19.18	17.74	17.39	18.47	17.72
	572	28.13	27.33	28.75	26.03	26.45	26.71	27.39	27.22
	511	8.13	7.33	8.13	3.42	5.16	6.21	4.46	4.43
	461	42.50	40.67	38.75	28.77	30.96	29.81	28.03	26.58
	403	35.00	32.00	31.25	20.55	24.52	23.60	21.02	20.89
	246	24.38	20.67	23.75	5.48	17.42	18.01	15.29	15.19
	226	29.38	26.67	29.38	10.27	25.16	25.47	21.66	22.15
	179	25.63	22.00	25.00	3.42	18.06	19.25	15.92	15.82
3	712	100	100	100	100	100	100	100	100
	591	20.51	20.70	21.01	18.47	21.66	21.02	21.02	19.75
	572	30.77	29.30	29.94	27.39	31.85	28.66	29.94	28.66
	511	8.33	7.64	8.28	7.01	7.64	5.09	6.37	4.78
	461	36.54	36.31	35.03	37.58	29.62	29.30	26.75	26.11
	403	29.49	28.34	26.75	29.94	24.20	21.02	19.75	19.75
	246	15.38	15.29	15.29	21.02	11.46	15.29	10.19	9.55
	226	18.27	19.11	19.11	27.39	15.29	15.29	14.65	15.29
	179	11.54	12.10	10.83	22.93	8.92	7.64	7.01	7.64

Discussion

The species present in the solutions were the same as observed in S / NH_3(l) solutions. Once again, the concentration of these species remained approximately constant over the course of the experiment. The addition of $SOCl_2$ to the liquid ammonia did not apparently influence the nature of the species present in the solution, but it is worth noting that no peaks for the NSO- ion itself were observed in the spectra, although it is quite possible that these were marked by the spectrum of NH_3(l), even after the subtraction of the background spectrum of NH_3(l).

xxii) Raman Spectroscopy on S / SO_2Cl_2 / NH_3(l) Solutions.

Method

In these experiments the solutions detailed in table .7. below were set up in Raman cells.

SO_2Cl_2 was added to $10cm^3$ NH_3(l) which had been collected in Schlenk tubes. (SO_2Cl_2 and NH_3(l) react to form sulphamide ($SO_2(NH_2)_2$) or its mono-or di-anion). The purpose of adding SO_2Cl_2 was to investigate if the presence of sulphamide ions would influence the nature of the species present in an NH_3(l) / S solution in any way.

Table .7.

Cell#	Amount of S /g	Amount of SO_2Cl_2 /cm^3
1	0.218	1
2	0.218	2
3	0.218	3

A Raman laser power of 250mW was used, and 20 scans were taken for each spectrum.

A blank spectrum of NH_3(l)was subtracted from the spectrum of each sample solution.

Results

See Table .8. for results.

Table .8. S / SO_2Cl_2 / NH_3(l) Raman.

Cell#	Wavenumber /cm^{-1}	TIME/HOURS						
		1	18	24	48	66	72	90
		INTENSITY/%						
1	712	100	100	100	100	100	100	100
	593	21.68	21.98	21.27	20.52	21.74	19.31	20.89
	572	29.49	29.32	29.07	28.36	28.62	28.27	30.59
	511	12.1	13.61	12.41	11.19	7.97	10.69	13.43
	461	45.10	47.38	43.97	43.28	41.30	45.51	45.52
2	712	100	100	100	100	100	100	100
	593	3.7	13.53	10.91	8.5	20.00	12.94	6.85
	572	7.48	23.31	20.91	18.18	32.00	22.35	20.55
	511	13.08	6.02	1.82	2.84	75.00	1.18	2.74
	461	31.78	43.61	40.91	39.77	41.00	47.06	41.10
3	712	100	100	100	100	100	100	100
	593	7.41	9.84	12.59	8.85	5.62	5.43	2.94
	572	19.76	20.49	20.98	20.35	17.98	22.83	8.82
	511	0.99	1.64	2.09	8.85	0.56	1.09	0.74
	461	34.58	37.70	38.46	38.93	31.46	32.61	23.53

Peak Assignments

712 cm^{-1} S_4N^-/Sulphamide
593 cm^{-1} S_2^-
572 cm^{-1} S_3N^-/Sulphamide
511 cm^{-1} S_4^-
461 cm^{-1} S_3^{2-}

Discussion

From the data in Table .8. it is again clear that the concentration of species present in the solutions (taken as a function of peak intensity) remains approximately constant with time. This would indicate that the species present are participating in equilibria with each other, or with components of the solution that are not Raman active and are therefore not visible in the spectrum; such that their concentration remains approximately constant.

The peak at $572cm^{-1}$ is due to sulphamide in the solution (this was ascertained by taking a Raman spectrum of pure sulphamide on its own). The other peaks are due to the species detailed at the foot of the results table, and are the same as those present in a solution of $S/NH_3(l)$. It is, therefore, possible to conclude that the presence of sulphamide in the solution has not influenced the nature of the other species present.

xxiii) Raman Spectroscopy on (S/Se)/NH_3(l) solutions.

Liquid ammonia was collected as previously described. Two cells were set up as detailed in Table .9. below.

Table .9.

Cell#	Amount of Selenium used
1	10% by weight
2	10% by mol

The percentage of selenium was based upon using 0.109g S. Raman spectra were taken over a 258 hour time period, as detailed in table ...; using a laser power of 300mW and 20 scans were taken for each spectrum. A blank spectrum of liquid ammonia was subtracted from the spectrum of each sample solution.

Results

See Table .10. for results.

Table .10. S/Se/NH_3(l) Raman.

		1	18	24	42	66	114	138	162	186	210
		Intensity/%									
Cell #	Wavenumber /cm^{-1}	Time/Hrs									
1	712	100	100	100	100	100	100	100	100	100	100
	590	21.28	13.42	17.96	15.04	21.30	19.17	17.75	14.98	21.33	14.41
	572	31.29	23.96	28.13	25.85	28.69	26.67	28.04	24.98	32.33	22.41
	510	16.89	5.75	11.72	7.52	13.91	10.83	11.21	8.49	14.67	6.94
	461	55.06	47.94	53.91	51.69	56.09	52.08	51.87	49.95	56.00	50.16
	403	48.81	39.31	45.70	42.29	47.83	45.83	44.39	41.46	48.33	41.62
	312	18.15	9.59	15.63	12.69	20.00	14.17	13.55	8.99	19.33	8.00
	237	30.66	75.74	60.15	43.70	34.78	35.33	35.04	34.46	54.00	36.29
	225	37.55	36.91	40.63	37.59	40.87	35.83	37.38	34.97	43.67	29.88
	182	31.41	29.72	34.77	30.55	34.35	32.08	30.84	27.97	38.33	24.01
2	712	100	100	100	100	100	100	100	100	100	100
	590	63.88	50.76	52.53	54.45	51.02	54.25	48.18	54.66	65.86	21.07
	572	63.14	52.79	56.49	55.44	53.45	57.87	49.58	56.56	68.73	23.74
	537	58.74	43.65	46.09	51.95	41.30	48.82	39.11	46.58	56.70	17.51
	460	63.88	60.91	62.93	63.94	60.25	62.39	59.36	61.79	80.76	30.86
	406	55.07	52.79	55.99	55.44	54.91	54.70	48.18	57.03	73.88	27.29
	230/237	32.31	55.33	50.55	35.46	33.04	32.55	77.51	34.69	64.72	24.63
	153	51.40	40.61	38.16	45.95	44.22	40.69	37.71	43.25	52.69	29.97

Discussion

It is clear from table .10. and by reference to table .4.($S/NH_3(l)$ expt.) that the only species present in solution are S-N species. The purpose of using a mixed S/Se system was to try and solubilise the Se with the S as it dissolved. (Se is insoluble on its own in liquid ammonia, but may be solubilised in the presence of a small amount of Na, but this yields a very cloudy solution unsuitable for Raman spectroscopy), but this was found not to be the case since no signals attributable to a mixed S/Se species were observed.

Again, it was observed that the quantity of each species present remained approximately constant over the course of the experiment.

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