THE PREPARATION OF METALLA-SULPHUR/SELENIUM COMPLEXES FROM REACTIONS IN LIQUID AMMONIA

J. Woollins

► To cite this version:

J. Woollins. THE PREPARATION OF METALLA-SULPHUR/SELENIUM COMPLEXES FROM REACTIONS IN LIQUID AMMONIA. Journal de Physique IV Proceedings, 1991, 01 (C5), pp.C5-217-C5-222. 10.1051/jp4:1991525 . jpa-00250649

HAL Id: jpa-00250649

<https://hal.science/jpa-00250649>

Submitted on 1 Jan 1991

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

THE PREPARATION OF METALLA-SULPHUR/SELENIUM COMPLEXES FROM REACTIONS IN LIQUID AMMONIA

J.D. WOOLLINS

Department of Chemistry, Imperial College London, GB-London SW7 2AY, Great-Britain

Abstract - The preparation of metalla-sulphur-nitrogen and metalla-selenium-nitrogen complexes from reactions in liquid ammonia is described. For example, reaction of $\text{PtCl}_2(\text{PR}_3)_2$ with $[\text{S}_4\text{N}_3]\text{Cl}$ in liquid ammonia yields $\text{Pt}(\text{S}_2\text{N}_2)(\text{PR}_3)_2$. Similar reactions with SOCl_2 , SO_2Cl_2 and SeCl_4 give complexes containing NSO^- , $[\text{SO}_2(\text{NH})_2]^{2-}$ and $\text{Se}_2\text{N}_2^{2-}$ ligands respectively.

The preparation of metalla-sulphur-nitrogen complexes is not a new area of research. Adducts of S_4N_4 with metal halides such as TiCl_4 were reported¹ in 1908. The first example was obtained² by reaction of PbI_2 with S_4N_4 in liquid ammonia and formulated as $\text{Pb}(\text{S}_2\text{N}_2)\cdot\text{NH}_3$ in 1904 by Ruff and Geisel although it was not until 1966 that Weiss established the structure by single crystal X-ray studies³. The area was developed in the 1950s by Margot Becke-Goehring and co-workers and has undergone a resurgence of interest in the past decade. There is now a wide range of metalla-sulphur-nitrogen complexes known with ligands ranging from the simple monodentate thionitrosyl NS , *via* bidentate $\text{S}_2\text{N}_2^{2-}$, S_3N^- , $\text{S}_3\text{N}_2^{2-}$ to tridentate S_4N_3^- , $\text{S}_3\text{N}_4^{2-}$ and $\text{S}_4\text{N}_4^{2-}$. It is interesting to note that many of the anions which are stabilised by coordination are otherwise not known. The area has been reviewed by ourselves⁴ and by Chivers and Edelmann⁵. The majority of the syntheses reported involve reactions of S_4N_4 or sulphur-nitrogen halides and although these reactions often proceed in good yield they are not mechanistically explicable in many cases. A particular problem is the explosive nature of S_4N_4 which makes this unsuitable as a starting material unless strict safety precautions are observed.

We have investigated the usefulness of reactions of a variety of S-N and sulphur halides in liquid ammonia since this solvent offers significant advantages for these syntheses: [1] It is obtained commercially quite cheaply in an extremely pure state [2] it will dissolve inorganic metal salts and starting materials easily and [3] for our reactions it may also provide a source of nitrogen atoms in the final molecule. The reactions described here were all performed in conventional glassware, under nitrogen. In typical reactions we take approximately 15 ml of liquid ammonia and add 1 mmol of the appropriate S-N species or sulphur/selenium halide followed by 1 mmol of $\text{PtCl}_2(\text{PR}_3)_2$ (1). The reaction is stirred at -78°C and gradually allowed to warm to room temperature during which time the ammonia evaporates off. The resulting solid may be extracted with an appropriate organic solvent such as dichloromethane to yield the final metal complex.

Our earliest studies centred around developing new routes to complexes containing $\text{S}_2\text{N}_2^{2-}$ and related ligands. We have prepared complexes of the type $\text{Pt}(\text{S}_2\text{N}_2)(\text{PR}_3)_2$ (2) and $[\text{Pt}(\text{S}_2\text{N}_2\text{H})(\text{PR}_3)_2]\text{X}$ (3) by a variety of routes. (3) are of particular interest since they form stacking structures in the solid state. Prior to our studies in liquid ammonia the most satisfactory routes to (2) and (3) involved reactions of either the very explosive $\text{Na}[\text{S}_3\text{N}_3]$ or $\text{S}_4\text{N}_4/\text{dbu}$ (dbu = diazabicycloundecane). Neither of these S-N starting materials is especially satisfactory, the former because it is explosive in its own right, and the latter because it is obtained from explosive S_4N_4 .

Initially we reacted the readily available (and non-explosive) $[\text{S}_4\text{N}_3]\text{Cl}$ with (1) in liquid ammonia to obtain good yields of (2) as shown in eqn 1. This reaction also proceeds well with Me_2SnCl_2 to give $[\text{Me}_2\text{Sn}(\text{S}_2\text{N}_2)]_2$ and with NiCl_2 or $[\text{Ni}(\text{NH}_3)_6]\text{Cl}_2$ to give $\text{Ni}(\text{S}_2\text{N}_2\text{H})_2$. Further studies reveal that there is actually no need to use a preformed S-N compound at all for these reactions and that SCL_2 provides an appropriate source of sulphur for the preparation of (2) in liquid ammonia (eqn 2)

The reaction according to eqn 1 and 2 can be extended to include the syntheses of SSeN_2^{2-} and $\text{Se}_2\text{N}_2^{2-}$ containing complexes (4) and (5). Thus reaction of mixtures of SeCl_4 and $[\text{S}_4\text{N}_3]\text{Cl}$ gives (4) whilst (5) is obtained from reaction of SeCl_4 . The structures of (2-5) as well as their protonated analogues have been established by X-ray crystallography.

(4)

(5)

The formation of (4) and (5) in a simple 'one-pot' reaction using liquid ammonia represents an extremely straightforward and hazard free synthesis. We have been able to prepare (5) via reactions involving Se_4N_4 but this compound is even more hazardous than S_4N_4 and should be avoided as far as possible. To date, we have not been able to prepare mixed S/Se ligands by any route which does not involve liquid ammonia. Surprisingly, attempts to prepare $\text{Ni}(\text{SeSN}_2\text{H})_2$ and $\text{Ni}(\text{Se}_2\text{N}_2\text{H})_2$ by analogous routes have been unsuccessful. Indeed in reactions involving NiCl_2 with SeCl_4 the metal salt appears to catalyse the formation of Se_4N_4 .

We have extended the above strategy and using similar reaction conditions have been able to synthesise *cis*- $\text{Pt}(\text{NSO})_2(\text{PR}_3)_2$ (6) and $\text{Pt}[(\text{HN})_2\text{SO}_2](\text{PR}_3)_2$ (7). In (6) the NSO ligands are bonded to the metal as simple σ -donors through nitrogen whilst in (7) the ligand is N-coordinated and isoelectronic with SO_4^{2-} . In all cases (2-7) are air stable solids, reflecting the ability of the metal centre to stabilise otherwise reactive S-N anions.

A simple way of defining many of the reactions we have observed is that the ammonia functions either to remove S(II) from an S-N starting material or it serves to deprotonate simple molecules such as sulphamide. Mechanistically, the formation of (2) is of some interest and we have investigated the nature of the S-N anion in liquid ammonia solution by ^{14}N NMR. If $[\text{S}_4\text{N}_3]\text{Cl}$, $[\text{S}_3\text{N}_2\text{Cl}]\text{Cl}$ or S_2Cl_2 is dissolved in liquid ammonia the ^{14}N NMR spectrum consists of the main signal due to NH_3 together with a signal at 148 ppm (with respect to liquid ammonia) which is readily identified as being due to the $[\text{S}_3\text{N}_3]^-$ anion. This observation is entirely compatible with our previous observation that (2) may be prepared from the $[\text{S}_3\text{N}_3]^-$ anion. ^{14}N NMR may also be used to identify the NSO^- anion in liquid ammonia ($\delta = 502$ ppm) and tentatively suggest the presence of the $[\text{Se}_3\text{N}_3]^-$ anion ($\delta = 180$ ppm). In contrast to the above solutions which have spectra that do not change with time dissolution of SCl_2 in liquid ammonia initially gives a dark red solution which changes with time to an intense blue. The red solution has signals at $\delta = 149, 141/51$ and 64 ppm which are assigned to $[\text{S}_3\text{N}_3]^-$, $[\text{S}_4\text{N}_5]^-$ and (tentatively) $\text{S}_\text{N}\text{NH}/\text{S}_\text{N}(\text{NH})_2$ respectively. After 16 hours a new peak at $\delta = 483$ ppm (S_4N^-) accounts for 5% of the nitrogen containing species whilst the amount of $[\text{S}_4\text{N}_5]^-$ has increased and the amount of $\text{S}_\text{N}\text{NH}/\text{S}_\text{N}(\text{NH})_2$ and $[\text{S}_3\text{N}_3]^-$ has decreased. With time the peaks due to $\text{S}_\text{N}\text{NH}/\text{S}_\text{N}(\text{NH})_2$ decrease in intensity whilst that due to S_4N^- increases.

We have also measured the ^{14}N NMR of solutions of S_4N_4 in liquid ammonia and observe peaks due to $[\text{S}_3\text{N}_3]^-$ and $[\text{S}_4\text{N}_5]^-$. ^{15}N labelled S_4N_4 was dissolved in liquid ammonia to determine if the nitrogen atoms in the S-N heterocycle exchange with the solvent. Figure 3 illustrates the decrease in the amount of ^{15}N in recovered S_4N_4 as a function of time as determined by mass spectrometry. It is clear that although $[\text{S}_3\text{N}_3]^-$ and $[\text{S}_4\text{N}_5]^-$ are formed upon initially dissolving S_4N_4 the ^{15}N label continues to be exchanged with the solvent suggesting the presence of a number of equilibria.

Figure 1 The X-Ray Crystal Structures^{12,14} of (6) and (7)

A somewhat surprising reaction occurs if $S_4N_4O_2$ is used: complexes (8) (Figure 2) containing an MS_2N_3 ring with an exocyclic SO_2NH_2 group are obtained.

Figure 2 The X-Ray Crystal Structure¹⁵ of $Pt(PMe_2Ph)_2(S_2N_3(SO_2NH_2))$.

Figure 3 ^{15}N content of S_4N_4 recovered from $[\text{S}_4^{15}\text{N}_3]\text{Cl}$ (open circles) and $\text{S}_4^{15}\text{N}_4$ (solid circles) in liquid ammonia.

In conclusion it is clear that liquid ammonia provides an excellent solvent for the preparation of M-S-N and M-Se-N compounds and we expect to see its use in this regard expand considerably. However, the speciation and mechanistics of the reactions remain difficult and further work is needed.

References

- 1 H. Wolbling, *Z.Anorg.Allg.Chem.*,1908,**57**,286.
- 2 O.Ruff and E.Geisel,*Ber.Dtsch.Chem.Ges.*,1904,**37**,1573.
- 3 J.Weiss, *Z.Anorg.Allg.Chem.*,1966,**343**,315.
- 4 P.F.Kelly and J.D.Woollins, *Polyhedron*,1986,**5**,607.
- 5 T.Chivers and F.Edelmann, *Polyhedron*,1986,**5**,1661.
- 6 P.S.Belton, I.P.Parkin, D.J.Williams and J.D.Woollins,*J.Chem.Soc.,Chem.Comm.*, 1988,1479.
- 7 C.A.O'Mahoney, I.P.Parkin, D.J.Williams and J.D.Woollins,*J.Chem.Soc.,Dalton Trans.*,1989,1179.
- 8 J.Tillet, V.C.Ginn and J.D.Woollins, unpublished.
- 9 C.A.O'Mahoney, I.P.Parkin, D.J.Williams and J.D.Woollins,*Polyhedron*,1989,**8**, 2215.
- 10 I.P.Parkin and J.D.Woollins, *J.Chem.Soc.,Dalton Trans.*,1990,925.
- 11 P.F.Kelly, I.P.Parkin, A.M.Z.Slawin, D.J.Williams and J.D.Woollins, *Angew.Chem.Int.Ed.Engl.*,1989,**28**,1047.
- 12 I.P.Parkin, A.M.Z.Slawin, D.J.Williams and J.D.Woollins, *J.Chem.Soc.,Chem.Comm.*, 1989,1061.
- 13 I.P.Parkin and J.D.Woollins, *J.Chem.Soc.,Dalton Trans.*,1990,519.
- 14 I.P.Parkin, A.M.Z.Slawin, D.J.Williams and J.D.Woollins,*Polyhedron*, 1989,**8**,835.
- 15 I.P.Parkin, A.M.Z.Slawin, D.J.Williams and J.D.Woollins, *J.Chem.Soc.,Chem.Comm.*, 1989,58.
- 16 I.P.Parkin, J.D.Woollins and P.S.Belton, *J.Chem.Soc.,Dalton Trans.*,1990,511.