Facile Synthesis of SN and S–N–O Complexes in Liquid Ammonia; *X*-Ray Structure of $Pt[(HN)_2SO_2](PPh_2Me)_2$

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Addition of SCl_2, $SOCl_2$, SO_2Cl_2, or $SeCl_4$ to liquid ammonia followed by $Pt(PR_3)_2Cl_2$ gives complexes of the type $Pt(S_2N_2)(PR_3)_2$, $Pt(NSO)_2(PR_3)_2$, $Pt[(HN)_2SO_2](PR_3)_2$, and $Pt(Se_2N_2)(PR_3)_2$ respectively; the *X*-ray structure of $Pt[(HN)_2SO_2](PPh_2Me)_2$ is reported.

A number of groups are involved in the synthesis of metalla-sulphur–nitrogen compounds.[1,2] These compounds are of interest since the metal centres stabilise otherwise unknown SN anions and some of the materials possess interesting solid state structures. The majority of the preparative routes involve a number of stages, typically including the isolation of one or more sulphur–nitrogen precursors. For example, we have described the synthesis of $Pt(S_2N_2)(PR_3)_2$ (**1**) from reactions[3,4] involving $Na[S_3N_3]$ or $S_4N_4H_4$. Although these reactions proceed in good yield $Na[S_3N_3]$ is explosive

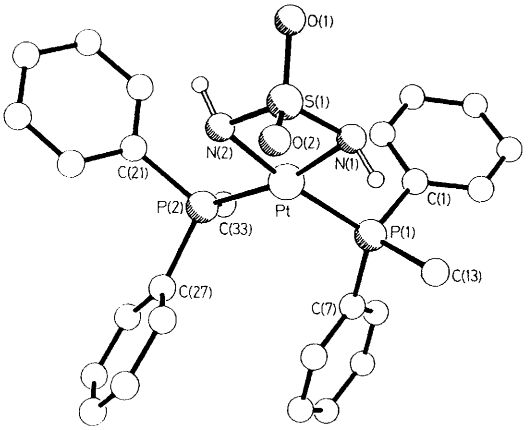

Figure 1. The *X*-ray structure of $Pt[(HN)_2SO_2](PPh_2Me)_2$ (**3**). Selected bond lengths and angles: Pt–N(1) 2.073(5), Pt–N(2) 2.061(5), N(1)–S(1) 1.614(5), S(1)–N(2) 1.636(5), Pt–P(1) 2.250(1), Pt–P(2) 2.249(1), S(1)–O(1) 1.436(5), S(1)–O(2) 1.454(6) Å; N(1)–Pt–N(2) 71.9(2), N(1)–Pt–P(1) 95.0(1), P(1)–Pt–P(2) 100.0(1), P(2)–Pt–N(2) 93.2(1), Pt–N(1)–S(1) 95.8(2), N(1)–S(1)–N(2) 96.6(2), S(1)–N(2)–Pt 95.5(2), O(1)–S(1)–O(2) 114.1(3)°.

and $S_4N_4H_4$ is obtained by reduction of S_4N_4 which is also difficult to handle. There have been some reports on the preparation of NSO^- complexes. We have[5] used $Hg(NSO)_2$ whilst Heberhold[6] and Roesky[7] used potassium salts of NSO^- and $RNSN^-$ which are very air sensitive and explode violently on contact with chlorinated solvents. Recently,[8—10] we have found that a number of SN compounds [*e.g.* S_4N_4, $S_4N_4O_2$, $S(NSO)_2$] dissolve and react to form metal complexes in liquid ammonia. Here, we report on simple 'one-pot' routes which do not require the isolation of any SN or SNO starting materials or special handling precautions (equations 1—3). Furthermore, we have also been able to apply this methodology to the synthesis of the first examples of complexes containing the bidentate $O_2S(NH)_2{}^{2-}$ or $Se_2N_2{}^{2-}$ ligands (equations 3 and 4).

$$2SCl_2 + 8NH_3(l) + PtCl_2(PR_3)_2 \rightarrow \underset{\mathbf{(1)}}{Pt(S_2N_2)(PR_3)_2} + 6NH_4Cl \qquad (1)$$

$$2SOCl_2 + 8NH_3(l) + PtCl_2(PR_3)_2 \rightarrow \underset{\mathbf{(2)}}{cis\text{-}Pt(NSO)_2(PR_3)_2} + 6NH_4Cl \qquad (2)$$

$$SO_2(NH_2)_2 + 2NH_3(l) + PtCl_2(PR_3)_2 \rightarrow \underset{\mathbf{(3)}}{Pt[(HN)_2SO_2](PR_3)_2} + 2NH_4Cl \qquad (3)$$

$$2SeCl_4 + 8NH_3(l) + PtCl_2(PR_3)_2 \rightarrow \underset{\mathbf{(4)}}{Pt(Se_2N_2)(PR_3)_2} \; 6NH_4Cl + 2Cl_2 \qquad (4)$$

In a typical reaction the sulphur halide or oxyhalide (1—2.5 mmol) is carefully added to $NH_3(l)$ (10 ml) at −78 °C. After stirring for *ca.* 30 min $PtCl_2(PR_3)_2$ (0.5—1.25 mmol) is added and the reaction is then allowed to warm slowly to room temperature with the ammonia being blown off under a stream of nitrogen. The final products are obtained by recrystallisation from CH_2Cl_2–petroleum ether. Yields are in the range 50—75%.

The products gave satisfactory microanalyses, and for (**1**) and (**2**) their spectroscopic properties are identical to those previously reported.[3,10] Compounds (**3**) and (**4**) have the expected n.m.r. properties† and in the case of (**3**; $PR_3 = PPh_2Me$) we have determined the *X*-ray structure.‡ The molecule (Figure 1) has the expected square planar geometry with Pt–P and Pt–N bond lengths that are typical for Pt^{II}. The PtN_2S ring is essentially planar (max. deviation 0.03 Å) with the oxygen atoms lying equidistant above and below the plane. The ring is rotated *ca.* 5° with respect to the P(1)–Pt–P(2) plane. The sulphamido ligand has slightly lengthened S=O bonds compared to sulphamide[11] and $SO_4{}^{2-}$ whilst the S–N bond lengths are intermediate between single and double and comparable to those in sulphamide. Both the sulphur and the nitrogen atoms are pyramidal, and within the four-membered ring the angles, of necessity, are reduced from their normal value; those at nitrogen and sulphur are *ca.* 96° whilst the N(1)–Pt–N(2) angle is appreciably reduced at 71.9(2)°. The Pt · · · S distance is 2.75 Å and the N(1) · · · N(2) distance is 2.43 Å. There is a weak intermolecular H-bond between N(1) and O(2) [3.10 Å, N(1)–H · · · O(2) 142°].

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† ^{31}P *N.m.r. data* for (**3**; $PR_3 = PPh_2Me$) δ −7.0 p.p.m. [$^1J(^{31}P–^{195}Pt)$ 3342 Hz]; (**4**; $PR_3 = PPh_2Me$) δ 45.7, 37.1 p.p.m. [$^2J(^{31}P–^{31}P)$ 10, ^1J 2817, 2627 Hz].

‡ *Crystal data* for (**3**; $PR_3 = PPh_2Me$): $C_{26}H_{28}N_2P_2O_2PtS$, $M = 689.6$, triclinic, $a = 10.645(2)$, $b = 10.823(2)$, $c = 12.132(3)$ Å, $\alpha = 83.31(2)$, $\beta = 88.36(2)$, $\gamma = 68.22(2)°$; $U = 1289$ Å^3, space group $P\bar{1}$, $Z = 2$, $D_c = 1.78$ g cm^{-3}, $\mu(Cu\text{-}K_\alpha) = 124$ cm^{-1}. Crystal dimensions 0.13 × 0.15 × 0.20 mm. Data were measured on a Nicolet R3m diffractometer with graphite monochromated Cu-K_α radiation using ω-scans. The structure was solved by the heavy atom method and refined using anisotropic thermal parameters and absorption corrected data, to give $R = 0.032$, $R_w = 0.034$ for 3416 independent observed reflections [$|F_o| > 3\sigma(|F_o|)$, $\theta \leq 58°$]. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.