The Preparation and *X*-Ray Structure of $Pt(PMe_2Ph)_2[S_2N_3(SO_2)(NH_2)]$

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Reaction of $S_4N_4O_2$ with $PtCl_2(PMe_2Ph)_2$ in liquid ammonia gives the title compound which is the first example of a PtS_2N_3 ring system, as shown by *X*-ray crystallography; the molecule consists of a square planar Pt^{II} with a puckered PtS_2N_3 ring.

Currently a number of groups are investigating routes to metalla-sulphur–nitrogen compounds[1,2] since they may possess interesting physical properties.[3] To date, simple sulphur–nitrogen rings and cages such as $S_4N_4H_4$, $S_3N_3Cl_3$, and S_4N_4 have been used as starting materials. In general, group 5 and 6 metals give complexes containing S_2N_3 and S_3N_2 moieties whilst group 8 metals usually give $S_2N_2H^-$ and S_3N^- complexes. Some attempts have been made to complex $S_4N_4O_2$ (**1**); oxygen co-ordinated $TiCl_4(S_4N_4O_2)$ and nitrogen co-ordinated $[Ag(S_4N_4O_2)][AsF_6]$ having been prepared.[2] Reaction of $S_4N_4O_2$ with $CoCl_2$ in methanol is also reported to give rise to $Co(S_3N)_2$ and $Co(S_2N_2H)(S_3N)$ in low yields.[4] In view of the known reactivity of SN species such as S_4N_4 in liquid ammonia and of $S_4N_4O_2$ with nucleophiles we have reacted liquid ammonia solutions of (**1**) with $PtCl_2(PR_3)_2$ (PR_3 = PPh_2Me, PMe_2Ph, and PEt_3). The major product, $Pt(PR_3)_2[S_2N_3(SO_2)(NH_2)]$ contains a PtS_2N_3 ring, as shown by *X*-ray crystallography, in the case of PR_3 = PMe_2Ph (**2**).

In a typical reaction $S_4N_4O_2$ (30 mg, 0.15 mmol) was dissolved in liquid ammonia (5 ml) at −78 °C. Solid $PtCl_2(PMe_2Ph)_2$ (80 mg, 0.15 mmol) was added. After stirring at −78 °C for 30 min the reaction was allowed to warm to room temperature and the ammonia evaporated under a stream of N_2. The residue was extracted with a minimum volume of

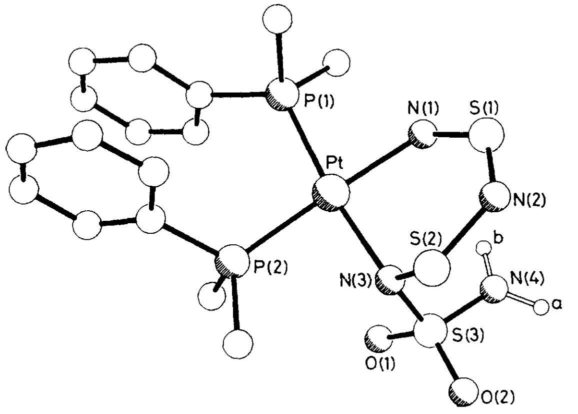

Figure 1. The *X*-ray crystal structure of $Pt(PMe_2Ph)_2[S_2N_3(SO_2)(NH_2)]$ (**2**). Selected bond lengths and angles: Pt–P(1) 2.253(2), Pt–P(2) 2.255(2), Pt–N(1) 2.048(6), Pt–N(3) 2.089(6), N(1)–S(1) 1.515(6), S(1)–N(2) 1.580(7), N(2)–S(2) 1.664(7), S(2)–N(3) 1.664(6), N(3)–S(3) 1.636(6), S(3)–O(1) 1.431(6), S(3)–O(2) 1.431(6), S(3)–N(4) 1.618(6) Å; P(1)–Pt–P(2) 98.5(1), N(1)–Pt–N(3) 88.7(2), Pt–N(1)–S(1) 126.2(4), N(1)–S(1)–N(2) 122.2(4), S(1)–N(2)–S(2) 124.1(4), N(2)–S(2)–N(3) 109.8(3), Pt–N(3)–S(2) 114.8(3), N(3)–S(3)–N(4) 111.7(3), N(3)–S(3)–O(1) 104.3(3), N(3)–S(3)–O(2) 109.4(3)°. The S(1)–N(2)–S(2)–N(3) torsion angle is 24.6°.

CH_2Cl_2–$CHCl_3$ and the pure product obtained as the CH_2Cl_2 solvate by addition of petroleum ether (0.06 mmol, 40%).†

The *X*-ray crystal structure‡ of (**2**) is shown in Figure 1. The molecule consists of a square planar Pt^{II} with a puckered PtS_2N_3 ring. The PtN_2P_2 co-ordination is planar within 0.026 Å [for N(3)]. Similarly, the N(1)–S(1)–N(2)–S(2) moiety is also planar [maximum deviation 0.007 Å for S(1)]. This latter plane is rotated 32° from the co-ordination plane and is essentially orthogonal to the S(3)–N(3) bond. Thus, the PtS_2N_3 ring can be regarded as a substituted PtN_2S_2 (ref. 5) ring with insertion of a $NSO_2(NH_2)$ group, the rigidity of the PtN_2S_2 group being retained. The geometry at N(3) is pyramidal, the nitrogen atom lying 0.31 Å out of the plane of its substituents. There are no intra-molecular H-bonding interactions although there are weak intermolecular N–H · · · O′ and N–H · · · N′ bonds [N(4)–H(b) · · · O(1)′; N · · · O 3.09, H(b) · · · O 2.18 Å, N–H · · · O angle 158°; N(4)–H(a) · · · N(2)′; N · · · N′ 3.04, H(a) · · · N′ 2.5 Å, N–H · · · N′ angle 128°]. There are no other intermolecular stacking interactions.

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† Satisfactory elemental analyses were given. $^{31}P-\{^1H\}$ N.m.r. ($CDCl_3$): δ −16.0 (^1J 3539 Hz), −19.1 p.p.m. (^1J 3178 Hz); ^2J 24 Hz. Fast atom bombardment (f.a.b.)-m.s.: MH^+ 658, $\{MH - [SO_2(NH_2)]\}^+$ 577, $\{MH - [NSO_2)]\}^+$ 563.

‡ *Crystal data* for (**2**): $C_{16}H_{24}O_2N_4S_3P_2Pt \cdot 0.5(CH_2Cl_2)$, $M = 700.1$, monoclinic, space group $P2_1/n$, $a = 9.054(1)$, $b = 17.494(2)$, $c = 15.826(2)$ Å, $\beta = 90.75(2)°$, $U = 2506$ Å^3, $Z = 4$, $D_c = 1.86$ g cm^{-3}, μ(Cu-K_α) = 153 cm^{-1}. 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 anisotropically using absorption corrected data to give $R = 0.039$, $R_w = 0.042$ for 2935 independent observed reflections $[|F_o| > 3\sigma(|F_o|), \theta \leqslant 55°]$. 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.

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