The Preparation and Crystal Structures of Platinum Stacking Compounds containing the $S_2N_2H^-$ Ligand: [Pt(S_2N_2H)(PMe₃)₂][PF₆] and [Pt(S_2N_2H)(PMe₂Ph)₂][BF₄]

Ray Jones, Paul F. Kelly, Christopher P. Warrens, David J. Williams, and J. Derek Woollins*

Department of Chemistry, Imperial College of Science and Technology, South Kensington, London SW7 2AY, U.K.

Reaction of *cis*-PtCl₂(PMe₃)₂ with $[Me_2Sn(S_2N_2)]_2$ and $[NH_4][PF_6]$ in dichloromethane gives $[Pt(S_2N_2H)(PMe_3)_2][PF_6]$, (1), or alternatively protonation of $[Pt(S_2N_2)(PMe_2Ph)_2]$ yields $[Pt(S_2N_2H)(PMe_2Ph)_2][BF_4]$,(2); the crystal structures of (1) and (2) reveal that the planar cations stack with significant close interactions.

We are investigating preparative routes to metalla-sulphurnitrogen complexes^{1—3} with particular interest in synthesising species which may make use of π -electron rich sulphurnitrogen ligands to stabilise stacking structures with the potential of one-dimensional conductivity. Currently there are no rational syntheses of platinum complexes containing $S_2N_2^{2-}$ or $S_2N_2H^-$ ligands and the variety of species known is limited.⁴ Complexes containing both phosphines and sulphurnitrogen ligands are particularly rare with only two examples reported^{4.5} for $S_2N_2^{2-}$ and none for $S_2N_2H^-$. Here we report a number of facile/rational synthetic routes together with the crystal structures of $[Pt(S_2N_2H)(PMe_3)_2][PF_6]$, (1), and $[Pt(S_2N_2H)(PMe_2Ph)_2][BF_4]$, (2). Compounds (1) and (2) are the first examples of a new class of platinum stacking compounds involving the $S_2N_2H^-$ ligand. We have obtained disulphurdinitrido complexes from *cis*-PtCl₂(PR₃)₂ [PR₃ = PMe₃, PMe₂Ph, PMePh₂, PPh₃, 1/2 1,2-bis(diphenylphosphino)ethane (dppe)] by making use of salt elimination reactions⁶ of Na(S₃N₃) [equation (1)], transmetallation reactions of [Me₂Sn(S₂N₂)]₂ {equation (2), dbu = 1,8-diazabicyclo[5.4.0]undec-7-ene}, or by use of S₄N₄H₄/dbu [equation (3)]. The disulphurdinitrido complexes may be protonated to give S₂N₂H⁻ complexes [equation (4)] or alternatively these latter compounds can be obtained directly from reactions with [Me₂Sn(S₂N₂)]₂ and [NH₄][PF₆] in dichloromethane which acts as the source of HCl. The identity of the various complexes has been established by microanalysis, i.r. and n.m.r. spectroscopy, and in a number of cases by X-ray crystallography. The i.r. spectra show the expected three v(SN) vibrations whilst the ³¹P n.m.r. spectra are AX systems



Figure 1. (a) The molecular structure of the cation in $[Pt(S_2N_2H)(PMe_3)_2][PF_6]$, (1), selected bond distances (Å) and angles (°): Pt-P(1) 2.263(1), Pt-P(2) 2.249(1), Pt-N(1) 2.038(12), Pt-S(2) 2.287(4), N(1)-S(1) 1.663(13), S(1)-N(2) 1.583(18), N(2)-S(2) 1.672(17); P(1)-Pt-P(2) 96.4(1), N(1)-Pt-S(2) 83.7(4), Pt-N(1)-S(1) 117.6(7), N(1)-S(1)-N(2) 101.9(8), S(1)-N(2)-S(2) 119.9(10), N(2)-S(2)-Pt 104.3(6). (b) $[Pt(S_2N_2H)(PMe_2Ph)_2][BF_4]$ (2), selected bond lengths (Å) and angles (°): Pt-P(1) 2.303(2), Pt-P(2) 2.261(2), Pt-N(1) 2.015(7), Pt-S(2) 2.283(2), N(1)-S(1) 1.595(7), S(1)-N(2) 1.538(9), N(2)-S(2) 1.649(8); P(1)-Pt-P(2) 94.3(1), N(1)-Pt-S(2) 84.6(2), Pt-N(1)-S(1) 121.4(4), N(1)-S(1)-N(2) 108.1(4), S(1)-N(2)-S(2) 121.6(5), N(2)-S(2)-Pt 104.4(3). (c) and (d) show overlap of the cations in (1) and (2) respectively. The uppermost cation is shown by a thick line, the next is shown by a broken line and the lowermost by a thin line. (e) Side view of the stacking of the cations in (2) showing the alternate stacking sequence.



Figure 2. Perspective view, down the crystallographic a axis, of the infinite stacking of anions and cations in (1).

with ${}^{1}J{{}^{195}Pt-{}^{31}P}$ couplings that are as anticipated for Pt^{II} complexes.

$$cis-PtCl_2(PR_3)_2 + 2Na(S_3N_3) \longrightarrow Pt(S_2N_2)(PR_3)_2 + 2NaCl + S_4N_4 \quad (1)$$

$$(60\% \text{ yield})$$

$$\begin{array}{c} \textit{cis-PtCl}_2(PR_3)_2 + 1/2[Me_2Sn(S_2N_2)]_2 \xrightarrow{dbu} \\ Pt(S_2N_2)(PR_3)_2 + Me_2SnCl_2 \\ (100\% \text{ by n.m.r. spectroscopy, not isolated}) \end{array}$$
(2)

$$cis-PtCl_2(PMe_2Ph)_2 + S_4N_4H_4/dbu \rightarrow Pt(S_2N_2)(PMe_2Ph)_2$$
(70% yield) (3)

$$Pt(S_2N_2)(PMe_2Ph)_2 + HBF_4 \rightarrow [Pt(S_2N_2H)(PMe_2Ph)_2][BF_4] \quad (4)$$
(2)
(60% yield)

$$cis$$
-PtCl₂(PR₃)₂ + 1/2[Me₂Sn(S₂N₂)]₂ + [NH₄][PF₆] →
[Pt(S₂N₂H)(PR₃)₂][PF₆] (5)
(1) R = Me
(40-50% yield)

The crystal structures of (1) and (2) reveal (Figure 1)[†] square planar co-ordination of the platinum with the $S_2N_2H^-$ ligands both having two short and one long SN distances comparable with those reported⁵ for Pt(S_2N_2)(PPh₃)₂. Of particular interest is the stacking arrangement both (1) and (2) adopt (Figures 1 and 2). In both cases the (PtS₂N₂) rings lie almost directly on top of each other with alternate cations reversed so as to accommodate the relatively bulky phosphine ligands. This results in structures with channels of cations and

[†] Crystal data: (1), C₆H₁₉N₂F₆P₃S₂Pt, orthorhombic, a = 8.402(2), b = 13.565(4), c = 16.049(5) Å, U = 1829 Å³, space group $P2_1nb$, Z = 4, M = 585.4, $D_c = 2.13$ g cm⁻³, μ (Cu- K_{α}) = 197 cm⁻¹. (2), C₁₆H₂₃BF₄N₂P₂S₂Pt, monoclinic, a = 8.568(2), b = 17.092(5), c = 16.135(4) Å, $\beta = 104.83(2)^\circ$, U = 2284 Å³, space group $P2_1/n$, Z = 4, M = 651.3, $D_c = 1.90$ g cm⁻³, μ (Cu- K_{α}) = 150 cm⁻¹. Data for both compounds were measured on a Nicolet R3m diffractometer with graphite monochromated Cu- K_{α} radiation using ω -scans. Both structures were solved by the heavy atom method and refined anisotropically using absorption corrected data to give for (1) R = 0.042, $R_w = 0.047$ for 1192 independent observed reflections $[|F_o|>3\sigma|F_o|$, $\theta \le 58^\circ$]; for (2) R = 0.034, $R_w = 0.038$ for 2244 independent observed reflections ($\theta \le 50^\circ$) respectively. In both structures the hydrogen atom positions were fixed except for H–N(1) which was allowed to refine isotropically. In both structures the N–H protons are involved in hydrogen-bonding interactions with the counter-ions. 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, 1986.

anions. In (1) [Figure 1(a,c)] the cations have their platinum atoms almost directly above/below the S(1) atom in their nearest neighbour with a Pt-S(1) distance of 3.90 Å. The distance of S(1) from the P(1)-P(2)-Pt-N(1)-S(2) plane is 3.8 Å. In (2) a different situation applies with the (PtS_2N_2) rings sheared with respect to each other compared with (1) [Figure 1(d)] and separation within the stacks resulting in dimer-like units [Figure 1(e)]. The closest inter-cation ('dimer') contact is between Pt and S(1) (3.62 Å) with the S(1) atom lying 3.5 Å above the mean plane. The longer 'dimer-dimer' separation has a Pt-S(1) distance of 5.05 Å and Pt-N(2) is 4.70 Å with S(1) lying 4.6 Å from the mean plane. The distortion in (2) probably comes about as a result of the increased bulk of PMe₂Ph compared with PMe₃. The interplanar separations observed for (1) and (2) compare favourably with those observed in dithiolene complexes7 although no directly analogous compounds are known. Particularly surprising is the formation of stacking structures in platinum complexes containing fairly bulky phosphine ligands.

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