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## A Thiophosphate Bridged Platinum–Zinc Hetero-bimetallic Complex: [(Me<sub>2</sub>PhP)<sub>2</sub>Pt{OSP(OR)<sub>2</sub>}<sub>2</sub>ZnCl<sub>2</sub>]

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 $Zn[S_2P(OR)_2]_2$  reacts with  $[PtCl_2(PMe_2Ph)_2]$  to give  $[PtS_2P(OR)_2(PMe_2Ph)_2]^+$  whereas  $Zn[OSP(OR)_2]_2$  (2) forms  $[(Me_2PhP)_2Pt{OSP(OR)_2}_2ZnCl_2]$ , (4) a hetero-bimetallic complex combining hard and soft metals co-ordinated by oxygen and sulphur respectively; both new compounds have been characterised by X-ray crystallography.

Zinc(dialkoxy)dithiophosphates (1) are important commercially as lubricant additives.<sup>1,2</sup> Industrially, the  $(RO)_2PS_2H$ acid is normally prepared by reaction of  $P_4S_{10}$  with an alcohol [equation (1)]. Neutralisation of this acid with ZnO gives (1). However, as can be seen in equation (1) the reaction liberates  $H_2S$  and is thus environmentally unfriendly. An alternative, related class of compounds, are the zinc(dialkoxy)monothiophosphates (2). Apart from its commercial applications (2) offers an opportunity to compare the co-ordination chemistry of the mixed O,S donor relative to that of the S,S donor. Although the reactivity of  $R_2PS_2^-$  has been studied<sup>3,4</sup> little work has been reported on  $R_2POS^-$  ligands and we know of no studies of  $(RO)_2POS^-$ . Reaction of (1) and (2)  $(R = Pr^i)$  with *cis*-[PtCl<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>2</sub>] proceeds as shown in equations (2)



Figure 1. The X-ray structure of one of the independent molecules in (3). Important bond lengths (Å) and angles (°) [second independent molecule in square brackets]: Pt–S(1) 2.383(4) [2.364(3)], Pt–S(2) 2.381(3) [2.367(3)], Pt–P(3) 2.254(3) [2.260(3)], Pt–P(4) 2.266(2) [2.267(3)], S(1)–P(1) 2.001(4) [1.997(4)], S(2)–P(1) 2.003(5) [2.012(4)], P(1)–O(1) 1.532(7) [1.549(7)], P(1)–O(2) 1.576(8) [1.555(6)]. S(1)–Pt–S(2) 83.2(1) [82.8(1)], P(3)–Pt–P(4) 93.8(1) [95.9(1)], Pt–S(1)–P(1) 86.1(2) [87.4(1)], S(1)–P(1)–S(2) 104.3(2) [102.6(1)], P(1)–S(2)–Pt 86.1(1) [87.0(1)].

and (3) respectively. To date, we have been unable to crystallise  $[Pt(S_2P(OR)_2)(PMe_2Ph)_2]^+$  as the chloride salt and so have performed the reaction in the presence of  $[NH_4][PF_6]$ .

$$P_4S_{10} + 8ROH \rightarrow 4(RO)_2PS_2H + 2H_2S$$
(1)

 $\frac{1}{2Zn}[S_2P(OR)_2]_2 + [PtCl_2(PMe_2Ph)_2] + [NH_4][PF_6] \rightarrow (1)$ 

$$[Pt{S_2P(OR)_2}(PMe_2Ph)_2][PF_6] + [NH_4]Cl + 1/2ZnCl_2 (2) (3)$$

$$Zn(OSP(OR)_{2})_{2} + [PtCl_{2}(PMe_{2}Ph)_{2}] \rightarrow$$
(2)
$$[(Me_{2}PhP)_{2}Pt\{OSP(OR)_{2}\}_{2}ZnCl_{2}] \quad (3)$$
(4)

In a typical reaction (2) (0.18 mmol) and  $[PtCl_2(PMe_2Ph)_2]$ (0.18 mmol) were stirred together in CH<sub>2</sub>Cl<sub>2</sub> (2 ml) for 4 h at room temperature; at this stage the <sup>31</sup>P NMR spectrum showed only (4). Recrystallisation from CH<sub>2</sub>Cl<sub>2</sub>–n-hexane gave crystals of (4) suitable for X-ray analysis.† Complex (3) was prepared in a similar fashion.

† Crystal data for (3), 2[C<sub>22</sub>H<sub>36</sub>O<sub>2</sub>P<sub>3</sub>S<sub>2</sub>PtPF<sub>6</sub>]·0.5CHCl<sub>3</sub>, triclinic, a = 10.913(3), b = 11.432(4), c = 29.463(12) Å,  $\alpha = 93.59(3)$ ,  $\beta = 91.79(3)$ ,  $\gamma = 106.60(2)^\circ$ , U = 3511 Å<sup>3</sup>, space group  $P\overline{1}$ , Z = 4 (2 crystallographically independent molecules), M = 859.5,  $D_c = 1.63$  g cm<sup>-3</sup>,  $\mu$ (Cu- $K_{\alpha}$ ) = 114 cm<sup>-1</sup>, F(000) = 1682. For (4),  $C_{28}H_50Cl_2O_6P_4PtS_2Zn$ , monoclinic, a = 11.748(3), b = 23.146(7), c = 15.714(4) Å,  $\beta = 104.91(2)^\circ$ , U = 4129 Å<sup>3</sup>, space group  $P_1/n$ , Z = 4, M = 1002.1,  $D_c = 1.61$  g cm<sup>-3</sup>,  $\mu$ (Cu- $K_{\alpha}$ ) = 110 cm<sup>-1</sup>, F(000) = 1984. Data were measured on a Nicolet R3m diffractometer with graphite monochromated Cu- $K_{\alpha}$  radiation using  $\omega$ -scans. The structures were solved by the heavy atom method and refined anisotropically using absorption-corrected data to give R = 0.061 and 0.034,  $R_w = 0.067$  and 0.032 for 6763 and 4854 independent observed reflections [ $|F_o| > 3\sigma(|F_o|)$ ,  $2\theta \le 100$ ,  $116^\circ$ ] for (3) and (4) respectively. 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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Figure 2. The X-ray structure of (A) (4) and (B) the central core in (4). Important bond lengths (Å) and angles (°): Pt-S(1) 2.402(1), Pt-S(2) 2.389(2), Pt-P(3) 2.258(2), Pt-P(4) 2.282(2), S(1)-P(1) 2.008(2), S(2)-P(2) 2.017(2), P(1)-O(1) 1.497(4), P(2)-O(2) 1.482(4), P(1)-O(3) 1.556(5), P(1)-O(4) 1.546(5), P(2)-O(5) 1.570(5), P(2)-O(6) 1.564(4), Zn-O(1) 1.942(4), Zn-O(2) 1.966(5), Zn-Cl(1) 2.221(2), Zn-Cl(2) 2.224(2). S(1)-Pt-S(2) 87.1(1), P(3)-Pt-P(4) 94.2(1), Pt-S(1)-P(1) 104.6(1), Pt-S(2)-P(2) 107.0(1), S(1)-P(1)-O(1) 114.4(4), S(2)-P(2)-O(2) 117.3(1), P(1)-O(1)-Zn 147.3(3), P(2)-O(2)-Zn 150.6(3), O(1)-Zn-O(2) 101.7(2), Cl(1)-Zn-Cl(2) 119.1(1), O-Zn-Cl in range 105.1(2)—110.4(1).

The S,S donor ligand forms a simple chelate complex whilst the O,S donor yields the novel hetero-bimetallic species where the sulphurs co-ordinate platinum and the oxygens co-ordinate zinc in accord with the relative hardness of the different donors and acceptors. Compounds (3) and (4) were characterised by microanalysis, IR, <sup>31</sup>P NMR [for (3)  $\delta$  -17.9, <sup>1</sup>*J*(<sup>31</sup>P-<sup>195</sup>Pt) 3323 Hz, and 92.5, <sup>2</sup>*J*(<sup>31</sup>P-<sup>195</sup>Pt) 275 Hz; for (4)  $\delta$  -11.7, <sup>1</sup>*J* 3264 Hz and 36.3 ppm, <sup>2</sup>*J* 66 Hz, referenced to 85% phosphoric acid] and *X*-ray crystallography.†

The X-ray structure of one of the two independent molecules of (3) is shown in Figure 1. One of the two independent molecules has approximate non-crystallographic  $C_2$  symmetry, whereas in the other (illustrated) this symmetry is broken by the orientation of the isopropyl groups. The co-ordination at platinum is slightly distorted in both independent molecules; the PtP<sub>2</sub> plane is twisted by 7 and 8° with respect to the PS<sub>2</sub> plane. The PtS<sub>2</sub>P ring is non-planar with the dihedral angle about S(1)-S(2) being 7 and 4° for the two independent molecules respectively. In consequence the P(1)atom lies 0.14 and 0.07 Å from the PtS<sub>2</sub> plane [cf. dihedral angle of 19.4° and P atom displacement of 0.48 Å in  $[Pt{S_2P(S)C_6H_4OMe}(PPh_3)_2]$ .<sup>5</sup> The transannular S ... S and Pt ... P distances are 3.16, 3.13 and 3.00, 3.03 Å respectively. The X-ray structure of (4) is shown in Figure 2. The eight-membered ring has distorted  $C_s$  symmetry with approximate square-planar co-ordination at platinum and tetrahedral co-ordination at zinc. All the bond lengths within the ring are reasonable for a bidentate fully delocalised R<sub>2</sub>POS<sup>-</sup> ligand. At platinum the PtP<sub>2</sub> plane is twisted by  $15^{\circ}$  relative to the PtS<sub>2</sub> plane. The ring conformation is similar to that observed for  $S_8^{2+}$ , *i.e.* intermediate between the crown  $S_8$  and cage  $S_4N_4$ structures.<sup>6</sup> The transannular Zn … Pt distance is 4.39 Å. The most unusual feature of the ring geometry is the exceptionally large angles at O(1) and O(2) [147.3(3) and  $150.6(3)^{\circ}$ 

respectively]. Furthermore, the  $ZnCl_2$  group is arranged with the two chlorine atoms symmetric above and below the  $ZnO_2P_2S_2$  'plane' rather than with Cl(1) axial and Cl(2) equatorial which would allow more normal (sp<sup>2</sup>) angles at O(1) and O(2).

The synthesis of (4) illustrates the utility of the mixed O,S (hard/soft) thiophosphate ligand for the formation of heterobimetallic species. Clearly, the range of systems which could be prepared by this strategy is very large; further work is under way.

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