A Thiophosphate Bridged Platinum–Zinc Hetero-bimetallic Complex: $[(Me_2PhP)_2Pt\{OSP(OR)_2\}_2ZnCl_2]$

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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.[1,2] 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[3,4] 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*-$[PtCl_2(PMe_2Ph)_2]$ proceeds as shown in equations (2)

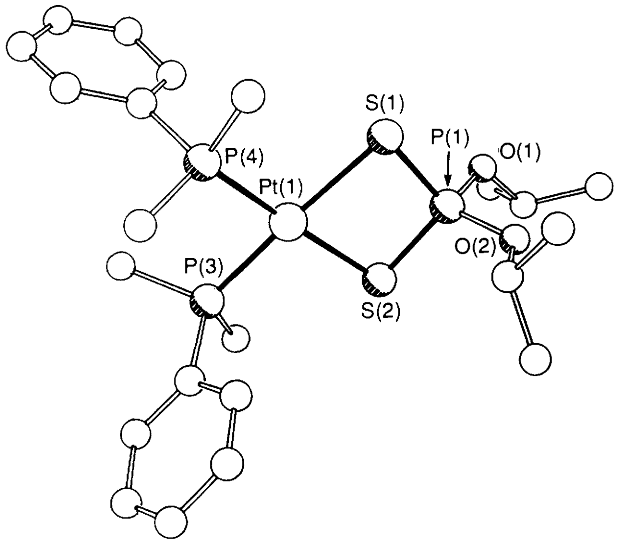

Figure 1. The *X*-ray structure of one of the independent molecules in (**3**). Important bond lengths (Å) and angles (°) [second independent molecule in square brackets]: Pt–S(1) 2.383(4) [2.364(3)], Pt–S(2) 2.381(3) [2.367(3)], Pt–P(3) 2.254(3) [2.260(3)], Pt–P(4) 2.266(2) [2.267(3)], S(1)–P(1) 2.001(4) [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 $[NH_4][PF_6]$.

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

$$\underset{(\mathbf{1})}{1/2Zn[S_2P(OR)_2]_2} + [PtCl_2(PMe_2Ph)_2] + [NH_4][PF_6] \rightarrow \underset{(\mathbf{3})}{[Pt\{S_2P(OR)_2\}(PMe_2Ph)_2][PF_6]} + [NH_4]Cl + 1/2ZnCl_2 \quad (2)$$

$$\underset{(\mathbf{2})}{Zn(OSP(OR)_2)_2} + [PtCl_2(PMe_2Ph)_2] \rightarrow \underset{(\mathbf{4})}{[(Me_2PhP)_2Pt\{OSP(OR)_2\}_2ZnCl_2]} \quad (3)$$

In a typical reaction (**2**) (0.18 mmol) and $[PtCl_2(PMe_2Ph)_2]$ (0.18 mmol) were stirred together in CH_2Cl_2 (2 ml) for 4 h at room temperature; at this stage the ^{31}P NMR spectrum showed only (**4**). Recrystallisation from CH_2Cl_2–n-hexane gave crystals of (**4**) suitable for *X*-ray analysis.† Complex (**3**) was prepared in a similar fashion.

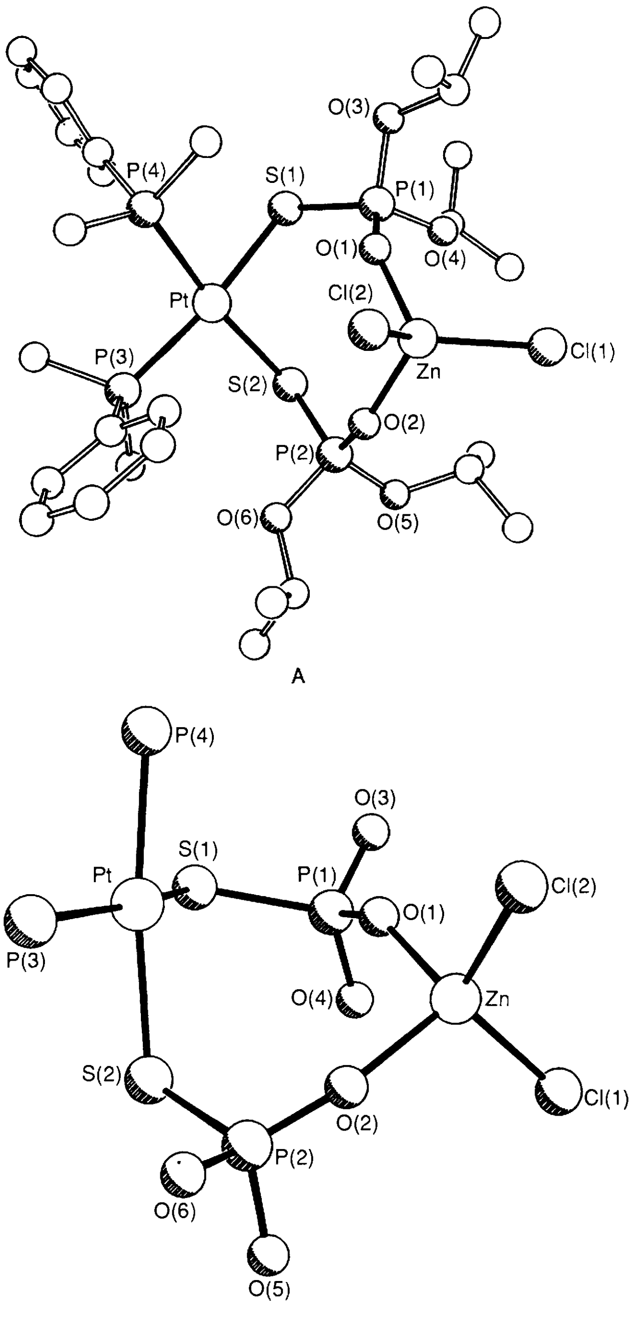

Figure 2. The *X*-ray structure of (A) (**4**) and (B) the central core in (**4**). Important bond lengths (Å) and angles (°): Pt–S(1) 2.402(1), Pt–S(2) 2.389(2), Pt–P(3) 2.258(2), Pt–P(4) 2.282(2), S(1)–P(1) 2.008(2), S(2)–P(2) 2.017(2), P(1)–O(1) 1.497(4), P(2)–O(2) 1.482(4), P(1)–O(3) 1.556(5), P(1)–O(4) 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) 2.231(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 charac-

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† *Crystal data* for (**3**), $2[C_{22}H_{36}O_2P_3S_2PtPF_6]\cdot 0.5CHCl_3$, triclinic, a = 10.913(3), b = 11.432(4), c = 29.463(12) Å, α = 93.59(3), β = 91.79(3), γ = 106.60(2)°, U = 3511 Å^3, space group $P\bar{1}$, Z = 4 (2 crystallographically independent molecules), M = 859.5, D_c = 1.63 g cm^{-3}, $\mu(Cu\text{-}K_\alpha)$ = 114 cm^{-1}, $F(000)$ = 1682. For (**4**), $C_{28}H_{50}Cl_2O_6P_4PtS_2Zn$, monoclinic, a = 11.748(3), b = 23.146(7), c = 15.714(4) Å, β = 104.91(2)°, U = 4129 Å^3, space group $P2_1/n$, Z = 4, M = 1002.1, D_c = 1.61 g cm^{-3}, $\mu(Cu\text{-}K_\alpha)$ = 110 cm^{-1}, $F(000)$ = 1984. Data were measured on a Nicolet R3m diffractometer with graphite monochromated Cu-K_α radiation using ω-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 $[|F_o| > 3\sigma(|F_o|), 2\theta \leqslant 100, 116°]$ 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.

terised by microanalysis, IR, ^{31}P NMR [for (**3**) δ -17.9, $^1J(^{31}P-^{195}Pt)$ 3323 Hz, and 92.5, $^2J(^{31}P-^{195}Pt)$ 275 Hz; for (**4**) δ -11.7, ^1J 3264 Hz and 36.3 ppm, ^2J 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_2 plane is twisted by 7 and 8° with respect to the PS_2 plane. The PtS_2P 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_2 plane [*cf.* dihedral angle of 19.4° and P atom displacement of 0.48 Å in $[Pt\{S_2P(S)C_6H_4OMe\}(PPh_3)_2]$.[5] 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_2POS^- ligand. At platinum the PtP_2 plane is twisted by 15° relative to the PtS_2 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.[6] 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)° 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^2) 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.

We are grateful to Exxon Chemicals for financial support. J. D. W. is currently the Sir Edward Frankland Fellow of the Royal Society of Chemistry.

Received, 5th April 1990; Com. 0/01548B

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