Synthesis and Structure of Bis[sulphato]tris[μ-bis(diphenylphosphino)methane]-*triangulo*-trimercury

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Bis[sulphato]tris[μ-bis(diphenylphosphino)methane]-*triangulo*-trimercury was prepared from $[Hg_2(\mu\text{-dppm})(dppm\text{–}P)_2(SO_4)_2]$ [dppm = bis(diphenylphosphino)methane] and elemental Hg, and has Hg–Hg distances of 2.764(1), 2.764(1), and 2.802(1) Å.

The mercury cations $[Hg_n]^{2+}$, $n = 2,3,4$, and the polymeric $Hg_{2.85}AsF_6$ contain almost linear mercury atom arrangements and formal mercury oxidation states $\leqslant +1$.[1,2] We report here on a triangular Hg_3^{4+} cluster (Figure 1) which contains mercury in the novel formal oxidation state of +4/3. The existence of the cluster is surprising, as soluble mercury derivatives in oxidation states of less than +2 are expected to be unstable towards disproportionation into mercury and mercury(II) in the presence of strong ligands, *e.g.*, phosphines.

$HgSO_4$ and dppm [dppm = bis(diphenylphosphino)methane] in a molar ratio of 2:3 react in $MeOH\text{–}CH_2Cl_2$ according to equation (1). Compound (**1**)† reacts with elemental mercury to give (**2**) as shown in equation (2). Complex (**2**) was isolated as stable colourless crystals‡ and is readily soluble in MeOH or MeCN.

The structure of (**2**) was established by *X*-ray diffraction§ (suitable crystals of $(\mathbf{2})\cdot1.5H_2O$ were obtained from MeCN–

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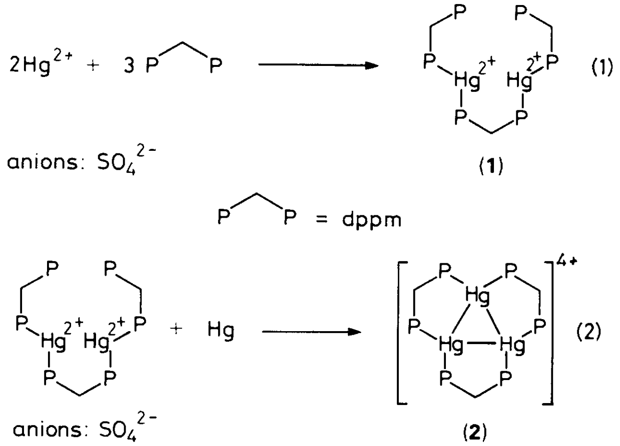
† *Spectroscopic data*: ^{31}P n.m.r. δ 48.9, −10.2 (dppm–P), 32.3 p.p.m. (μ-dppm), 193 K, relative to 85% H_3PO_4.

‡ M.p. 171 °C decomp., ^{31}P n.m.r. δ 42.8 p.p.m., ^{199}Hg n.m.r. δ 2552 p.p.m., relative to aqueous $Hg(ClO_4)_2$ (1 mmol HgO cm^{-3} 60% $HClO_4$).

§ *Crystal data* for $(\mathbf{2})\cdot1.5\,H_2O$: Enraf–Nonius CAD-4 diffractometer, Mo-K_α radiation, $\lambda = 0.71069$ Å, graphite monochromator, $T = 22\,°C$. $C_{75}H_{66}Hg_3O_8P_6S_2\cdot1.5H_2O$, $M = 1974.121$, monoclinic, space group $P2_1/n$ (No. 14) with $a = 15.069(2)$, $b = 24.025(2)$, $c = 22.405(2)$ Å, $\beta = 93.88(1)°$, $U = 8092.8$ Å^3, $D_c = 1.620$ g cm^{-3}, $\mu(\text{Mo-}K_\alpha) = 58.9\ cm^{-1}$, $Z = 4$, $F(000) = 3828$. 15721 Reflections were measured, 14152 of which were unique, and 6782 with $I \geqslant 2.0\sigma(I)$ 'observed' ($R_{int} = 0.033$, $(\sin\theta/\lambda)_{max} = 0.594$ Å^{-1}, *hkl*-range +18, + 29, ± 28, θ-2θ scans, $\Delta\omega = 0.8 + 0.35\tan\theta$). Lorentz-polarisation and empirical absorption corrections were applied (relative transmission: 0.80—1.00). A decay of −16.7% was observed during data collection and was corrected for. The structure was solved by automated Patterson methods (SHELXS-86). Refinement converged at $R(R_w) = 0.061$ (0.064), $w = 1/\sigma^2(F_0)$ for 355 refined parameters (anisotropic, phenyl rings as idealized rigid hexagons with individual isotropic displacement parameters, all hydrogen atoms calculated, SHELX-76). The residual electron density was +1.58/−0.81e Å^{-3}. 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.



H_2O), which showed a triangular Hg_3^{4+} cluster with all the edges spanned by bridging dppm ligands (Figure 1). The two SO_4^{2-} counter anions are weakly co-ordinated to the three Hg atoms. An overall C_{3v} symmetry of the cluster is only violated by the conformation of the phenyl rings (not shown in Figure 1) and the five-membered Hg–Hg–P–CH_2–P rings. Of these, two CH_2 groups are located 'below' the Hg_3 plane and one 'above' (Figure 1).

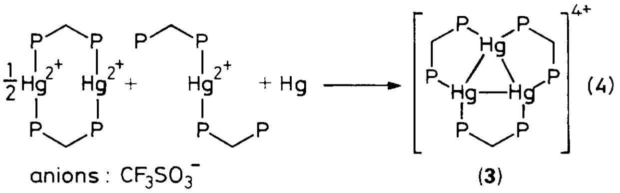
Related dicationic clusters of palladium and platinum, $[M_3(\mu\text{-dppm})_3(\mu_3\text{-CO})]^{2+}$ have been reported[3,4] and are used as starting materials for much varied chemistry.[5] A similar structure without formal metal–metal bonds, $[Ag_3(\mu_3\text{-Br})_2(\mu\text{-dppm})_3]^+$, is also known.[6]

The Hg–Hg distances in (**2**) are 2.764(1), 2.764(1), and 2.802(1) Å (the metal–metal distances in the palladium, platinum, and silver complexes mentioned above are 2.576(1)—2.610(2) Å, 2.613(1)—2.650(1) Å, and 3.192(3)—3.362(3) Å, respectively) which compare with a range of 2.4—2.7 Å found in linear mercury polycations, and 3.0 Å in elemental mercury.[1,2] Usually the Hg–Hg bond lengths in various Hg_2^{2+} salts centre around 2.5 Å.[1]

Formally, the +4 charge can be considered to result from a Hg^{2+} cation bridging a $[Hg\text{–}Hg]^{2+}$ unit. $M_2(\mu\text{-}Hg^{II})$ clusters are known[7] where mercury, in the formal oxidation state +2, bridges two transition metals joined by a metal–metal bond. In the light of the present results, it seems possible that the exchange reaction[8] shown in equation (3) involves a Hg_3^{4+} intermediate.

$$[\mathbf{Hg}\text{–}Hg]^{2+} + Hg^{2+} \rightleftharpoons \mathbf{Hg}^{2+} + [Hg\text{–}Hg]^{2+} \qquad (3)$$

A mixture of $[Hg_2(\mu\text{-dppm})_2](O_3SCF_3)_4$[9] and $[Hg(dppm\text{–}P)_2](O_3SCF_3)_2$[10] contained in a solution of $[Hg(Me_2SO)_6](O_3SCF_3)_2$ and dppm in the ratio of 2:3, reacts with elemental mercury to yield the trifluoromethanesulphonate (**3**) (equation 4).



The ^{31}P chemical shift of (**3**) (δ 53.1 p.p.m.) appears at higher frequencies than (**2**), thus indicating non-co-ordinating $CF_3SO_3^-$ anions.[4]

The salt (**3**) is also formed from $Hg_2(O_3SCF_3)_2$ and dppm according to equation (5) or by reduction of $[Hg_2(\mu\text{-dppm})_2](O_3SCF_3)_4$ by for example $NaBH_4$.

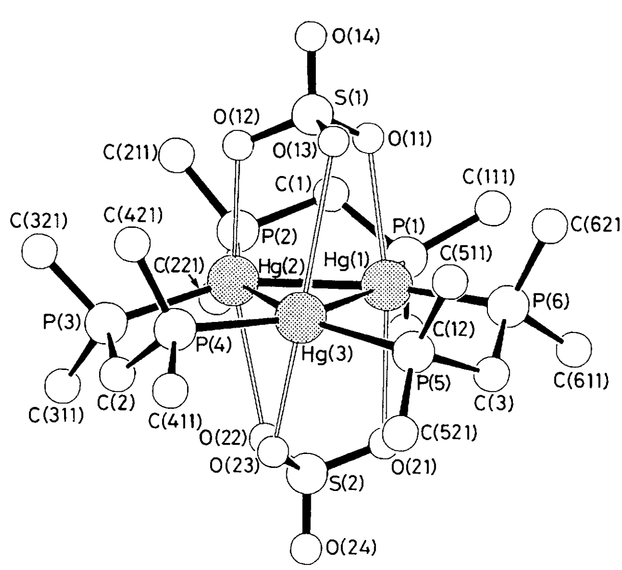


Figure 1. Molecular structure and atomic numbering scheme of (**2**) (SCHAKAL plot; atoms with arbitrary radii; for clarity, only the *ipso*-carbon atoms of the phenyl rings are drawn, and the hydrogen atoms are omitted). Important distances (Å) and angles (°): Hg(1)–Hg(2) 2.764(1), Hg(1)–Hg(3) 2.764(1), Hg(2)–Hg(3) 2.802(1), Hg(1)–P(1) 2.526(6), Hg(1)–P(6) 2.510(6), Hg(1)–O(11) 2.70(2), Hg(1)–O(21) 2.88(2), Hg(2)–P(2) 2.533(6), Hg(2)–P(3) 2.511(6), Hg(2)–O(12) 2.56(1), Hg(2)–O(22) 2.96(2), Hg(3)–P(4) 2.516(6), Hg(3)–P(5) 2.549(6), Hg(3)–O(13) 3.25(2), Hg(3)–O(23) 2.54(2), Hg(3)–O(21) 3.33(2); Hg(2)–Hg(1)–Hg(3) 60.9(1), Hg(1)–Hg(2)–Hg(3) 59.6(1), Hg(2)–Hg(3)–Hg(1) 59.5(1).

$$2\,Hg_2(O_3SCF_3)_2 + 3\,P\frown P \rightarrow (\mathbf{3}) + Hg \qquad (5)$$

The analogous methanesulphonate compound (**4**), (^{31}P n.m.r. δ 48.5 p.p.m.), displays a broadened methyl ^1H n.m.r. spectral signal at 303 K (δ 2.58). At 203 K, there are two resonances (δ 2.27 and 2.98, integral ratio 1:1), thus indicating a solution structure of $[Hg_3(\mu\text{-dppm})_3(O_3SMe)_2](O_3SMe)_2$.

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References

1 C. A. McAuliffe, 'The Chemistry of Mercury,' McMillan Press, London, 1977; A. F. Wells, 'Structural Inorganic Chemistry,' Clarendon Press, Oxford, 1984.

2 R. B. King, *Polyhedron*, 1988, **7**, 1813.

3 L. Manojlovic-Muir, K. W. Muir, B. R. Lloyd, and R. J. Puddephatt, *J. Chem. Soc., Chem. Commun.*, 1983, 1336.

4 G. Ferguson, B. R. Lloyd, and R. J. Puddephatt, *Organometallics*, 1986, **5**, 344.

5 For example, R. Ramachandran, N. C. Payne, and R. J. Puddephatt, *J. Chem. Soc., Chem. Commun.*, 1989, 128; G. Douglas, M. C. Jennings, L. Manojlovic-Muir, K. W. Muir, and R. J. Puddephatt, *ibid.*, 1989, 159.

6 A. A. M. Aly, D. Neugebauer, O. Orama, U. Schubert, and H. Schmidbaur, *Angew. Chem., Int. Ed. Engl.*, 1978, **90**, 125.

7 For example, R. Fahmy, K. King, E. Rosenberg, A. Tiripicchio, and M. Tiripicchio-Camellini, *J. Am. Chem. Soc.*, 1980, **102**, 3626; P. R. Sharp, *Inorg. Chem.*, 1986, **25**, 4185.

8 P. Peringer, *J. Chem. Res.*, 1980, (*S*) 194; (*M*) 2757 and references cited therein.

9 M. Lusser and P. Peringer, *Chem. Ber.*, 1985, **118**, 2140.

10 P. Peringer and M. Lusser, *Inorg. Chem.*, 1985, **24**, 109.