Synthesis and crystal structure of the subvalent mercury cluster [*triangulo*-$Hg_3(\mu\text{-dmpm})_4][O_3SCF_3]_4$ (dmpm = $Me_2PCH_2PMe_2$)

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The subvalent mercury cluster [*triangulo*-$Hg_3(\mu\text{-dmpm})_4][O_3SCF_3]_4$ [dmpm = bis(dimethylphosphino)methane], involving the +4/3 oxidation state of mercury, was formed by reaction of $[Hg_2]^{2+}$ with 2 equivalents of dmpm or by reduction of a mixture of $[Hg(Me_2SO)_6][O_3SCF_3]_2$ and dmpm in the molar ratio 2:4 with elemental Hg. The cation consists of a Hg_3 triangle [Hg–Hg 276.68(14), 280.99(14) and 295.53(14) pm] in which two edges are bridged by one dmpm ligand and the third edge is doubly bridged by a pair of dmpm ligands. The three Hg atoms and the phosphorus atoms of the singly bridging dmpm ligands are nearly in a plane. The dihedral angles of the Hg_3 triangle and the mean planes formed by the doubly bridged Hg atoms and the phosphorus atoms of the two bridging dmpm ligands respectively are 61 and 46°. The complex is fluxional on the ^{31}P NMR time-scale at 81 MHz at ambient temperature due to intramolecular exchange between the two different types of dmpm ligands.

An interesting feature of the chemistry of mercury is the existence of subvalent cationic clusters.[1,2] Mercury is unique in forming linear systems of directly bonded metal atoms. The simplest example is the mercury(I) ion $[Hg–Hg]^{2+}$ which can be regarded as a complex $[HgL]^{2+}$ with L = Hg^0.[2] Many salts and complexes of $[Hg–Hg]^{2+}$ are known.[3] The formal co-ordination of one or two Hg^0 atoms to $[Hg–Hg]^{2+}$ leads to $[Hg–Hg–Hg]^{2+}$ [4–9] or $[Hg–Hg–Hg–Hg]^{2+}$.[10–12] Infinite arrangements of Hg atoms are present in $[Hg_{3-\delta}]^-$ which contain either infinite linear chains[12–16] or planes[17] of Hg atoms. All the clusters mentioned above involve formal oxidation states ⩽1.

The cyclic system $[Hg_3]^{4+}$, in which Hg has an oxidation number of +4/3, is the sole subvalent mercury cluster with a formal oxidation state >1. This can be formally regarded as an Hg^0 atom donating to two mercury(II) ions resulting in three-centre two-electron bonding. In D_{3h} symmetry the overlap of the s orbitals generates a bonding a_1' molecular orbital and two degenerate weakly antibonding e′ orbitals. The a_1' orbital is filled with two electrons, the e′ orbitals are empty.[18] So far two examples containing the $[Hg_3]^{4+}$ system are known: the mineral terlinguaite, $Hg_4Cl_2O_2$, an insoluble co-ordination polymer,[19–21] is composed of separate $[Hg_3]^{4+}$ and Hg^{2+} elements. The cluster [*triangulo*-$Hg_3(\mu\text{-dppm})_3][O_3SCF_3]_4$ **1** [dppm = bis(diphenylphosphino)methane], the second example, is a molecular complex of $[Hg_3]^{4+}$ entities and is soluble in common organic solvents.[22]

The existence of compound **1** indicates an important difference between subvalent clusters with formal oxidation states ⩽1 and >1: most complexes of oxidation state ⩽1 are co-ordinated by oxygen- or nitrogen-donor ligands or halides, but are unstable towards disproportionation into Hg^0 and Hg^{II} in the presence of strong ligands, *e.g.* phosphines. It has been shown that PPh_3 always causes disproportionation of $[Hg–Hg]^{2+}$, while weaker donors, *e.g.* $PPh_2(CF_3)$ or PF_3, cause disproportionation only if present in a ligand to $[Hg–Hg]^{2+}$ ratio of >1:1 if at all.[23,24] In contrast, each Hg atom of the $[Hg_3]^{4+}$ cluster **1** is co-ordinated by two phosphorus atoms of the alkyldiarylphosphine dppm. This difference is now confirmed by the synthesis of the $[Hg_3]^{4+}$ cluster [*triangulo*-$Hg_3(\mu\text{-dmpm})_4]^{4+}$ **2** [dmpm = bis(dimethylphosphino)methane]: the trialkylphosphine dmpm is strongly basic, and up to three P-donor atoms are co-ordinated per mercury.

There is current interest in the luminescent properties of cluster chromophores. The photoluminescence of compound **1**[18] as well as of heterometallic *triangulo*-clusters[25] has recently been investigated. The related cluster complexes [*triangulo*-$Pt_3(\mu\text{-CO})(\mu\text{-dmpm})_4]^{2+}$ **3**[26] and [*triangulo*-$Ni_3(\mu_3\text{-CO})(\mu\text{-dmpm})_4]^{2+}$ **4**[27] have been reported.

Results and Discussion

Synthesis

Reaction of a mixture of $[Hg(Me_2SO)_6][O_3SCF_3]_2$ and dmpm in the molar ratio 2:4 with elemental Hg at ambient temperature gives the cluster **2** [equation (1)]. Alternatively, **2** was prepared

$$2[Hg(Me_2SO)_6][O_3SCF_3]_2 + 4\ \text{dmpm} + Hg \longrightarrow [Hg_3(\mu\text{-dmpm})_4][O_3SCF_3]_4 + 12\ Me_2SO \quad (1)$$

by reaction of $Hg_2(O_3SCF_3)_2$ with dmpm according to equation (2). Crystals of **2** suitable for X-ray diffraction analysis were

$$2[Hg_2][O_3SCF_3]_2 + 4\ \text{dmpm} \longrightarrow [Hg_3(\mu\text{-dmpm})_4][O_3SCF_3]_4 + Hg \quad (2)$$

obtained upon standing of a solution of $[Hg(Me_2SO)_6][O_3SCF_3]_2$ and dmpm in the ratio 2:3 in MeOH–water.† In this reaction dmpm is thought to act as a reducing agent, since dmpm oxides were identified in the reaction mixture. Complex **2** is soluble in Me_2SO and dimethylformamide (dmf) and has a very limited solubility in CH_2Cl_2, MeOH or acetone.

Crystal structure

The structure of complex **2** was determined by single-crystal X-ray analysis and is shown in Fig. 1. Crystal data are in Table 1, selected bond distances and angles in Table 2. The structure contains four $CF_3SO_3^-$ anions for each $[Hg_3(\mu\text{-dmpm})_4]^{4+}$ cation confirming the +4/3 oxidation state of Hg. The cation consists

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† In a solution of this composition the manxane-type complex $[Hg_2(\mu\text{-dmpm})_3][O_3SCF_3]_4$ is formed.[28]

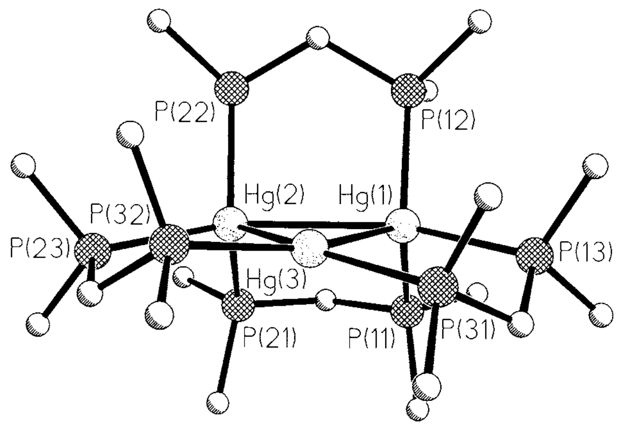

Fig. 1 View of [*triangulo*-Hg_3(μ-dmpm)$_4$]$^{4+}$ **2**

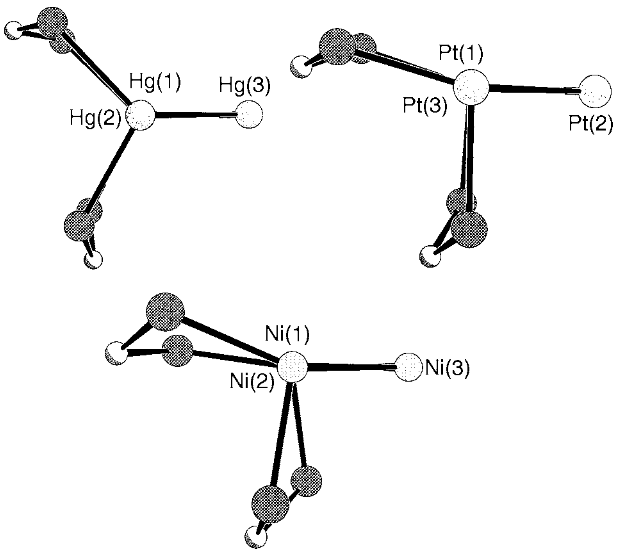

Fig. 2 View along the vector of the doubly bridged Hg atoms of [*triangulo*-Hg_3(μ-dmpm)$_4$]$^{4+}$ **2** and analogous projections of [*triangulo*-[Pt_3(μ-CO)(μ-dmpm)$_4$]$^{2+}$ **3** and [*triangulo*-Ni_3($μ_3$-CO)(μ-dmpm)$_4$]$^{2+}$ **4** showing the different co-ordination geometries of the doubly bridging dmpm ligands

Table 1 Crystal data and structure refinement for complex **2**

Molecular formula	$C_{24}H_{56}F_{12}Hg_3O_{12}P_8S_4$
M	1742.46
Colour, habit	Colourless prism
Crystal size/mm	0.3 × 0.25 × 0.25
Crystal system	Monoclinic
Space group	*C*2/*m* (no. 12)
a/pm	2391.0(10)
b/pm	1305.5(4)
c/pm	3616.0(10)
β/°	107.17(3)
U/nm^3	10.784(6)
Z	8
T/K	173(2)
Radiation (λ/pm)	Mo-Kα (71.073)
D_c/Mg m^{-3}	2.146
μ/mm^{-1}	9.000
F(000)	6624
θ Range for data collection/°	3.02–24.28
hkl Ranges	−15 to 23, −13 to 14, −39 to 38
Reflections collected	7691
Independent reflections (R_{int})	6779 (0.0542)
Reflections with $I > 2\sigma(I)$	4408
Absorption correction	ψ Scan
Maximum and minimum transmission	1.00, 0.74
Data, restraints, parameters	6757, 9, 479
Goodness of fit on F^2	1.072
Final *R*1, *wR*2 [$I > 2\sigma(I)$]	0.0570, 0.1111
(all data)*	0.1098, 0.1488
Largest difference peak, hole/e nm^{-3}	1834, −1180

* Weighting scheme $w = 1/[\sigma^2(F_o)^2 + (0.0211P)^2 + 2.15P]$ where $P = (F_o^2 + 2F_c^2)/3$.

Table 2 Selected bond lengths (pm) and angles (°) for complex **2**

Hg(1)–P(11)	253.4(5)	Hg(1)–P(13)	253.7(6)
Hg(1)–P(12)	253.8(5)	Hg(1)–Hg(3)	276.68(14)
Hg(1)–Hg(2)	295.53(14)	Hg(2)–P(23)	253.7(6)
Hg(2)–P(21)	254.9(6)	Hg(2)–P(22)	254.9(5)
Hg(2)–Hg(3)	280.99(14)	Hg(3)–P(32)	251.7(5)
Hg(3)–P(31)	255.0(6)	Hg(3)–O(1)	274(2)
Hg(3) · · · F(12^I)	307(2)	P(11)–C(21)	184(2)
P(12)–C(12)	184(2)	P(13)–C(13)	184(2)
P(23)–C(23)	183(2)	P(21)–C(21)	181(2)
P(31)–C(13)	178(2)	P(22)–C(12)	179(2)
		P(32)–C(23)	180(2)
P(11)–Hg(1)–P(13)	104.1(2)	P(11)–Hg(1)–P(12)	107.3(2)
P(13)–Hg(1)–P(12)	108.7(2)	P(11)–Hg(1)–Hg(3)	126.54(13)
P(13)–Hg(1)–Hg(3)	90.46(13)	P(12)–Hg(1)–Hg(3)	116.13(13)
P(11)–Hg(1)–Hg(2)	91.52(13)	P(13)–Hg(1)–Hg(2)	148.60(13)
P(12)–Hg(1)–Hg(2)	91.83(13)	Hg(3)–Hg(1)–Hg(2)	58.71(3)
P(23)–Hg(2)–P(21)	105.9(2)	P(23)–Hg(2)–P(22)	108.6(2)
P(21)–Hg(2)–P(22)	105.7(2)	P(23)–Hg(2)–Hg(3)	90.77(14)
P(21)–Hg(2)–Hg(3)	127.83(13)	P(22)–Hg(2)–Hg(3)	115.19(13)
P(23)–Hg(2)–Hg(1)	147.55(14)	P(21)–Hg(2)–Hg(1)	91.71(13)
P(22)–Hg(2)–Hg(1)	91.91(14)	Hg(3)–Hg(2)–Hg(1)	57.29(3)
P(32)–Hg(3)–P(31)	106.6(2)	P(32)–Hg(3)–Hg(1)	156.84(13)
P(31)–Hg(3)–Hg(1)	96.16(14)	P(31)–Hg(3)–Hg(2)	159.2(2)
P(32)–Hg(3)–Hg(2)	93.78(13)	Hg(1)–Hg(3)–Hg(2)	64.00(4)
C(21)–P(11)–Hg(1)	110.8(6)	C(21)–P(21)–Hg(2)	111.3(6)
C(12)–P(12)–Hg(1)	111.2(6)	C(13)–P(31)–Hg(3)	106.6(7)
C(13)–P(13)–Hg(1)	110.9(7)	P(21)–C(21)–P(11)	116.4(10)
C(12)–P(22)–Hg(2)	111.6(6)	P(32)–C(23)–P(23)	114.6(12)
C(23)–P(23)–Hg(2)	113.6(8)	C(23)–P(32)–Hg(3)	107.7(8)
		P(22)–C(12)–P(12)	118.3(10)
		P(31)–C(13)–P(13)	115.4(11)

Symmetry transformation used to generate equivalent atoms: I −*x*, *y*, $-z + \frac{1}{2}$.

of a Hg_3 triangle, two edges of which are spanned by one dmpm ligand whilst the third edge is doubly bridged by a pair of dmpm ligands. Correspondingly, the atoms Hg(1) and Hg(2) are surrounded by three phosphorus and two Hg atoms respectively. Atom Hg(3) is surrounded by two phosphorus, two Hg and one CF_3SO_3 oxygen atom. The three Hg atoms and the phosphorus atoms of the singly bridging dmpm ligands are nearly in a plane. The dihedral angles of the Hg_3 triangle and the mean planes Hg(1)Hg(2)P(12)P(22) and Hg(1)Hg(2)-P(11)P(21), *i.e.* the planes formed by the doubly bridged Hg atoms and the phosphorus atoms of the two bridging dmpm ligands, are 61 and 46° respectively (Fig. 2). Both Hg(1)Hg(2)-P_2C rings adopt envelope conformations with P–Hg–Hg–P torsion angles near zero. The co-ordination geometry of the doubly bridged Hg atoms makes a major difference to the related platinum and nickel complexes **3**[26] and **4**:[27] both contain roughly planar M_3(μ-dmpm)$_3$ groupings, whilst the fourth dmpm is co-ordinated roughly perpendicular to the M_3(μ-dmpm)$_3$ planes (Fig. 2). Therefore, the two types of dmpm ligands have been termed latitudinal and longitudinal. The Hg–Hg distances in **2** are 276.68(14), 280.99(14) and 295.53(14) pm. The metal–metal distance in elemental mercury is 299 pm. All Hg–Hg separations are shorter than the P · · · P bites of the corresponding dmpm ligands [P(11) · · · P(21) 316.0(8), P(12) · · · P(22) 312.2(8), P(13) · · · P(31) 306.1(8), P(23) · · · P(32) 306.3(8) pm]. The distance between the doubly bridged atoms Hg(1) and Hg(2) is distinctly longer than the separations Hg(1)–Hg(3) and Hg(2)–Hg(3) involving the single bridges. The Hg–Hg distances in **1**[22] are 276.4(1), 276.4(1) and 280.2(1) pm, a mean 277.7 pm, compared with 284.4 pm for **2**. In contrast, there is little variety in the Pt–Pt bond lengths of **3**, the distance between the doubly bridged Pt atoms (264.8 pm) being very close to the distances between the singly bridged Pt atoms (262.8 and 262.0 pm). The mean Pt–Pt bond length of **3** (263.2 pm) is almost identical to the average value in $[Pt_3(\mu_3\text{-}CO)(\mu\text{-}dppm)_3]^{2+}$ (263.4 pm).[29] This has been interpreted to imply that the extra electrons in **3** do not occupy strongly antibonding orbitals.[26] The Hg–P bond lengths cover a range of 251.7(5)–255.0(6) pm and no obvious sensitivity to the environment can be observed. One oxygen atom of a $CF_3SO_3^-$ ion has a contact to Hg(3) at 274(3) pm.

NMR spectroscopy

The $^{31}P\text{-}\{^1H\}$ NMR spectrum of complex **2** in dmf at 297 K consists of three broad signals which sharpen upon cooling to 243 K. At 333 K there is only one slightly broadened resonance at the average value of the signals observed at 297 K; this is flanked by ^{199}Hg satellites [*J*(HgP) 791 Hz] implying the presence of intramolecular exchange between the two different types of dmpm ligands present. The exchange on the ^{31}P NMR time-scale (81 MHz) appears to be slow at 243 K and approaches the fast limit at 333 K. In contrast, the related platinum complex **3** is kinetically stable on the NMR time-scale at ambient temperature.[26] The nickel complex **4** shows a rapid intramolecular rotation of the axial dmpm ligand about the Ni_3 triangle.[27] There is no interconversion of the dmpm ligands positioned in the Ni_3 plane and the axial dmpm. Rotation about the M_3 triangle thus occurs in both the complexes of Hg and Ni. However, all dmpm ligands in the mercury complex exchange only because of the equivalence of the two doubly bridging dmpm ligands.

The signal at highest frequencies is attributed to atoms P(31) and P(32) (labelling as in Fig. 1) because the phosphorus-31 shift usually decreases as the co-ordination number of a d^{10} metal increases.[30] The other two types of phosphorus atoms [P(11), P(12), P(21), P(22) and P(13), P(23) respectively] are readily assigned according to the intensity of the signals. The $^{31}P\text{-}\{^1H\}$ NMR spectrum of the isotopomer without ^{199}Hg nuclei consists of a AA′XX′YY′Y′Y″Y‴ spin system. The pattern is very complex and insufficiently resolved even at 11.744 T. Efforts to analyse the spectrum were unsuccessful. The patterns of the isotopomers containing ^{199}Hg nuclei are broadened, presumably due to chemical shift anisotropy (CSA) relaxation processes. No $^{199}Hg\text{-}\{^1H\}$ NMR spectrum could be obtained.

Mass spectrometry

The use of gentle ionisation techniques has enabled the characterisation of ionic high-molecular-weight cluster complexes. The mass spectra of the related subvalent nickel complexes [*triangulo*-$Ni_3(\mu_3\text{-}L)(\mu_3\text{-}I)(\mu\text{-}dmpm)_4]^{n+}$ and [{*triangulo*-$Ni_3(\mu_3\text{-}I)(\mu\text{-}dmpm)_4\}_2(\mu_3,\mu_3'\text{-}\eta^1,\eta^{1\prime}\text{-}CN{-}R{-}NC)]^{2+}$ [R = $(CH_2)_6$ or 1,4-C_6H_4] were recently measured by plasma desorption and fast atom bombardment (FAB) mass spectrometry.[31] These clusters are neutral, mono- or di-cations. The mass spectrum of **2** was measured by FAB mass spectrometry. The molecular-ion signal enables the determination of the molecular weight.

Experimental

All reactions were carried out in Schlenk glassware by using standard inert-atmosphere techniques. The ^{31}P NMR spectra were recorded on a Bruker AC 200 spectrometer at 81.015 MHz and are referenced against external H_3PO_4, mass spectra on a Finnigan MAT 95 instrument with the FAB technique. Microanalyses were by the Mikroanalytisches Laboratorium, Institut für Physikalische Chemie, Universität Wien. The complex $[Hg(Me_2SO)_6][O_3SCF_3]_2$ was prepared as described previously;[32] dmpm was obtained from Strem Chemical Corp.

Synthesis of $[Hg_3(\mu\text{-}dmpm)_4][O_3SCF_3]_4$ 2

(*a*) To a dmf (0.5 cm^3) solution of $[Hg(Me_2SO)_6][O_3SCF_3]_2$ (72.6 mg, 0.075 mmol) were added dmpm (0.0225 cm^3, 0.15 mmol) and elemental Hg (0.1 cm^3). After stirring for 12 h the dmf phase was separated and the solvent removed under reduced pressure. The residue was washed with MeOH (0.5 cm^3) leaving the product as a white powder in almost quantitative yield, m.p. 268–270 °C (decomp.) (Found: C, 16.45; H, 2.9. $C_{24}H_{56}F_{12}Hg_3O_{12}P_8S_4$ requires C, 16.55; H, 3.25%). $^{31}P\text{-}\{^1H\}$ NMR (243 K, $[^2H_6]$ dmf): δ 39.9 [m, P(31), *J*(HgP) *ca.* 1300], 12.9 [m, P(13), *J*(HgP) *ca.* 1500], 7.7 [m, P(11), *J*(HgP) *ca.* 1650 and 850 Hz], labelling as in Fig. 1. FAB mass spectrum: *m/z* 1747 (M^+, 1.7), 1598 $\{[Hg_3(dmpm)_4(O_3SCF_3)_3]^+$, 2.3}, 1462 $\{[Hg_3(dmpm)_3(O_3SCF_3)_3]^+$, 5.0}, 1396 $\{[Hg_2(dmpm)_4(O_3SCF_3)_3]^+$, 3.1}, 1260 $\{[Hg_2(dmpm)_3(O_3SCF_3)_3]^+$, 10.9}, 1124 $\{[Hg_2(dmpm)_2(O_3SCF_3)_3]^+$, 28.6} and 1111 $\{[Hg_2(dmpm)_3(O_3SCF_3)_2]^+$, 2.0}.

(*b*) To a MeOH (0.5 cm^3) solution of $[Hg(Me_2SO)_6][O_3SCF_3]_2$ (72.6 mg, 0.075 mmol) was added elemental Hg (0.1 cm^3) and the mixture stirred for 10 min producing a solution of $[Hg_2][O_3SCF_3]_2$.[31] The compound dmpm (0.0225 cm^3, 0.15 mmol) was added and the mixture was stirred for 10 min. The MeOH phase was discarded and the residue was treated with dmf (0.5 cm^3). The dmf phase was separated and processed as in (*a*).

(*c*) Single crystals of complex **2** were obtained upon standing a solution of $[Hg(Me_2SO)_6][O_3SCF_3]_2$ (48.4 mg, 0.05 mmol) and dmpm (0.011 cm^3, 0.075 mmol) in water (0.6 cm^3) and MeOH (0.4 cm^3). Their identity with the products of methods (*a*) and (*b*) was checked by ^{31}P NMR spectroscopy.

Crystallography

The crystallographic data were acquired on a Siemens P4 diffractometer. The structure was solved by direct methods (SHELXS 86)[33] and refined by a full-matrix least-squares procedure using F^2 (SHELXL 93).[34] All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were included in the refinement at calculated positions using a riding model.

Three of the four $CF_3SO_3^-$ ions are located in general positions. The fourth is disordered in two positions with 50% occupancy. One of the disordered anions lies near the two-fold axis and could be refined without further difficulties. The other lies near an inversion centre with two or three possible directions of the S–C ion axis. An exact analysis of this disorder failed, because of different occupancy and overlying of the O, F and C atoms. Therefore only the two major orientations were refined with constrained S–C and C–F bond lengths. A crystal structure analysis of another crystal of complex **2** showed the same phenomenon.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/418.

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