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FULL PAPER

Host–guest chemistry of the cluster $[Hg_3(\mu\text{-dppm})_3]^{4+}$ [dppm = bis(diphenylphosphino)methane] with oxo- and fluoro-anions

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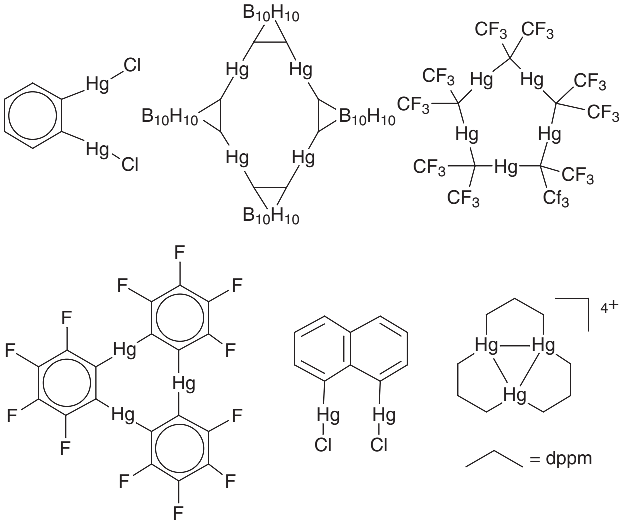
The subvalent mercury clusters $Hg_3(\mu\text{-dppm})_3(SiF_6)_2$ and $Hg_3(\mu\text{-dppm})_3(PF_6)_4$ with weakly co-ordinating octahedral fluoro-anions have been prepared from HgO, H_2SiF_6 or HPF_6, dppm and elemental mercury. The solid state structures of these clusters were determined by single crystal X-ray structure analysis as well as those of $Hg_3(\mu\text{-dppm})_3(O_3SCF_3)_4$, $Hg_3(\mu\text{-dppm})_3(O_3SCF_3)_4\cdot MeOH$, $Hg_3(\mu\text{-dppm})_3(O_3SCH_3)_4$ and $Hg_3(\mu\text{-dppm})_3(O_3SCH_3)_4\cdot 4H_2O$. The $[Hg_3(\mu\text{-dppm})_3]$ clusters are bifunctional recognition hosts and two anions of all the clusters are found inside the two cavities formed by the 12 phenyl groups of the dppm ligands and the Hg_3 triangle. The anion dependence of the ^{31}P NMR shift of the clusters is attributed to a varying occupancy of the cavities in solution.

Introduction

The design of multidentate Lewis acids is a current area of research. Scheme 1 summarises various previously studied multidentate Lewis acidic compounds of mercury.[1–9]



Scheme 1

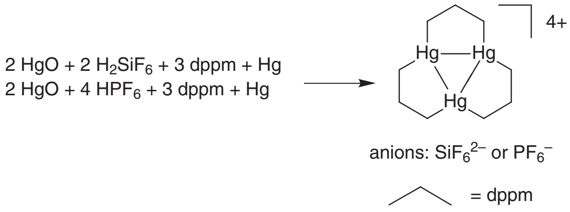
In this paper we report on the interaction of the tridentate Lewis acid $[Hg_3(\mu\text{-dppm})_3]^{4+}$ (Scheme 1) with the formal oxidation state +4/3 for Hg with different oxo- and fluoro-anions.

The host–guest chemistry of the related Group 10 metal members of the unsaturated $[M_3(\mu\text{-dppm})_3]$ type clusters with anionic and neutral ligands has been intensively studied. These complexes were shown to be bifunctional recognition hosts due to the hydrophobic cylindrical cavities formed by the phenyl groups of the dppm ligands and the Lewis acidic M_3 triangle.[10,11] In contrast to the Group 10 metal $[M_3(\mu\text{-dppm})_3]$ type clusters in which at least one cavity is persistently occupied by a one atom bridging ligand, *e.g.* CO, both cavities of the Hg cluster are accessible to host–guest interactions. The X-ray structure of $Hg_3(\mu\text{-dppm})_3(SO_4)_2$ has been previously determined and both cavities were found to be occupied by SO_4 anions.[12] The ^{31}P NMR shifts of $Hg_3(\mu\text{-dppm})_3(SO_4)_2$ and $Hg_3(\mu\text{-dppm})_3(O_3SCF_3)_4$ in solution are surprisingly different (10 ppm)[12] and this may be attributed to the different size and donor abilities of the anions involved. In order to investigate the host–guest interactions of the $[Hg_3(\mu\text{-dppm})_3]^{4+}$ cluster in solution and in the solid state we have synthesised and structurally characterised the hitherto unknown clusters with the weakly co-ordinating octahedral fluoro-anions PF_6^- and SiF_6^{2-} and also report on the X-ray structures of the previously reported[12] Hg clusters involving the $CF_3SO_3^-$ and $CH_3SO_3^-$ anions.

Results

Synthesis and NMR spectroscopy

The new subvalent clusters $Hg_3(\mu\text{-dppm})_3(SiF_6)_2$ **1** and $Hg_3(\mu\text{-dppm})_3(PF_6)_4$ **2** with the formal oxidation state of +4/3 were prepared according to eqn. (1) in almost quantitative yield.



(1)

The phosphorus-31 chemical shift of the PF_6 cluster **2** (60.5 ppm) is the highest value hitherto observed for a $Hg_3(\mu\text{-dppm})_3$ cluster. Table 1 summarises the phosphorus-31 shifts of **1** and **2** together with those of the previously reported clusters $Hg_3(\mu\text{-dppm})_3(SO_4)_2$ **3**, $Hg_3(\mu\text{-dppm})_3(CF_3SO_3)_4$ **4** and $Hg_3(\mu\text{-dppm})_3(CH_3SO_3)_4$ **5**. The shifts of these compounds cover a range of *ca.* 15 ppm and this is surprisingly large in view of the fact that each mercury atom is already strongly bound to two Hg and two phosphorus atoms. The NMR parameters appear to be related to the presence of the anions in the cavities which is thought to be controlled by the donor abilities and the size of the anions. Phosphorus shift data for the corresponding

Pd and Pt clusters exhibit a similar anion dependence. The solid state structure of $[Pd_3(\mu\text{-dppm})_3(\mu_3\text{-CO})][PF_6]_2$ shows that the PF_6 anion is located outside the cavity. The "empty" cluster exhibits unusual distortions of the Pd_3P_6 fragment when compared to clusters in which an anion is found inside the cavity *e.g.* $[Pd_3(\mu\text{-dppm})_3(\mu_3\text{-CO})(CF_3CO_2)][PF_6]$.[10]

Crystallography

The crystal data of the clusters **1**·$2H_2O$·$C_4H_8O_2$, **2**·$2CH_2Cl_2$, **4**·MeOH, **4**, **5**·$4H_2O$ and **5** are collected in Table 2. As exemplified for the SiF_6 cluster **1** depicted in Fig. 1 and for the PF_6 cluster **2** sketched in Fig. 2, all clusters invariably consist of Hg_3 triangles whose edges are bridged by three dppm ligands.

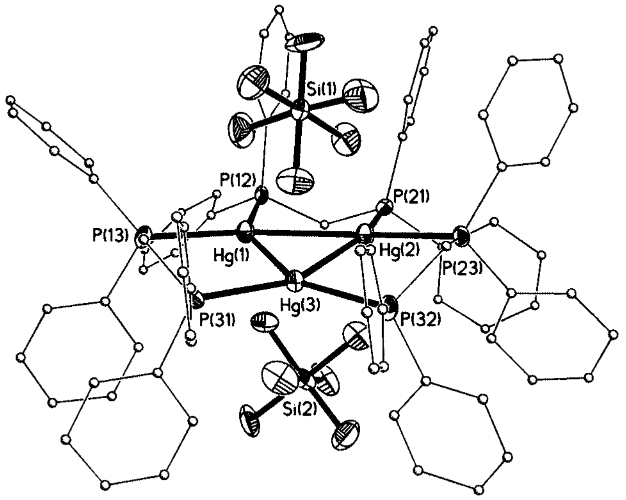


Fig. 1 An ORTEP[23] representation of **1**.

Table 1 ^{31}P NMR chemical shifts of the cluster $[Hg_3(\mu\text{-dppm})_3]^{4+}$ with different oxo- and fluoro-anions (solvent: CH_2Cl_2)

Anion	δ ^{31}P	Ref.
SO_4^{2-}	44.7	This work, 12[a]
$CH_3SO_3^-$	49.4	This work, 12[a]
SiF_6^{2-}	49.9	This work
$CF_3SO_3^-$	54.7	This work, 12[a]
PF_6^-	60.5	This work

[a] Slightly different shifts were reported for different solvents.

Two of the CH_2 groups lie above and one below the Hg_3 triangle resulting in four equatorial and two axial phenyl groups above the Hg_3 triangle and two equatorial and four axial phenyl groups below the Hg_3 triangle forming two cavities. The cavities of all clusters are occupied by anions. This is also observed for the structure of $Hg_3(\mu\text{-dppm})_3(SO_4)_2$, where both SO_4 anions are found to be contained in the cavities.[12] In the case of the anions CH_3SO_3, CF_3SO_3 and PF_6, there are two peripheral counterions outside of the cavities which do not have any contacts with mercury within the sum of the appropriate van der Waals radii.

Table 3 summarises the Hg–Hg distances of the $[Hg_3(\mu\text{-dppm})_3]^{4+}$ clusters which cover a range of 271.7(2)–286.49(13) pm. Interestingly, both extremes are observed for CF_3SO_3 clusters, the lowest value for **4**·MeOH and the highest value for **4** and this renders doubtful any correlation of the Hg–Hg distances with the anions involved. The mineral terlinguaite $Hg_4Cl_2O_2$[13] and $Hg_9As_4O_{16}$,[14] which both possess Hg_3 triangles, have values of 270.3(1); 266.2, 266.8 and 269.6 pm, respectively. In elemental mercury each atom has six nearest neighbours at 299 and six more at 347 pm.

Table 4 summarises the Hg–O and Hg–F distances between the mercury atoms of the Hg_3 triangle and the anions contained in

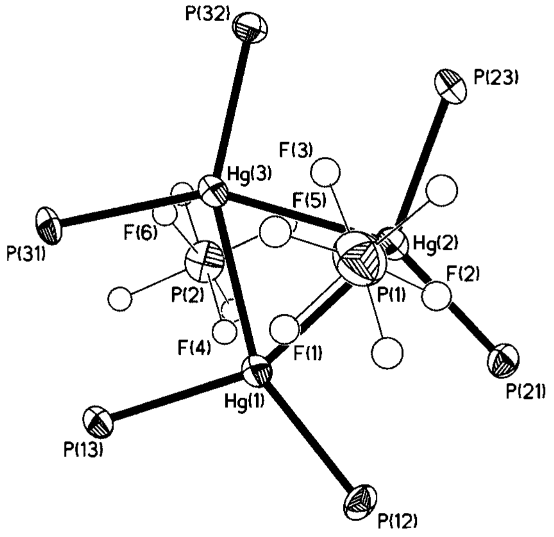


Fig. 2 An ORTEP representation of **2** showing that the phosphorus atoms of the PF_6 anions are not positioned exactly above and below the midpoint of the Hg_3 triangle; for clarity, only the *ipso* carbon atoms of the phenyl groups are drawn.

Table 2 Crystal data of the cluster $[Hg_3(\mu\text{-dppm})_3]^{4+}$ with different oxo- and fluoro-anions

Compound	**1**·$2H_2O$·$C_4H_8O_2$	**2**·$2CH_2Cl_2$	**4**·MeOH	**4**	**5**·$4H_2O$	**5**
Formula	$C_{75}H_{66}F_{12}Hg_3OP_6Si_2$	$C_{75}H_{66}F_{24}Hg_3P_{10}$	$C_{79}H_{66}F_{12}Hg_3O_{12}P_6S_4$	$C_{79}H_{66}F_{12}Hg_3O_{12}P_6S_4$	$C_{79}H_{78}Hg_3O_{12}P_6S_4$	$C_{79}H_{78}Hg_3O_{12}P_6S_4$
M	2163.18	2504.60	2383.19	2351.15	2207.31	2135.24
Crystal system	Orthorhombic	Monoclinic	Triclinic	Monoclinic	Triclinic	Monoclinic
a/pm	2228.0(4)	1455.9(4)	1483.1(5)	1439.2(3)	1492.0(3)	2395.0(2)
b/pm	2066.5(4)	4442.1(11)	1504.5(5)	2677.3(5)	1503.6(3)	2175.2(3)
c/pm	1690.9(4)	1511.3(3)	2319.0(5)	2372.3(2)	2218.2(3)	1959.4(3)
α/°	—	—	100.74(3)	—	83.19(2)	—
β/°	—	115.12(2)	96.81(4)	99.51(3)	71.49(2)	111.13(1)
γ/°	—	—	112.99(4)	—	65.96(2)	—
U/nm^3	7.785(3)	8.850(4)	4.574(2)	9.015(3)	4.3092(14)	9.521(2)
T/K	213(2)	213(2)	188(2)	293(2)	293(2)	293(2)
Space group	$Pca2_1$	$P2_1/c$	$P\bar{1}$	$P2_1/c$	$P\bar{1}$	$P2_1/c$
Z	4	4	2	4	2	4
μ(Mo-Kα)/mm^{-1}	6.134	5.586	5.299	5.375	5.601	5.064
Reflections total, independent, R_{int}	6390, 5702, 0.0404	9046, 7567, 0.0650	7223, 6887, 0.0338	13090, 10753, 0.700	14022, 12409, 0.0465	9256, 7432, 0.0680
Final *R*1	0.078	0.0646	0.0649	0.0656	0.0642	0.0612

Table 3 Hg–Hg distances in **1**–**5** (pm)

	Hg1–Hg2	Hg1–Hg3	Hg2–Hg3	mean Hg–Hg	Ref.
1·$2H_2O·C_4H_8O_2$	279.57(12)	281.04(12)	273.46(12)	278.02	This work
2·$2CH_2Cl_2$	280.7(2)	279.5(2)	281.7(2)	280.6	This work
3·$1.5H_2O$	276.4(1)	276.4(1)	280.2(1)	277.7	12
4·CH_3OH	271.7(2)	274.8(2)	278.1(2)	274.9	This work
4	275.26(11)	286.49(13)	284.09(13)	281.95	This work
5·$4H_2O$	281.91(9)	274.49(11)	277.80(9)	278.07	This work
5	277.76(13)	275.45(13)	279.94(13)	277.72	This work

Table 4 Hg–O/F distances in **1**–**5** (pm); values exceeding the appropriate upper van der Waals limit are in parentheses

	Hg1–O/F1	Hg1–O/F4	Hg2–O/F2	Hg2–O/F5	Hg3–O/F3	Hg3–O/F6	Ref.
1·$2H_2O·C_4H_8O_2$	307(2)	269(2)	265(2)	266.9(14)	257.9(14)	298(2)	This work
2·$2CH_2Cl_2$	299(2)	291(2)	279(2)	[401(3)]	313(2)	280(2)	This work
3·$1.5H_2O$	270	288	256	296	325	254	12
4·CH_3OH	321(2)	286(2)	302(2)	289(2)	279(2)	[347(3)]	This work
4	283(2)	[349(2)]	336(2)	273(2)	273(2)	290(2)	This work
5·$4H_2O$	263.0(11)	[397(2)]	298.1(11)	268.5(10)	326.4(11)	251.6(12)	This work
5	294(2)	322(6)	370(3)	263(2)	264(2)	[348(7)]	This work

the cavities. In order to discuss the values of the Hg–O distances it is useful to have a look at the van der Waals sum of Hg and oxygen. On the basis of Hg–Hg distances in metallic mercury, Grdenic proposed a van der Waals radius of 150 pm for Hg, but also suggested some sort of bonding within a value of 173 based on the 346 pm contacts in elemental mercury.[15] Canty and Deacon proposed a general Hg radius of 173 and a possible range of 170 to 200 pm. In combination with 140 for oxygen this amounts to a Hg–O van der Waals sum between 290 and 340 pm.[16] There are two reviews compiling experimental Hg–O distances.[17,18] Reference to Table 4 reveals that four of the five clusters have three Hg–O distances below the lower limit of 290, while the other distances exceed this value and in part also the higher limit of 340 pm. Typically, the short distances to oxygen atoms are formed by different mercury atoms within the Hg_3 system.

The van der Waals radius for fluorine is 135 pm, thus resulting in a range of 285–335 pm for Hg···F distances. According to Table 3, four Hg···F interactions of the SiF_6 cluster and two of the PF_6 cluster are within the lower limit whilst all Hg···F interactions of the SiF_6 cluster and five of the PF_6 cluster are within the upper limit. One Hg atom (Hg2) of the SiF_6 cluster has two short Hg···F contacts.

Discussion

Since all anions are contained in the cavities in the solid state, the ^{31}P chemical shift phenomena appear not to be caused by the different size of the anions. This is in contrast to the corresponding palladium clusters $[Pd_3(\mu\text{-dppm})_3(\mu_3\text{-CO})]^{2+}$ whose cavity is too small to accommodate the PF_6 anion in the solid state. The size of the cavities in $M_3(\mu\text{-dppm})_3$ clusters is governed by the M–M and M–P distances which are larger for Hg (Hg: Hg–Hg 271.7–286.5, Hg–P 247.3–254.8 pm) than for the Pd clusters (Pd: Pd–Pd 258–263, Pd–P 230–235 pm).[10,11] The size of the cavities has also been tuned by modification of the dppm ligands. In a recent paper the arsenic analogue of dppm, dpam [dpam = bis(diphenylarsino)methane], has been used to increase the size of the cavity of the Pd cluster and one PF_6 anion of $[Pd_3(\mu\text{-dpam})_3(\mu_3\text{-CO})][PF_6]_2$ is now contained in the cavity as has been established by the X-ray structure.[19] Another approach involves the substitution of the phenyl rings of dppm in $Pt_3(\mu\text{-dppm})_3$ clusters.[20]

The Hg···O/F interactions are thought to be of largely electrostatic nature: the Hg···F distances of the hexafluorosilicate ion are distinctly shorter (mean 277.3 pm) compared with the substantially smaller hexafluorophosphate ion (mean 310.5 pm), and this is attributed to the charge of the respective anions. The same reason is thought to be responsible for the shorter Hg–O distances of the sulfate ion compared to the methanesulfonate and trifluoromethanesulfonate ions. The ^{31}P NMR shift phenomena in solution are thus attributed to a varying dissociation of the different anions depending on the strength of the electrostatic binding in the cavities of the clusters. In view of the relatively long Hg···O/F distances observed, we propose that the large range of ^{31}P chemical shifts observed for $Hg_3(\mu\text{-dppm})_3$ clusters with oxo- and fluoro-anions is not directly caused by the co-ordination of the anions to the Hg_3 Lewis acid, but indirectly by distortions of the $Hg_3(\mu\text{-dppm})_3$ skeleton when the cavities are filled by anions.

The ^{31}P chemical shift is thought to indicate the occupancy. A single resonance is observed in all cases, indicating, that the anion dissociation/association processes [*e.g.* eqn. (2)] occur rapidly on the ^{31}P NMR timescale.

$$[Hg_3(\mu\text{-dppm})_3]^{4+} + O_3SCF_3^- \rightleftharpoons [Hg_3(\mu\text{-dppm})_3(O_3SCF_3)]^{3+}$$

$$[Hg_3(\mu\text{-dppm})_3(O_3SCF_3)]^{3+} + O_3SCF_3^- \rightleftharpoons [Hg_3(\mu\text{-dppm})_3(O_3SCF_3)_2]^{2+} \quad (2)$$

In this context it is interesting to note, that the exchange of CH_3SO_3 anions located inside and outside the cavities has been shown to reach the slow exchange limit on the ^1H NMR timescale at temperatures below 213 K,[12] whereas the SO_4^{2-} transfer between $Hg_3(\mu\text{-dppm})_3(SO_4)(O_3SCF_3)_2$, which is formed by the reaction of equimolar amounts of $Hg_3(\mu\text{-dppm})_3(SO_4)_2$ and $Hg_3(\mu\text{-dppm})_3(O_3SCF_3)_4$ as indicated in eqn. (3), and $Hg_3(\mu\text{-dppm})_3(O_3SCF_3)_4$ occurs slowly on the ^{31}P NMR time scale at ambient temperature.

$$Hg_3(\mu\text{-dppm})_3(SO_4)_2 + Hg_3(\mu\text{-dppm})_3(O_3SCF_3)_4 \longrightarrow 2\ Hg_3(\mu\text{-dppm})_3(SO_4)(O_3SCF_3)_2 \quad (3)$$

In all cases the solid state structure has no three-fold symmetry whereas the equivalence of the dppm ligands in solution is indicated by ^{31}P NMR. This fluxional behaviour reflects the relatively weak association of the anions.

Experimental

NMR spectra were recorded on a Bruker AC 200 spectrometer. Microanalyses were acquired by the Institut für Physikalische Chemie of the Universität Wien.

Synthesis of $Hg_3(\mu\text{-dppm})_3(SiF_6)_2$ 1

A suspension of yellow HgO (43.2 mg, 0.2 mmol) in H_2O (0.2 cm^3) is treated with a 25% aqueous solution of H_2SiF_6 until a clear solution is obtained. Elemental Hg (*ca.* 100 mg), dppm (115.2 mg, 0.3 mmol) and CH_2Cl_2 (0.5 cm^3) is added and the mixture is stirred for 1 h. According to ^{31}P NMR spectroscopy, the products are formed in almost quantitative yield. The volatiles are evaporated under reduced pressure and the residue is recrystallised from ethyl acetate–methanol (1 : 1) to give colourless crystals of **1**·$2H_2O$ (160 mg, 74%) (Found: C, 44.0; H, 3.4. $C_{75}H_{66}F_{12}Hg_3P_6Si_2\cdot 2H_2O\cdot C_4H_8O_2$ requires: C, 43.86; H, 3.63%).

Synthesis of $Hg_3(\mu\text{-dppm})_3(SO_4)_2$ 3

A mixture of $HgSO_4$ (59.3 mg, 0.2 mmol), dppm (115.2 mg, 0.3 mmol), CH_2Cl_2 (0.6 ml) and CH_3OH (0.9 ml) is stirred until a clear solution is obtained. Elemental mercury (*ca.* 100 mg) is added and the mixture is stirred for 24 h. The volatiles are evaporated and the residue is suspended in 1 cm^3 of H_2O and dissolved by addition of a minimal amount of CH_3CN at reflux. Upon slow cooling to ambient temperature, 160 mg (81%) of colourless crystals of **3**·$1.5H_2O$ are obtained (Found: C, 45.8; H, 3.5. $C_{75}H_{66}Hg_3O_8P_6S_2\cdot 1.5H_2O$ requires: C, 45.63; H, 3.52%).

Synthesis of $Hg_3(\mu\text{-dppm})_3(PF_6)_4$ 2, $Hg_3(\mu\text{-dppm})_3(O_3SCF_3)_4$ 4 and $Hg_3(\mu\text{-dppm})_3(O_3SCH_3)_4$ 5

The clusters were obtained similarly to **1** except for the use of a 60% aqueous solution of HPF_6, neat HO_3SCF_3 or HO_3SCH_3 instead of H_2SiF_6. **2**: (200 mg, 80% from ethyl acetate–dichloromethane) (Found: C, 37.4; H, 2.8. $C_{75}H_{66}F_{24}Hg_3P_{10}\cdot 2CH_2Cl_2$ requires: C, 36.92; H, 2.82%) **4**: (155 mg, 66% from ethyl acetate–dichloromethane) (Found: C, 40.5; H, 2.9. $C_{79}H_{66}F_{12}Hg_3O_{12}P_6S_4$ requires: C, 40.36; H, 2.83%) **5**: (128 mg, 60% from ethyl acetate–dichloromethane) (Found: C, 44.3; H, 3.7. $C_{79}H_{78}Hg_3O_{12}P_6S_4$ requires: C, 44.44; H, 3.68%). The solvate content of the solvates of **4** and **5** was confirmed by integration of the ^1H NMR spectra.

The asymmetric cluster $Hg_3(\mu\text{-dppm})_3(SO_4)(O_3SCF_3)_2$ was formed immediately upon mixing equimolar amounts of $Hg_3(\mu\text{-dppm})_3(SO_4)_2$ and $Hg_3(\mu\text{-dppm})_3(O_3SCF_3)_4$ and was not isolated.

Crystallography

Suitable crystals of $Hg_3(\mu\text{-dppm})_3(SiF_6)_2\cdot 2H_2O\cdot C_4H_8O_2$ were grown from ethyl acetate saturated with H_2O–methanol; of $Hg_3(\mu\text{-dppm})_3(PF_6)_4\cdot 2CH_2Cl_2$ from ethyl acetate–dichloromethane; of $Hg_3(\mu\text{-dppm})_3(O_3SCF_3)_4$ from ethyl acetate–dichloromethane; of $Hg_3(\mu\text{-dppm})_3(O_3SCF_3)_4\cdot MeOH$ from ethyl acetate–methanol; of $Hg_3(\mu\text{-dppm})_3(O_3SCH_3)_4$ from ethyl acetate–dichloromethane; of $Hg_3(\mu\text{-dppm})_3(O_3SCH_3)_4\cdot 4H_2O$ from ethyl acetate saturated with H_2O–dichloromethane. All crystals were examined by similar procedures. Crystals were mounted on a glass fiber, X-ray data were collected on a Siemens P4 diffractometer (Mo-Kα radiation, monochromator: highly oriented graphite crystal, ω-scan). Unit cell parameters were determined and refined from 22 to 32 randomly selected reflections in the θ range of 5.0 to 12.5°, obtained by *P*4 automatic routine. Every 97 reflections three standard reflections were measured. Data were corrected for Lorentz-polarisation and absorption effects (ψ-scans). The structures were solved by direct methods and subsequent difference Fourier techniques (SHELXS-86).[21] Refinement on F^2 with all measured reflections was carried out by full-matrix least-squares techniques (SHELXL-93).[22]

Because of the poor quality of some crystals, not all non-hydrogen atoms could be refined anisotropically. Only for **5**·$4H_2O$ the anisotropic refinement of all non-hydrogen atoms was possible. In all structures, at least the Hg and P atoms and the co-ordinated anions were refined anisotropically. All hydrogen atoms were placed at calculated ideal positions (riding model).

The peripheral O_3SCF_3 anions of **4**·MeOH were found to be disordered over three positions with occupancies of 0.75, 0.75 and 0.5. For the latter, an inversion center lies in the middle of the S–C bond and therefore three pairs of O- and F-atoms were refined with equal co-ordinates. The O_3SCH_3 anions of **5** were found to be disordered over four positions with occupancies of 0.66, 0.66, 0.33 and 0.33.

Crystal data and numerical details of structure determination and refinement are collected in Table 2.

CCDC reference number 186/1520.

See http://www.rsc.org/suppdata/dt/1999/2525/ for crystallographic files in .cif format.

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