Synthesis and Structure of the Cluster [*triangulo*-$AgHg_2(\mu\text{-dppm})_3]^{3+}$ [dppm = bis(diphenylphosphino)methane]

Anna Knoepfler, Klaus Wurst and Paul Peringer*

Institut für Allgemeine, Anorganische und Theoretische Chemie der Universität Innsbruck, Innrain 52a, A-6020 Innsbruck, Austria

The title cluster, which formally contains Ag^+ and Hg_2^{2+}, is formed from $Hg(O_3SCF_3)_2$, $Ag(O_3SCF_3)$, dppm and elemental mercury and has a Hg–Hg bond length of 265.98(14), and Ag–Hg distances of 280.5(2) and 285.3(2) pm.

We report here on the subvalent triangular cluster $[AgHg_2(\mu\text{-dppm})_3]^{3+}$ (**1**, Fig. 1). Mercury is known to form bonds with a wide variety of metals,[1–4] but we are unaware of reports relating to the existence of silver–mercury clusters. There are only a few examples of molecular mixed-metal compounds containing Hg_2 fragments, although in different structural environments: $[HgCo(np_3)]_2$ [np_3 = tris(2-diphenylphosphinoethyl)amine] contains an essentially linear Co–Hg–Hg–Co grouping.[5] In the clusters $[Os_{18}Hg_2C_2(CO)_{42}]^{n-}$ (n = 2, 4), the dimercury fragment is embedded between two parallel Os_3 triangles in a way that each Hg atom links an edge of one Os_3 triangle with a corner of the other. Each Hg and the Os atoms bonded to it lie approximately in a plane.[6,7] A weak Hg···Hg interaction [322.5(1) pm] was reported for $[\{Pt_3Hg(\mu\text{-CO})_3(PPhPr^i{}_2)_3\}_2]$ in which each mercury caps a Pt_3 unit.[8] Subvalent homometallic clusters based on the *triangulo*-M_3-(μ-dppm)$_3$ unit have been reported for M = Ni, Pd, Pt[9] and Hg.[10]

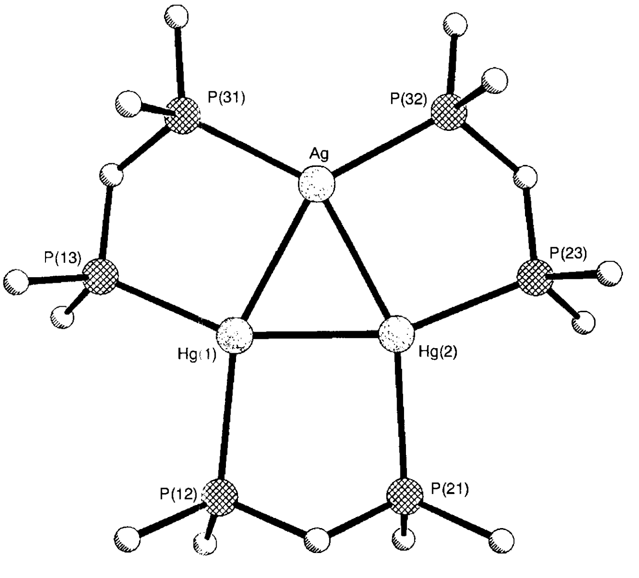
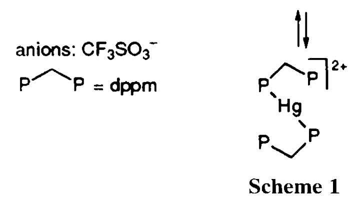


Fig. 1 Molecular structure of the cation of **1**; only the *ipso* carbon atoms of the phenyl rings are drawn; selected distances (pm) and angles (°): Hg(1)–Hg(2) 265.98(14), Hg(1)–Ag 285.3(2), Hg(2)–Ag 280.5(2), Hg(1)–P(12) 263.4(5), Hg(1)–P(13) 252.0(6), Hg(2)–P(21) 265.0(5), Hg(2)–P(23) 251.2(6), Ag–P(31) 247.0(6), Ag–P(32) 248.7(6), Hg(2)–Hg(1)–Ag 61.05(4), Hg(1)–Hg(2)–Ag 62.87(4), Hg(2)–Ag–Hg(1) 56.08(4)



Scheme 1

A solution of $Hg(O_3SCF_3)_2$, $Ag(O_3SCF_3)$ and dppm in the molar ratio of 1 : 1 : 3 in dichloromethane contains a mixture of $[AgHg(\mu\text{-dppm})_2][O_3SCF_3]_3$,[11,12] $[Ag_2(\mu\text{-dppm})_3][O_3SCF_3]_2$[13,14] and $[Hg(dppm)_2][O_3SCF_3]_2$.[11,15] The reaction of this mixture with elemental mercury leads to an almost complete conversion to the yellow silver–mercury cluster **1** (Scheme 1) which could be isolated in nearly quantitative yield.

A single-crystal structure analysis of **1** establishes the structure shown in Fig. 1.† The molecular structure consists of an $AgHg_2$ triangle, each edge of which is bridged by a dppm ligand. The charge of the $[AgHg_2(\mu\text{-dppm})_3]$ cation is +3 as indicated by the number of trifluoromethanesulfonate anions. Formally, this charge can be considered to result from an Ag^+ and an η^2-Hg_2^{2+} cation.

The Hg–Hg distance in **1** is 265.98(14) pm compared to 265.1(4) in $[\{HgCo(np_3)\}_2]$,[5] and 274.4(5) and 282.0(3) in $[Os_{18}Hg_2C_2(CO)_{42}]^{n-}$, ($n$ = 2, 4), respectively.[6,7] The Hg–Hg length in the related *triangulo*-Hg_3^{4+} clusters $[Hg_4O_2Cl_2]$[16] and $[Hg_3(\mu\text{-dppm})_3][SO_4]_2$[10] are 270.30(7) and 276.4(1), 280.2(1) pm, respectively. The Hg–Hg bond lengths in linear cations Hg_n^{2+} (n = 2–4), fall in the range of 240–270 pm.[17] The Ag–Hg distances are 280.5(2) and 285.3(2) pm. The metal–metal distances in elemental silver and mercury are 289 and 299 pm.

Silver and mercury have essentially planar coordination groups of two metals and two phosphorus atoms; additionally, there are interactions with oxygen atoms: two $CF_3SO_3^-$ anions are located in the two cavities formed by the six upper and six lower dppm phenyl groups. The Hg–O and Ag–O distances are: Hg(1)–O(1) 274(2), Hg(1)–O(4) 314(2), Hg(2)–O(5) 277(2), Hg(2)–O(2) 313(2), Ag–O(3) 318(2) and Ag–O(6) 443(2) pm [the oxygen atoms O(1)–O(3) and O(4)–O(6) belong to one $CF_3SO_3^-$ anion respectively]. Complex **1** is readily soluble in dichloromethane or acetone. The $^{31}P\{^1H\}$ NMR spectrum is a superposition of the patterns of six isotopomers, as both Ag and Hg have magnetically active nuclei. The species without ^{199}Hg nuclei give rise to two AA′BB′MM′X spin systems (X = $^{107/109}Ag$). Efforts to analyse the spectrum are currently being undertaken.‡

According to preliminary results, the copper and gold analogues of **1** are formed in a similar way, but so far we have not succeeded in growing single crystals of these clusters.

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Footnotes

† *Crystal data for* **1**: $C_{78}H_{66}AgF_9Hg_2O_9P_6S_3$, M = 2109.36, monoclinic, space group $P2_1/n$, a = 1525.6(3), b = 2802.8(8), c = 2186.3(3) pm, β = 92.14(1)°, U = 9.342(4) nm^3, Z = 4, D_c = 1.500 g cm^{-3}, μ(Mo-Kα) = 3.721 nm^{-1}. Crystal dimensions: 0.8 × 0.4 × 0.25 mm. Data were measured at 298(2) K on a Siemens P4 automatic diffractometer with a highly oriented graphite crystal monochromated Mo-Kα radiation using ω scans. The structure was solved by direct methods and refined using absorption corrected data to give R_1 = 0.0648 for 5046 independent observed reflections [$I > 2\sigma(I)$] and 598 parameters. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic

Data Centre. See Information for Authors, Issue No. 1.

‡ *Partial spectroscopic data for* **1**: $^{31}P\{^1H\}$ NMR (CH_2Cl_2) δ 51.4 (m), 46.2 (m), 21.5 (m), ref. 85% H_3PO_4. ^{199}Hg NMR (CH_2Cl_2) δ 2727 (m), ref. aqueous $Hg(ClO_4)_2$ (1 mmol HgO cm^{-3}, 60% $HClO_4$).

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