Mercury(II) halide complexes of tertiary phosphines
Part XV*. Crystal structure of the mercury(II) halide–phosphine complex of unusual stoichiometry, $(Me_3P)_2(HgI_2)_3$

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Abstract

Crystals of the complex are triclinic, space group $P\bar{1}$ with $a=9.439(2)$, $b=8.108(6)$, $c=8.532(1)$ Å, $\alpha=105.74(8)$, $\beta=88.48(3)$, $\gamma=103.64(3)°$. The structure was solved using the heavy atom method and refined to a final R of 0.1033 for 1740 observed diffractometer data. The structure contains Hg in two very different environments and comprises octahedrally coordinated mercury in which linear $(Me_3P)_2Hg^{2+}$ cations are weakly linked to $4HgI_3^-$ anions, resulting in chains along c. The trigonal HgI_3^- units link in pairs via further weak Hg---I interactions to form highly asymmetric $Hg_2I_6^{2-}$ dimers, thereby linking the chains together.

Introduction

We have earlier carried out extensive structural and spectroscopic studies of a range of mercury(II) halide–tertiary phosphine complexes having 1:1 and 1:2 stoichiometry. The $HgX_2(PR_3)_2$ complexes have a monomeric pseudotetrahedral arrangement, the degree of distortion depending on the σ-donor ability of the phosphine [1–5]. The 1:1 complexes in contrast show a much greater variety of structural types, ranging from monomeric units, albeit weakly linked in a variety of ways to form polymeric chains for strong σ-donors such as Me_3P, to discrete dimers for weak phosphine donors such as Ph_3P [5–15]. The factors affecting the extent of association in the 1:1 complexes and the magnitude of geometrical parameters for both series of complexes have been discussed in Parts XII [4] and XIV [14]. As part of our continuing studies in this area, examining more thoroughly the effect of halogen on the structures adopted, we intended to determine the structure of Me_3PHgI_2 since earlier X-ray work had shown that it was not isostructural with the corresponding bromo and chloro complexes, the latter containing $[Me_3PHgCl]^+Cl^-$ units, weakly linked to form a trigonal bipyramidal polymeric arrangement [8]. Additionally the low frequency infrared spectrum of Me_3PHgI_2, contrary to earlier assertions [15], is not interpretable in terms of a discrete centrosymmetric dimeric arrangement [12]. It is however, similar to that of α-Pr_3PHgI_2 which has a non-centrosymmetric dimeric structure in which both phosphine ligands are coordinated to the same mercury atom [14]. Unfortunately, a crystal chosen for X-ray analysis from a long-time prepared sample of $MePHgI_2$ was found to have the stoichiometry $(Me_3P)_2(HgI_2)_3$ and we herein report the structure of this compound. Though this is the first mercury(II) halide–tertiary phosphine complex of this stoichiometry subjected to X-ray crystallographic analysis, Mann and co-workers [16] in their pioneering work in 1940 isolated tertiary phosphine and arsine complexes of mercury(II) halides having such stoichiometry. Preliminary X-ray work showed that $(Et_3As)_2(HgI_2)_3$ had no centre of symmetry, whereas $(Pr_3As)_2(HgCl_2)_3$ and $(Bu_3As)_2(HgBr_2)$ contained a centre of symmetry and more detailed structural studies of the latter showed it to be a molecular compound of the 1:1 dimeric complex $(Bu_3AsHgBr_2)_2$ and $HgBr_2$ [16].

Experimental

The complex of stoichiometry Me_3PHgI_2 was prepared as described [8] and left for several years in

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a closed bottle. A crystal of this material was selected for X-ray analysis. Structural studies indicated that it did not have the expected 1:1 stoichiometry and subsequent chemical analysis of the bulk sample showed it to be $(Me_3P)_2(HgI_2)_3$. *Anal.* Found: C, 4.98; H, 1.08. Calc.: C, 4.75; H, 1.19%.

Crystallographic studies

A crystal of approximate dimensions 0.12 × 0.25 × 0.18 mm was mounted with its b axis coincident with the ω axis of a Stoe Stadi-2-two-circle diffractometer. Data were collected using the background–ω scan–background technique and with graphite monochromated Mo Kα radiation. A total of 2071 unique reflections was measured of which 1740 had $I/\sigma(I) \geqslant 4.0$ and were used for subsequent analysis. Data were corrected for Lorentz and polarisation effects but the application of absorption corrections did not significantly improve the data.

Crystal data

$C_6H_{18}Hg_3P_2I_6$, $M = 1515.3$, triclinic, $a = 9.439(2)$, $b = 8.108(6)$, $c = 8.532(1)$ Å, $\alpha = 105.74(8)$, $\beta = 88.48(3)$, $\gamma = 103.64(3)°$, $U = 610$ Å^3, $F(000) = 642$, space group $P\bar{1}$, $Z = 1$, $D_c = 4.12$ g cm^{-3}, Mo Kα radiation, $\lambda = 0.71069$ Å, μ(Mo Kα) = 252 cm^{-1}.

One of the two mercury atoms was located on a centre of symmetry at 0, 0.5, 0. The remaining non-hydrogen atoms were located from successive Fourier electron density maps and refined by full matrix least-squares. Hydrogen atoms were included in ideal positions (C–H, 1.08 Å) and given a common isotropic temperature factor ($U = 0.050(29)$ Å^2) while all other atoms were assigned anisotropic thermal parameters. Complex neutral-atom scattering factors [17] were employed throughout the refinement and in the final cycles of refinement the weighting scheme $\omega = 1.0000/[\sigma^2(F_o) + 0.018931(F_o)^2]$ was adopted and refinement converged at $R = 0.1033$, $R' = 0.0986$. All calculations were performed using an IBM 4341 computer using the SHELX computing package [18]. Final positional parameters are given in Table 1, bond distances and angles in Table 2. See also 'Supplementary material'.

TABLE 1. Final fractional coordinates (Hg × 10^5, other atoms × 10^4)

	x	y	z
Hg(1)	0	5000	0
Hg(2)	28172(13)	40842(19)	53761(14)
P	2003(6)	7436(8)	1256(7)
I(1)	732(2)	3181(2)	2970(2)
I(2)	4610(2)	7462(2)	6237(2)
I(3)	2239(2)	2524(2)	7827(2)
C(1)	1712(27)	8395(37)	3342(29)
C(2)	2257(26)	9123(34)	228(25)
C(3)	3728(27)	6796(46)	1167(38)

TABLE 2. Bond lengths (Å) and bond angles (°) with e.s.d.s in parentheses[a]

Distances	
Hg(1)–P	2.413(6)
Hg(1)–I(1)	3.417(2)
Hg(1)–I(3)^{ii}	3.422(2)
Hg(2)–I(1)	2.710(2)
Hg(2)–I(2)	2.774(2)
Hg(2)–I(3)	2.706(2)
Hg(2)–I(2)^{iv}	3.113(2)
Hg(2)...Hg(2)^{iv}	4.134(1)
P–C(1)	1.78(2)
P–C(2)	1.78(2)
P–C(3)	1.82(3)
Angles	
P–Hg(1)–I(1)	85.4(1)
P–Hg(1)–I(3)^{ii}	93.5(1)
I(1)–Hg(1)–I(3)^{ii}	82.5(0)
I(1)–Hg(2)–I(3)	117.1(1)
I(1)–Hg(2)–I(2)	119.8(1)
I(2)–Hg(2)–I(3)	115.4(1)
I(1)–Hg(2)–I(2)^{iv}	105.4(1)
I(2)–Hg(2)–I(2)^{iv}	91.0(1)
I(3)–Hg(2)–I(2)^{iv}	101.3(1)
Hg(1)–I(1)–Hg(2)	134.9(1)
Hg(1)–I(3)^{ii}–Hg(2)^{ii}	99.1(1)
Hg(2)–I(2)–Hg(2)^{iv}	89.0(1)
Hg(1)–P–C(1)	112(1)
Hg(1)–P–C(2)	111(1)
Hg(1)–P–C(3)	112(1)
C(1)–P–C(2)	108(1)
C(2)–P–C(3)	106(1)
C(1)–P–C(3)	108(1)

[a] i: $-x$, $1-y$, $-z$; ii: x, y, $-1+z$; iii: $-x$, $1-y$, $1-z$; iv: $1-x$, $1-y$, $1-z$.

Results and discussion

Although mercury(II) halides form tertiary phosphine complexes of several stoichiometries, the most important being HgX_2L_n ($n = 1$, 2), a number of complexes having less common stoichiometry are known. For example we have earlier determined the structure of $(Me_2EtP)_3(HgCl_2)_2$ which contains $[(Me_2EtP)_2HgCl]^+$ and $[Hg(Me_2EtP)Cl_3]^-$ weakly linked by chlorine bridges to form chains [19]. In pursuing structural studies of 1:1 HgI_2 complexes with tertiary phosphines we inadvertently obtained $(Me_3P)_2(HgI_2)_3$. Compounds of this type have previously been prepared from HgX_2L ($L = R_3P$, R_3As) and excess HgX_2 in hot ether or acetone [16] but in our case Me_3PHgI_2 appears to have lost one third of a mole of trimethylphosphine over several years to yield $(Me_3P)_2(HgI_2)_3$.

The structure contains mercury in two very different environments and can best be described as comprising $Hg(PMe_3)^{2+}$ cations linked via weak Hg–I interactions to four HgI_3^- anions to give chains running along the *c*-direction (Fig. 1.). The HgI_3^- units are grouped in pairs and further weak Hg...I interactions give rise to $Hg_2I_6^{2-}$ dimers, thereby linking the chains together. The PMe_3–Hg(1)–PMe_3 cation is required, crystallographically, to be linear and this together with the four Hg(1)...$IHgI_2$ linkages give rise to an octahedral coordination about Hg(1). The Hg...I interactions are, however, likely to be extremely weak given that the distances are just within the sum of the van der Waals' radii (3.417 and 3.422 Å compared with 3.45 Å). Certainly the Hg–P distance of 2.413(6) Å is indicative of a strong interaction and comparable with that found for $(R_3P)_2HgX_2$ complexes containing strong σ-phosphine donors [4]. Bond angles about Hg(1) range from 82.5(0) to 97.5(1)°.

Although surrounded by four iodines, coordination about Hg(2) can be described as trigonal, given that the fourth iodine lies at a considerably larger distance from Hg(2) than do the other three (3.113(2) Å compared to 2.706(2), 2.710(2) and 2.774(2) Å). However, the HgI_3 units are not planar, the sum of the bond angles about Hg(2) being only 352.3°, and the Hg–$I(2)^{iv}$ distance of 3.113(2) Å is well within the sum of the van der Waals; radii (3.45 Å), such that pairs of HgI_3^- anions are loosely linked into centrosymmetric $[I_2Hg(\mu\text{-}I)_2HgI_2]^{2-}$ dimers. The latter are, however, highly asymmetric, the two bridging distances being 2.774(2) and 3.113(2) Å.

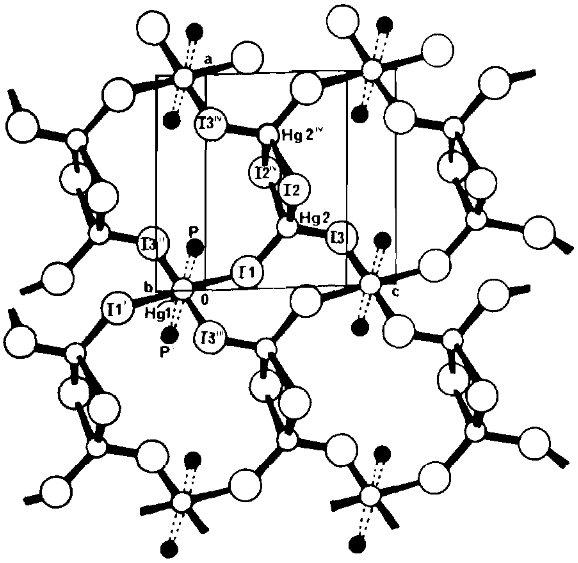

Fig. 1. Structure of $(Me_3P)_2(HgI_2)_3$ along *c* showing the $(Me_3P)_2Hg^{2+}$ and HgI_3^- units: CH_3 groups omitted for clarity.

The trend from discrete HgI_3^- to $[Hg_2I_6]^{2-}$ anions is illustrated by the series $MHgI_3$ (M = Bu_4N [20], Me_3S [21], Ph_4P [22]). The former contains discrete HgI_3^- anions, the closest approach of different anions being 7.4 Å, whereas Me_3SHgI_3 contains approximately planar HgI_3^- units as in the structure described herein but differs in having weak apical links extending the coordination round mercury to a trigonal bipyramidal arrangement. Ph_4PHgI_3 contains four-coordinate mercury in the $[Hg_2I_6]^{2-}$ anion with the bridging distances (2.864(1), 2.962(1) Å) differing little.

Detailed structures of two other compounds of stoichiometry $(HgX_2)_3(L)_2$ (X = Cl; L = thiourea [23], dimethylsulfoxide [24] have been determined but both differ from the present complex. The thiourea complex consists of infinite chains of Hg(tu)Cl units bridged by further Cl atoms with the chains interleaved with discrete $HgCl_2$ molecules [23]. The Me_2SO complex also contains linear $HgCl_2$ units with four long Hg...Cl contacts from dimeric $[Me_2SOHgCl_2]_2$ units in which double oxygen bridges link the mercury atoms [24].

Supplementary material

Hydrogen positions, thermal parameters, observed and calculated structure factors are available from the authors on request.

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