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Mercuric Halide Complexes of Tertiary Phosphines.
Part II.* Crystal Structures of 1:1 Complexes of Trimethylphosphine and Triethylphosphine, and a Rationalisation of Structural Differences in the $HgX_2(PR_3)$ Series

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The crystal structures of the complexes $HgCl_2(PMe_3)$ *and* $HgCl_2(PEt_3)$ *have been completely characterised by single crystal X-ray analysis. In each case the structures are polymeric, with mercury atoms in distorted trigonal bipyramidal environments, but the actual arrangements are different. Whereas* $HgCl_2(PEt_3)$ *may be regarded as an extended chlorine-bridged chain with essentially covalent bonding throughout, a very large P–Hg–Cl angle, and other structural features, characterise the trimethylphosphine complex as being of ionic formulation,* $[HgCl(PMe_3)]^+Cl^-$. *Preliminary single crystal photographs show that* $HgBr_2(PMe_3)$ *is isostructural with chloride, but* $HgI_2(PMe_3)$ *is apparently structurally different.*

The structures found are thus in marked contrast to those previously reported for 1:1 adducts of mercuric chloride with bulkier phosphines, and the origins of the differences are discussed.

Introduction

We have recently reported the crystal structures of 1:1 complexes of mercuric chloride with triphenylphosphine, 1,2,5-triphenylphosphole, and tributylphosphine [1], and were able to show how differences in the structures of these compounds, some rather subtle, could be rationalised in terms of the different donor properties of the phosphorus ligands. Because the three ligands chosen for this earlier study all gave rise to closely related structures for the complexes, we have now extended the range considerably, in the direction of the trend suggested by the earlier work. Thus the present paper is concerned with complexes of the small, strong σ-donors PMe_3 and PEt_3. Preliminary results have appeared [2].

Experimental

Although the complexes described in this paper have been prepared previously [3], we have developed a particularly convenient method for the PMe_3 series as follows.

To an aqueous solution of $[Et_4N]_2[HgCl_4]$ [4] was added dropwise an equimolar aqueous solution of $AgNO_3(PMe_3)$ [5], whereupon a yellow-white precipitate, comprising a mixture AgCl + $HgCl_2(PMe_3)$, formed immediately. After the addition was complete, the product was collected and dried by suction. The required $HgCl_2(PMe_3)$ complex was extracted with hot formdimethylamide and recovered on addition of water. The bromo-analogue was obtained similarly, while for the iodide an analogous method was adopted but with the $[Et_4N]_2[HgI_4]$ starting material dissolved in acetone. All compounds subsequently studied gave satisfactory elemental analysis.

The general methods for obtaining the spectroscopic and crystallographic data were as described previously [1].

Crystal Data

These are summarised in Table I.

X-Ray Intensity Measurements

Crystals of $HgCl_2(PMe_3)$ and $HgCl_2(PEt_3)$, having approximate dimensions 0.15 × 0.12 × 0.27 mm and 0.33 × 0.17 × 0.23 mm respectively, were mounted such that a real axis (*c* and *a* respectively) was coincident with the ω-axis of a Stöe Stadi 2 two-circle diffractometer. Data were collected using the background-ω scan-background technique. Lorentz and polarisation corrections have been applied and corrections for absorption effects were made for the PMe_3 complex.

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*Part I: see reference 1.

TABLE I. Crystal Data and Details of Data Collection.

	HgCl$_2$(PMe$_3$)	HgCl$_2$(PEt$_3$)
Crystal Data		
M_r	347.58	389.66
Crystal System	triclinic	monoclinic
a/Å	6.408(6)	7.454(8)
b/Å	8.894(9)	11.543(10)
c/Å	7.270(9)	13.673(12)
α/°	89.13(5)	
β/°	92.00(5)	105.94(5)
γ/	95.83(5)	
U/Å^3	411.9	1131.3
D_m/g cm^{-3}	2.79	2.31
Z	2	4
D_c/g cm^{-3}	2.80	2.29
F(000)	312	720
μ(Mo–$K\alpha$)/cm^{-1}	187.1	136.3
Space Group	$P\bar{1}$	$P2_1/c$
Collection of Intensity Data		
Reflections collected	1732	1467
No. of observed reflections[a]	1674	1240
$I/\sigma(I)$	3.0	4.0
Final R value	0.057	0.087

[a] Those reflections having $I/\sigma(I)$ greater than the indicated value were considered to be observed. The net intensity $I = T - B$, where T = scan count, B = mean background count over the scan width; $\sigma(I) = (T + Bc/2t)^{1/2}$, where c = scan time, t = time for background measurements at each end of the scan.

Structure Determination and Refinement

The Patterson function was used to locate the mercury atoms in both compounds and remaining non-hydrogen atoms were located from successive electron-density maps. Scattering factors were calculated [6] using an analytical approximation. Full-matrix refinement was used with anisotropic temperature factors applied to mercury, chlorine, and phosphorus atoms, and with isotropic temperature factors assigned to all carbons. Unit weights were used throughout and final atomic parameters are listed in Table II; bond distances and angles are in Table III. Observed and calculated structure factors and thermal parameters have been deposited and are available from the Editor.

Structure Calculations

All calculations, apart from preliminary data processing, were carried out on an IBM 370/165 computer using the SHELX computing package [7].

Results

HgCl$_2$(PEt$_3$) is a chlorine–bridged polymer (Fig. 1) containing mercury atoms in distorted trigonal bipyramidal co-ordination. The equatorial positions are occupied by a close phosphorus atom [2.35(1) Å] and the two nearest Cl atoms [2.42(1) and 2.56(1) Å], and although the four atoms are essentially coplanar, there is considerable distortion of the trigonal grouping with the angles around mercury varying from 98.9(3)° [Cl(2)–Hg–Cl(1)] to 145.4(3)° [P–Hg–Cl(2)]. The two axial Hg–Cl contacts [3.04(1) and 3.21(1) Å] are close to linear [170.8(3)°], with the bridging angles, Hg–Cl(1)–Hg$^{\text{iii}}$ and Hg–Cl(2)–Hg$^{\text{iv}}$, of 93.2(3) and 91.3(3)°, respectively.

This polymeric arrangement resembles the more regular structures found for a number of trichloromercurate(II) salts [8, 9] and for HgCl$_2$(2,4,6-trimethylpyridine) [10], and may be regarded as an extension of the association of dimeric units found to occur in tetrameric α-HgCl$_2$(PBu$_3$) [1].

Although the structure of HgCl$_2$(PMe$_3$) also appears to be polymeric, it is very different to that of HgCl$_2$(PEt$_3$) and shows a number of distinguishing features. The most prominent of these is the presence of a terminal Hg–Cl bond which is notably short [2.355(4) Å] and which forms part of a near-linear Cl–Hg–P arrangement [162.1(1)°]. The other near neighbours to mercury are three other Cl atoms at substantially longer distances [2.782(4), 2.941(4), and 3.489(4) Å]. These features lend themselves towards describing the structure as ionic in nature, comprising [Cl–Hg–PMe$_3$]$^+$ cations and Cl$^-$ anions alternately arranged in a zig-zag chain manner (Fig. 2). The chain is very regular, with centres of symmetry associated with each four-membered ring and with all the atoms of the chain being almost coplanar (deviations 0.142 Å or less). The structure thus resembles that found [11] for HgCl$_2$(tetrahydrothiophene), but the ionic formulation is less appropriate in the latter case (Cl–Hg–S angle of 142.8°).

Preliminary single-crystal X-ray photographs indicate that HgBr$_2$(PMe$_3$) is isostructural with the corresponding chloride, but that HgI$_2$(PMe$_3$) is not.

Discussion

The results obtained in the present study are in marked contrast to those reported for other 1:1 complexes of HgCl$_2$ with phosphine type donors [1]. Apart from the gross differences in structure, there are more subtle variations in the mercury environment (Table IV [1, 12]) which, contrary to earlier indications [13], cannot be attributed simply to changes in the ligand size. For example, there appears to be no obvious cause, in terms of phosphine ligand 'bulkiness', why the two compounds described in the present paper should be of different structure.

A more acceptable rationalisation of the structures adopted extends arguments put forward by us recently [2]. Thus we deduce that the tendency for the phosphine to impart a linear ClHgP arrangement at mercury, with corresponding displacement of a Cl atom

TABLE II. Final Fractional Coordinates ($\times 10^4$) for Non-Hydrogen Atoms with Estimated Standard Deviations in Parentheses.

$HgCl_2(PMe_3)$				$HgCl_2(PEt_3)$			
	x	y	z		x	y	z
Hg	1928(1)	99(1)	2989(1)	Hg	2185(2)	5142(1)	4392(1)
Cl(1)	2666(6)	132(4)	6782(6)	Cl(1)	4371(14)	5878(9)	6063(7)
Cl(2)	2032(7)	2727(4)	2482(6)	Cl(2)	1047(13)	3415(8)	5023(7)
P	2099(6)	−2510(4)	2525(6)	P	1995(16)	6305(12)	2960(8)
C1	−498(26)	−3529(18)	2378(24)	C1	−52(66)	7101(36)	2553(34)
C2	3384(28)	−3359(20)	4465(26)	C2	1680(130)	5132(79)	1808(65)
C3	3462(33)	−2915(23)	450(30)	C3	3801(93)	7301(58)	3196(50)
				C4	−2050(85)	6377(50)	2095(42)
				C5	2300(92)	5792(52)	933(45)
				C6	4141(89)	8071(54)	4015(49)

TABLE III. Bond lengths (Å) and Angles (°) with Estimated Standard Deviations in Parentheses.

Symmetry Code

none x, y, z

(^{i}) $-x, -y, 1.0 - z$ (^{iii}) $1.0 - x, 1.0 - y, 1.0 - z$

(^{ii}) $1.0 - x, -y, 1.0 - z$ (^{iv}) $-x, 1.0 - y, 1.0 - z$

Metal Coordinations

Distances (Å)			
$HgCl_2(PMe_3)$		$HgCl_2(PEt_3)$	
Hg–P	2.365(3)	Hg–P	2.35(1)
Hg–Cl(1)	2.782(4)	Hg–Cl(1)	2.56(1)
Hg–Cl(1^{i})	2.941(4)	Hg–Cl(1^{iii})	3.04(1)
Hg–Cl(1^{ii})	3.489(4)	Hg–Cl(2)	2.42(1)
Hg–Cl(2)	2.355(4)	Hg–Cl(2^{iv})	3.21(1)
Hg···Hg^{i}	3.884(2)	Hg···Hg^{iii}	4.081(2)
Hg···Hg^{ii}	4.838(2)	Hg···Hg^{iv}	4.057(2)
Angles (°)			
$HgCl_2(PMe_3)$		$HgCl_2(PEt)_3$	
P–Hg–Cl(1)	98.2(1)	P–Hg–Cl(1)	115.6(3)
P–Hg–Cl(1^{i})	95.2(1)	P–Hg–Cl(1^{iii})	84.9(3)
P–Hg–Cl(1^{ii})	78.4(1)	P–Hg–Cl(2)	145.4(3)
P–Hg–Cl(2)	162.1(1)	P–Hg–Cl(2^{iv})	91.9(4)
Cl(1)–Hg–Cl(1^{i})	94.6(1)	Cl(1)–Hg–Cl(1^{iii})	86.8(3)
Cl(1)–Hg–Cl(1^{ii})	79.6(1)	Cl(1)–Hg–Cl(2)	98.9(3)
Cl(1)–Hg–Cl(2)	98.2(1)	Cl(1)–Hg–Cl(2^{iv})	86.7(3)
Cl(1^{i})–Hg–Cl(1^{ii})	170.6(1)	Cl(1^{iii})–Hg–Cl(2)	98.8(3)
Cl(1^{i})–Hg–Cl(2)	90.6(1)	Cl(1^{iii})–Hg–Cl(2^{iv})	170.8(3)
Cl(1^{ii})–Hg–Cl(2)	97.6(1)	Cl(2)–Hg–Cl(2^{iv})	88.7(3)
Hg–Cl(1)–Hg^{i}	85.4(1)	Hg–Cl(1)–Hg^{iii}	93.2(3)
Hg–Cl(1)–Hg^{ii}	100.4(1)	Hg–Cl(2)–Hg^{iv}	91.3(3)

Ligand Geometries

Distances (Å)			
$HgCl_2(PMe_3)$		$HgCl_2(PEt_3)$^{a}	
P–C1	1.81(2)	P–C	1.84
P–C2	1.80(2)	C–C	1.55
P–C3	1.83(2)		
Angles (°)			
$HgCl_2(PMe_3)$		$HgCl_2PEt_3)$^{a}	
Hg–P–C1	111.4(7)	Hg–P–C	109.7
Hg–P–C2	111.0(7)	C–P–C	109.3
Hg–P–C3	113.5(7)	P–C–C	115.2
C1–P–C2	104.6(9)		
C1–P–C3	107.7(9)		
C2–P–C3	108.2(9)		

[a] Ethyl groupings are not well resolved and average bond distances and angles are given.

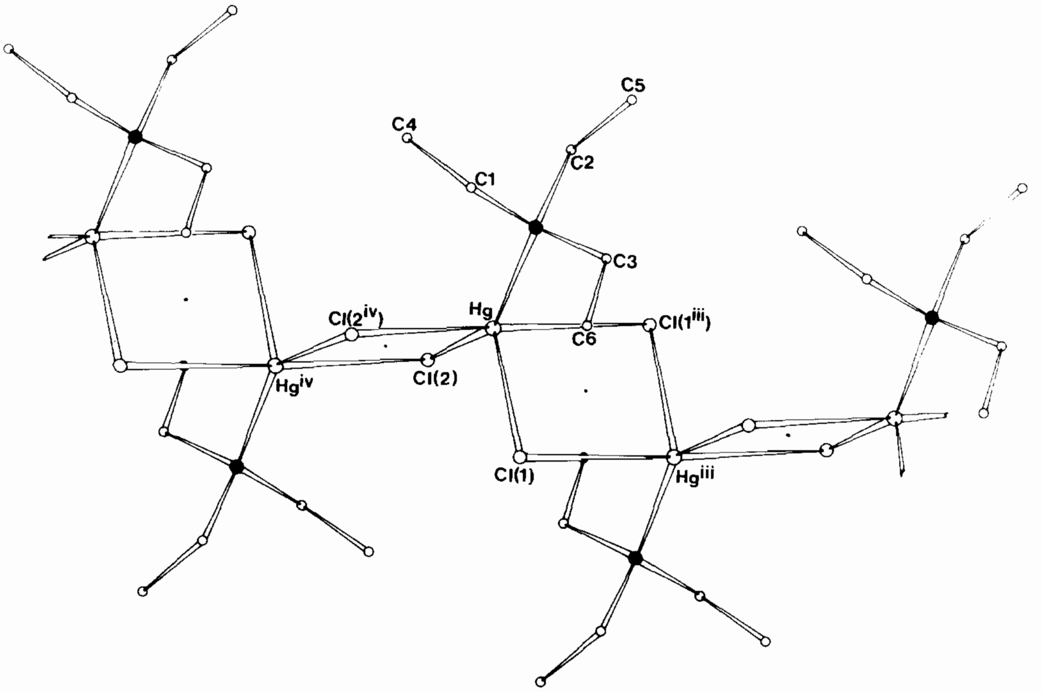

Fig. 1. $HgCl_2(PEt_3)$. Atom numbering and part of the chain running parallel to *a*.

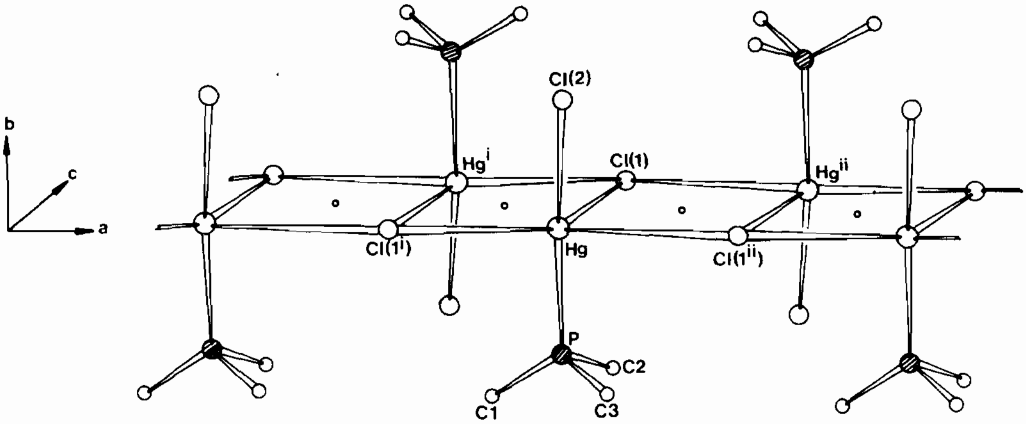

Fig. 2. The chain structure and atom numbering scheme of $HgCl_2(PMe_3)$.

to form a structure approaching an ionic formulation of type $[ClHgP]^+Cl^-$, is a consequence of enhanced σ-donor strength of the phosphine. In support of this correlation we cite the following:

(a) Enthalpies of formation of 1:1 adducts of $HgCl_2$ with selected phosphines in benzene solution at 30 °C have been determined [14]. Although not all the phosphines studied in the present work were included in the thermodynamic study, it was found that the weakest interaction takes place with PPh_3 and 1,2,5-triphenylphosphole, while PBu_3 interacts more strongly. Thus the solid state effects are compatible with the solution phase results.

(b) The enthalpy data referred to in (a), for the full range of phosphines studied, correlate remarkably with the sum of the Taft constants of the groups attached to the phosphorus atoms, thereby emphasising the dominance of electronic influences in these systems.

(c) There is a *general* tendency for the Hg–P distances to be shorter in the complexes of the stronger donor ligands (Table IV). This is compatible with the stronger donors tending towards the ionic $[ClHgP]^+Cl^-$ structure in which the Cl^- anions provide weak links in the structure.

TABLE IV. Selected Structural Parameters for 1:1 Complexes of HgCl$_2$ with Phosphine Type Donors.

	Solid State Structure	Coordination polyhedron about Hg	Hg–P/A	Hg–Cl$_t$/A[a]	Hg–Cl$_b$/A[a]	P–Hg–Cl$_t$	Reference
HgCl$_2$(TPP)[b]	centrosymmetric dimer	distorted tetrahedron	2.438(10)	2.404(11)	2.542(13), 2.747(14)	127.8(5)	[1]
HgCl$_2$(PPh$_3$)	centrosymmetric dimer	distorted tetrahedron	2.406(7)	2.370(10)	2.623(8), 2.658(8)	128.7(4)	[1]
β-HgCl$_2$(PBu$_3$)	centrosymmetric dimer	distorted tetrahedron	2.378(6)	2.348(7)	2.718(6), 2.737(6)	150.8(3)	[12]
α-HgCl$_2$(PBu$_3$)	tetramer	^{i}distorted tetrahedron	2.363(21)	2.289(21)	2.626(19), 2.709(20)	147.8(7)	[1]
		^{ii}distorted trigonal bipyramid	2.337(19)	2.304(21)	2.664(18), 2.895(21), 3.375(25)	150.6(7)	
HgCl$_2$(PEt$_3$)	polymer	distorted trigonal bipyramid	2.35(1)	2.42(1)	2.56(1), 3.04(1), 3.21(1)	145.4(3)	p.w.[c]
HgCl$_2$(PMe$_3$)	polymer	distorted square pyramid	2.365(3)	2.355(4)	2.782(4), 2.941(4), 3.489(4)	162.1(1)	p.w.[c]

[a] Cl$_t$ – chlorine atom closest to mercury; Cl$_b$ – further chlorine atoms within or close to the sum of the van der Waals' radii (3.45 Å). [b] TPP = 1,2,5-triphenylphosphole. [c] p.w. = present work.

(d) In complexes HgCl$_2$(PR$_3$)$_2$, large P–Hg–P angles and long Hg–Cl distances are associated with the observed trends shows quite conclusively that the the observed trends show quite conclusively that the structural variations, particularly the extent to which linear coordination around mercury is achieved, have their origin in electronic rather than steric 'bulkiness' effects.

It must, of course, be acknowledged that bulky substituent groups on the phosphorus atom will tend to increase the internal C–P–C angle and thereby influence the availability of the phosphorus lone pair. Indeed, Mason and Meek [16] consider the difference between steric and electronic effects involving tertiary phosphines to be 'semantic'. However, the present series of results does lend itself to an acceptable rationalisation in terms of the strength of electronic interactions between the mercury atoms and the phosphorus donors, and does not support the notion that the bulkiness of the phosphine (Brown's 'Face-strain' [17]) plays a major role.

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