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Mercury(II) Halide Complexes of Tertiary Phosphines.
Part XIV*. Structural Variations within the Series $Pr_3P \cdot HgX_2$ (X = Cl, Br, I)

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Abstract

Marked structural variations have been found along the series Pr_3PHgX_2 (X = Cl, Br or I). The chloride and bromide are halogen-bridged dimers with increasing asymmetry in the HgX_2Hg bridge and therefore weaker association from chloride to bromide. The β-form of the iodide complex consists of approximately trigonal planar $PHgI_2$ monomeric units in which coordination of mercury is increased to five by weak association via very long Hg...I interactions with two neighbouring molecules. This loosely associated chain arrangement results in approximately trigonal bipyramidal coordination around mercury, elongated in the axial directions. These variations may be rationalised in terms of the increased donor capacity of halide to mercury, from chloride to iodide, reducing the additional electron density required by the metal, thereby resulting in looser association. α-Pr_3PHgI_2 is unique among all the 1:1 tertiary phosphine–mercury(II) halide complexes in having a non-centrosymmetric dimeric structure in which one of the mercury atoms is coordinated to both phosphine groups analogous to that previously established for the mixed metal complex $(Pr_3P)_2Hg(\mu\text{-}I)_2CdI_2$.

Introduction

Structural and spectroscopic studies of a wide range of tertiary phosphine complexes of mercury(II) halides $(R_3P)_nHgX_2$ (n = 1 or 2; X = Cl, Br or I) have shown that the structures adopted and some of their molecular parameters are very dependent on the σ-donor ability of the phosphine. Additionally these are also affected by both the nature of the halogen and the tendency of mercury to acquire linear coordination [1–14]. The 2:1 complexes have an essentially monomeric pseudotetrahedral constitution in which the magnitude of the P–Hg–P angle and $^{199}Hg–^{31}P$ coupling constant are significantly influenced by the nature of the phosphine [1–6]. For example in the triethylphosphine (pK_a, 8.69) complex P–Hg–P is 158.5(5)° [2] whereas for the tris(2-thienyl)phosphine analogue this angle is much less, being only 128.6(1) [3]. Such features have been discussed in ref. 4.

The 1:1 complexes show a much greater variety of structural types varying from halogen-bridged dimers to five-coordinate polymers and all are based on the centrosymmetric dimeric arrangement, albeit in some cases associated to give a polymeric structure [5, 8–14]. Although we have shown from structural studies of an extensive range of 1:1 tertiary-phosphine–mercury(II) chloride complexes that the σ-donor ability of the phosphine plays a dominant role in the extent of association of such complexes, also resulting in short Hg–P bonds and large P–Hg–$Cl_{terminal}$ bond angles for strong σ-donors as compared to weak σ-donors [5, 8–11], we have not carried out an extensive study of the effect of the nature of the halogen. Within the series $(Ph_3PHgX_2)_2$ (X = Cl, Br or I) the halogen does not appear to have a major effect on the structure adopted and all are centrosymmetric halogen-bridged dimers [8, 14]. The smaller more strongly σ-donating trialkylphosphines such as Me_3P and Et_3P [9] in their complexes with mercury(II) chloride have monomeric structures which loosely associate to form chains and thus competition by more strongly donating bromide or iodide ligands may have a marked effect on structural parameters. In addition our earlier far infrared studies [13] have indicated that the α-form of Pr_3PHgI_2 has a structure uncharacterised by X-ray analysis and this has been confirmed in a preliminary report of its structure [7]. Thus we herein report detailed structural analyses of the series Pr_3PHgX_2 (X = Cl, Br or I).

Experimental

The complexes Pr_3PHgX_2 (X = Cl, Br or I) were prepared as described previously [13, 15] and gave

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TABLE 1. Crystal data and details of data collection

	Pr_3PHgCl_2 (I)	Pr_3PHgBr_2 (II)	α-Pr_3PHgI_2 (III)	β-Pr_3PHgI_2 (IV)
Crystal data				
M_r	3453.8	4165.0	4917.0	4917.0
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Crystal size (mm)	0.32 × 0.44 × 0.60	0.12 × 0.50 × 0.84	0.40 × 0.25 × 0.16	0.30 × 0.05 × 0.10
a (Å)	18.474(5)	11.777(5)	10.707(3)	8.670(8)
b (Å)	11.328(1)	8.758(5)	13.766(5)	13.174(9)
c (Å)	13.891(6)	16.761(1)	22.399(8)	14.893(8)
β (°)	101.17(5)	116.18(8)	96.5(1)	106.57(5)
U (Å^3)	2852.3	1551.5	3280.3	1630.7
D_m (g cm^{-3})	2.00	2.25	2.50	2.47
D_c (g cm^{-3})	2.02	2.23	2.49	2.50
Z	4	4	4	4
$F(000)$	1632	1920	2208	2208
μ(Mo Kα) (cm^{-1})	108.2	146.8	126.3	127.1
Space group	$B2_1/a$ [a]	$P2_1/c$	$P2_1/c$	$B2_1/a$ [a]
Collection of intensity data				
Axis mounted about	c	b	a	a
Reflections collected	1876	2285	2620	1022
No. observed reflections[b]	1446	1431	1638	582
$I/\sigma(I)$	3.0	2.0	3.0	2.0
Final R value	0.069	0.052	0.103	0.0924
Final R' value	0.070	0.039	0.103	0.0973
Weighting scheme[c] a	1.0000	1.0000	1.0000	2.6953
b	0.09116	0.000162	0.016547	0.002123

[a] Non-standard setting of $P2_1/c$. [b] Those reflections having $I/\sigma(I)$ greater than the indicated value were considered to be observed. [c] For the weighting scheme $w = a/(\sigma^2(F_o) + b(F_o)^2)$ values of a and b are as shown.

satisfactory elemental analyses. The iodide complex occurs in two forms (α,β) depending upon conditions of preparation and recrystallisation. Crystals of the complexes were mounted with one 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. Data were corrected for Lorentz and polarisation effects and although absorption corrections were also applied for α-Pr_3PHgI_2, this did not significantly improve the R value nor reduce the errors. Details of the crystal data and the X-ray data collection for the four complexes studied are listed in Table 1.

Structure Determination and Refinement

The mercury coordinates for all the complexes were determined from the three dimensional Patterson maps. The remaining atoms were located from successive difference Fourier maps and refined by full matrix least-squares techniques. Hydrogen atoms were included for the chloride and bromide in ideal positions (C–H, 1.08 Å) and were given a common isotropic temperature factor. All other atoms were assigned anisotropic thermal parameters. For the α- and β-forms of the iodide only Hg, I and P atoms were assigned anisotropic thermal parameters and in the former due to the presence of many heavy atoms it was impossible to include H atoms in the refinement. For the β-form interlayer scaling was applied and it was impossible to even assign positions for the carbon atoms due to the small number of reflections available and the presence of a number of heavy atoms.

Complex neutral atom scattering factors [16] were employed throughout the refinements and in the final cycles of refinement weighting schemes were adopted as detailed in Table 1. Final positional parameters are given in Tables 2–5, bond distances and angles in Tables 6–9. See also 'Supplementary Material'. All calculations were performed using an IBM 4341 computer using the SHELX computing package [17].

Results and Discussion

The complexes Pr_3PHgX_2 (X = Cl, Br or I) show very marked structural variations. Compounds **I** and **II** (X = Cl, Br respectively) are centrosymmetric halogen-bridged dimers (Figs. 1 and 2) whereas the structure of the α-form of Pr_3PHgI_2 (**III**) is an unsymmetrical halogen-bridged dimer (Fig. 3) in which

TABLE 2. Final fractional coordinates (Hg × 10^5, other atoms × 10^4) $[Pr_3PHgCl_2]_2$ with e.s.d.s in parentheses

	x	*y*	*z*
Hg	−7296(4)	37958(6)	−3011(5)
Cl1	−1593(3)	4242(5)	683(3)
Cl2	456(2)	4031(4)	1089(4)
P	−451(2)	2811(4)	−1680(3)
C11	508(8)	2987(16)	−1782(14)
C12	1055(10)	2399(22)	−1056(18)
C13	1810(10)	2499(31)	−1303(28)
C21	−992(9)	3408(17)	−2786(12)
C22	−1772(11)	3525(20)	−2786(17)
C23	−2223(20)	4065(27)	−3772(25)
C31	−642(13)	1228(14)	−1694(18)
C32	−1274(17)	882(22)	−1270(26)
C33	−1386(16)	−394(22)	−1209(23)

TABLE 3. Final fractional coordinates (Hg × 10^5; other atoms × 10^4) for $[Pr_3PHgBr_2]_2$ with e.s.d.s in parentheses

	x	*y*	*z*
Hg	−16426(6)	52282(6)	38966(4)
Br1	−3155(2)	3161(2)	3827(2)
Br2	443(2)	3661(2)	4180(1)
P	−1812(4)	7871(4)	3463(3)
C11	−2632(15)	8877(16)	3984(10)
C12	−3943(17)	8287(22)	3752(13)
C13	−4623(19)	9126(25)	4191(16)
C21	−290(13)	8774(15)	3802(9)
C22	462(15)	8110(19)	3349(10)
C23	1661(16)	9002(23)	3580(12)
C31	−2684(14)	8132(16)	2283(9)
C32	−2838(17)	9830(19)	1987(11)
C33	−3613(15)	9966(20)	985(11)

TABLE 4. Final fractional coordinates for α-Pr_3PHgI_2 (× 10^4) with e.s.d.s in parentheses

	x	*y*	*z*
Hg1	6109(2)	1511(2)	6051(1)
Hg2	2373(2)	2357(2)	5958(1)
I1	4608(4)	2804(3)	6798(2)
I2	3685(4)	946(3)	5281(2)
I3	764(4)	1423(3)	6601(2)
I4	1739(5)	3917(3)	5270(3)
P1	6478(15)	99(11)	6719(7)
P2	6946(15)	2768(11)	5454(7)
C11	7831(55)	−643(44)	6468(25)
C12	8187(76)	−1455(57)	6989(34)
C13	8949(108)	−2100(85)	6746(48)
C21	5102(50)	−709(37)	6617(23)
C22	4008(59)	−250(46)	6902(25)
C23	2949(75)	−1009(57)	6827(34)
C31	6630(56)	453(44)	7500(24)
C32	7979(49)	1024(39)	7633(24)
C33	8064(65)	1277(47)	8325(30)
C41	7320(77)	3895(62)	5881(35)
C42	8265(60)	3736(48)	6418(28)
C43	8680(111)	4712(92)	6665(47)
C51	8188(56)	2555(45)	5102(25)
C52	8327(53)	1539(41)	4958(25)
C53	9363(89)	1446(63)	4674(38)
C61	5464(83)	3108(72)	4799(39)
C62	5796(77)	3922(63)	4422(36)
C63	4677(85)	3885(65)	3853(40)

TABLE 5. Final fractional coordinates (Hg × 10^5, other atoms × 10^4) for β-Pr_3PHgI_2 with e.s.d.s in parentheses

	x	*y*	*z*
Hg	27729(40)	47693(23)	4650(17)
I1	4289(7)	6567(3)	392(3)
I2	573(6)	4308(4)	−1184(3)
P	3500(24)	3720(15)	1844(11)

both phosphine groups are coordinated to the same mercury atom. For **I** and **II** the distortion from a regular tetrahedral arrangement around the mercury atom is considerable, the angles ranging from 96.5(2) to 148.7(2)° and from 102.5(1) to 135.9(1)° respectively. In both cases however, there is only a slight degree of distortion from tetrahedral around the phosphorus atom (106.4(8) to 113.6(7)° and 107.3(7) to 112.8(4)° respectively). The former has a very symmetrical bridged HgX_2Hg arrangement ($Hg–Cl_{br}$, 2.638(4), 2.780(4) Å) whereas in the latter this bridge is extremely asymmetric with the bridging distances ($Hg–Br_{br}$, 2.667(2), 3.051(2) Å) differing markedly. The trend of increasing asymmetry in the HgX_2Hg bridges from X = Cl to X = I, earlier noted for $(Ph_3PHgX_2)_2$ (X = Cl, I) [8, 14] is even more marked within the series studied herein when β-Pr_3PHgI_2 (**IV**) is considered. ($Hg–I_{br}$, 2.715(5), 2.726(5), 3.579(5), 3.627(5) Å). The structure of **IV** at first sight appears to consist of a single $(HgI_2)_n$ polymeric chain with each mercury atom coordinated to four iodine and one phosphorus atoms (Fig. 4). The mercury atom lies at the centre of an extended distorted trigonal bipyramidal environment, analogous to that found for $(Et_3PHgCl_2)_n$ [9], with bond angles around mercury varying from 85.8(2) to 169.7(2)°. Close examination of bond distances and angles however around mercury indicates that the complex is best described as weakly linked, approximately trigonal planar Pr_3PHgI_2 monomeric units, having two Hg–I distances of 2.715(5) and 2.726(5) Å and an Hg–P bond length of 2.406(17) Å, with these three atoms surrounding mercury in an approximately planar arrangement (sum of angles around Hg = 359.7°). Five coordination is completed by interaction of the mercury atom with iodine atoms from two adjacent molecules, approximately

TABLE 6. Bond angles (°) and bond lengths (Å) of $[Pr_3PHgCl_2]_2$ with e.s.d.s in parentheses

Bond lengths (Å)			
Hg–Cl1	2.348(5)	C11–C12	1.45(3)
Hg–Cl2	2.638(4)	C12–C13	1.51(3)
Hg–P	2.358(4)	C21–C22	1.45(3)
Hg–Cl2′	2.780(4)	C22–C23	1.58(4)
P–C11	1.815(16)	C31–C32	1.46(3)
P–C21	1.795(17)	C32–C33	1.47(3)
P–C31	1.827(17)	Hg- - -Hg′	3.813
Bond angles (°)			
Cl2–Hg–Cl1	96.5(2)	C11–P–C21	106.4(8)
P–Hg–Cl1	148.7(2)	C11–P–C31	107.2(9)
P–Hg–Cl2	111.2(2)	C21–P–C31	106.6(10)
Cl1–Hg–Cl2′	103.6(2)	P–C11–C12	117.2(15)
Cl2–Hg–Cl2′	90.6(2)	P–C21–C22	115.1(14)
P–Hg–Cl2′	90.8(2)	P–C31–C32	115.3(16)
Hg–P–C11	112.4(6)	C11–C12–C13	111(2)
Hg–P–C21	110.1(6)	C21–C22–C23	113(2)
Hg–P–C31	113.6(7)	C31–C32–C33	115(2)
		Hg–Cl2–Hg′	89.4(1)

Primed atoms (′): $-x, 1-y, -z$.

TABLE 7. Bond angles (°) and bond lengths (Å) for $[Pr_3PHgBr_2]_2$ with e.s.d.s in parentheses

Bond lengths (Å)			
Hg–Br1	2.507(2)	C11–C12	1.507(18)
Hg–Br2	2.667(2)	C12–C13	1.499(20)
Hg–P	2.408(4)	C21–C22	1.514(17)
Hg–Br2′	3.051(2)	C22–C23	1.507(18)
P–C11	1.794(14)	C31–C32	1.553(17)
P–C21	1.806(14)	C32–C33	1.521(19)
P–C31	1.796(14)	Hg- - -Hg′	4.022
Bond angles (°)			
Br2–Hg–Br1	102.5(1)	Hg–P–C11	108.4(5)
P–Hg–Br1	135.9(1)	Hg–P–C21	112.8(4)
P–Hg–Br2	119.7(1)	Hg–P–C31	112.7(5)
Br1–Hg–Br2′	105.6(1)	P–C11–C12	114.6(11)
Br2′–Hg–Br2	90.9(1)	C11–C12–C13	114.4(15)
Br2′–Hg–P	87.2(1)	P–C21–C22	113.1(10)
C11–P–C21	107.7(7)	C21–C22–C23	111.2(13)
C11–P–C31	107.7(7)	P–C31–C32	113.8(11)
C21–P–C31	107.3(7)	C31–C32–C33	110.8(14)
		Hg–Br2–Hg′	89.1(1)

Primed atoms (′): $-x, 1-y, 1-z$.

perpendicular to the I_2HgP trigonal plane (I_2''–Hg–I′ = 169.7(2)°) but as these distances (3.579(5), 3.627(5) Å) are longer than the sum of the van der Waals' radii (3.45 Å) these interactions are considered to be very weak.

Complex **III**, the α-form of Pr_3PHgI_2 differs from **I** and **II** in that, although a dimer, both phosphine groups are coordinated to the same mercury atom.

TABLE 8. Bond lengths (Å) and bond angles (°) for [α-Pr_3PHgI_2] with e.s.d.s in parentheses

Bond distances (Å)			
Hg1–I1	3.027(4)	P2–C61	2.09(9)
Hg1–I2	3.050(5)	C11–C12	1.63(9)
Hg1–P1	2.457(14)	C12–C13	1.36(11)
Hg1–P2	2.421(15)	C21–C22	1.53(8)
Hg2–I1	2.937(5)	C22–C23	1.54(9)
Hg2–I2	2.921(4)	C31–C32	1.64(8)
Hg2–I3	2.694(4)	C32–C33	1.58(8)
Hg2–I4	2.685(5)	C41–C42	1.50(9)
P1–C11	1.91(6)	C42–C43	1.50(12)
P1–C21	1.84(5)	C51–C52	1.45(7)
P1–C31	1.81(6)	C52–C53	1.35(9)
P2–C41	1.84(9)	C61–C62	1.47(11)
P2–C51	1.65(6)	C62–C63	1.65(11)
Bond angles (°)			
I1–Hg1–I2	89.5(1)	C21–P1–C31	105(3)
I1–Hg1–P1	100.8(4)	Hg1–P2–C41	113(3)
I1–Hg1–P2	98.0(4)	Hg1–P2–C51	121(2)
I2–Hg1–P1	102.2(4)	Hg1–P2–C61	104(3)
I2–Hg1–P2	102.4(4)	C41–P2–C51	105(3)
P1–Hg1–P2	149.1(5)	C41–P2–C61	106(4)
I1–Hg2–I2	93.9(1)	C51–P2–C61	107(3)
I1–Hg2–I3	106.3(2)	P1–C11–C12	106(4)
I1–Hg2–I4	109.6(2)	C11–C12–C13	105(7)
I2–Hg2–I3	109.5(1)	P1–C21–C22	110(4)
I2–Hg2–I4	109.8(2)	C21–C22–C23	105(5)
I3–Hg2–I4	123.6(2)	P1–C31–C32	106(4)
Hg1–I1–Hg2	88.1(1)	C31–C32–C33	104(4)
Hg1–I2–Hg2	88.0(1)	P2–C41–C42	113(6)
Hg1–P1–C11	109(2)	C41–C42–C43	108(7)
Hg1–P1–C21	109(2)	P2–C51–C52	113(4)
Hg1–P1–C31	112(2)	C51–C52–C53	108(6)
C11–P1–C21	105(2)	P2–C61–C62	111(6)
C11–P1–C31	116(3)	C61–C62–C63	103(7)

TABLE 9. Bond angles (°) and bond lengths (Å) for [β-Pr_3PHgI_2] with e.s.d.s in parentheses

Bond lengths (Å)			
Hg–I1	2.726(5)	Hg- - -Hg′	4.501(4)
Hg–I1′	3.617(5)	Hg- - -Hg″	4.501(4)
Hg–I2	2.715(5)		
Hg–I2″	3.579(5)		
Hg–P	2.406(17)		
Bond angles (°)			
I2–Hg–I1	112.4(2)	I2″–Hg–I1′	169.7(2)
P–Hg–I2	126.1(5)	Hg–I1–Hg′	89.3(2)
P–Hg–I1	121.4(5)	Hg–I2–Hg″	94.2(2)
I1–Hg–I1′	90.7(2)	P–Hg–I1′	89.0(5)
I2″–Hg–I1	99.1(2)	P–Hg–I2″	88.7(5)
I2–Hg–I2″	85.8(2)		
I1′–Hg–I2	87.4(2)		

Symmetry code: ′: $1-x, 1-y, -z$; ″: $-x, 1-y, -z$.

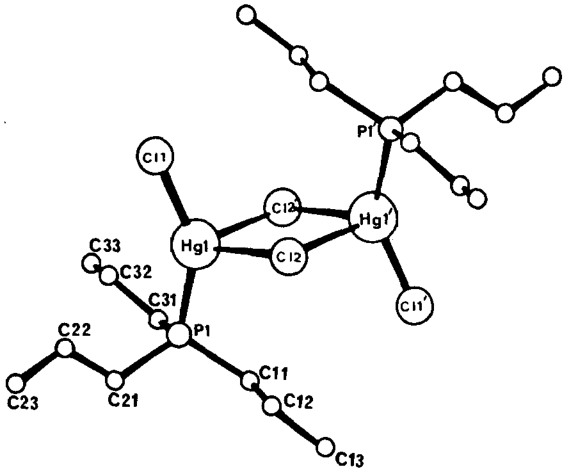

Fig. 1. Molecular structure of $(Pr_3PHgCl_2)_2$, hydrogen atoms omitted for clarity.

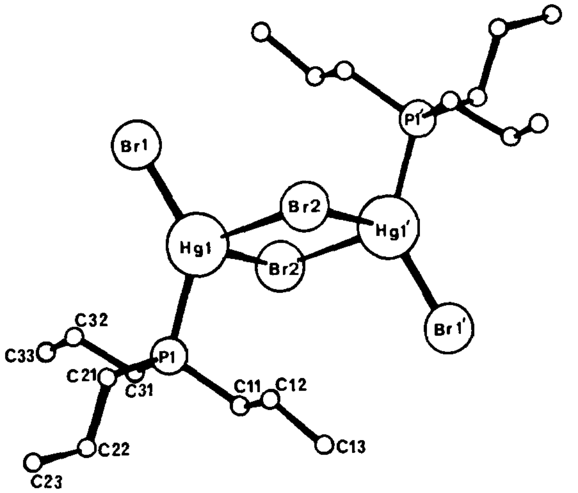

Fig. 2. Molecular structure of $(Pr_3PHgBr_2)_2$, hydrogen atoms omitted for clarity.

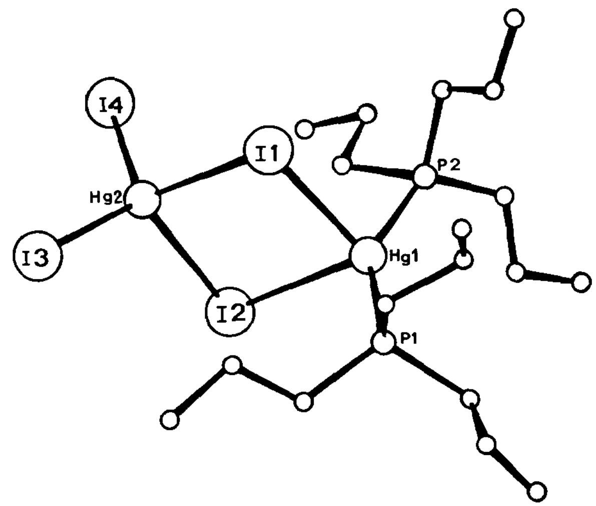

Fig. 3. Molecular structure of $(Pr_3P)_2Hg(\mu\text{-}I)_2HgI_2$ (α-Pr_3PHgI_2), hydrogen atom positions not determined.

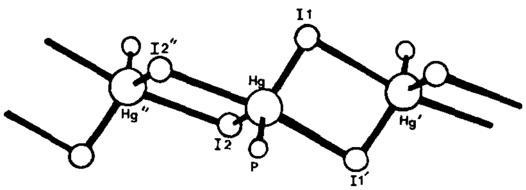

Fig. 4. $(PHgI_2)_n$ chain arrangement in β-Pr_3PHgI_2.

This complex is unique in being the only 1:1 mercury(II) halide complex of this type whose structure in the solid state has been substantiated by X-ray analysis, although ^{31}P NMR studies [18–20] have indicated the presence of such an unsymmetrical dimer as a minor component in solutions of Bu_3PHgX_2 (X = Br, I). The geometry about Hg(1) to which both phosphine groups are coordinated is highly distorted from tetrahedral with angles ranging from 89.5(1) to 149.1(5)° and there is significant tetrahedral distortion around phosphorus, angles varying from 104(3) to 121(2)°. The distortion about Hg(2) is much less, angles ranging from 93.9(1) to 123.6(2)°. The Hg–I_t distances (2.685(5), 2.694(4) Å) are markedly shorter than the bridging distances. Comparison of the structure of this complex with that of $(Pr_3P)_2Hg(\mu\text{-}I)_2CdI_2$ [21] shows remarkable similarity in both having a double iodine-bridged structure with two phosphine groups coordinated to the same mercury atom. The geometry about the cadmium atom and the mercury atom which is also linked to two terminal iodine atoms is only slightly distorted from tetrahedral while the geometry about the other mercury atoms are in each case highly distorted from tetrahedral (89.5(1)–149.1(5)° in **III** and 88.6(1)–152.8(1)° in the mixed metal analogue). The similarity in structure is perhaps not totally unexpected as α-Pr_3PHgI_2 may be prepared from $(Pr_3P)_2Hg(\mu\text{-}I)_2CdI_2$ by displacement of CdI_2 with excess HgI_2 [15]. Surprisingly the ^{31}P NMR data for **III** [13] shows little similarity to that of the mixed cadmium–mercury analogue [21] but is very similar to that for **IV** [13] indicating that in solution the centrosymmetric halogen-bridged dimer predominates under the conditions in which the NMR experiments were performed.

The geometry about Hg(1) may be compared with that found in the 2:1 complexes $(R_3P)_2HgX_2$ in which the short Hg–P distances (2.421(15), 2.457(14) Å) and large P–Hg–P angle (149.1(5)°) (cf. Hg–P, 2.557(3), 2.574(3) Å; P–Hg–P, 108.95(9)° in $(Ph_3P)_2HgI_2$ [6]) result from a strongly σ-donating R_3P ligand [4 and refs. therein].

For R_3PHgCl_2, small strong σ-donor tertiary phosphine ligands give rise to monomeric units which weakly link to form extended chain structures. For example Me_3P [9], Et_3P [9] and Bu_3P(α-form) [8] have weakly extended structures whereas a weak σ-donor such as Ph_3P results in a centrosymmetric dimeric arrangement [8]. Exceptionally Cy_3PHgCl_2 [11] and Pr_3PHgCl_2 described herein both have discrete halogen-bridged dimeric structures despite both ligands having high pK_a values (9.7 and 8.64 respectively [22]). Although the bulky nature of the cyclohexyl group could inhibit extension it is not clear why Pr_3PHgCl_2 is only dimeric. Additionally the P–Hg–Cl_t angle is an effective indicator of the σ-donor ability of the phosphine to mercury(II) halides and this is illustrated by the following data for R_3PHgCl_2 (R = Me, (pK_a, 8.65) 162.1(1)° [9], R = Et(pK_a, 8.69) 145.4(3)° [9], R = Pr(pK_a, 8.64) 148.7(2)°, cf. R = Ph (pK_a, 2.73) 128.7(4)° [8].

The structure of only one other bromide complex has been determined, $(NCC_2H_4)_3PHgBr_2$ but as it contains one molecule of acetone, weakly coordinated to mercury, comparison with the unsolvated propyl analogue described herein may not be meaningful.

Structure of three 1:1 mercury(II) iodide complexes with tertiary phosphines have been established, namely that for Ph_3P [14] and the α- and β-forms of Pr_3PHgI_2 described herein. Although these complexes have vastly different structures there is surprisingly little variation in bond lengths and angles, despite the differing pK_a values of the phosphines (2.73 and 8.64 respectively [22]). The average Hg–P bond lengths (2.472(8), 2.44(1), 2.41(2) Å respectively), Hg–I_t bond lengths (2.677(2), 2.690(5), 2.720(5) respectively) and P–Hg–I_t angles (127.5(2)° for $(Ph_3PHgI_2)_2$ and 123.8(5) for **IV**) are not markedly different despite the vastly different donor character of the phosphine ligands.

Our previous studies of 1:1 tertiary phosphine mercury(II) halide complexes have been dominated by the effect of the nature of the phosphine on the structure adopted while studies of the effect of varying the halogen have been limited and also rather *ad hoc*. However, the structures described herein together with our earlier work on Ph_3PHgX_2 (X = Cl, I) [8, 14] provides the opportunity for a rationalisation of the effect of varying the halogen on the geometry and extent of association in such complexes. In both series, the steric and electronic effects of the phosphine may be ignored. The relative donor strength of halides (Cl^-, Br^-, I^-) towards mercury(II) increases with decreasing electronegativity of the halogen, chloride being the weakest. This is indicated by comparison of the first stepwise formation constants ($\log K_1$) for HgX^+ [X = Cl, 6.74; X = Br, 9.05; X = I, 12.87 [23]) and also by X-ray and NMR techniques for the series $(Ph_3P)_2HgX_2$ (X = Cl, Br, I, CF_3, CN, SCN, NO_2) [2] in which the X–Hg–X grouping predominates over the P–Hg–P unit, tending towards linearity with longer Hg–P bonds and smaller ^{199}Hg–^{31}P coupling constants than for complexes involving weaker anions.

As for $(Ph_3PHgX_2)_2$ (X = Cl, I) [14] the larger Hg–X_t distance and X_{br}–Hg–X_{br} angles in **I**, **II** and **IV** may be readily attributed to the increasing size of halogen. The P–Hg–X_t angle however shows a decrease from X = Cl to X = I (148.7(2), 135.9(1), 123.7(6) av. respectively) and these variations are also accompanied by an increase in the Hg–P bond lengths (2.358(4) (**I**); 2.408(4) (**II**); 2.439(15) (**III**) av. Å). Both these trends were found for Ph_3PHgX_2 (X = Cl, I) [14] and result from the greater donor strength of iodide compared to chloride. The stronger donor ability of iodide in these complexes also manifests itself in the iodides having lower ^{199}Hg–^{31}P coupling constants than chlorides [13, 14] and also in the asymmetry of the HgX_2Hg bridges which in turn reflects the strength of association of monomeric R_3PHgX_2 units. Thus for both $(Ph_3PHgX_2)_2$ (X = Cl, I) [14] and for **I**, **II** and **IV**, it is clear that looser association takes place with increasing donor capacity of halide for both series of 1:1 complexes. Thus as the electron density donated by the halide to the metal is reduced (I → Cl) so the additional electron density required by the metal is obtained by having a more extended structure through a greater extent of halogen bridging.

Supplementary Material

Hydrogen positions (for **I** and **II**), thermal parameters and observed and calculated structure factors are available from the authors on request.

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