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Mercury(II) Halide Complexes of Tertiary Phosphines.
Part VIII. Structural Characterisation of the Mixed Cadmium–Mercury Complex $I_2Cd(\mu\text{-}I)_2Hg(PPr_3)_2$

NORMAN A. BELL, MICHAEL GOLDSTEIN, LORRAINE A. MARCH and IAN W. NOWELL*

Department of Chemistry, Sheffield City Polytechnic, Pond Street, Sheffield S1 1WB, U.K.

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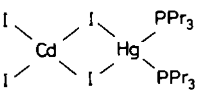
Reaction of equimolar amounts of $Cd_2I_4(PPr_3)_2$ *and* $Hg_2I_4(PPr_3)_2$ *leads to formation of the complex* $CdHgI_4(PPr_3)_2$*. Phosphorus-31 and mercury-199 nmr studies show both phosphines to be co-ordinated to mercury in solution, and a single crystal X-ray analysis confirms the unsymmetrical nature of the complex in the solid state also:* $I_2Cd(\mu\text{-}I)_2Hg(PPr_3)_2$*. The crystals of the complex are monoclinic, space group* $P2_1/c$*, with* $a = 10.694(6)$*,* $b = 13.794(7)$*,* $c = 22.415(9)$ *Å,* $\beta = 96.25(5)°$*. The structure was solved via the heavy-atom method and refined to an* R *value of 0.048 for 3053 observed diffractometer data. The* $[CdI_2Hg]$ *ring is almost planar and each metal atom is four co-ordinate. The coordination polyhedron about mercury is highly irregular and the large P–Hg–P angle of 152.8(1)° is attributed both to the presence of two strong σ-donor phoshines and to the bridging nature of the halogen atoms attached to mercury. The far-i.r. spectrum of the complex is discussed.*

Introduction

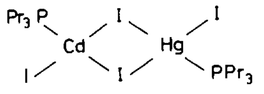
In our studies of tertiary phosphine complexes of mercury(II) and cadmium(II) we have shown [1–8] that the σ-donating ability of the phosphine ligand plays a significant role in determining the solid state structures of the complexes $MX_2(PR_3)_n$ (M = Cd or Hg; X = Cl, Br, or I; n = 1 or 2). In addition, phosphine nmr coordination shifts indicate that the mercury–phosphine bond is stronger than the cadmium–phosphine bond [9]. The relative affinities of mercury and cadmium towards phosphorus are readily seen by the structural characterisation of the mixed-metal complex $CdHgI_4(PPr_3)_2$ herein reported.

Results and Discussion

Reaction of either $CdI_2(PPr_3)_2$ with HgI_2 or $Cd_2I_4(PPr_3)_2$ with $Hg_2I_4(PPr_3)_2$ leads to formation of the mixed-metal complex $CdHgI_4(PPr_3)_2$ [10]. Phosphorus-31, and mercury-199 nmr data are similar to those reported [9] for $CdHgI_4(PBu_3)_2$ and are consistent with the formulation of the complex in solution as *1*. The 1:2:1 triplet nature of the ^{199}Hg nmr spectrum ($\delta = -621 \pm 2$ ppm) confirmed the bonding of two equivalent phosphine ligands to mercury with a coupling constant the same as that derived from the phosphorus spectrum, 4340 ± 2.5 Hz. The ^{31}P spectrum gave a single sharp resonance ($\delta = 17.5 \pm 0.1$ ppm) with ^{199}Hg satellites at ambient temperature, and although rapid exchange may occur at room temperature, no change in the spectrum was detected on cooling the solution to –90 °C. The ^{31}P chemical shift and J(Hg–P) values are markedly different from those found for the two forms of Pr_3PHgI_2 [11], providing further support that in solution more than one phosphine ligand is bonded to mercury. The nmr data thus strongly point to the unsymmetrical arrangement *1* rather than the symmetrical structure *2* originally proposed in the pioneering work of Mann and Purdie [10].



(*1*)



(*2*)

In order to determine whether this apparent discrepancy is real or whether it arises from a difference in phase, we have sought firstly to utilise far-i.r. spectroscopy, drawing upon our detailed studies

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*Author to whom correspondence should be addressed.

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TABLE I. Far-i.r. Data for Cadmium(II) and Mercury(II) Iodide Complexes of Tertiary Phosphines.

Complex type	Number of examples	$\nu(MI)_t$		$\nu(MI)_b$	
		No. bands	cm^{-1}	No. bands	cm^{-1}
$Cd_2I_4(PR_3)_2$	3 [12]	1	175–161	1–2	132–126
$Hg_2I_4(PR_3)_2$	6 [11]	1	165–151	1–2	112–90
$CdHgI_4(PPr_3)_2$	1	2	172, 147	2	118, 87

TABLE II. Selected Bond Lengths and Angles.

(a) *Bond lengths* (Å)			
Hg–I(1)	3.077(1)	Cd–I(4)	2.705(2)
Hg–I(2)	3.056(1)	P(1)–C(11)	1.829(16)
Hg–P(1)	2.424(4)	P(1)–C(21)	1.790(14)
Hg–P(2)	2.410(4)	P(1)–C(31)	1.850(17)
Cd–I(1)	2.866(1)	P(2)–C(41)	1.819(18)
Cd–I(2)	2.882(1)	P(2)–C(51)	1.805(20)
Cd–I(3)	2.705(2)	P(2)–C(61)	1.826(25)
(b) *Bond angles* (°)			
I(1)–Hg–I(2)	88.6(1)	Hg–I(2)–Cd	87.3(1)
I(1)–Hg–P(1)	100.6(1)	Hg–P(1)–C(11)	111.4(5)
I(1)–Hg–P(2)	101.4(1)	Hg–P(1)–C(21)	111.6(5)
I(2)–Hg–P(1)	99.9(1)	Hg–P(1)–C(31)	111.5(5)
I(2)–Hg–P(2)	96.4(1)	C(11)–P(1)–C(21)	107.6(7)
P(1)–Hg–P(2)	152.8(1)	C(11)–P(1)–C(31)	108.2(7)
I(1)–Cd–I(2)	96.3(1)	C(21)–P(1)–C(31)	106.3(7)
I(1)–Cd–I(3)	110.3(1)	Hg–P(2)–C(41)	113.2(6)
I(1)–Cd–I(4)	110.9(1)	Hg–P(2)–C(51)	113.6(7)
I(2)–Cd–I(3)	108.3(1)	Hg–P(2)–C(61)	108.3(8)
I(2)–Cd–I(4)	110.0(1)	C(41)–P(2)–C(51)	107.0(10)
I(3)–Cd–I(4)	118.6(1)	C(41)–P(2)–C(61)	107.8(12)
Hg–I(1)–Cd	87.2(1)	C(51)–P(2)–C(61)	106.6(12)

of the parent mercury(II) [6, 11] and cadmium(II) [8, 12] systems. Solution-phase far-i.r. studies in the significant region (50–200 cm^{-1}) were not practical, but for the solid complex a very clear pattern of four intense bands was observed: 87, 118, 147, and 172 cm^{-1}. There is little doubt that these are all metal–iodine modes. The observation of this number of bands gives little clue as to the geometrical arrangement of the complex, since for both *1* and *2* six i.r.-active metal–iodide bands are predicted (four due to in-plane deformations of the bridge, two arising from terminal stretching). However, intuitively one expects that the two bridging modes which are i.r.-inactive in a strictly centro-symmetric dimer $(L)IMI_2MI(L)$, would be significantly weaker in the i.r. spectrum of *2*. This tends to favour *2* as the structure. On the other hand, the pattern of the bands and their wavenumbers are comparable with either arrangement as shown in Table I.

Consequently we have undertaken a full X-ray analysis to elucidate the crystal and molecular structure. The results confirm that the unsymmetrical arrangement *1* is retained in the solid state (Fig. 1); selected bond lengths and bond angles are given in Table II.

The four-membered ring is approximately planar (maximum deviation from the best least-squares plane being 0.077 Å, Cd) and the angles within the ring range from 87.2(1) to 96.3(1)°. Each metal atom is four co-ordinate but while the extent of distortion from a regular tetrahedral arrangement is not large for cadmium, the co-ordination polyhedron of the mercury atom is highly irregular. In particular, the P–Hg–P angle is found to be 152.8(1)° and is comparable to the value of 158.5(5)° found in the monomeric complex $HgCl_2(PEt_3)_2$ [2]. The magnitude of the P–Hg–P angle in the latter complex may be attributed to the strong σ-donor properties of

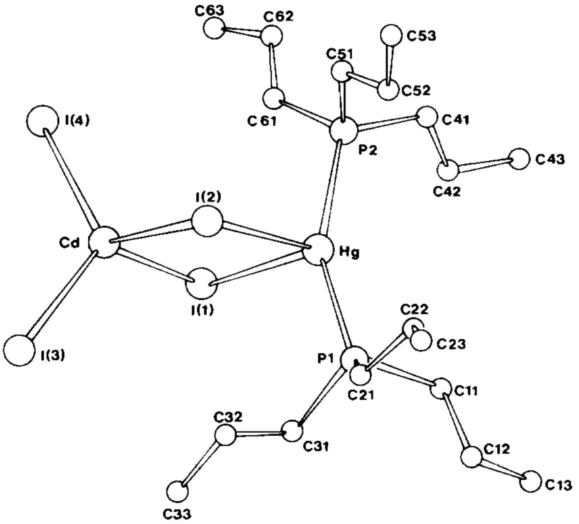

Fig. 1. Molecular structure of $I_2Cd(\mu\text{-}I)_2Hg(PPr_3)_2$.

triethylphosphine and also to the tendency of mercury(II) towards linear co-ordination. In contrast, there is far less angular distortion in $HgCl_2(PPh_3)_2$ (P–Hg–P, 134.1(1)°) [7], while an almost regular tetrahedral arrangement is found in $HgI_2(PPh_3)_2$ (P–Hg–P, 108.95(9)°) [13]. The more regular tetrahedral arrangements found in $HgX_2(PPh_3)_2$ (X = Cl, I) compared with $HgCl_2(PEt_3)_2$ [2] reflects the weaker σ-donor properties of (i) Ph_3P compared with Et_3P, and (ii) Cl^- compared with I^-. The far greater distortion about mercury in $CdHgI_4(PPr_3)_2$, compared with $HgI_2(PPh_3)_2$, can be interpreted in terms of the presence of more strongly σ-donating phosphine ligands and indeed the Hg–P distances in the present complex (2.410(4), 2.424(4) Å) are significantly shorter than those in $HgI_2(PPh_3)_2$ (2.557(3), 2.574(3) Å) [13]. However, a contributing factor to the magnitude of the P–Hg–P angle must also be the bridging nature of the iodine atoms attached to mercury, which will facilitate a stronger interaction between mercury and the phosphine ligands.

The $Cd\text{–}I_{bridging}$ distances of 2.866(1) and 2.882(1) Å lie close to the values found in the dimeric complex $Cd_2I_4(PEt_3)_2$ (2.862(1), 2.878(1) Å) [8] and the overall geometry about cadmium is strikingly similar to that reported for the iodine-bridged anion $[Cd_2I_6]^{2-}$ [14, 15].

The far-i.r. spectrum of the complex can thus be interpreted as in Table I, with $\nu(CdI)_t$ at 172 and 147 cm^{-1}, and $\nu(CdI_2Hg)_b$ modes at 118 and 87 cm^{-1}. The assignments are fully compatible with results on the parent $M_2I_4(PR_3)_2$ species [11, 12].

TABLE III. Final Fractional Co-ordinates (Hg, Cd, I × 10^5; other atoms × 10^4) with Estimated Standard Deviations in Parentheses.

Atom	*x*	*y*	*z*
Hg	38275(5)	15282(4)	89433(2)
Cd	75301(10)	23481(8)	90295(5)
I(1)	62807(9)	9624(7)	97105(4)
I(2)	53776(10)	28099(9)	81895(5)
I(3)	92599(11)	14569(9)	84250(5)
I(4)	82386(14)	39229(10)	97022(7)
P(1)	3529(4)	127(3)	8290(2)
P(2)	3068(4)	2818(3)	9533(2)
C(11)	2200(15)	–611(10)	8471(6)
C(12)	1882(19)	–1464(14)	8056(9)
C(13)	984(28)	–2118(19)	8222(11)
C(21)	3231(13)	474(11)	7518(6)
C(22)	2062(16)	1038(12)	7378(7)
C(23)	1756(19)	1291(14)	6693(8)
C(31)	4947(16)	–649(11)	8348(7)
C(32)	6017(15)	–271(12)	8069(7)
C(33)	7112(17)	–966(14)	8137(8)
C(41)	1672(15)	2490(14)	9884(8)
C(42)	1614(19)	1505(15)	10081(9)
C(43)	452(18)	1268(15)	10381(8)
C(51)	2699(24)	3916(14)	9113(9)
C(52)	1812(21)	3847(17)	8597(10)
C(53)	1408(26)	4787(18)	8272(11)
C(61)	4305(23)	3128(20)	10130(11)
C(62)	4196(29)	3820(23)	10513(14)
C(63)	5330(24)	3774(19)	11094(11)

Experimental

The compound was prepared as described previously [10] from equimolar amounts of $(Pr_3P)_2CdI_2$ and HgI_2 in hot ethanol and recrystallised from ethanol as colourless needles.

The nmr spectra were kindly recorded as solutions in dichloromethane by Dr. B. F. Taylor at the University of Sheffield. The ^{199}Hg spectrum was obtained at 71.67 MHz using a Bruker 400 MHz spectrometer and the ^{31}P nmr spectrum was recorded using a JEOL PFT-100 Fourier-transform nmr spectrometer at 40.48 MHz with proton noise decoupling. Chemical shifts are reported on a δ scale with respect to external 85% H_3PO_4 or neat $HgMe_2$, shifts to high field being negative in sign.

The far-i.r. spectrum was obtained using a Beckmann-RIIC FS-720 spectrometer with the sample as a Nujol mull cooled to approximately liquid nitrogen temperature.

Crystallographic Studies

A crystal of approximate dimensions 0.21 × 0.19 × 0.25 mm was mounted with its *a*-axis coincident with the ω-axis of a Stöe Stadi 2 two circle diffractometer. Data were collected using the background-ω scan-background technique and with graphite monochromated Mo-K_α radiation. 4157 unique reflections were measured of which 3053 had $I/\sigma(I) \geqslant 3.0$ and were used for subsequent analysis. Data were corrected for Lorentz, polarisation and absorption effects.

Crystal data

$C_{18}H_{42}CdHgI_4P_2$, M = 1141.1, Monoclinic, a = 10.694(6), b = 13.794(7), c = 22.415(9) Å, β = 96.25(5)°, U = 3286.7 Å^3, $F(000)$ = 2080, space group $P2_1/c$, Z = 4, D_m (by flotation) = 2.29, D_c = 2.31 g cm^{-3}, Mo-K_α radiation, λ = 0.71069 Å, μ(Mo-K_α) = 86.2 cm^{-1}.

The structure was solved *via* the heavy-atom method and refined by full-matrix least squares. Hydrogen atoms were included in ideal positions (C–H, 1.08 Å) and given common isotropic temperature factors; all other atoms were assigned anisotropic thermal parameters. Complex neutral-atom scattering factors [16] were employed throughout the refinement and in the final cycles of refinement the weighting scheme $w = 1.7507/[\sigma^2(F_o) + 0.0009(F_o)^2]$ was adopted. The converged residuals were R = 0.048 and R' = 0.052. Table III lists the final atomic parameters while hydrogen positions, thermal parameters, observed and calculated structure factors have been deposited and are available from the Editor.

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References

1 N. A. Bell, M. Goldstein, T. Jones and I. W. Nowell, *J. Chem. Soc., Chem. Commun.*, 1039 (1976); *Inorg. Chim. Acta, 43,* 87 (1980).

2 N. A. Bell, T. D. Dee, P. L. Goggin, M. Goldstein, R. J. Goodfellow, T. Jones, K. Kessler, D. M. McEwan and I. W. Nowell, *J. Chem. Res., (S)*, 2; *(M)*, 201 (1981).

3 N. A. Bell, M. Goldstein, T. Jones and I. W. Nowell, *Inorg. Chim. Acta, 48,* 185 (1981).

4 N. A. Bell, T. D. Dee, M. Goldstein and I. W. Nowell, *Inorg. Chim. Acta, 38,* 191 (1980); *70,* 215 (1983).

5 N. A. Bell, M. Goldstein, T. Jones, L. A. March and I. W. Nowell, *Inorg. Chim. Acta, 61,* 83 (1982).

6 N. A. Bell, M. Goldstein, T. Jones and I. W. Nowell, *Inorg. Chim. Acta, 69,* 155 (1983).

7 N. A. Bell, T. D. Dee, M. Goldstein, P. J. McKenna and I. W. Nowell, *Inorg. Chim. Acta, 71,* 135 (1983).

8 N. A. Bell, T. D. Dee, M. Goldstein and I. W. Nowell, *Inorg. Chim. Acta, 65,* L87 (1982).

9 R. Colton and D. Dakternicks, *Aust. J. Chem., 33,* 1677 (1980).

10 F. G. Mann and D. Purdie, *J. Chem. Soc.*, 1230 (1940).

11 N. A. Bell, M. Goldstein, T. Jones and I. W. Nowell, *Inorg. Chim. Acta, 75,* 21 (1983).

12 N. A. Bell, T. D. Dee, M. Goldstein and I. W. Nowell, to be published.

13 L. Fälth, *Chem. Scripta, 9,* 71 (1976).

14 P. L. Orioli and M. Ciampolini, *J. Chem. Soc., Chem. Commun.*, 1280 (1972).

15 P. J. H. A. M. Van der Leemput, J. A. Cras and J. Willemse, *Rec. Trav. Chim., 96,* 288 (1977).

16 'International Tables for X-ray Crystallography', Kynoch Press, Birmingham, 1974, vol. 4.