Phosphite and Phosphonate Complexes. Part IV.[1] *trans*-Influence in Mercury(II) Complexes. *X*-Ray Crystal Structure Analysis of Bis(dimethyl phosphonato)Mercury(II)

By **G. G. Mather** and **A. Pidcock**,* School of Molecular Sciences, University of Sussex, Brighton BN1 9QJ

Crystals of the title compound are monoclinic, space group $I2/c$, with $Z = 4$ in a cell of dimensions: $a = 8{\cdot}869(13)$, $b = 6{\cdot}930(9)$, $c = 17{\cdot}797(27)$ Å, $\alpha = \gamma = 90°$, $\beta = 91° 16'(20')$. The structure was determined from photographic *X*-ray data by Patterson and Fourier methods and refined by full-matrix least-squares techniques to R 0·116 for 804 observed reflections. The mercury atom forms strong bonds with only two phosphorus atoms, the angle P–Hg–P being 165·9°, and molecules of $[Hg\{(MeO)_2PO\}_2]$ are clearly distinguishable. Two phosphoryl oxygen atoms from neighbouring molecules interact weakly with mercury (Hg · · · O *ca.* 2·54 Å) forming with the two phosphorus atoms a very distorted tetrahedral arrangement about mercury. The molecular association results in the formation of chains parallel to the *a* axis. Hg–P distance (2·41 Å) is significantly longer than in $[HgCl\{(EtO)_2PO\}]$, which confirms that the *trans*-influence formalism is useful in digonal mercury(II) complexes and that effects through the metal σ electrons are dominant.

THE tendency of phosphorus ligands to weaken bonds in *trans*-relationship in square-planar and octahedral complexes of transition metals has been established in a wide range of situations by a variety of physical techniques.[2] It was shown that the Hg–Cl bond in the approximately digonal complex of the phosphorus donor, diethyl phosphonate, was longer than the average value in octahedral complexes of $HgCl_2$ with oxygen donors. The high *trans*-influence of the phosphonato-ligand in mercury(II) complexes was also inferred from the much smaller n.m.r. coupling constant ^1J(Hg–P) for $[Hg\{(EtO)_2PO\}_2]$ (7·50 kHz) than for $[HgCl\{(EtO)_2PO\}]$ (12·67 kHz), but since this inference involved the assumption of similar valence angles about mercury in the two complexes, we have undertaken an *X*-ray structure analysis of a bis(phosphonato)-complex to compare the angles and the Hg–P distances with those found for the chloro-complex. Crystals of bis(dimethyl phosphonato)mercury(II) were selected as they were much more readily obtained than those of the analogous ethyl compound, and measurements of ^1J(Hg–P) in the methyl complexes [7·51 kHz for the bis(phosphonato)-complex and 12·90 kHz for chloro-complex] gave values expectedly similar to those of the ethyl compounds.

EXPERIMENTAL

Complex.—The complex was prepared by the method of ref. 3 and recrystallised from methanol–ether, m.p. 120—122 °C (lit.,[3] 121·6—123 °C) (Found: C, 11·3; H, 2·75. Calc. for $C_4H_{12}HgO_6P_2$: C, 11·45; H, 2·85%). The ^{31}P n.m.r. spectrum of a solution in dichloromethane was recorded as previously described.[1] The central resonance was 2·5 p.p.m. to high field of external P_4O_6 and $^1J(^{199}Hg–^{31}P)$ was 7·51 kHz, which confirms the value 7·50 kHz given earlier[1] for an impure sample of the bis(diethyl phosphonato)-complex.

Crystal Data.—$C_4H_{12}HgO_6P_2$, $M = 418{\cdot}6$, Monoclinic, $a = 8{\cdot}689(13)$, $b = 6{\cdot}930(9)$, $c = 17{\cdot}797(27)$ Å, $\alpha = \gamma = 90°$, $\beta = 91° 16'(20')$, $U = 1071{\cdot}4$ Å^3, $Z = 4$, $D_c = 2{\cdot}595$, $F(000) = 776$. Space group $I2/c$ from systematic absences: hkl, $h + k + l = 2n + 1$; $h0l$, $l = 2n + 1$. Cu-K_α radiation, $\lambda = 1{\cdot}542$ Å; μ(Cu-K_α) = 311·3 cm^{-1}.

Crystallographic Measurements.—Cell dimensions were obtained from precession photographs taken with Mo-K_α radiation ($\lambda = 0{\cdot}7107$ Å). Three dimensional *X*-ray intensity data were collected from equi-inclination Weissenberg photographs of the levels 0—$7kl$ taken with Cu-K_α radiation. The crystals were unstable to *X*-irradiation and decomposed after a few days exposure. Fresh crystals of cross-section of *ca.* 0·5 × 0·25 mm were used for the recording of each level over 24 h; no significant fall-off in intensity was obtained during this period. Intensities were estimated by use of a Joyce–Loebl flying spot integrating densitometer. Data were corrected for Lorentz polarisation effects, but not for absorption, since a fresh crystal had to be used for each layer. A total of 814 independent reflections were obtained. Initially the various layers were assumed to be on the same scale; individual layer scale-factors were obtained later by correlation of the observed with the calculated structure amplitudes.

Structure Analysis.—All calculations were carried out on the ATLAS computer of the S.R.C. Chilton Laboratory,

---

[1] Part III, J. Bennett, A. Pidcock, C. R. Waterhouse, P. Coggon, and A. T. McPhail, *J. Chem. Soc.* (*A*), 1970, 2094.

[2] A. Pidcock, ' Heavy Group VB Donors,' Macmillan, London, ch. 1, in the press.

[3] R. B. Fox and D. L. Venezky, *J. Amer. Chem. Soc.*, 1956, **78**, 1664.

using the ' X-Ray '63 ' set of programmes.[4] Interpretation of the three-dimensional Patterson synthesis gave the co-ordinates of the mercury atom. The fractional co-ordinates $x/a = 0{\cdot}0$ and $z/c = 0{\cdot}25$ were held constant throughout the course of the analysis.

A three-dimensional Fourier synthesis phased by the mercury atom (R 26·8%) gave approximate co-ordinates for the two phosphorus atoms. A Fourier synthesis based on all three (R 26%) gave approximate co-ordinates for two of the oxygen atoms, and a difference-Fourier synthesis (R 24%) then revealed the third oxygen atom position. Three cycles of full-matrix least-squares adjustment of the co-ordinates and isotropic thermal parameters reduced R to 15%. Anisotropic thermal parameters were then assigned to mercury, and improved positions and thermal parameters were obtained from several cycles of Fourier and least-squares refinement. At the end of each cycle, bond lengths and valency angles were examined, and atoms giving unreasonable bond lengths or angles were omitted and relocated in more likely positions. The approximate positions of all the atoms were thus located and R was reduced to 13·7%. A further three cycles of least-squares refinement gave R 12%. At this stage a weighting scheme was introduced of the form: $\sqrt{w} = 1$ for $|F_o| < 150{\cdot}0$ and $\sqrt{w} = 150{\cdot}0/F_o$ for $|F_o| > 150{\cdot}0$.

Full-matrix least-squares refinement was carried out until parameter shifts were $<0{\cdot}4\sigma$. The final R over 804 reflections was 0·116. The scattering factors used for neutral mercury, phosphorus, oxygen, carbon, and hydrogen were taken from ref. 5.

RESULTS AND DISCUSSION

Final atomic co-ordinates and temperature-factor parameters together with their standard deviations are given in Table 1. Observed and calculated structure factors are listed in Supplementary Publication No. SUP 20588 (2 pp., 1 microfiche).* Table 2 lists interatomic distances and valence angles, and Table 3 contact distances. Figure 1 shows the mercury atom with the two strongly bound phosphonato-ligands and the arrangement of molecules in the unit cell is shown in Figures 2 and 3.

TABLE 1

Fractional atomic co-ordinates and thermal parameters with standard deviations in parentheses

Atom	x/a	y/b	z/c	$B/\text{Å}^2$
Hg	1·000(0)	0·1047(3)	0·250(0)	†
P	0·795(1)	0·062(1)	0·1580(5)	1·76(0·2)
O(1)	0·734(5)	−0·168(5)	0·163(2)	5·6(0·8)
O(2)	0·843(6)	0·057(7)	0·078(3)	7·3(1·0)
O(3)	0·646(5)	0·150(6)	0·172(2)	6·3(0·9)
O(1)	0·841(6)	−0·319(7)	0·151(3)	4·1(0·9)
C(2)	0·907(6)	0·231(7)	0·036(3)	4·2(1·0)

† For the mercury atom, an anisotropic temperature factor of the form $\exp[-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl)]$ was employed, with parameters ($\times 10^4$):

b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
35(17)	156(4)	10(1)	0	−(9)1	0

Molecules of $[\text{Hg}\{(\text{MeO})_2\text{PO}\}_2]$ are clearly distinguishable in the solid state. The P–Hg–P angle (165·9°) is significantly different from 180°. The co-ordination sphere of mercury is completed by two weakly bound phosphoryl oxygen atoms at 2·54 Å giving a very distorted tetrahedral environment around mercury with O–Hg–O *ca.* 96° and P–Hg–O *ca.* 95°. The co-ordination number of mercury is lower than in $[\text{HgCl}\{(\text{EtO})_2\text{PO}\}]$,

TABLE 2

Interatomic distances (Å) and valency angles (°)

(*a*) Bond lengths

Hg–P	2·411(9)	P–O(3)	1·46(4)
P–O(1)	1·68(4)	O(1)–C(1)	1·42(6)
P–O(2)	1·50(5)	O(2)–C(2)	1·53(7)

(*b*) Valency angles

P–Hg–P	165·9(0·3)	O(1)–P–O(3)	96·2(2·2)
Hg–P–O(1)	108·1(1·4)	O(2)–P–O(3)	116·5(2·5)
Hg–P–O(2)	115·6(1·9)	P–O(1)–C(1)	119·4(3·3)
Hg–P–O(3)	118·4(1·7)	P–O(2)–C(2)	123·7(3·6)
O(1)–P–O(2)	96·7(2·3)		

TABLE 3

Contact distances (Å)

(*a*) Intramolecular contact <3·7 Å

Hg · · · O(1)	3·34(4)	P · · · C(2)	2·66(5)
Hg · · · O(2)	3·34(5)	O(2) · · · O(3)	2·52(6)
Hg · · · O(3)	3·36(4)	O(2) · · · C(1)	2·92(7)
Hg · · · C(1)	3·68(5)	O(3) · · · C(1)	3·69(7)
P · · · C(1)	2·68(5)	O(3) · · · C(2)	3·40(7)

(*b*) Intermolecular contacts <4·0 Å

Hg · · · P^{II}	3 842(9)	O(3) · · · $\text{O}(3^{\text{II}})$	3·55(6)
Hg · · · $\text{O}(1^{\text{III}})$	3·99(4)	C(1) · · · $\text{O}(1^{\text{V}})$	3·42(6)
Hg · · · $\text{O}(3^{\text{II}})$	2·54(4)	O(2) · · · $\text{O}(1^{\text{VII}})$	3·79(6)
Hg · · · $\text{C}(1^{\text{III}})$	4·00(5)	C(2) · · · $\text{O}(2^{\text{VII}})$	3·71(7)
P · · · $\text{O}(3^{\text{II}})$	3·64(4)	C(2) · · · $\text{C}(1^{\text{I}})$	3·78(7)
P · · · $\text{C}(1^{\text{III}})$	3·99(5)	C(2) · · · $\text{O}(1^{\text{VII}})$	3·95(7)
O(1) · · · $\text{O}(1^{\text{III}})$	3·32(6)	C(2) · · · $\text{O}(3^{\text{IV}})$	3·26(7)
O(1) · · · $\text{C}(1^{\text{III}})$	3·40(6)	C(2) · · · $\text{O}(2^{\text{VIII}})$	3·61(7)
O(2) · · · $\text{O}(3^{\text{IV}})$	3·70(6)	C(2) · · · $\text{C}(2^{\text{VIII}})$	3·82(7)
O(3) · · · $\text{O}(1^{\text{III}})$	3·89(6)	C(1) · · · $\text{O}(3^{\text{V}})$	3·52(7)
O(3) · · · $\text{O}(3^{\text{VI}})$	3·79(6)		

Roman numerals as superscripts refer to the following co-ordinate transformations:

I	$x, 1 + y, z$	V	$\frac{1}{2} + x, -\frac{1}{2} - y, z$
II	$\frac{1}{2} - x, \frac{1}{2} - y, \frac{1}{2} - z$	VI	$1 - x, y, \frac{1}{2} - z$
III	$\frac{1}{2} - x + 1, -\frac{1}{2} - y, \frac{1}{2} - z$	VII	$\frac{1}{2} - x + 1, \frac{1}{2} + y, -z$
IV	$\frac{1}{2} + x, \frac{1}{2} - y, z$	VIII	$2 - x, -y, -z$

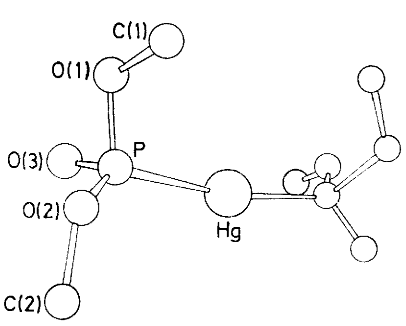

FIGURE 1 A view of the molecule

---

* For details see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No.20 (items less than 10 pp. are sent as full size copies).

[4] ' X-Ray '63,' system of programmes (amended 1969), J. M. Stewart, University of Maryland Technical Report TR 64.6.

[5] ' International Tables for X-Ray Crystallography,' Kynoch Press, Birmingham, 1962, vol. III.

probably owing to the presence of two bulky phosphonato-ligands. The effect of the molecular association is to form chains parallel to the *a* axis. The chains are separated by >4 Å, so the interaction between them must be weak, which accounts for the crystals being easily cleaved parallel to the *a* axis.

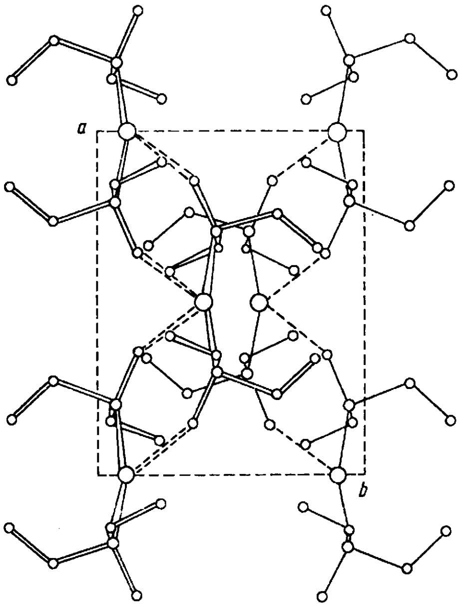

FIGURE 2 Packing diagram in the *ab* plane; dotted lines show close Hg · · · O contact

The neglect of absorption in the presence of atoms such as mercury introduces rather large errors, especially in the oxygen and carbon atomic positions. The P–O and O–C lengths and related angles have therefore been obtained with only low precision. The P=O length (1·46 Å) and the mean of the P–O(C) lengths (1·59 Å) are in good agreement with those found in [HgCl{(EtO)$_2$PO}] [1·44 (P=O) and 1·59 Å (P–OC)],[1] and the mean C–O distance (1·47 Å) compares with that (1·44 Å) in the chloro-complex. These distances are in good agreement with other literature values.[1]

The association of molecules in the crystals of the bis(phosphonato)- and chloro-complexes causes similar and fairly small deviations from digonal stereochemistry for the strongly bound ligands. In solution, both complexes are probably dimeric [1] and on the basis of the solid-state structures it is likely that the association causes similar small deviations from a 180° bond-angle in the two complexes. There is therefore no reason to suppose that the *s* characters of the Hg–P bonds in the two complexes differ significantly by virtue of different mercury valence angles, so the solid-state structures support the suggestion that the Hg–P coupling constants are strongly affected by electronic factors akin to the *trans*-influence in transition-metal square-planar and octahedral complexes.[1] Further support for the interpretation of the coupling constants is obtained from examination of the Hg–P lengths. The Hg–P length is 2·41(1) Å in [Hg{(MeO)$_2$PO}$_2$] and the mean of the four independent values in [HgCl{(EtO)$_2$PO}] is 2·36(1).[1] The mercury–phosphorus bond is therefore significantly longer [6] when *trans* to the phosphonate than *trans* to chloride and this correlates with the smaller Hg–P coupling constant in the bis(phosphonato)-complex.

Thus the measurements of Hg–Cl and Hg–P lengths and of Hg–P coupling constants imply that the mutual interaction of ligands in approximately digonal mercury complexes has the same characteristics as between *trans*-ligands in platinum(II) complexes.[7] Mercury–ligand vibration frequencies and indirect n.m.r. coupling constants involving ^{199}Hg in digonal complexes lead to the same conclusion for other ligands.[8] The similarity of results for mercury and other transition metals in positive oxidation states is strong evidence that the *trans*-influence of ligands is dominated by electrons in the metal–ligand σ orbitals, and it further suggests that metal d_σ orbitals, which are probably little involved in bonding in mercury(II), are not essential for the existence of a strong *trans*-influence.

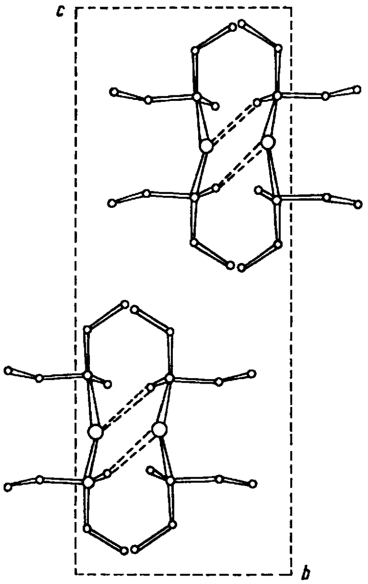

FIGURE 3 Packing diagram in the *bc* plane

We thank the S.R.C. for a research studentship (to G. G. M.), and G. M. McLaughlin for assistance.

[2/1984 *Received*, 21*st August*, 1972]

---

[6] D. L. Weaver, *Inorg. Chem.*, 1970, **9**, 2250.

[7] F. H. Allen, A. Pidcock, and C. R. Waterhouse, *J. Chem. Soc.* (*A*), 1970, 2087.

[8] P. L. Goggin, R. J. Goodfellow, S. R. Haddock, and J. G. Early, *J.C.S. Dalton*, 1972, 647.