160. ^{31}P-NMR and X-Ray Studies of the Complexes [HgX$_2$(*1*)]. (*1* = 2,11-Bis(diphenylphosphinomethyl)benzo[*c*]phenanthrene, X = Cl, I)

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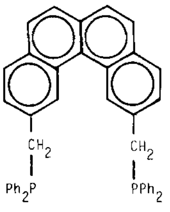
Summary

The $^{31}P\{^1H\}$-NMR characteristics of the complexes [HgX$_2$(**1**)] and [HgX$_2$(PPh$_2$Bz)$_2$] (X = NO$_3$, Cl, Br, I, SCN, CN) and the solid state structures of the complexes [HgCl$_2$(**1**)] and [HgI$_2$(**1**)] (**1** = 2,11-bis(diphenylphosphinomethyl)benzo[*c*]phenanthrene) have been determined.

The $^1J(^{199}Hg, ^{31}P)$ values increase in the order CN < I < SCN < Br < Cl < NO$_3$. The two molecular structures show a distorted tetrahedral geometry about mercury. Pertinent bond lengths and bond angles from the X-ray analysis are as follows: Hg-P = 2.485(7) Å and 2.509(8) Å, Hg-Cl = 2.525(8) Å and 2.505(10) Å, P-Hg-P = 125.6(3)°, Cl-Hg-Cl = 97.0(3)° for [HgCl$_2$(**1**)] and Hg-P = 2.491(10) Å and 2.500(11) Å, Hg-I = 2.858(5) Å and 2.832(3) Å, P-Hg-P = 146.0(4)°, I-Hg-I = 116.9(1)° for [HgI$_2$(**1**)]. The equation, derived previously, relating $^1J(^{199}Hg, ^{31}P)$ and the angles P-Hg-P and X-Hg-X is shown to be valid for **1**.

1. Introduction. – There are a number of reports concerned with the ^{31}P-NMR characteristics of trigonal and tetrahedral phosphine complexes of Hg(II) [1–9]. We have recently reported ^{31}P-NMR and X-ray structural data for complexes of the type [HgX$_2$(PPh$_3$)$_2$] [10] and find that the values $^1J(^{199}Hg, ^{31}P)$ and the molecular structures for these species are markedly dependent on the anion X. An increase in the value $^1J(^{199}Hg, ^{31}P)$ is associated with an increase in the P-Hg-P bond angle and Hg-X bond length and/or a decrease in the Hg-P bond length and X-Hg-X angle. The molecular geometry approaches a tetrahedron when the anion X is a strong donor, such as I$^-$ or CN$^-$, and distorts significantly when the anion is weakly coordinated, *e.g.* the P-Hg-P angle for [Hg(NO$_3$)$_2$(PPh$_3$)$_2$] is 132°, the O-Hg-O angle is 70°. We have utilized the structural data as a basis for extended *Hückel* calculations [10] and found that the one-bond Hg, P-coupling is more sensitive to the P-Hg-P angle than the Hg-P distance. Given this observation we



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have attempted to restrict this angle *via* the use of bidentate ligands containing organic skeletons in which the P-Hg-P angle should be relatively inflexible. The first of these ligands was *cis*-bis(diphenylphosphino)ethylene which restricts the angle P-Hg-P to about 80°. In the complexes $[HgX_2(Ph_2PCH=CHPPh_2)]$, $^1J(^{199}Hg, ^{31}P)$ decreases by > 1,000 Hz relative to the values for the PPh_3-complexes, thereby supporting the predictions stemming from the *Hückel* calculations [11]. A second attempt, with the intention of opening the P-Hg-P angle, concerns the ligand 2,11-bis(diphenylphosphinomethyl)benzo[*c*]phenanthrene, which we abbreviate as **1**. This diphosphine has been shown to be capable of spanning *trans*-positions in square planar d^8-complexes [12], although, for complexes of group Ib, significant deviations from P-M-P angles of 180° have been found [13]. We report here ^{31}P-NMR results from solution studies and X-ray solid state studies on Hg-complexes of **1**. For comparison, we also consider the ^{31}P-NMR properties of the molecules $[HgX_2(PBzPh_2)_2]$ $(Bz=CH_2Ph)$.

2. Experimental. - The complexes $[HgX_2(\mathbf{1})]$ and $[HgX_2(PPh_2Bz)_2]$ were prepared by literature methods [4] [14] starting from HgX_2 and either two equivalents of PPh_2Bz or one equivalent of **1**. All the complexes afforded satisfactory microanalyses (see *Table 1*).

$^{31}P\{^1H\}$-NMR spectra were measured on a *Bruker HX-90* in 10-mm sample tubes. The chemical shifts (relative to external H_3PO_4) and coupling constants are estimated to be correct to ±0.1 ppm and 3 Hz, respectively. The $^1J(^{199}Hg, ^{31}P)$ value for $[HgI_2(\mathbf{1})]$ was measured using a *Varian XL-200*.

Table 1. *Analytical Results for the Complexes*

Complex $[HgX_2(\mathbf{1})]$	% C Found (Calc.)	% H Found (Calc.)	% P Found (Calc.)
X			
NO_3	55.97 (55.67)	3.91 (3.61)	6.35 (6.53)
Cl	58.16 (58.97)	3.86 (3.82)	6.16 (6.91)
Br	49.05 (48.97)	3.97 (3.48)	5.41 (6.29)
I	49.05 (48.97)	3.30 (3.18)	5.60 (5.74)
SCN	59.83 (58.68)	3.91 (3.65)	5.90 (6.58)
$[HgX_2(PPh_2Bz)_2]$			
NO_3	50.92 (52.03)	3.97 (3.91)	7.25 (7.06)
Cl	55.70 (55.38)	4.50 (4.16)	7.85 (7.52)
Br	49.90 (49.99)	3.85 (3.75)	6.86 (6.78)
I	45.22 (45.32)	3.46 (3.40)	6.24 (6.15)
SCN	55.20 (55.26)	4.02 (3.95)	7.33 (7.12)
CN	58.23 (59.66)	4.27 (4.26)	8.97 (7.69)

Crystal Data. Colorless crystals of $[HgCl_2(\mathbf{1})]$ and of $[HgI_2(\mathbf{1})] \cdot \overline{O(CH_2)_3C}HCH_2OH$ were obtained from tetrahydrofurfuryl alcohol solutions. A summary of the crystal data, together with data collection details, is given in *Table 2.*

Intensity Measurements. Intensities were measured with an automatic diffractometer *Syntex P2*$_1$. Data were processed as described previously [15], with $p = 0.004$ for $[HgCl_2(\mathbf{1})]$ and 0.008 for $[HgI_2(\mathbf{1})]$ as calculated from the variance of the standard reflections [16], and corrected for *Lorentz* and polarization effects.

Structure Analysis and Refinement. The structures were solved by *Patterson* and *Fourier* methods and refined by least-squares analysis. The isotropic refinements converged at $R = 0.080$ and 0.097 for $[HgCl_2(\mathbf{1})]$ and $[HgI_2(\mathbf{1})]$, respectively. In the subsequent cycles H-atoms were included at fixed positions[1]), while the heavier atoms were allowed to vibrate anisotropically. The H-atoms were then repositioned and included in the final structure factor calculations.

During the analysis of $[HgI_2(\mathbf{1})]$ the presence of a molecule of tetrahydrofurfuryl alcohol per molecule of complex became evident. When included in the refinement, the high thermal parameters of some atoms and the diffuse electron density, which appeared on *Fourier* maps, gave a clear indication of disorder. No satisfactory model of disorder was found although several attempts were made. Therefore six C-atoms and the alcoholic O-atom were introduced into the found positions and not refined.

Table 2. *Crystal Data for* $[HgCl_2(\mathbf{1})]$ *and* $[HgI_2(\mathbf{1})]$

Compd.	$[HgCl_2(\mathbf{1})]$	$[HgI_2(\mathbf{1})] \cdot \overline{O(CH_2)_3C}HCH_2OH$[a])
Formula	$C_{44}H_{34}Cl_2HgP_2$	$C_{49}H_{44}HgI_2O_2P_2$
Fw	896.20	1181.24
a(Å)	15.127(4)	16.354(4)
b(Å)	14.133(4)	12.690(3)
c(Å)	17.810(5)	11.798(3)
α(deg)	90.	105.67(2)
β(deg)	98.27(2)	99.48(2)
γ(deg)	90.	105.75(2)
V(Å^3)	3767.9(18)	2192.8(8)
Z	4	2
Density, gcm^{-3} (calcd.)	1.580	1.789
(obsd.)[b])	1.54(1)	1.74(1)
Space group	$P2_1/c$	P_1
Crystal dimensions (mm^3)	$0.05 \times 0.10 \times 0.18$	$0.05 \times 0.08 \times 0.12$
Radiation	Graphite monochromatized MoK	
μ, cm^{-1}	43.40	59.11
Scan mode	ω-scan	ω-scan
Scan range (deg)	0.9	0.9
Bkgd counts	Scan time at + 0.65°; Scan time at + 0.69° from the center of the scan range	
2θ limits (deg)	3-56	3-56
Observations, total no.	9785	8442
No. unique data $F_o^2 > 3\sigma(F_o^2)$	2265	2176
Final no. of variables	164	154
Final $R(R_w)$	0.061, 0.080	0.070, 0.097

[a]) A molecule of tetrahydrofurfuryl alcohol per molecule of complex was found during the analysis.

[b]) Measured by flotation in ZnI_2-solutions.

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[1]) C–H = 1.0 Å, C–C–H = 120° (sp^2), H–C–H = 109.5° (sp^3), dihedral angle 90°; each H-atom was assigned an isotropic thermal parameter equal to that of the C-atom to which it is attached.

For $[H_gCl_2(\mathbf{1})]$ and $[HgI_2(\mathbf{1})]$ a two-block approximation of the normal equations matrix was used. The quantity minimized was $\Sigma w(|F_o| - |F_c|)^2$ with $w = \sin\theta/\lambda$. The phenyl rings were refined as rigid groups (D_{6h}-symmetry, C–C = 1.392 and C–H = 1.0 Å). Atomic scattering factors and anomalous dispersion terms were taken from [17]. The calculations were performed using local programs on the *UNIVAC 1100/20* computer of the University of Rome [18] and on the *HP 21MX* minicomputer of the CNR Research Area [19]. Final positional parameters for the non-H-atoms of the two compounds are included as supplementary material[2]).

3. Results and Discussion. – a. *^{31}P-NMR Spectroscopy.* The ^{31}P-NMR results for the complexes $[HgX_2(\mathbf{1})]$ ($X = NO_3$, Cl, Br, I, SCN, CN) are shown in *Table 3* and are in qualitative agreement with other ^{31}P-NMR data of related molecules. For comparison we show the data for the analogous PPh_2Bz-complexes which were prepared in order to have a data base for a phosphine with a donor capacity similar to that of **1**. In both series the values $^1J(^{199}Hg, ^{31}P)$ increase in the order $CN < I < SCN < Br < Cl < ONO_2$, and this trend is in keeping with the capability of the ligand atom to coordinate to the metal. The PPh_2Bz-series shows larger $^1J(^{199}Hg, ^{31}P)$ values than found earlier for the PPh_3-complexes [10] and this can be correlated with the different basicities of the two phosphines. A similar observation has been made for $P(cyclohexyl)_3$-[7] and $PBu_{(3-n)}Ph_n$-[9] complexes of Hg. Changes in $J(M,P)$ with increasing substitution of alkyl for aryl groups have also been found for Cd-[20] and Sn-[21] phosphine complexes.

Figure 1 shows a plot of $^1J(^{199}Hg, ^{31}P)$ for the PPh_2Bz-complexes against the M,P-coupling in complexes of *a*) PPh_3 and *b*) **1**. We observe a linear correlation between the coupling constants stemming from the monodentate ligands and this is reasonable since we do not expect the effect of the X-group to vary markedly in these monodentate phosphine complexes. The good correlation between the coupling constants for **1** and PPh_2Bz-complexes was not necessarily to be expected. Constraints stemming from a coordinated molecule of **1** could lead to a micro-

Table 3. *^{31}P-NMR Data for the Complexes $[HgX_2P_2]$*[a])

X	Phosphine Ligand					
	1[b])		PPh_2Bz[c])		PPh_3[d])	
	$^1J(^{199}Hg, ^{31}P)$	δ	$^1J(^{199}Hg, ^{31}P)$	δ	$^1J(^{199}Hg, ^{31}P)$	δ
NO_3	5710	45.6	6003	49.7	5925	40.4
Cl	4671	29.1	5084	32.0	4675	28.3
Br	4219	23.5	4615	25.9	4156	21.8
SCN	4189	33.2	4297	35.3	3725	31.3
I	3624	14.9	3624	11.9	3074	1.2
CN	2914	15.0	2629	18.3	2617	17.9

[a]) Chemical shifts are in ppm, coupling constants in Hz, $CDCl_3$-solutions.

[b]) NO_3, Cl, Br at 300° K; I at 250° K; SCN at 220° K; CN at 215° K.

[c]) NO_3 at 220° K; Cl and Br at 230° K; I and SCN at 210° K; CN at 200° K.

[d]) Data from [10].

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[2]) Tables of positional parameters for the non-H-atoms can be obtained from *F.C.*

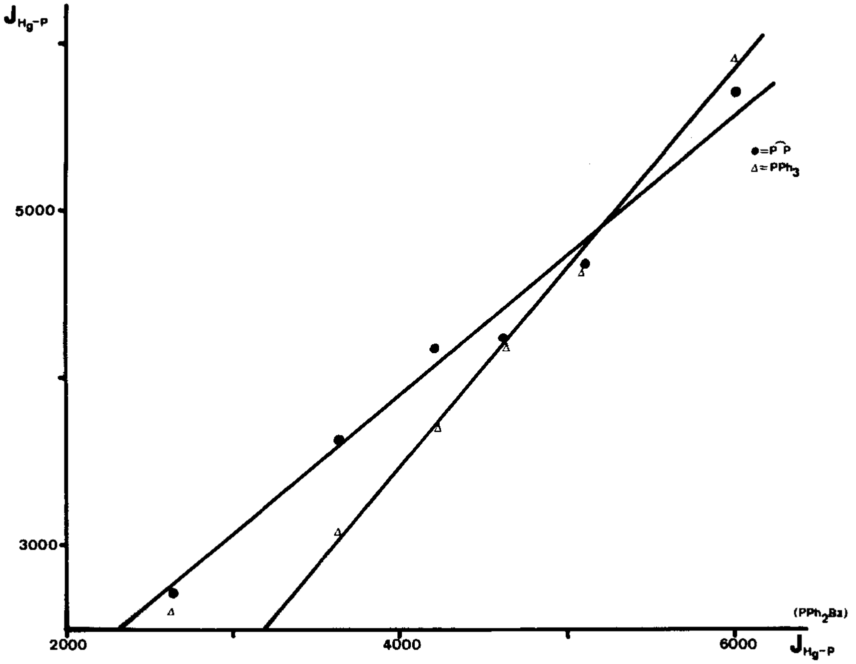

Fig. 1. *Plot of* $^1J(^{199}Hg,\ ^{31}P)$ *for* $[HgX_2(PPh_2Bz)_2]$ vs. $^1J(^{199}Hg,\ ^{31}P)$ *for* $[HgX_2(PPh_3)_2]$ *and* $[HgX_2(\mathbf{1})]$

geometry about the Hg-atom which is determined by considerations other than the nature of the anionic ligand, *e.g.* a geometric limitation of the P-Hg-P angle might lead to a smaller range of $^1J(^{199}Hg,\ ^{31}P)$ values. However, this is not the case, with the total range of values for both series differing only slightly (see *Table 3*). Interestingly, for X = NO_3, Cl, Br, the coupling constant is larger for $[HgX_2(PPh_2Bz)_2]$ than for $[HgX_2(\mathbf{1})]$, but the reverse is true for X = CN^-. Based on $^1J(^{199}Hg,\ ^{31}P)$, it would seem that **1** is not significantly hindered from coordinating to mercury in a fashion analogous to that of the monodentate ligands.

Our previous calculations [10] [11] have shown that $^1J(^{199}Hg,\ ^{31}P)$ depends on both the X-Hg-X and P-Hg-P angles θ_X and θ_P [11] such that: $J(^{199}Hg,\ ^{31}P) = 5{,}851\ Hz + 25.1\ \theta(P\text{-}Hg\text{-}P)\ Hz/deg - 48.7\ \theta(X\text{-}Hg\text{-}X)\ Hz/deg$ where J is the experimental value for the compound in question. Given the experimental X-Hg-X bond angles for $[HgX_2(PPh_3)_2]$ (X = NO_3, SCN, I) and assuming that replacing two PPh_3 by ligand **1** does not change the X-Hg-X angles for a given X, our measured one-bond Hg,P-coupling constants suggest the P-Hg-P angles for $[HgCl_2(\mathbf{1})]$, $[HgBr_2(\mathbf{1})]$ and $[HgI_2(\mathbf{1})]$ should be approximately 125, 120 and 110°, respectively.

b. *Structural Studies.* To test the capability of our NMR data to estimate structural parameters and to further investigate molecular distortions in molecules of the type $[HgX_2P_2]$ we have determined the structures of the complexes $[HgCl_2(\mathbf{1})]$ and $[HgI_2(\mathbf{1})]$, using X-ray methods.

i. *[$HgCl_2$(1)]*. Crystals of [$HgCl_2$(**1**)] contain monomeric molecules in which the Hg-atom is coordinated to two P-atoms and two Cl^--ions in a distorted tetrahedral arrangement. A diagram of the molecular structure of the complex with the numbering scheme is shown in *Figure 2* and a selection of bond lengths and valence angles is given in *Table 4*.

The Hg-P vectors, of lengths 2.485(7) and 2.509(8) Å, subtend a rather large angle [125.6(3)°] and are shorter than the sum of the tetrahedral covalent radii, 1.48 Å for Hg [22] and 1.10 Å for P [23]. *Table 5* shows that the Hg-P distances lie in the middle of the observed range for related complexes [24–28], with the value 2.39 Å found for [$HgCl_2(PEt_3)_2$] worthy of note [28].

A comparison of these Hg-P bond-lengths and P-Hg-P bond-angles confirms the trend described earlier [10] [11] in which larger P-Hg-P angles are associated with shorter Hg-P bonds.

The Hg-Cl bonds, of lengths 2.528(8) and 2.505(10) Å, subtend a rather small angle [97.0(3)°], and are slightly longer than expected from the covalent radii of Hg, 1.48 Å [22], and Cl, 0.99 Å [23]. These Hg-Cl separations also lie within the range illustrated by our model complexes in *Table 5* [29] [30], but interestingly are about 0.16 Å shorter than those found for [$HgCl_2(PEt_3)_2$].

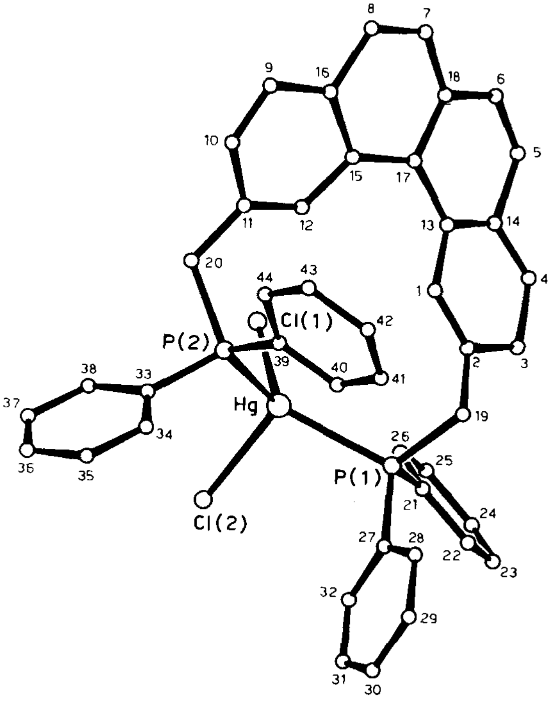

Fig. 2. *Computer-generated drawing of the molecule of [$HgCl_2$(1)]*

Table 4. *Selection of Bond Lengths (Å) and Angles (deg)* (Standard deviations are given in parentheses)

	[HgCl$_2$(**1**)]	[HgI$_2$(**1**)]		[HgCl$_2$(**1**)]	[HgI$_2$(**1**)]
Hg–P(1)	2.485 (7)	2.491 (10)	P(1)–Hg–P(2)	125.6 (3)	146.0 (4)
Hg–P(2)	2.509 (8)	2.500 (11)	P(1)–Hg–X(1)[a]	116.7 (3)	99.2 (3)
Hg–X(1)	2.525 (8)	2.858 (5)	P(1)–Hg–X(2)	100.8 (3)	99.2 (2)
Hg–X(2)	2.505 (10)	2.832 (3)	P(2)–Hg–X(1)	102.8 (3)	96.5 (3)
P(1)–C(19)	1.87 (3)	1.84 (5)	P(2)–Hg–X(2)	110.3 (3)	100.3 (2)
P(1)–C(21)	1.82 (2)	1.80 (3)	X(1)–Hg–X(2)	97.0 (3)	116.9 (1)
P(1)–C(27)	1.85 (2)	1.78 (4)	Hg–P(1)–C(19)	115.0 (9)	112.9 (13)
P(2)–C(20)	1.87 (2)	1.86 (4)	Hg–P(1)–C(21)	114.2 (8)	107.7 (10)
P(2)–C(33)	1.82 (2)	1.78 (4)	Hg–P(1)–C(27)	109.0 (7)	115.5 (16)
P(2)–C(39)	1.80 (2)	1.83 (2)	C(19)–P(1)–C(21)	103.3 (12)	100.7 (21)
C(2)–C(19)	1.50 (5)	1.53 (6)	C(19)–P(1)–C(27)	107.4 (12)	111.6 (19)
C(11)–C(20)	1.47 (5)	1.47 (6)	C(21)–P(1)–C(27)	107.6 (11)	107.3 (16)
			Hg–P(2)–C(20)	113.0 (10)	112.4 (14)
			Hg–P(2)–C(33)	114.2 (8)	114.9 (11)
			Hg–P(2)–C(39)	114.1 (8)	107.6 (10)
			C(20)–P(2)–C(33)	102.4 (12)	107.0 (18)
			C(20)–P(2)–C(39)	107.0 (14)	108.0 (14)
			C(33)–P(2)–C(39)	105.2 (11)	106.7 (15)
			C(2)–C(19)–P(1)	108.1 (21)	114.7 (40)
			C(11)–C(20)–P(2)	115.2 (20)	109.9 (30)

[a] X = Cl for [HgCl$_2$(**1**)], X = I for [HgI$_2$(**1**)].

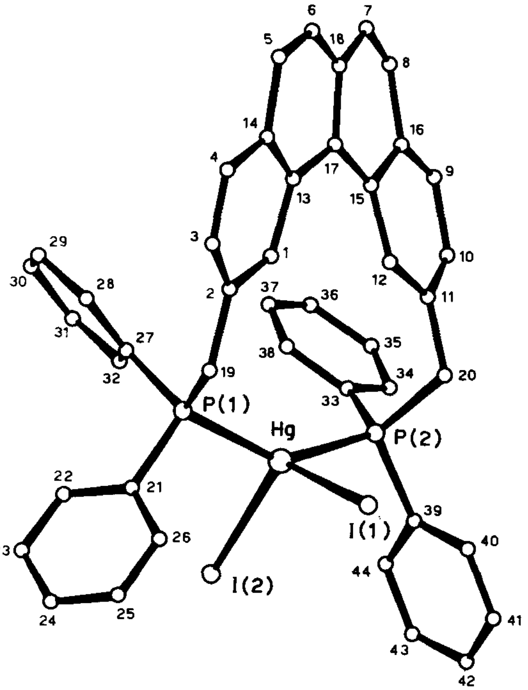

Fig. 3. *Computer-generated drawing of the molecule [HgI$_2$(1)]*

Once again a trend is apparent; here smaller Cl-Hg-Cl angles correspond to longer Hg-Cl bonds.

The considerable distortion of bond angles at the Hg-atom in [$HgCl_2$(**1**)], presumably arises from the nature of the ligand. Interestingly, the P-Hg-P angle is one of the smallest P-M-P angles observed in complexes of **1** [12] [13], and supports the suggestion [13] that the aromatic backbone can be distorted such that this ligand allows a wider range of complex geometries than originally envisioned.

The observed P-Hg-P bond angle is in agreement with our prediction based on the ^{31}P coupling-constant data. Using the observed values of θ_P and θ_X we calculate a ^1J of 4,280 Hz, which is ≈8.4% smaller than the experimental result. We note that the sum of the P-Hg-P and Cl-Hg-Cl angles in [$HgCl_2$(**1**)] is only slightly larger than the sum of two tetrahedral angles, which is consistent with the assumption we made in our earlier extended *Hückel* calculations [10] [11].

ii. *[HgI_2(**1**)].* Table 4 also contains a compilation of bond distances and angles for [HgI_2(**1**)] and a view of this molecule is given in *Figure 3.*

The crystal of [HgI_2(**1**)] contains monomeric molecules with the Hg-atom in an even more distorted tetrahedral arrangement than in [$HgCl_2$(**1**)]. In fact, the coordination tetrahedron appears flattened along a direction perpendicular to the directions P....P and I....I. The Hg-P bond lengths, 2.491(10) and 2.500(11) Å, subtend an angle of 146.0(4)°. The Hg-P distances are shorter than the 2.566 Å value found for [$HgI_2(PEt_3)_2$] [31] but similar to the bond lengths found in [$HgI_2((Ph_2PCH_2CH_2)_2S)$] 2.531 and 2.493 Å [32].

The Hg-I bond-lengths at 2.823(3) Å and 2.858(5) Å are long relative to [$HgI_2(Ph_2PCH_2CH_2)_2S$] 2.808 Å [32], [HgI_4]$^{2-}$ 2.785 Å [33], or [$HgI_2(PEt_3)_2$], 2.748 Å [31].

Table 5. *Bond Distances and Bond Angles in Some Model Hg(II) Complexes with Halogen (X) Ligands*[a])

Complex	l(Hg–X)	θ(X–Hg–X)	l(Hg–P)	θ(P–Hg–P)	Ref.
[$HgCl_2(PEt_3)_2$]	2.68	109	2.39	158	[28]
[$HgCl_2(SCH_2CH(NH_3)CO_2H)$][b])	2.614	91			[40]
[$HgCl_2$(**1**)]	2.515	97	2.497	126	
[$HgCl_2(Et_2NCH_2CH_2PPh_2)$]	2.444	109	2.417	78[c])	[41]
[$(HgCl_2)_2$(1,4,8,11-tetra-thiacyclotetradecane)][d])	2.413	122			[30]
[$HgCl_2(Ph_3AsO)_2$]	2.33	147			[29]
[$HgCl_2(\mu\text{-}Cl)_2Pt(PMe_2Ph)_2$][e])	2.371	157			[42]
[HgI_2(**1**)]	2.84	116	2.51	145	
[$HgI_2((Ph_2PCH_2CH_2)_2S)$]	2.808	113	2.515	123	[32]
HgI_4^{2-}	2.785				[33]
[$HgI_2(Ph_2P(CH_2)_5PPh_2)$] (polymeric)	2.772	110	2.579	101	[24]
[$HgI_2(PPh_3)_2$]	2.748	110	2.566	109	[31]

[a]) Distances in Å, angles in degrees.

[b]) Contains bridging S-atoms.

[c]) N–Hg–P angle.

[d]) The macrocycle acts as a bidentate to two distinct $HgCl_2$-moieties.

[e]) Data for the terminal halogen atoms.

The I-Hg-I angle of [HgI_2(**1**)] at 116.9(1)° is the largest of the set *(Table 5)*. Obviously, a completely different trend is apparent for [HgI_2(**1**)] since *both* the angles θ_P and θ_X are relatively large. For [HgI_2(**1**)], **1** avoids a value of 110° for θ_P, although smaller angles are possible, *e.g.* for *cis*-[$PtCl_2$(**1**)] the P-Pt-P angle is 104.8° [34]. [HgI_2(**1**)] finds a compromise by lengthening the Hg-I bonds and opening both θ_P and θ_X.

Assuming that our equation governing $^1J(^{199}Hg, ^{31}P)$, θ_P and θ_X is valid, we calculate a coupling constant of 3,823 Hz, using the experimental values for θ_P and θ_X. This is only 5.5% more than the observed 3,624 Hz value and lies within the confidence boundaries of our model. We would not have been able to make an accurate prediction of either θ_P or θ_X, based on $^1J(^{199}Hg, ^{31}P)$ alone using our equation. This stems, in part, from the inadequacy of our assumption that the sum ($\theta_P + \theta_X$) should be approximately 220°. Obviously, when both angles are free to change, the problem has one unknown too many. However, assuming a chelating dianion, perhaps one such as *ortho*-$C_6H_4O_2^{2-}$ or oxalate, $C_2O_4^{2-}$, where θ_X can be estimated, it should be possible to estimate θ_P for Hg-complexes of **1** or other new bidentate ligands. Returning to the possible distortions of **1**, it is curious that for [$HgCl_2$(**1**)], ($\theta_P + \theta_X$) is 222.6°, but jumps to 263° in [HgI_2(**1**)]. The ligand allows itself to be 'squeezed' with the poorer donor Cl^-, but refuses, and seeks a different energy minimum for the better donor, I^-. In this connection the structure of [$HgBr_2$(**1**)] might be informative; however, since both subtle electronic and steric effects may be at work (I^- is also a larger ligand as well as a better donor than Cl^-) a clear answer may prove difficult.

The bidentate ligand **1** has been shown to coordinate to transition metal ions with two conformations [12] [13] [34–37], one of which is characterized by having the two CH_2-P bonds, C(19)-P(1) and C(20)-P(2), oriented in the same direction relative to the mean of the benzo[*c*]phenanthrene plane, while the other is characterized by having the two CH_2-P bonds oriented in opposite directions. In both conformations the geometry of the $CH_2-C_{18}H_{10}-CH_2$ moiety is the same. The parameters which characterize the two conformations involve the internal torsion angles of the twelve-membered ring formed by chelation of **1** to the metal, and specifically the torsion angles (ν) around C(2)–C(19) and C(11)–C(20), and those (τ) around C(19)–P(1) and C(20)–P(2). Generally, in the first type of conformation the ν and τ angles have opposite signs, whereas for the second type of conformation the angles have the same sign. The first conformation has been found in complexes in which the two P-atoms are coordinated in *trans* (or almost

Table 6. *Torsion Angles Defining the Conformation of 1 in [$HgCl_2$(1)] and [HgI_2(1)]*

		[$HgCl_2$(**1**)]	[HgI_2(**1**)]
C(1)–C(2)–C(19)–P(1)	(γ)	92.0 (3)	–45.0 (5)
C(2)–C(19)–P(1)–Hg	(τ)	–57.0 (2)	89.0 (3)
C(12)–C(11)–C(20)–P(2)	(γ)	51.0 (4)	90.0 (4)
C(11)–C(20)–P(2)–Hg	(τ)	–80.0 (2)	–88.0 (2)

trans) position with the P-M-P angle larger than 160°, but also in [Ag(Cl$_3$Sn)(**1**)] which has a P-Ag-P angle of 142.2° [38].

The second type of conformation is present in [AgX(**1**)], (X = NO$_3$, Cl, BF$_4$) [39] and in [CuCl(**1**)] [13] with P-M-P angles ranging from 130° to 150°. For our Hg(II) complexes we find the first conformation in [HgI$_2$(**1**)], the second in [HgCl$_2$(**1**)] (*Table 5*).

4. Conclusion. – The structures of [HgCl$_2$(**1**)] and [HgI$_2$(**1**)] both show distorted tetrahedral coordination at the metal. The iodide is noteworthy in that the P-Hg-P and I-Hg-I angles are large and exceed those of the chloride by $>18°$. These structures clearly show that **1** can distort somewhat more than expected to accommodate the electronic requirements of mercury. Our original goal in this work, the use of **1** to produce [HgX$_2$P$_2$] complexes with larger P-Hg-P angles *has* been achieved. The limited predictive value of $^1J(^{199}\mathrm{Hg}, {}^{31}\mathrm{P})$ is understandable and a clear sign of the complexity and subtleties which are involved even in these relatively simple Hg-compounds.

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