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Multidentate Lewis Acids. Crystal Structure of the 2:1 Adduct of 1,2-Phenylenedimercury Dichloride with Tetraphenylphosphonium Chloride

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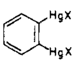
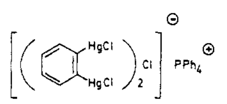
Abstract: The compound belongs to the $P\bar{1}$ space group, with a = 13.351 (8) Å, b = 16.420 (8) Å, c = 20.200 (17) Å, α = 108.43 (6)°, β = 94.48 (6)°, γ = 105.41 (6)°, Z = 4 $(C_6H_5)_4P[(C_6H_4Hg_2Cl_2)_2Cl]\cdot{}^1/_2CH_2Cl_2$ units per cell. The structure was solved from 8176 significantly observed Cu Kα reflections to an R factor of 0.040. The unit cell contains well-separated $[(C_6H_5)_4P]^+$ cations and $[(C_6H_4Hg_2Cl_2)_2Cl]^-$ anions. The anions consist of two entwined $C_6H_4Hg_2Cl_2$ molecules, with an additional chloride ion embraced by the network of C-Hg-Cl arms. There are two types of symmetry-independent anions in the cell. In anions of one type, the additional chloride ion forms four bonds to mercury in the range 2.91-3.10 Å. In the second type, two of the Hg-Cl$^-$ bonds are short (2.857, 2.934 Å) and two are longer (3.335, 3.177 Å). Both anions are stabilized by extra Hg···Cl contacts involving terminal chlorine atoms. The general significance of these structural features is discussed.

The coordination chemistry of multidentate Lewis acids and their use as stoichiometric or catalytic reagents are promising new areas of research.[1] We have recently described the unusual coordination chemistry of a series of bidentate Lewis acids, the 1,2-phenylenedimercury dihalides **1-3**.[1a] Unlike simple monodentate organomercuric halides, bidentate acids **1** and **2** react with halides to give isolable adducts. These are the only known anionic complexes of organomercury compounds.[2] To obtain more information about the bonding in these novel complexes, we have determined the crystal structure of the 2:1 adduct **4** of dichloro-1,2-phenylenedimercury (**1**) with tetraphenylphosphonium chloride.



1 (X=Cl)
2 (X=Br)
3 (X=I)



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Experimental Section

Crystal Data: $(C_6H_5)_4P[(C_6H_4Hg_2Cl_2)_2Cl]\cdot{}^1/_2CH_2Cl_2$, fw = 1513.7, triclinic, $P\bar{1}$, a = 13.351 (8) Å, b = 16.420 (8) Å, c = 20.200 (17) Å, α = 108.43 (6)°, β = 94.48 (6)°, γ = 105.41 (6)°, V = 3986.0 Å^3, D_c = 2.522 g cm^{-3}, Z = 4, λ(Cu K$\bar{\alpha}$) = 1.54178 Å (graphite monochromator), μ(Cu Kα) = 334.8 cm^{-1}, T = 293 K.

Crystallographic Measurements and Structure Resolution. Crystals of complex **4** suitable for X-ray work were obtained by recrystallization from CH_2Cl_2/hexanes. The specimen used had the following distances (mm) between the indicated pairs of faces: 0.090($\bar{1}$00-100) × 0.090-(00$\bar{1}$-001) × 0.520(1$\bar{1}$0-$\bar{1}$10). It was mounted in a random orientation on an Enraf-Nonius CAD-4 diffractometer, and a set of 25 reflections was created by the automatic search routine and centered in the counter aperture. The indexation procedure yielded the reduced triclinic cell given above, which was used throughout this work. This cell was checked by means of long-exposure oscillation photographs taken along the three crystallographic axes. These photographs revealed no symmetry and showed the expected layer-line spacings. The Niggli coefficients unambiguously indicated that the lattice could not be described in higher symmetry.

The intensity data were collected as described elsewhere.[3] The three standard reflections showed random variation within ±2.8% during the experiment. A set of 11 812 nonequivalent hkl, $hk\bar{l}$, $h\bar{k}\bar{l}$, and $h\bar{k}l$ reflections was measured within a sphere limited by 2θ = 120°. On the basis of the criterion $I > 3.0\sigma(I)$, a set of 8176 measurements significantly above background was retained for structure determination. These data were corrected for the Lorentz effect, polarization, and absorption (Gaussian integration, grid 8 × 8 × 8, transmission range = 0.027-0.117).

The structure was solved in the centric space group $P\bar{1}$ with a limited set of 3057 nonzero intensity data ($2\theta \leqslant 70°$). The $P\bar{1}$ asymmetric unit contains eight mercury atoms, which were located by direct methods (MULTAN package).[4] The remaining non-hydrogen atoms were progressively found by standard structure-factor and difference-Fourier (ΔF) calculations. Isotropic refinement by full-matrix least-squares calculations converged to $R = \sum||F_o| - |F_c||/\sum|F_o|$ = 0.150 and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$ = 0.160. The full data set was used for the rest of the refinement. The hydrogen atoms were fixed at idealized positions (C-H = 0.95 Å, B = 4.0 Å^2). Their parameters were not refined, but the coordinates were recalculated after each least-squares cycle. The non-hydrogen atoms were finally refined anisotropically. Convergence was reached for R = 0.040, R_w = 0.047, and a goodness-of-fit ratio of 1.53 for 858 parameters varied. The highest residuals on the final ΔF map were in the range ±(0.9-1.7) e Å^{-3} near Hg and below ±0.9 e Å^{-3} elsewhere. The refined coordinates are listed in Table II.

The scattering curves were those of Cromer and Waber,[5] except for hydrogen.[6] The f' and f'' contributions to anomalous dispersion were included in the structure-factor calculations for Hg, Cl, and P.[7]

Description of the Structure

The asymmetric unit contains two $[(C_6H_5)_4P]^+$ cations, two nonequivalent $[(C_6H_4Hg_2Cl_2)_2Cl]^-$ anions, and one CH_2Cl_2 solvent molecule. The two nonequivalent $[(C_6H_4Hg_2Cl_2)_2Cl]^-$ ions have similar structures (a and b in Figure 1). Both possess an approximate twofold axis running through the central Cl$^-$ ion and rotating one aromatic ring into the other. Selected distances and angles involving the mercury atoms in the two anions are listed in Table I. In anion **5** (Figure 1a), two of the Hg-Cl$_i$[8] distances (2.857 (4), 2.934 (4) Å) are much shorter than the other two

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[1] For recent references, see: (a) Wuest, J. D.; Zacharie, B. *Organometallics* **1985**, *4*, 410-411. (b) Wuest, J. D.; Zacharie, B. *J. Am. Chem. Soc.* **1985**, *107*, 6121-6123. (c) Wuest, J. D.; Zacharie, B., unpublished results. (d) Katz, H. E. *J. Am. Chem. Soc.* **1985**, *107*, 1420-1421. (e) Karol, T. J.; Hutchinson, J. P.; Hyde, J. R.; Kuivila, H. G.; Zubieta, J. A. *Organometallics* **1983**, *2*, 106-114.

[2] (a) The isolation and elemental analysis of halide complexes of perfluoroalkylmercury compounds have been reported: Emeléus, H. J.; Lagowski, J. J. *J. Chem. Soc.* **1959**, 1497-1501. However, this work has been criticized: Downs, A. J. *Ibid.* **1963**, 5273-5278. (b) A zwitterionic iodide complex of an organomercuric iodide has been studied: Baenziger, N. C.; Flynn, R. M.; Swenson, D. C.; Holy, N. L. *Acta Crystallogr.* **1978**, *B34*, 2300-2301.

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[5] Cromer, D. T.; Waber, J. T. *Acta Crystallogr.* **1965**, *18*, 104-109.

[6] Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175-3187.

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[8] Cl$_i$ refers to the additional chloride ion, whereas Cl$_t$ indicates a strongly bonded terminal chlorine.

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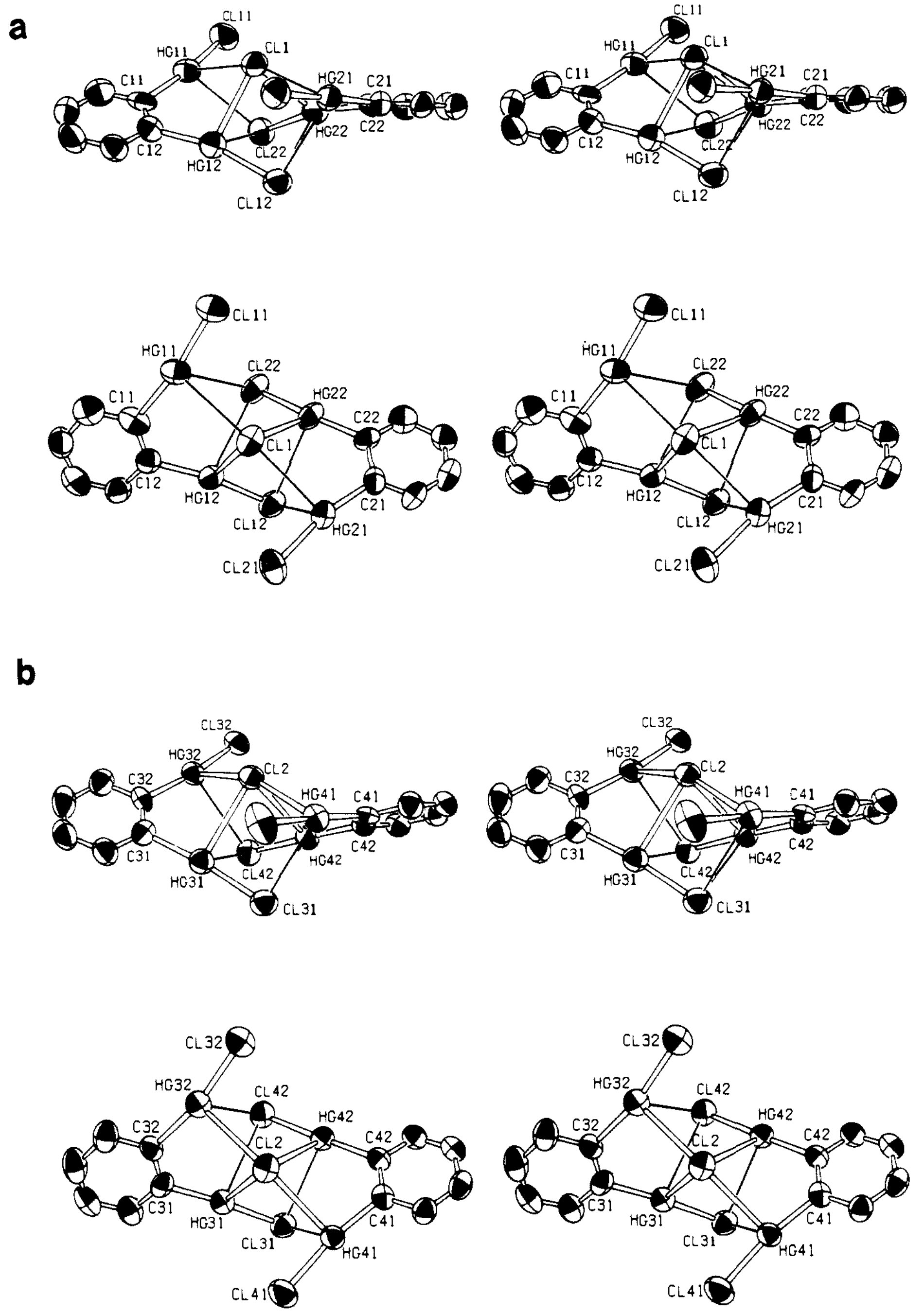

Figure 1. (a) Stereoviews of anion **5**, with all hydrogens omitted for simplicity. The ellipsoids correspond to 50% probability, and single lines represent Hg···Cl contacts shorter than 3.40 Å. The dihedral angle between the aromatic rings is 42°. (b) Stereoviews of anion **6**, with all hydrogens omitted for simplicity. The ellipsoids correspond to 50% probability, and single lines represent Hg···Cl contacts shorter than 3.40 Å. The dihedral angle between the aromatic rings is 65°. To facilitate comparisons, the anion **6** shown here is related to the coordinates of Table II by the $(-x,-y,-z)$ transformation.

(3.335 (4), 3.177 (4) Å), whereas in anion **6** (Figure 1b) the four Hg–Cl$_i$ distances span a much narrower range (2.910–3.095 Å, σ = 0.004 Å). The more compact anion **6** probably better reflects the ideal structure of the free anion and will be discussed first.

This anion (Figure 1b) consists of two entwined $C_6H_4Hg_2Cl_2$ molecules, with an additional chloride ion embraced by the network of C–Hg–Cl arms. This structure follows two general trends in the coordination chemistry of Hg(II), which are obeyed particularly well by organomercury compounds: (i) Hg(II) shows a marked preference for forming two strong collinear (primary) bonds and (ii) it retains appreciable acidity in the plane perpendicular to these primary bonds, permitting secondary coordinative interactions to take place. In agreement with the first trend, each mercury atom forms only one strong Hg–Cl$_t$[8] bond in addition to the Hg–C bond. The Hg–C distances in anion **6** (2.051–2.074 Å, av 2.062 Å, σ = 0.013 Å) are similar to those found in other arylmercury compounds.[9] The lengths of the primary Hg–Cl$_t$ bonds (2.310–2.344 Å, σ = 0.004 Å, mean = 2.334 Å) are comparable to those found in other organomercury compounds[9] and various complex salts containing discrete $HgCl_2$ units.[10] The coordination is not perfectly linear (C–Hg–Cl$_t$ = 167.4–176.9°, σ = 0.4°, mean = 172.0°) but very far from the 120° value expected for normal three-coordinate geometry. Furthermore, the small departure from linearity does not appear to occur in direct response to binding with the additional chloride ion, since the Hg–Cl$_t$ bond is not displaced in the plane defined by the atoms C–Hg–Cl$_i$. This is clearly illustrated in Figure 2, which shows

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[9] For references, see: Wardell, J. L. In "Comprehensive Organometallic Chemistry"; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, 1982; Vol. 2, pp 863–978.

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Table I. Selected Interatomic Distances and Bond Angles

Distances (Å)			
Hg(11)-Cl(11)	2.288 (4)	Hg(31)-Cl(31)	2.344 (4)
Hg(11)-C(11)	2.084 (14)	Hg(31)-C(31)	2.074 (13)
Hg(11)-Cl(1)	3.335 (4)	Hg(31)-Cl(2)	3.064 (4)
Hg(11)-Cl(22)	3.266 (4)	Hg(31)-Cl(42)	3.274 (4)
Hg(12)-Cl(12)	2.348 (4)	Hg(31)-Cl(11)[b]	3.494 (5)
Hg(12)-C(12)	2.068 (14)	Hg(32)-Cl(32)	2.337 (4)
Hg(12)-Cl(1)	2.857 (4)	Hg(32)-C(32)	2.072 (12)
Hg(12)-Cl(22)	3.409 (4)	Hg(32)-Cl(2)	2.910 (4)
Hg(21)-Cl(21)	2.332 (4)	Hg(32)-Cl(42)	3.286 (4)
Hg(21)-C(21)	2.059 (13)	Hg(41)-Cl(41)	2.310 (4)
Hg(21)-Cl(1)	3.177 (4)	Hg(41)-C(41)	2.051 (12)
Hg(21)-Cl(12)	3.296 (4)	Hg(41)-Cl(2)	2.998 (4)
Hg(21)-Cl(41)[a]	3.401 (5)	Hg(41)-Cl(31)	3.326 (4)
Hg(22)-Cl(22)	2.334 (4)	Hg(41)-Cl(21)[a]	3.591 (5)
Hg(22)-C(22)	2.011 (15)	Hg(42)-Cl(42)	2.344 (4)
Hg(22)-Cl(1)	2.934 (4)	Hg(42)-C(42)	2.052 (14)
Hg(22)-Cl(12)	3.330 (4)	Hg(42)-Cl(2)	3.095 (4)
C(1)-Cl(3)	1.75 (2)	Hg(42)-Cl(31)	3.310 (4)
C(1)-Cl(4)	1.75 (2)	Hg(42)-Cl(32)[b]	3.361 (4)
		Hg(42)-Cl(42)[b]	3.502 (4)
Angles (deg)			
C(11)-Hg(11)-Cl(11)	170.3 (4)	C(31)-Hg(31)-Cl(31)	172.8 (4)
C(11)-Hg(11)-Cl(1)	93.6 (4)	C(31)-Hg(31)-Cl(2)	94.9 (4)
C(11)-Hg(11)-Cl(22)	105.9 (4)	C(31)-Hg(31)-Cl(42)	101.8 (4)
Cl(11)-Hg(11)-Cl(1)	95.5 (1)	Cl(31)-Hg(31)-Cl(2)	92.1 (1)
Cl(11)-Hg(11)-Cl(22)	80.8 (1)	Cl(31)-Hg(31)-Cl(42)	82.1 (1)
Cl(1)-Hg(11)-Cl(22)	67.4 (1)	Cl(2)-Hg(31)-Cl(42)	72.5 (1)
C(12)-Hg(12)-Cl(12)	165.2 (4)	C(32)-Hg(32)-Cl(32)	167.4 (4)
C(12)-Hg(12)-Cl(1)	102.7 (4)	C(32)-Hg(32)-Cl(2)	97.7 (4)
C(12)-Hg(12)-Cl(22)	104.3 (4)	C(32)-Hg(32)-Cl(42)	101.2 (4)
Cl(12)-Hg(12)-Cl(1)	91.9 (1)	Cl(32)-Hg(32)-Cl(2)	94.6 (1)
Cl(12)-Hg(12)-Cl(22)	81.9 (1)	Cl(32)-Hg(32)-Cl(42)	84.6 (1)
Cl(1)-Hg(12)-Cl(22)	70.9 (1)	Cl(2)-Hg(32)-Cl(42)	74.2 (1)
C(21)-Hg(21)-Cl(21)	168.4 (4)	C(41)-Hg(41)-Cl(41)	170.9 (4)
C(21)-Hg(21)-Cl(1)	102.3 (4)	C(41)-Hg(41)-Cl(2)	96.5 (4)
C(21)-Hg(21)-Cl(12)	93.2 (4)	C(41)-Hg(41)-Cl(31)	99.3 (4)
Cl(21)-Hg(21)-Cl(1)	89.0 (1)	Cl(41)-Hg(41)-Cl(2)	92.3 (1)
Cl(21)-Hg(21)-Cl(12)	92.7 (1)	Cl(41)-Hg(41)-Cl(31)	84.6 (1)
Cl(1)-Hg(21)-Cl(12)	71.0 (1)	Cl(2)-Hg(41)-Cl(31)	76.6 (1)
C(22)-Hg(22)-Cl(22)	165.4 (4)	C(42)-Hg(42)-Cl(42)	176.9 (4)
C(22)-Hg(22)-Cl(1)	106.6 (4)	C(42)-Hg(42)-Cl(2)	97.0 (4)
C(22)-Hg(22)-Cl(12)	95.3 (4)	C(42)-Hg(42)-Cl(31)	100.0 (4)
Cl(22)-Hg(22)-Cl(1)	87.3 (1)	Cl(42)-Hg(42)-Cl(2)	86.0 (1)
Cl(22)-Hg(22)-Cl(12)	83.9 (1)	Cl(42)-Hg(42)-Cl(31)	81.3 (1)
Cl(1)-Hg(22)-Cl(12)	73.4 (1)	Cl(2)-Hg(42)-Cl(31)	75.6 (1)
Hg(11)-Cl(1)-Hg(12)	71.1 (1)	Hg(31)-Cl(2)-Hg(32)	74.4 (1)
Hg(11)-Cl(1)-Hg(21)	157.7 (1)	Hg(31)-Cl(2)-Hg(41)	87.2 (1)
Hg(11)-Cl(1)-Hg(22)	92.8 (1)	Hg(31)-Cl(2)-Hg(42)	77.7 (1)
Hg(12)-Cl(1)-Hg(21)	89.6 (1)	Hg(32)-Cl(2)-Hg(41)	159.0 (1)
Hg(12)-Cl(1)-Hg(22)	83.1 (1)	Hg(32)-Cl(2)-Hg(42)	92.7 (1)
Hg(21)-Cl(1)-Hg(22)	73.1 (1)	Hg(41)-Cl(2)-Hg(42)	73.3 (1)
Cl(3)-C(1)-Cl(4)	113.6 (12)		

[a] $-x$, $1-y$, $1-z$. [b] $-x$, $-y$, $1-z$.

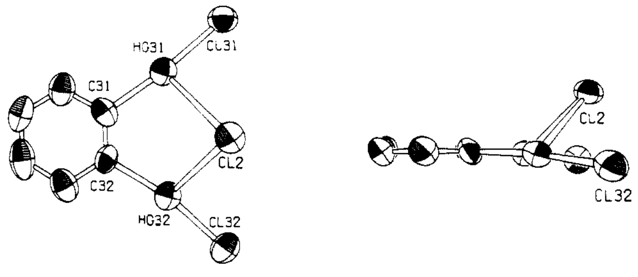

Figure 2. Two views of a fragment of anion **6** showing the small geometrical changes that occur in the $C_6H_4Hg_2Cl_2$ units.

that interaction with the additional chloride ion leaves the $C_6H_4Hg_2Cl_2$ units approximately planar.[11] Binding of the additional chloride ion *above* the plane of the molecule results in a displacement of the terminal $Hg-Cl_t$ bonds by only about 10°, most of which occurs *in* the molecular plane. Some strain may be introduced at positions 1 and 2 of the phenylene rings, since the four internal angles C(31)-C(32)-Hg(32), C(32)-C(31)-Hg(31), C(41)-C(42)-Hg(42), and C(42)-C(41)-Hg(41) are, on the average, 5.2° greater than the four external angles C(33)-C(32)-Hg(32), C(36)-C(31)-Hg(31), C(43)-C(42)-Hg(42), and C(46)-C(41)-Hg(41). However, it is possible that this distortion already existed in the uncoordinated $C_6H_4Hg_2Cl_2$ molecule.[12]

In conclusion, the additional chloride ion does not increase the primary coordination of mercury to trigonal but instead makes efficient use of residual acidity in the equatorial plane of each of the four metal atoms, which retain their primary two-coordination. The residual acidity of the metals is also expressed by four intramolecular $Hg\cdots Cl_t$ contacts shorter than 3.35 Å (Table II; single lines in Figure 1b). Complex anion **6** therefore exhibits three distinct levels of mercury-chlorine bonding interactions. This is typical of $HgCl_3^-$ salts, in which there are two roughly collinear

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[11] The geometry of the aromatic rings is described in detail in the supplementary material.

[12] Attempts to determine the crystal structure of dichloro-1,2-phenylenedimercury (**1**) itself have not yet been successful.

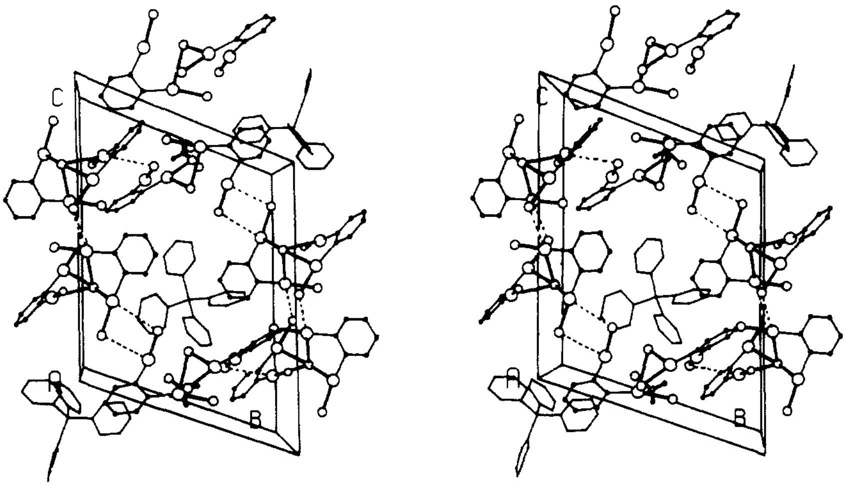

Figure 3. Stereoview of the molecular packing in complex **4**. Atoms in the anions are represented by spheres of arbitrary size (large for Hg, medium for Cl, small for C).

Hg–Cl$_t$ primary bonds (2.30–2.40 Å), interactions with the additional chloride ion (2.74–2.84 Å) and longer Hg···Cl$_t$ contacts (3.10–3.27 Å)[10].

Anion **5** (Figure 1a) is formally derived from anion **6** by a small rotation and separation of the two $C_6H_4Hg_2Cl_2$ units. The dihedral angle between the aromatic rings becomes 42°, whereas it is 65° in anion **6**. In addition, the Hg···Cl$_t$ contacts in anion **5** are, on the average, slightly longer than in anion **6**. This makes two of the Hg–Cl$_i$ bonds shorter (2.857 (4), 2.934 (4) Å) at the expense of the other two (3.335 (4), 3.177 (4) Å).

The unit cell contains two symmetry-independent $[(C_6H_5)_4P]^+$ cations. They show no particular interactions with the rest of the structure, so they appear to serve simply as inert counterions. Phosphorus has its usual tetrahedral environment, and the P–C distances (mean = 1.791 Å) are normal.[13] Other geometrical details are provided in the supplementary material.

Crystal packing is illustrated in Figure 3. The $[(C_6H_4Hg_2Cl_2)_2Cl]^-$ anions exist as centrosymmetrically related pairs along crystallographic axes. Anions of type **5** face each other across the inversion center at the midpoint along *b*, whereas those of type **6** occupy analogous positions along *c*. Pairs of type **6** anions are connected across the inversion center by two complementary Hg(42)···Cl(32) contacts of 3.361 (4) Å. Contacts between pairs of type **5** anions, involving Hg(22) and Cl(22), are very weak (3.998 Å). Successive pairs are interconnected by at least one rather short Hg···Cl$_t$ contact, thereby defining a continuous crown of connected $[(C_6H_4Hg_2Cl_2)_2Cl]^-$ units all around the *bc* face (Figure 3). This crown leaves a channel in the middle of the face, where half of the $[(C_6H_5)_4P]^+$ cations (those containing P(1)) are nested. Similar channels in the cell corners, down the *a* axis, are occupied by the remaining $[(C_6H_5)_4P]^+$ cations. The cations found in these channels do not lie on the *bc* face, but between $^1/_4$ and $^3/_4$ along *a*, so that they provide a separating layer between successive crowns. In the *a* direction, the structure therefore consists of alternating layers of anions and cations.

The unit cell also contains two CH_2Cl_2 solvent molecules. These occupy space near the middle of the *ab* face but seem to have no important effect on the structure of the complex anions. Although such solvates of volatile molecules are often unstable, complex **4** did not lose CH_2Cl_2 at room temperature. This may be due to the presence of moderately short contacts between the hydrogens of CH_2Cl_2 and terminal Cl$_t$ atoms of nearby anions. This undoubtedly involves some C(1)—H···Cl$_t$ hydrogen bonding, since the C(1)–Cl(11) and C(1)–Cl(22) distances (3.68 (2) and 3.77 (2) Å) are not much longer than the upper limit accepted for N—H···Cl hydrogen bonds (3.52 Å).[14] Furthermore, the C–H bonds are appropriately oriented toward the acceptor Cl$_t$ atoms, producing C(1)–H(2)–Cl(11) and C(1)–H(1)–Cl(21) angles of 142 and 152°.

Discussion

Adduct **4** is the only anionic halide complex of an organomercury compound that has been isolated and structurally characterized.[2] Despite the uniqueness of this complex, certain features of its structure are likely to have general significance. These generalizations provide tentative answers to a number of interesting questions about the coordination chemistry of bidentate Lewis acids **1**–**3** and related compounds.

For example, it is now possible to understand why bidentate acid **1** forms an isolable complex with added chloride, whereas monodentate chlorophenylmercury does not. The crystal structure of adduct **4** shows that anions **5** and **6** both use all four atoms of mercury to bind the additional chloride ion. Since Lewis acid **1** is bidentate and rigid, this strong bonding is not entropically costly. Anionic aggregates **5** and **6** are also held together by four weaker Hg···Cl$_t$ interactions. Two of these (Hg(31)···Cl(42) and Hg(42)···Cl(31) in anion **6**, for example) arise from the normal antiparallel pairing of organomercuric halides.[15] However, the other two (Hg(32)···Cl(42) and Hg(41)···Cl(31) in anion **6**) are formed at little additional entropic cost because the $C_6H_4Hg_2Cl_2$ unit is bidentate. These features may make the formation constant of adduct **4** greater than those of analogous complexes of monodentate organomercuric halides. Dichloro-1,8-naphthalenedimercury (**7**)[1a,16] may fail to form an analogous chloride complex for subtle geometrical reasons. Since the C–Hg–Cl arms in this molecule are parallel, stable C_{2h} dimers are likely to be formed by antiparallel self-association. The stability of this arrangement may prevent the coordination of added chloride, which appears to require additional sites of Lewis acidity. Even if coordination of the added chloride is strong enough to interrupt an antiparallel pair in the C_{2h} dimer, the two freed C–Hg–Cl arms would be geometrically unable to assume the orientations observed in complexes **5** and **6**. In addition, geometrical factors may also help account for the observed instability of analogous chloride complexes of diiodo-1,2-phenylenedimercury (**3**).[1a] In this case, the long Hg–I$_t$ bonds would create large Hg–Hg separations in antiparallel dimers and lead to potentially destabilizing changes in the distance Hg–Cl$_i$ and the angle Hg–Cl$_i$–Hg.

Anions **5** and **6** share the basic structural motifs **8** and **9**, which simultaneously satisfy three conditions: the primary bonds to

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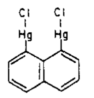

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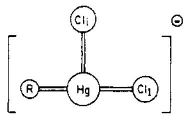
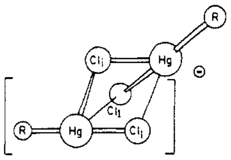


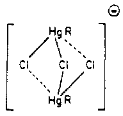
8



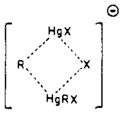
9

mercury are approximately collinear, the secondary coordinative interactions are nearly orthogonal to the primary bonds, and roughly antiparallel dimers are formed in **9** by weaker Hg···Cl$_t$ contacts (single lines). Spectroscopic studies have already suggested that the fugitive 1:1 complexes of monodentate organomercuric halides with additional halide adopt structures like **8**.[17] Our crystallographic results reinforce this hypothesis and indicate that 2:1 complexes of monodentate organomercuric halides with additional halide may favor structure **9**.

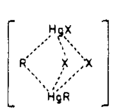
This geometrical information is particularly important for the following reason: structures analogous to **9** = **9** are closely related to the transition states involved in the well-known redistribution reactions of organomercuric halides (eq 1).[9,18] For similar redistributions, Hughes and Ingold have favored a transition state like structure **10**, with one bridging halide,[18c] whereas Jensen and Rickborn have suggested that a doubly bridged transition state (**11**) is involved.[18b] Structural analogies could not previously be used to support either of these hypotheses, since related anionic complexes of organomercury compounds were unknown. However, the close formal similarity of structures **11** and **9** = **9′** now reinforces the proposal of Jensen and Rickborn.



9′



10

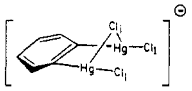


11

$$2\,RHgX + X^{\ominus} \rightleftharpoons R_2Hg + HgX_3^{\ominus} \qquad (1)$$

Decomposition of adduct **4** via redistribution reactions may be kinetically unfavorable, since formation of transition state **11** from anions **5** or **6** would require significant changes in the binding of the additional chloride by the bidentate $C_6H_4Hg_2Cl_2$ units. Strong bonding of the additional chloride may therefore stabilize adduct **4** kinetically as well as thermodynamically, by preventing it from readily attaining the geometry required for subsequent redistribution reactions.

Although we isolate 2:1 complex **4**, spectroscopic studies indicate that a 1:1 complex is preferred in solution.[1a] Complex **12** corresponds to this stoichiometry and is also a fundamental structural motif in anions **5** and **6**. As expected, the primary bonds to mercury in this unit are approximately collinear, and the secondary coordinative interactions are nearly orthogonal to the primary bonds. We therefore propose that the 1:1 complex adopts structure **12** in solution.



12

Dichloro-1,2-phenylenedimercury (**1**) also forms isolable 2:1 adducts with tetraphenylphosphonium bromide and iodide.[1a] Since Raman and far-infrared spectroscopy indicate that the $C_6H_4Hg_2Cl_2$ units remain intact in these adducts,[1c] their crystal structures are probably similar to those of anions **5** or **6** (a and b, Figure 1), with Cl(1) or Cl(2) replaced by Br or I. It is interesting that a single tetradentate aggregate, formed by the antiparallel dimerization of two $C_6H_4Hg_2Cl_2$ molecules, can accommodate such a wide range of anionic substrates. The structural differences between anions **5** and **6** show that the $[(C_6H_4Hg_2Cl_2)_2Cl]^-$ unit can in fact accept substantial distortions without breaking apart, by trading Hg···Cl$_t$ contact interactions for stronger Hg–Cl$_i$ bonding. Similar distortions presumably permit the formation of $[(C_6H_4Hg_2Cl_2)Br]^-$ and $[(C_6H_4Hg_2Cl_2)I]^-$ as stable aggregates.

We are eager to use this structural flexibility and our detailed knowledge of the bonding in complex **4** to build macrocyclic, multidentate Lewis acids from 1,2-phenylenedimercury units.

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Supplementary Material Available: Tables of refined coordinates and equivalent temperature factors of the non-hydrogen atoms (Table II), anisotropic temperature factors of non-hydrogen atoms (Table III), fixed coordinates of the hydrogen atoms (Table IV), weighted least-squares plane calculations (Table V), geometry of the tetraphenylphosphonium ions (Table VI), geometry of the rings in the $[(C_6H_4Hg_2Cl_2)_2Cl]^-$ ions (Table VII), observed and calculated structure-factor amplitudes (Table VIII) (64 pages). Ordering information is given on any current masthead page.

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