Multidentate Lewis Acids. Crystal Structure of the 1:1 Complex of Dichloro-1,2-phenylenedimercury with Dimethylformamide

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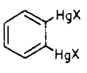
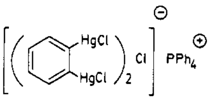
The 1:1 complex was obtained by slow recrystallization of dichloro-1,2-phenylenedimercury from dimethylformamide. The crystals are monoclinic, space group $P2_1/c$, with a = 9.275 (6) Å, b = 16.086 (6) Å, c = 8.634 (9) Å, β = 91.02 (6)°, and Z = 4. The structure was refined on 1583 nonzero Mo K$\bar{\alpha}$ reflections collected at 175 K to R = 0.040. The unit cell contains discrete 1:1 molecules. The oxygen-bonded dimethylformamide bridges the two Hg atoms of the dichloro-1,2-phenylenedimercury molecule. The bound dimethylformamide is planar and lies perpendicular to the aromatic ring, close to the approximate mirror plane bisecting the ring. The oxygen donor lies above the plane containing the two –Hg–Cl substituents, and the Hg···O distances (2.777 (13) and 2.681 (13) Å) correspond to moderately strong secondary bonds with the metal. The structure is stabilized by a number of intermolecular Hg···Cl contacts.

We are interested in designing multidentate Lewis acids that can recognize, bind, and activate particular molecules by interacting with their basic sites.[1-3] For example, bidentate Lewis acids like dichloro-1,2-phenylenedimercury (1)[1a,c] form complexes with halides. Compound 1 reacts with tetraphenylphosphonium chloride to give a 2:1 complex 3 in which the added chloride forms strong bonds to all four atoms of mercury. In addition, related compounds like bidentate trifluoroacetate 2 can be used to promote the reductive desulfurization of reactive thioketones.[1b] Spectroscopic evidence suggests that the first step in these reductions is complexation and activation of the thioketone by the bidentate Lewis acid. This step presumably involves binding of the sulfur atom of the thioketone to both mercury atoms of the receptor. Unfortunately, this hypothesis has not yet been confirmed directly by X-ray crystallography, since the high reactivity of the complexes makes them difficult to isolate and crystallize. However, we have successfully studied a related complex, the 1:1 adduct 4 of dichloro-1,2-phenylenedimercury with dimethylformamide. The structure of this complex is described below.



1 (X=Cl)

2 (X=OOCCF$_3$)



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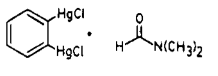

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Experimental Section

Crystal Data. $C_9H_{11}Cl_2Hg_2NO$: fw 621.28, monoclinic, $P2_1/c$, a = 9.275 (6) Å, b = 16.086 (6) Å, c = 8.634 (9) Å, β = 91.02 (6)°, V = 1288.0 Å^3, Z = 4, D_{calcd} = 3.203 g cm^{-3}, λ(Mo K$\bar{\alpha}$) = 0.71069 Å (graphite monochromator), μ(Mo Kα) = 241.9 cm^{-1}, T = 175 K.

Table I. Refined Coordinates of the Non-Hydrogen Atoms (×10^4; Hg × 10^5) and Equivalent Temperature Factors (×10^3)

atom	x	y	z	U_{eq}, Å^2
Hg1	1916 (7)	21504 (4)	27425 (8)	26
Hg2	–1359 (7)	–1067 (4)	24126 (7)	22
Cl1	1835 (5)	2991 (3)	1455 (6)	38
Cl2	995 (5)	–1006 (3)	673 (5)	31
C1	–1325 (16)	1475 (10)	3889 (18)	22
C2	–1397 (17)	588 (12)	3836 (17)	24
C3	–2458 (19)	185 (11)	4757 (19)	28
C4	–3366 (19)	623 (12)	5627 (18)	30
C5	–3282 (21)	1481 (12)	5677 (21)	38
C6	–2298 (19)	1890 (11)	4846 (22)	33
O10	2153 (15)	895 (8)	2119 (16)	41
N10	4158 (16)	1125 (10)	732 (19)	36
C10	2791 (20)	943 (12)	853 (22)	35
C11	4784 (23)	1223 (15)	–787 (24)	48
C12	4994 (24)	1349 (16)	2126 (30)	62

Crystallographic Measurements and Structure Resolution. Crystals of complex 4 suitable for X-ray work were obtained by slow crystallization of dichloride 1 from dimethylformamide. The specimen used had the following distances (mm) between the indicated pairs of faces: 0.28 (010–0$\bar{1}$0) × 0.26 (101–$\bar{1}$0$\bar{1}$) × 0.49 (10$\bar{1}$–$\bar{1}$01). It was sealed in a capillary and mounted on an Enraf-Nonius CAD4 diffractometer. A set of 25 reflections randomly distributed in reciprocal space was centered in the counter aperture. Indexation yielded the reduced cell, which was checked by means of oscillation photographs taken along the three axes. These photographs showed the expected layer–line spacings. A mirror plane was observed for oscillation along the 16.086-Å axis, identifying this direction as the unique axis of a monoclinic cell. The Niggli matrix unambiguously indicated that no higher symmetry was present. The initial cell edges were interchanged to define the conventional monoclinic cell described above.

The intensity data were collected following the procedure described elsewhere[4]. The peaks were integrated by the ω–2θ scan technique at a constant speed of 1.67° min^{-1}. Seven standard reflections checked every hour showed random fluctuations of ±3% about their respective means during the experiment. A set of 2353 independent Mo K$\bar{\alpha}$ reflections (hkl and $hk\bar{l}$, 2$\theta \leq$ 50°) was collected at 175 K. Inspection of these data revealed two conditions of systematic absence ($0k0$, $k \neq 2n$, $h0l$, $l \neq 2n$) consistent only with space group $P2_1/c$. The 98 systematically absent reflections were rejected, leaving a data set of 2255 independent reflections, of which 1583 ($I > 4\sigma(I)$) were retained for structure determination. These measurements were corrected for the Lorentz effect, polarization, and absorption (Gaussian integration, transmission range = 0.0044–0.0419).

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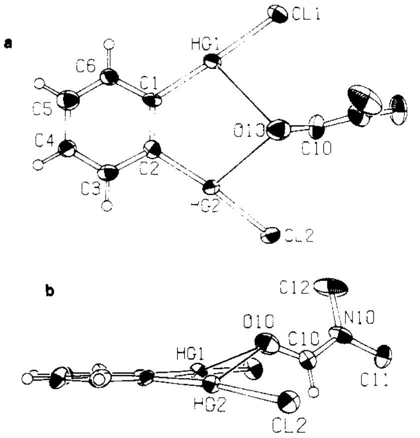

Figure 1. (a) View of the 1:1 complex of dichloro-1,2-phenylenedimercury with dimethylformamide with the aromatic ring in the plane of the figure and (b) a view perpendicular to this plane. The ellipsoids correspond to 50% probability. Hydrogens are shown as spheres of arbitrary size. The hydrogens of the C11 and C12 methyl groups were not located.

The structure was solved by the heavy-atom method and refined on $|F_o|$ by full-matrix least-squares procedures. The two independent Hg atoms were located from a Patterson map. The remaining non-hydrogen atoms were found by standard structure factor and difference Fourier (ΔF) map calculations. Isotropic refinement of the non-hydrogen atoms converged to $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.074$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} = 0.082$. These atoms were then refined anisotropically. Hydrogen atoms of the formyl group and the aromatic ring were fixed at idealized positions (C–H = 0.95 Å; B = 3.0 Å^2). Those of the methyl groups were not visible in the ΔF map. The hydrogen parameters were not refined, but the coordinates were recalculated after each cycle of refinement. Anisotropic refinement converged to $R = 0.040$ and $R_w = 0.048$. The goodness-of-fit ratio was 1.54 for 136 parameters varied. The final ΔF map was essentially featureless, with a general background below ±0.8 e Å^{-3} and several peaks in the range $\pm|1.0–1.8|$ e Å^{-3} within 1.1 Å from Hg or Cl. The refined coordinates are listed in Table I. . The scattering curves were from standard sources.[5] The contributions of Hg and Cl to anomalous dispersion[6] were included in structure factor calculations.

Description of the Structure

The complex (parts a and b of Figure 1) has an approximate plane of symmetry that bisects the aromatic ring and includes the non-hydrogen atoms of the bound dimethylformamide. Binding involves interactions of the oxygen atom of the amide with both mercury atoms of dichloro-1,2-phenylenedimercury. The two mercury–oxygen distances (2.777 (13) and 2.681 (13) Å; Table II) are very similar and are comparable to those found in complexes of inorganic mercuric halides with amides.[3b,7] Since the van der Waals radii of oxygen and mercury are approximately 1.40 and 1.5–1.73 Å[8,9] respectively, the mercury–oxygen interactions in complex 4 are moderately strong.

Table II. Interatomic Distances and Bond Angles

Distances (Å)

Hg1–Cl1	2.334 (5)	C2–C3	1.43 (2)
Hg1–C1	2.047 (16)	C3–C4	1.34 (2)
Hg2–Cl2	2.346 (4)	C4–C5	1.38 (3)
Hg2–C2	2.044 (16)	C5–C6	1.34 (3)
Hg1–O10	2.777 (13)	C6–C1	1.40 (2)
Hg2–O10	2.681 (13)	C10–O10	1.26 (2)
Hg1–Cl2^a	3.454 (4)	C10–N10	1.31 (2)
Hg2–Cl2^b	3.296 (4)	N10–C11	1.45 (3)
C1–C2	1.43 (2)	N10–C12	1.46 (3)

Angles (deg)

C1–Hg1–Cl1	176.6 (4)	Cl1–Hg1–Cl2^a	84.6 (1)
C2–Hg2–Cl2	171.5 (5)	C1–Hg1–Cl2^a	92.1 (4)
C1–Hg1–O10	99.6 (5)	Cl2–Hg2–Cl2^a	85.5 (1)
Cl1–Hg1–O10	83.9 (3)	C2–Hg2–Cl2^a	93.2 (5)
C2–Hg2–O10	101.0 (5)	Hg2–Cl2^a–Hg2^a	94.5 (1)
Cl2–Hg2–O10	86.9 (3)	Hg1–Cl2^a–Hg2^a	97.3 (1)
Hg1–O10–Hg2	84.0 (4)	Hg1–C1–C2	123.1 (12)
Hg1–O10–C10	116.4 (12)	Hg1–C1–C6	119.1 (12)
Hg2–O10–C10	120.4 (12)	Hg2–C2–C1	122.6 (12)
O10–C10–N10	123.8 (17)	Hg2–C2–C3	119.5 (12)
C10–N10–C11	120.0 (16)	C2–C3–C4	121.3 (16)
C10–N10–C12	119.3 (17)	C3–C4–C5	120.5 (17)
C11–N10–C12	120.1 (17)	C4–C5–C6	120.7 (17)
C2–C1–C6	117.6 (15)	C5–C6–C1	122.1 (17)
C1–C2–C3	117.8 (15)		

^{a} $-x$, $1/2 + y$, $1/2 - z$. ^{b} $-x$, $-y$, $-z$.

Strong complexation should create geometrical and electronic differences between bound and unbound dimethylformamide. We expected the carbon–nitrogen bond in complex 4 to become shorter and the carbon–oxygen bond to become longer. Our results do not disagree with this prediction, since the C–O and C–N distances in complex 4 are 1.26 (2) and 1.31 (2) Å, respectively, whereas they are 1.24 (1) and 1.35 (2) Å for uncomplexed dimethylformamide in the liquid phase.[10] However, the variations are significant only at the $\sim 1\sigma$ level. In general, complexes of dimethylformamide with one or two simple metal cations have structures only slightly different from those of dimethylformamide trapped in the crystal lattices of solvates (Table III, supplementary material). Our X-ray results are similar and therefore do not provide unambiguous evidence for changes in bond orders.

Vibrational spectra are often more sensitive to these changes. Strengthening of the carbon–nitrogen bond and weakening of the carbon–oxygen bond help explain why the amide band at 1670 cm^{-1} in the infrared spectrum of dimethylformamide (neat liquid) shifts to 1655 cm^{-1} in the spectrum of complex 4 (KBr). Although the binding is moderately strong, irreversible decomplexation occurs slowly at room temperature when complex 4 is left in open air and faster when it is exposed to high vacuum. Under these conditions, transparent crystals of complex 4 are reduced to a white powder consisting of pure dichloro-1,2-phenylenedimercury (1). For this reason, the crystal selected for X-ray study was sealed in a capillary and intensities were measured at 175 K.

The particular orientation of bound dimethylformamide and dichloride 1 shown in parts a and b of Figure 1 min-

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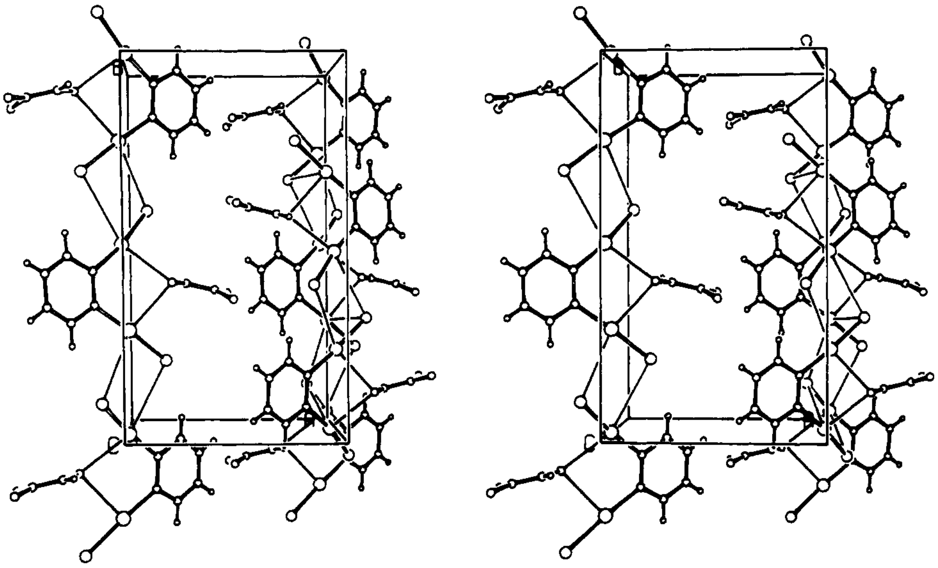

Figure 2. Stereoview of the unit cell down the *c* axis. The atoms are represented by spheres of arbitrary size (large for Hg, medium for Cl, and small for non-hydrogen atoms). Single lines correspond to Hg···O bonds and Hg···Cl contacts.

imizes interaction of the dimethylamino group with the bidentate Lewis acid and is presumably favored for steric reasons. Dimethylformamide bridges two sodium atoms in a similar way in the 2:1 complex with $NaClO_4$.[12] Attempts to prepare a complex of dichloride 1 with 1,1,3,3-tetramethylurea have failed, probably because interaction of a dimethylamino group with the bidentate Lewis acid is unavoidable.

The structure of the complex shown in parts a and b of Figure 1 obeys two general trends in the coordination chemistry of Hg(II), which are followed particularly closely 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 in complex 4 forms strong bonds to carbon and chlorine only. The mercury–carbon distances (2.047 (16) and 2.044 (16) Å) are similar to those found in other arylmercury compounds.[9] The lengths of the mercury–chlorine bonds (2.334 (5) and 2.346 (4) Å) are comparable to those found in other organomercury chlorides[9] and various complexes containing discrete $HgCl_2$ units.[7,8,13] The coordination is not perfectly linear (C–Hg–Cl = 176.6 (4) and 171.5 (5)°) but very far from the 120° value expected for normal three-coordinate geometry. Furthermore, the small departure from linearity does not appear to be a direct response to binding with the oxygen atom of dimethylformamide, since the mercury–chlorine bonds are not displaced in the planes defined by the atoms C–Hg–O. This is clearly illustrated in Figure 1b, which shows that interaction with dimethylformamide leaves the $C_6H_4Hg_2Cl_2$ units approximately planar. The distances to the plane of the aromatic ring are significant, but small, for Hg1 (−0.0876 (7) Å) and Cl1 (−0.148 (5) Å). They correspond to a displacement of the C1–Hg1–Cl1 arm as a whole by 2° toward the dimethylformamide molecule. The distances are greater for Hg2 (0.1180 (6) Å) and Cl2 (0.500 (4) Å), and these atoms lie on the opposite side of the plane. The C2–Hg2 and Hg2–Cl2 bonds make angles of 3° and 6°, respectively, with the plane. These unequal values suggest that pressure, probably arising from packing forces, acts on the terminal Cl2 atom and not only displaces the C2–Hg2–Cl2 arm from the plane but also introduces a small out-of-plane contribution of ~3° to the nonlinearity about Hg2. In conclusion, binding of dimethylformamide *above* the plane of the molecule results in displacement of the terminal mercury–chlorine bonds by less than 9°, most of which occurs *in* the molecular plane. The geometrical consequences of binding dimethylformamide are therefore very similar to those of binding chloride.[1a]

The residual acidity of mercury is also expressed in the packing pattern shown in Figure 2. As in chloride complex 3, intermolecular Hg···Cl interactions are present throughout the unit cell and typically involve antiparallel pairing of the Hg–Cl arms via two complementary Hg···Cl contacts. Pairing is obvious in the repetition pattern along the *b* axis. The flat molecules are approximately coplanar, and their Hg–Cl arms, roughly perpendicular to the propagation direction, are directed alternately inside and outside the unit cell. This orientation allows antiparallel pairing to take place, and two complementary Hg···Cl contacts are formed within any pair of successive molecules. However, these contacts are rather long (Hg1–Cl2 = 3.454 (4) Å, Hg2–Cl1 = 3.586 (5) Å). The resulting infinite ribbons, repeated in the *c* direction, define layers in the *bc* plane. Cohesion between the ribbons again involves Hg···Cl contacts, which are on the average shorter than those within the ribbons. One ribbon is shifted by ~*b*/4 with respect to the next, which allows a Hg2–Cl2 arm in one to interact with a symmetry-equivalent Hg2–Cl2 arm in another, forming a pair across the corner of the unit cell and leading to two equivalent Hg2–Cl2 contacts of 3.296 (4) Å. This arrangement does not permit the Hg1–Cl1 arm to find an antiparallel partner in a nearby ribbon, but a single Hg1···Cl1 contact of 3.532 (5) Å is established.

The dimethylformamide molecules occupy the interlayer region at $x \sim {}^1/_2$. They are paired in van der Waals contacts across inversion centers. One such pair is shown in Figure 2 in the middle of the unit cell. In order to avoid abnormally short contacts, the dimethylamino groups are displaced in opposite directions. This probably explains why dimethylformamide is not found exactly on the approximate mirror plane bisecting the aromatic ring, where it would be expected to lie in an isolated molecule of the complex.

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Comparison of complex 4 with the 1:1 adduct of dimethylformamide and the tridentate Lewis acid tris(chloromercury)acetaldehyde (**5**)[3b] is very informative.

$(ClHg)_3C-CHO$
5

This complex incorporates only two mercury-oxygen interactions with dimethylformamide that are shorter than the sum of their van der Waals radii. One is moderately strong (2.75 (5) Å) and comparable to the bonds in complex 4, but the other is quite weak (3.03 (6) Å). We believe that the symmetrical, cooperative binding of dimethylformamide by dichloro-1,2-phenylenedimercury (1) results from a particularly favorable orientation of the two sites of Lewis acidity. Cooperative binding requires that the complexed oxygen atom be approximately 2.6-2.7 Å from each mercury atom. At the same time, each mercury-oxygen bond should be perpendicular to the primary bonds of the mercury atom. Dichloro-1,2-phenylenedimercury (1) can satisfy these two conditions simultaneously, but tris(chloromercury)acetaldehyde (**5**) cannot unless the oxygen atom lies close to the plane defined by the atoms Hg-C-Hg. This indicates that bidentate and multidentate Lewis acids derived from 1,2-phenylenedimercury are particularly promising reagents for the binding and activation of carbonyl compounds and related substrates.

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Registry No. 1, 35099-05-9; 4, 105253-41-6; dimethyl formamide, 68-12-2.

Supplementary Material Available: Tables of mean interatomic distances and bond angles in free and bound dimethylformamide, anisotropic temperature factors, idealized coordinates of the hydrogen atoms, distances to the weighted least-squares planes, and geometry of dimethylformamide in crystal structures (11 pages); a listing of structure factor amplitudes (9 pages). Ordering information is given on any current masthead page.

Polar Substituent Effects on NMR Chemical Shifts of Group 14 Elements: Synthesis and NMR (^{13}C, ^{29}Si, ^{119}Sn, and ^{207}Pb) Substituent Chemical Shifts (SCS) of 4-Substituted Bicyclo[2.2.2]oct-1-ylbutanes, -trimethylsilanes, -trimethylstannanes, and -trimethylplumbanes ($M(CH_3)_3$, M = C, Si, Sn, and Pb) and 4-Substituted Bicyclo[2.2.1]hept-1-yltrimethylstannanes[1]

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An extensive series of 4-substituted bicyclo[2.2.2]oct-1-yltrimethylstannanes (**2a**) and 4-substituted bicyclo[2.2.1]hept-1-yltrimethylstannanes (**3a**) has been synthesized and characterized and the ^{119}Sn chemical shifts measured. A remarkably wide range of substituent chemical shifts (SCS; ca. 20 ppm) are obtained for system **2a**, and these have been analyzed in terms of possible substituent-probe interactions. Comparisons have been made between systems **2a** and **3a**, but the signs of the ^{119}Sn substituent chemical shifts (SCS) for the two systems are diametrically opposed, indicating a different blend of "through-space" and "through-bond" effects. Some 4-substituted 1-*tert*-butylbicyclo[2.2.2]octanes (**2b**) as well as more restricted series of trimethylsilanes and trimethylplumbanes (**2c** and **2d**, respectively) have also been acquired and their ^{13}C, ^{29}Si, and ^{207}Pb SCS measured and compared with those of the stannane series. Synthetic approaches that provide efficient access to some 1,4-disubstituted bicyclo[2.2.2]octyl systems are outlined.

Introduction

Organic derivatives of the group 14 elements (silicon, germanium, tin, and lead) have featured prominently in studies of periodicity, and much effort has been devoted to comparisons of spectra, reactivity, etc. In this regard, nuclear magnetic resonance studies, generally utilizing ^{1}H or ^{13}C nuclei, have provided considerable, if at times conflicting, insights into molecular characteristics and the types of effects that groups incorporating these elements may exert. The increasing ease of acquiring NMR spectra of the group 14 nuclei themselves, i.e., ^{29}Si, ^{119}Sn, and ^{207}Pb in particular, and the recognition that these nuclei respond fairly sensitively to changing molecular characteristics, have resulted in a blossoming interest in such spectra.[2-5]

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