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(Bromodichloromethyl)phenylmercury

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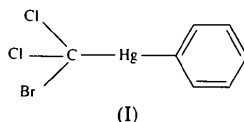
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Abstract

[Hg(C₆H₅)(CBrCl₂)] exists as a dimer in the solid state through weak Lewis acid–base interactions between the mercury centers and the halogen atoms. However, these interactions are too weak to significantly perturb the C—Hg—C angles [178.3 (6) and 179.5 (6)°].

Comment

Relatively few organomercury compounds have been characterized to date. Furthermore, most of the examples reported in the literature are Lewis base adducts rather than free compounds. Though it is only of moderate thermal stability, (bromodichloromethyl)phenylmercury, (I), crystallizes easily even in the absence of a Lewis base. Interestingly, even in this case the mercury center still possesses weak Lewis acid character in the solid state. This acidic nature of the metal center results in the formation of a dimer *via* mercury–halogen interactions.



As expected for a mercury(II) center bound by two ligands, the coordination geometry is approximately linear with C—Hg—C angles of 178.3 (6) and 179.5 (6)°. The observed intramolecular bond distances are consistent with those previously reported. The Hg—C(phenyl) bond distances are 2.048 (15) and 2.046 (14) Å, compared with 2.096 (16) Å in (C₆F₄H)₂Hg (Brown, Massey & Wickens, 1980) and 2.062 Å (average) in (C₆H₄)(HgCl)₂·[Ph₄P]Cl (Beauchamp, Oliver, Wuest & Zcharie, 1986). The Hg—C(alkyl) distances are 2.136 (15) and 2.12 (2) Å *versus* 2.110 (10) and 2.121 (14) Å, respectively, in (C₆H₅)C(HgCl)₂C(OCH₃)₂(C₆H₅) (Bassetti & Bocelli, 1990), 2.067 (22) and 2.042 (23) Å in [Ph₄P]Cl·Hg(CF₃)₂ (Korpar-Colig, Popovic, Bruvo & Vickovic, 1988), and 2.10 (6) Å in 2-(chloromercurio)-3-acetoxycyclo[2.2.1]heptane (Halfpenny, Small & Thorpe, 1978).

The two independent Hg atoms make intermolecular contacts with a halide atom on the adjacent molecule

forming a loose halogen-bridged dimer in the solid state. The six-membered ring formed by these interactions adopts a chair-like conformation with the phenyl rings occupying equatorial positions. These weak bridging distances are 3.468 (3) Å (Hg1···X22) and 3.516 (4) Å (Hg2···X11). These distances are significantly longer than those found in [Ph₄P]Cl·Hg(CF₃)₂ [2.823 (3) and 2.837 (4) Å] (Korpar-Colig, Popovic, Bruvo & Vickovic, 1988) but comparable with the longest contacts found in (C₆H₄)(HgCl)₂·[Ph₄P]Cl [3.266 (4)–3.591 (5) Å] (Beauchamp, Oliver, Wuest & Zcharie, 1986). Furthermore, these contacts are about the same length as the sum of the van der Waals radii for Hg and Cl (3.4 Å) and approximately 0.1 Å shorter than that of Hg and Br (3.6 Å) (Huheey, 1983).

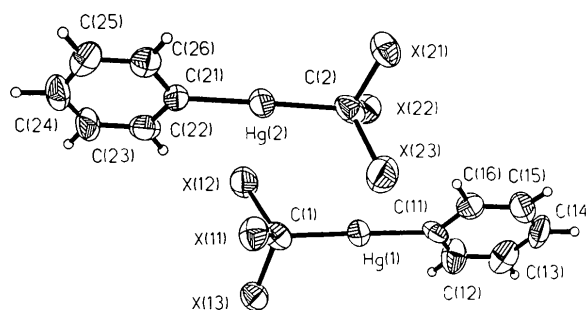


Fig. 1. View of the two independent [Hg(C₆H₅)(CBrCl₂)] molecules showing the labelling of the non-H atoms and the intermolecular mercury–halogen interactions. Displacement ellipsoids are shown at 50% probability levels; H atoms are drawn as small circles of arbitrary radii.

Experimental

The title compound was obtained as described by Seyferth and co-workers (Seyferth, Jula, Hadwig & Pereyre, 1967; Seyferth & Lambert, 1969).

Crystal data

[Hg(C₆H₅)(CBrCl₂)]
M_r = 440.51
 Monoclinic
*P*2₁/*c*
a = 9.426 (2) Å
b = 17.744 (4) Å
c = 12.137 (2) Å
 β = 102.04 (3)°
V = 1985.3 (7) Å³
Z = 8
D_x = 2.948 Mg m⁻³

Mo *K*α radiation
 λ = 0.71073 Å
 Cell parameters from 25 reflections
 θ = 6.93–16.55°
 μ = 20.003 mm⁻¹
T = 293 (2) K
 Needle
 0.4 × 0.1 × 0.1 mm
 Colorless

Data collection

Rigaku AFC-5S diffractometer

*R*_{int} = 0.0475
 θ_{\max} = 25°

ω scans $h = 0 \rightarrow 10$
 Absorption correction: $k = 0 \rightarrow 21$
 ψ scan $l = -14 \rightarrow 14$
 $T_{\min} = 0.7679$, $T_{\max} = 1.000$
 3677 measured reflections 3 standard reflections
 3452 independent reflections monitored every 150
 1988 observed reflections reflections
 $[I > 2\sigma(I)]$ intensity decay: 10.9%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.0467$
 $wR(F^2) = 0.0738$
 $S = 1.099$
 3436 reflections
 206 parameters
 H atoms calculated with riding model
 $w = 1/\sigma^2(F_o^2)$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.893 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -1.186 \text{ e } \text{\AA}^{-3}$

Extinction correction:
SHELXL93 (Sheldrick, 1993)

Extinction coefficient:
 $4.2(6) \times 10^{-7}$

Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

C13—C14	1.40 (2)	C23—C24	1.34 (2)
C14—C15	1.35 (2)	C24—C25	1.38 (2)
C15—C16	1.38 (2)	C25—C26	1.36 (2)
C11—Hg1—C1	178.3 (6)	C21—Hg2—C2	179.5 (6)
X11—C1—X13	107.5 (7)	X21—C2—X22	107.8 (7)
X11—C1—X12	105.3 (8)	X21—C2—X23	106.0 (7)
X13—C1—X12	107.8 (7)	X22—C2—X23	108.3 (8)
X11—C1—Hg1	111.8 (7)	X21—C2—Hg2	110.3 (8)
X13—C1—Hg1	109.7 (7)	X22—C2—Hg2	110.6 (6)
X12—C1—Hg1	114.4 (6)	X23—C2—Hg2	113.7 (7)
C12—C11—C16	117.9 (15)	C26—C21—C22	117.1 (14)
C12—C11—Hg1	120.2 (12)	C26—C21—Hg2	122.9 (12)
C16—C11—Hg1	121.9 (12)	C22—C21—Hg2	120.0 (12)
C11—C12—C13	121.4 (16)	C23—C22—C21	119.8 (16)
C12—C13—C14	120.9 (17)	C24—C23—C22	121.5 (16)
C15—C14—C13	117.5 (16)	C23—C24—C25	120.8 (16)
C14—C15—C16	120.6 (16)	C26—C25—C24	118.1 (16)
C15—C16—C11	121.6 (15)	C25—C26—C21	122.7 (15)

During the structure refinement, it was found that the Cl and Br atoms were distributed over the halogen-atom positions of each molecule. This disorder problem was modeled by creating a composite atom of Cl and Br. The Br population was refined so that its total contribution for all three sites on each methyl group summed to 1. The Cl population at each site was then set equal to one minus the Br population. The refinement converged with the Br atoms showing an unsymmetrical distribution. For the methyl group centered at C1, the bromine populations at X11, X12 and X13 were 0.21, 0.49 and 0.30, respectively, while the corresponding values for X21, X22 and X23 were 0.18, 0.35 and 0.47, respectively. The chemical composition was verified by mass spectrometry. The parent ion displayed an isotopic distribution that agreed with that calculated for the formula C₇H₅BrCl₂Hg. Because of this disorder problem, the composite halogen atoms are represented by the symbol *X* in the tables.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *SHELXTL/PC* (Sheldrick, 1990b). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990a). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *SHELXTL/PC*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: MD1001). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)

The halogen atoms were disordered and modeled as composite atoms of Br and Cl. The Br and Cl compositions were constrained to equal 1 at each location and the total Br occupancy for all three halogen sites on an individual methyl group was constrained to also sum to unity. The Br occupancies at each site refined to the following values: X11, 21; X12, 49; X13, 30; X21, 18; X22, 35; X23, 47%. $U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$

	x	y	z	U_{eq}
Hg1	0.04942 (7)	0.59406 (3)	0.17142 (5)	0.0452 (2)
X11	-0.1667 (4)	0.4944 (2)	0.2942 (2)	0.0614 (14)
X12	-0.2892 (3)	0.53229 (14)	0.0567 (2)	0.0750 (12)
X13	-0.0459 (3)	0.41908 (15)	0.1166 (2)	0.0573 (11)
C1	-0.1147 (17)	0.5097 (8)	0.1597 (11)	0.050 (4)
C11	0.2105 (16)	0.6727 (8)	0.1808 (12)	0.044 (4)
C12	0.3073 (19)	0.6669 (10)	0.1142 (13)	0.068 (5)
C13	0.4178 (18)	0.7182 (11)	0.1202 (13)	0.065 (5)
C14	0.4310 (18)	0.7794 (10)	0.1941 (14)	0.067 (5)
C15	0.3350 (19)	0.7841 (9)	0.2629 (14)	0.065 (5)
C16	0.2232 (17)	0.7332 (9)	0.2538 (12)	0.055 (4)
Hg2	-0.38088 (7)	0.63560 (3)	0.38131 (5)	0.0492 (2)
X21	-0.2401 (4)	0.7988 (2)	0.4525 (2)	0.0615 (14)
X22	-0.1753 (3)	0.7313 (2)	0.2457 (2)	0.0579 (11)
X23	-0.0292 (3)	0.6745 (2)	0.4765 (2)	0.0795 (12)
C2	-0.2042 (17)	0.7106 (8)	0.3891 (11)	0.056 (4)
C21	-0.5509 (16)	0.5627 (8)	0.3728 (13)	0.048 (4)
C22	-0.5674 (17)	0.5021 (8)	0.2981 (12)	0.059 (5)
C23	-0.6814 (18)	0.4530 (9)	0.2933 (14)	0.060 (5)
C24	-0.7775 (19)	0.4617 (9)	0.3592 (14)	0.059 (5)
C25	-0.7681 (17)	0.5221 (10)	0.4321 (12)	0.060 (5)
C26	-0.6560 (17)	0.5715 (9)	0.4368 (11)	0.050 (4)

Table 2. Selected geometric parameters (\AA , $^\circ$)

Hg1—C11	2.048 (15)	Hg2—C21	2.046 (14)
Hg1—C1	2.136 (15)	Hg2—C2	2.12 (2)
X11—C1	1.820 (13)	X21—C2	1.808 (14)
X12—C1	1.890 (15)	X22—C2	1.855 (15)
X13—C1	1.849 (14)	X23—C2	1.878 (14)
C11—C12	1.34 (2)	C21—C26	1.39 (2)
C11—C16	1.38 (2)	C21—C22	1.39 (2)
C12—C13	1.37 (2)	C22—C23	1.38 (2)

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Di(aqua)bis[(η^5 -cyclopentadienyl)tris-(dimethylphosphito-*P*)cobalt-*O, O', O''*]-lanthanum(III) Chloride

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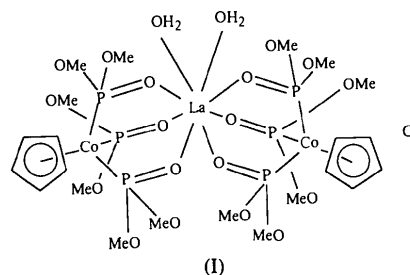
Abstract

The La atom in the title compound, diaqua- $1\kappa^2$ O-bis[2,3(η^5 -cyclopentadienyl)]hexakis(μ -dimethyl phosphito)- $1\kappa^3$ O:2 κ^3 P;1 κ^3 O:3 κ^3 P-dicobaltlanthanum chloride, [Co₂La(C₂H₆O₃P)₆(C₅H₅)₂(H₂O)₂]Cl, is eight-coordinate. The coordination polyhedron around the La atom is nearly a square antiprism, consisting of eight O atoms contributed by two tripodal Co-complex ligands and two water molecules.

Comment

Transition metal complexes containing the O-donor tripodal ligands L_{OR} [$L_{OR} = (C_5H_5)Co[P(O)(OR)_2]_3$, $R = CH_3, C_2H_5$] have been studied widely (Klaui, 1990). Cyclopentadienyl(aqua)-metal complexes of the type [CpM(H₂O)₃]²⁺ ($M = Cr, Co, Rh, Ru$) have been characterized (Spreer & Shar, 1981; Kolle & Fuss, 1984; Kolle & Klaui, 1991). We report here the crystal

structure of the title compound, (I). To our knowledge this structure is the first characterized of an aqua complex of an early lanthanide metal with such a tripodal ligand.



The coordination polyhedron around the La atom is nearly a square antiprism, consisting of O1, O2, O3, O4, O5 and O6 contributed by two tripodal groups, and OW and OW2 from two water molecules. One square face (O3, O4, OW2, O5) is nearly planar with no atom displaced by more than 0.044 (5) Å from its mean plane; another (O1, O2, OW1, O6) is almost planar, within 0.115 (5) Å of its mean plane [folded quadrilateral angle about O2...O6 168 (1)°]. The La atom is displaced from the plane of O3, O4, OW2 and O5 by 1.327 (2) Å. The angles of the square corners in the square faces are in the range 85.9 (1)–90.0 (2)° and the lengths of the square edges range from 2.843 (6) to 3.147 (6) Å. The twist angle of the square planes is 45 (3)°, which is the mean rotational angle of a square plane from eclipsed square planes (Wilson, 1992).

The average distance (Wilson, 1992) from the La atom to tripodal O atoms is 2.48 (2) Å, which is similar to the distance from the La atom to the phosphine oxide [2.422 (12) or 2.456 (11) Å] in [La{S₂P(OEt)₂}₃(OPPh₃)₂] (Pinkerton & Schwarzenbach, 1977). The distances La—OW1 and La—OW2 are 2.651 (5) and 2.619 (5) Å, respectively, which are longer than the La—O(water) distances in La(OH₂)₆(ClO₄)₃ (2.48 (3) Å; Glaser & Johansson, 1981), and similar to those in La(acac)₃(OH₂)₂ (2.56, 2.58 Å; Phillips, Sands & Wagner, 1968). Hydrogen bonding occurs between the Cl ion and H atoms of the coordinated water molecules [Cl...H1W(1-x, 1/2+y, 3/2-z) 2.20, Cl...H4W(1-x, y+1/2, 3/2-z) 2.14 Å]. The bond distances between P and O atoms attached to the La atom [average P—O 1.49 (1) Å] are shorter than the bond distances between P and O atoms attached to the methyl group [average P—O 1.59 (3) Å]. These distances are slightly longer than the average P=O distance, 1.46 (5) Å (Corbridge, 1992), in a variety of tetrahedral phosphate compounds, and lie in the range between P—O single and double bonds (Wilson, 1992). These values are similar to those in [CpCo{P(O)(OMe)₂}₂{P(OMe)₃}].H₂O (Towle, Landon, Brill & Tulip, 1982).