

Organomercury compounds

XXX *. The synthesis and crystal and molecular structure of bis(2,4,6-trichlorophenoxyethyl)mercury

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Abstract

Bis(2,4,6-trichlorophenoxyethyl)mercury has been prepared by reaction of bis(bromomethyl)mercury with thallium(I) 2,4,6-trichlorophenoxide. The compound has a centrosymmetric structure with linear C–Hg–C bonding (Hg–C 2.11(1) Å). Each mercury has contacts with two intramolecular and two intermolecular oxygen atoms (Hg···O 2.970(6) and 3.105(6) Å, respectively) and with an *ortho*-chlorine from each trichlorophenyl ring (Hg···Cl 3.419(2) Å). The other *ortho*-chlorines have contacts with a methylene hydrogen (H···Cl 2.874(3) Å).

Introduction

Heteroatom functionalised methylmercury compounds, R_nECH_2HgX or $(R_nECH_2)_2Hg$, are of interest both because of differences in properties from those of unsubstituted methylmercurials and because of possible $E \cdots Hg$ secondary interactions. Methylmercurials substituted by Group 16 atoms are mainly restricted to sulfur derivatives [1,2]. Phenylthiomethyl- and benzenesulfonylmethyl-mercury compounds, e.g. $(PhSCH_2)_2Hg$ [3,4], $[(PhS)_2CH]_2Hg$ [5] and $(PhSO_2CH_2)_2Hg$ [6], have been prepared by the organolithium route, and derivatives of disulfones, $(RSO_2)_2CHHgO_2CMe$ [7] and $(RSO_2)_2CHHgR'$ [8], have been prepared by mercuration. By contrast, organooxymethylmercury compounds, $(ROCH_2)_2Hg$ or $ROCH_2HgX$, are a neglected class of mercury organometallics [1,2]. They have an intermediate position between the oxymercuration products, $ROCH_2CH_2HgX$, or their symmetrization derivatives, $(ROCH_2CH_2)_2Hg$, and unsubstituted methylmercury compounds. Impure $(MeOCH_2)_2Hg$ and $MeHgCH_2OMe$ have been pre-

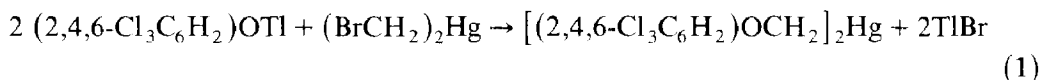
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pared by Grignard and organolithium methods, respectively, and identified by ^1H NMR spectroscopy [9]. The compounds decompose slowly into mercury metal at room temperature. We now report the synthesis and crystal structure of a stable aryloxymethylmercury compound.

Results and discussion

(a) Synthetic and spectroscopic studies

We examined three synthetic approaches to organooxymethylmercurials, organolithium/Grignard reactions, CH_2 insertion (from CH_2N_2) into a Hg–O bond, and nucleophilic substitution in a halogenomethylmercurial. Only the last was successful. Thus, bis(2,4,6-trichlorophenoxymethyl)mercury was prepared by reaction of bis(bromomethyl)mercury in ether with thallium(I) 2,4,6-trichlorophenoxide in tetrahydrofuran.



The synthesis is novel for Group 16-substituted methylmercurials, but a related substitution reaction has been used to give nitrogen-functionalised methylmercurials, viz. conversion of $(\text{ICH}_2)_2\text{Hg}$ by trimethylamine into an unseparated mixture of $[(\text{Me}_3\text{NCH}_2)_2\text{Hg}]\text{I}_2$ and $(\text{Me}_3\text{NCH}_2\text{HgCH}_2\text{I})\text{I}$ [10].

The ^{199}Hg NMR spectrum of bis(2,4,6-trichlorophenoxymethyl)mercury showed a pentet owing to coupling to the four methylene protons. Although $^2J(\text{HgH})$ (47.2 Hz) is significantly lower than values for Me_2Hg (102 Hz) [1] and $(\text{PhSCH}_2)_2\text{Hg}$ (121 Hz) [4], it is similar to coupling constants for $(\text{MeOCH}_2)_2\text{Hg}$ (48 Hz) [9], $\text{McHgCH}_2\text{OMc}$ ($^2J(\text{HgCH}_2)$ 50 Hz) and $(\text{ClCH}_2)_2\text{Hg}$ (61.1 Hz, this work). A medium intensity infrared band at 575 cm^{-1} can be attributed to $\nu_{\text{as}}(\text{HgC})$, which is observed at 542, 535 and $535/517\text{ cm}^{-1}$ for Me_2Hg , Et_2Hg and $(\text{ClCH}_2)_2\text{Hg}$ respectively [1].

In contrast with the behaviour of $(\text{MeOCH}_2)_2\text{Hg}$ [9], no spontaneous decomposition into metallic mercury was observed at room temperature. Preparation of a wider range of organooxymethylmercurials is in progress.

(b) Crystal structure of bis(2,4,6-trichlorophenoxymethyl)mercury

Final positional parameters are given in Table 1 and structurally significant bond distances and angles in Table 2*. The molecular structure with the atom numbering scheme is shown in Fig. 1, and a packing diagram showing intermolecular $\text{Hg} \cdots \text{O}$ contacts is given in Fig. 2. The structure solution indicates a centrosymmetric molecule with strictly linear C–Hg–C bonding. Slight deviations from linearity in C–Hg–C bonds are known, and are generally associated with steric, electronic or coordination effects of neighbouring substituents [1,11,12]. The Hg–C distance (Table 2) is slightly greater than that (2.083(5) Å) in dimethylmercury [13] and than the sum (2.07 Å) of the mercury digonal covalent radius [14] and the $\text{C}(sp^3)$ covalent radius [15]. Lengthening ($> 2.09\text{ Å}$) is generally associated with electron-

* Other bond distances and angles, final anisotropic thermal parameters, equations to the planes of all ligands, and Tables of observed and calculated structure factors may be obtained from the authors.

Table 1

Atomic parameters for C₁₄H₈Cl₆HgO₂ (e.s.d. values in parentheses)

Atom	x	y	z	U_{eq} (Å ²) ^a
Hg	0.5	0.5	0.5	0.0514(2)
Cl(1)	0.0675(2)	-0.2343(4)	0.0953(7)	0.0697(9)
Cl(2)	0.4063(2)	0.0548(4)	0.6993(9)	0.0823(12)
Cl(3)	0.1699(2)	0.4590(4)	0.7507(8)	0.0728(10)
O	0.3460(4)	0.3852(9)	0.8989(15)	0.058(2)
C(1)	0.3899(6)	0.5458(13)	0.7234(26)	0.064(4)
C(2)	0.2825(5)	0.2462(12)	0.6957(20)	0.044(3)
C(3)	0.2995(5)	0.0782(13)	0.5890(23)	0.049(3)
C(4)	0.2365(5)	-0.0688(13)	0.4062(23)	0.050(3)
C(5)	0.1516(5)	-0.0489(12)	0.3237(21)	0.047(3)
C(6)	0.1304(5)	0.1136(12)	0.4219(22)	0.049(3)
C(7)	0.1976(5)	0.2590(12)	0.6113(21)	0.045(3)

$$^a U_{eq} = 1/3 \sum_i \sum_j U_{ij} a_i^* a_j^* \bar{a}_i \cdot \bar{a}_j.$$

withdrawing substituents in the organic group or with secondary coordination to mercury from donor atoms in the organic group (see data in [1]), but not necessarily with steric crowding, e.g. Hg–C 2.077(6), 2.083(6) Å for (2,4,6-Bu^t₃C₆H₂)₂Hg [16]. The C(2)–O distance (Table 2) is significantly shorter than a C–O single bond length (e.g. C(1)–O (Table 2); average aliphatic C–O [17] 1.44 Å) and is comparable with that of phenols (average C–O [17] 1.36 Å). Partial double bond character can be attributed to conjugation of oxygen lone pairs with the aromatic rings, presumably enhanced by the inductive electron-withdrawing character of the chlorine substituents. Thus, the 2,4,6-trichlorophenoxy substituents in the methyl groups are strongly electron-withdrawing, and this may contribute to the slight Hg–C bond lengthening (see above). Mean plane calculations show that O, Cl(1), Cl(2) and Cl(3) are 0.087(6), 0.029(3), 0.022(3) and 0.076(3) Å, respectively, out of the plane through

Table 2

Bond lengths (Å) and selected angles (°) for bis(2,4,6-trichlorophenoxymethyl)mercury^a

Hg–C(1)	2.11(1)	Hg–C(1)–O	111.1(7)
C(1)–O	1.46(1)	C(1)–O–C(2)	114.6(6)
O–C(2)	1.363(9)	O–C(2)–C(3)	121.0(8)
C(2)–C(3)	1.40(1)	O–C(2)–C(7)	121.5(8)
C(3)–C(4)	1.36(1)	C(2)–C(3)–Cl(2)	118.6(6)
C(4)–C(5)	1.39(1)	C(2)–C(7)–Cl(3)	120.0(6)
C(5)–C(6)	1.38(1)		
C(6)–C(7)	1.39(1)		
C(7)–C(2)	1.37(1)		
C(5)–Cl(1)	1.742(8)		
C(3)–Cl(2)	1.746(9)		
C(7)–Cl(3)	1.734(9)		
<i>Intramolecular contacts</i>			
Hg···O	2.970(6)	Hg···Cl(2)	3.419(3)
Hg···O ^b	3.105(6)	H(11)···Cl(3)	2.874(3)

^a E.s.d.'s in parentheses. ^b (0, 0, +); intermolecular contact.

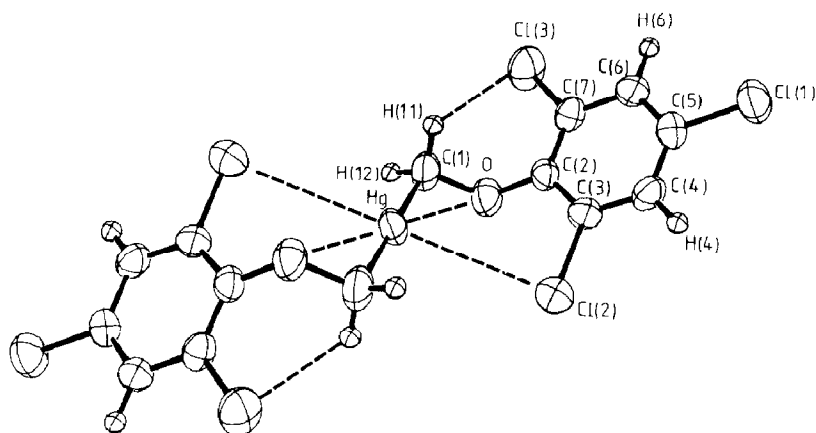


Fig. 1. Structure of bis(2,4,6-trichlorophenoxy)methylmercury showing the numbering of the atoms. Dotted lines show intramolecular contacts at distances (Table 2) approximately equal to the sum of the appropriate Van der Waals radii.

atoms C(2) to C(7) inclusive. All are displaced in the opposite direction to the methylene carbon (1.17 Å out of the aromatic plane).

Mercury has intramolecular contacts with the two oxygen atoms and with one *ortho*-chlorine from each ring (Fig. 1 and Table 2). There are also two short $\text{H}(\text{CH}_2) \cdots \text{Cl}$ contacts (Table 2). The $\text{Hg} \cdots \text{O}$ distance is greater than the sum (2.90 Å) of the Van der Waals radii of oxygen [15] and mercury [14], if the minimum value (1.50 Å) [14] for the latter is taken. There is a strong case for a radius of 1.73 Å [18], and this would possibly enable $\text{Hg} \cdots \text{O}$ to be regarded as weakly bonding. However, *gem* substituents can often approach within the sum of their Van der Waals radii without bonding (see e.g. CCl_4 [17]), hence the present assessment should be based on the minimum Van der Waals radius for mercury. Confirmation that $\text{Hg} \cdots \text{O}$ is non-bonding is provided by the $\text{Hg}-\text{C}(1)-\text{O}$ angle (Table 2), which

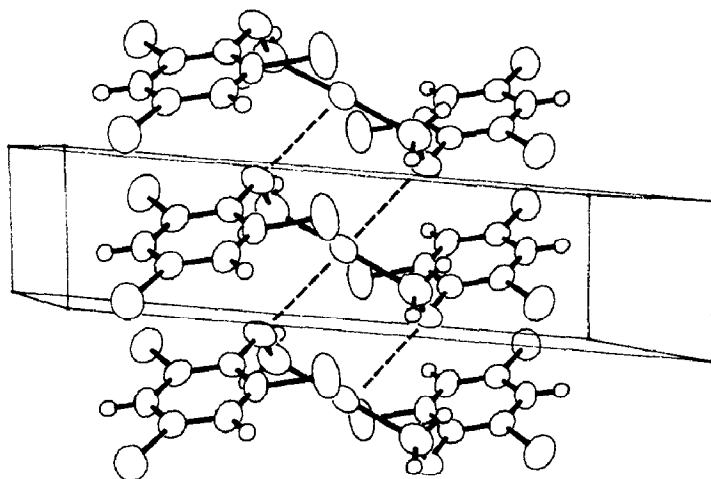


Fig. 2. Packing diagram showing the unit cell and intermolecular $\text{Hg} \cdots \text{O}$ contacts.

shows that C(1)–O is not bent towards mercury. Although $\text{Hg} \cdots \text{Cl}$ (Table 2) is slightly less than the sum (3.58 Å) of the Van der Waals radii of chlorine [15] and mercury (using 1.73 Å), there is no clear evidence from bond angles [O–C(2)–C(3) and C(2)–C(3)–Cl(2)] for a $\text{Hg} \cdots \text{Cl}$ interaction. Moreover, the short C(2)–O distance is a significant factor in bringing Hg and Cl(2) into proximity. The $\text{H} \cdots \text{Cl}$ contact is less than the sum (3.05 Å) of the appropriate Van der Waals radii, if an intermediate value (1.2 Å) [15] is used for hydrogen, but again this contact is affected by the short C(2)–O bond and there is no evidence from bond angles [O–C(2)–C(7); C(2)–C(7)–Cl(3)] for significant hydrogen bonding.

The packing diagram (Fig. 2) shows the molecules to be stacked in columns with intermolecular $\text{Hg} \cdots \text{O}$ contacts of 3.105 Å. Although these are longer than the intramolecular contacts, they may be of more significance and contribute to the intermolecular packing. The structure of $\text{PhHg}(\text{ox})$ (ox = quinolin-8-olate) shows the compound to be stacked in columns with intermolecular $\text{Hg} \cdots \text{O}$ contacts of 3.3–3.4 Å [19]. Evidence from molecular weight data and mass spectroscopy [20] (and the structure of $\text{PhHg}(\text{meox})$ [19]; (meox = 2-methylquinolin-8-olate)) indicates that these contacts are weakly bonding, corresponding to a Van der Waals radius of 1.9–2.0 Å for mercury in intermolecular stacking [20]. Thus, the intermolecular $\text{Hg} \cdots \text{O}$ contacts in the present structure may also be weakly bonding.

Experimental

(a) General

Microanalyses were by the Australian Microanalytical Service, Melbourne. Mass spectra were recorded with a V.G. Micromass 7050F spectrometer. The listed m/z values for ions containing one or more polyisotopic atoms are the most intense peaks of clusters with the expected isotope patterns, unless indicated otherwise (below). NMR spectra were recorded with a Bruker AM300 spectrometer. ^1H chemical shifts are in ppm downfield from internal Me_4Si , whilst ^{199}Hg chemical shifts are referenced to external neat Me_2Hg . IR spectra of Nujol and Fluorolube or hexachlorobutadiene mulls were recorded with a Perkin–Elmer 180 spectrometer, and listed bands are restricted to intense features.

(b) Reagents

Mercuric bromide, thallium(I) ethoxide and 2,4,6-trichlorophenol were from Aldrich. Diazomethane was prepared by a standard method [21]. Thallium(I) 2,4,6-trichlorophenoxide was precipitated on addition of thallium(I) ethoxide (2.53 g) to 2,4,6-trichlorophenol (2.00 g) in ethanol following by heating (yield, 96%), m.p. 239.5–240 °C. (Found: C, 18.0; H, < 0.4%. $\text{C}_6\text{H}_2\text{Cl}_3\text{OTl}$ calc.: C, 18.0; H, 0.5%). IR: 1430s, 1415s, 1385m, 1280s, 1247m, 858s, 785m, 745s, 725m cm^{-1} . Mass spectrum: m/z 400[1%, M^+], 205[12, Tl^+], 196[100, $\text{C}_6\text{H}_3\text{Cl}_3\text{O}^+$]. ^1H NMR spectrum [$(\text{CD}_3)_2\text{SO}$]: 7.07, s, H3,5. Bis(chloromethyl)mercury was prepared by the reported method [22]. ^1H NMR spectrum: 3.55, s with ^{199}Hg satellites $^2J(\text{HgH})$ 61.1 Hz, CH_2 .

(c) Preparation of bis(2,4,6-trichlorophenoxy)methylmercury

Bis(bromomethyl)mercury [23] was prepared 'in situ' by addition of a solution of diazomethane in ether dropwise to an ether solution of mercuric bromide (1.12 g,

3.11 mmol) until the colour of diazomethane just persisted. To the filtered solution (30 ml) was added thallium(I) 2,4,6-trichlorophenoxide (2.20 g, 6.02 mmol) in tetrahydrofuran (50 ml). The reaction mixture was stirred overnight at 30–40 °C and filtered. On cooling, fine colourless needles of the title compound crystallized and were collected and washed with cold 95% ethanol (yield, 0.70 g, 37%), m.p. 134 °C (Found: C, 27.4; H, 1.5; Cl, 34.0; Hg, 32.5. $C_{14}H_8Cl_6HgO_2$ calc.: C, 27.1; H, 1.3; Cl, 34.2; Hg, 32.3%). IR: 1568m, 1551m, 1461s, 1440s, 1429m, 1409s, 1381m, 1366m, 1276s, 1201m, 1190m, 1130m, 1078m, 938s, 863m, 850s, 815m, 800m, 783m, 722s, 685s, 575m cm^{-1} . 1H NMR spectrum ($CDCl_3$): 4.75, s with ^{199}Hg satellites $^2J(HgH)$ 47.2 Hz, 4H, CH_2 ; 7.31, s, 4H, H3,5. ^{199}Hg NMR spectrum ($CDCl_3$): -741.4, p (s decoupled), $^2J(HgH)$ 47.2 Hz. Mass spectrum: m/z 622 [0.4%, M^+], 420 [0.2, $C_{14}H_8Cl_6O_2^+$ -incomplete isotope pattern observed], 223 [58, $C_8H_6Cl_3O^+$], 209 [100, $C_7H_4Cl_3O^+$], 202 (20, Hg^+] overlapping 196 [50, $C_6H_3Cl_3O^+$].

(d) Crystallography

Crystals for the structure determination were deposited from $CDCl_3$ /hexane. An acicular crystal, $0.33 \times 0.06 \times 0.06$ mm was selected.

Crystal data. $C_{14}H_8Cl_6HgO_2$: M 621.52, triclinic, space group $P\bar{1}$ (No. 2), a 15.648(12), b 7.462(10), c 3.960(5) Å, α 94.13(7), β 95.60(5), γ 106.23(14)°, U 439.39 Å³, D_m , 2.34(2), D_c 2.35 $g\ cm^{-3}$ for $Z = 1$, $F(000)$ 290, Mo- K_α radiation, 0.7107 Å, μ (Mo- K_α) 96.8 cm^{-1} . The unit cell parameters were obtained by least-squares refinement of the angular settings of 24 medium-angle reflections and are the mean of six refinements of these reflections which were used to monitor the crystal stability during data collection.

Data collection, structure solution and refinement. The intensities of 2571 unique reflections were measured using a Philips PW 1100 automatic four-circle diffractometer, equipped with a graphite monochromator, in the $\theta/2\theta$ scan mode with $6^\circ < 2\theta < 60^\circ$, a scan width of $(1.20 + 0.3 \tan \theta)^\circ$ in θ and at a scan speed of $0.04^\circ\ s^{-1}$ [24]. Three standard reflections, monitored every 3 hours, indicated that there had been a 14% decomposition during the data collection period; a correction for decomposition was applied together with the Lorentz and polarization corrections [25] and 1590 reflections that were considered to be above background [$F_o > 6\sigma(F_o)$] were used in the subsequent refinement. A numerical absorption correction, based on indexed crystal faces, was applied to the data [26].

Since there was only one molecule in the unit cell, the mercury atom was conveniently placed on the centre of symmetry at the centre of the cell and the remaining non-hydrogen atoms located in the subsequent difference Fourier synthesis. Following insertion of hydrogen atoms in their geometrically calculated positions, refinement of positional and thermal parameters (anisotropic for non-hydrogen atoms and a single isotropic parameter for the hydrogen atoms) for several full-matrix least-squares cycles resulted in the calculations converging at R 0.051 and R_w at 0.047 ($R_w = \sum \omega^{1/2} (|F_o| - |F_c|) / \sum \omega^{1/2} F_o$; $\omega = 1/\sigma^2(F_o)$). The atomic scattering factors for neutral atoms [27] were corrected for anomalous dispersion. All calculations were carried out on the Monash University DEC VAX 11/780 computers; the major program used was that of Sheldrick [26].

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