Organo(organooxo)mercury(II) chemistry — Synthesis and structure of methyl(phenoxo)mercury(II)[1]

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Abstract: Methyl(phenoxo)mercury(II) may be obtained from the reaction of methyl(chloro)mercury(II) with silver(I) oxide, followed by addition of phenol. The dominant motif of the structure is a pair of independent MeHgOPh aggregates (Hg—C,O 2.05(2) Å, 2.06(1) Å (x2); C-Hg-O 176.6(5)°, 176.3(5)°) loosely associated about a quasi-inversion centre by Hg⋯O interactions (2.702(9) Å, 2.719(9) Å) to form a dimer (Hg-O-Hg′ 106.0(4)°, 106.5(4)°; O-Hg-O′ 73.0(3)°, 72.6(3)°), the dimer stacking up the short crystallographic c axis (= 6.914(1) Å) at spacings $c/2$. Vibrational spectroscopic studies are insensitive to the associative interactions.

Key words: mercury, methylmercury, organomercury, structure, aryloxide, phenoxide.

Résumé : On peut obtenir du méthyl(phénoxo)mercure(II) par réaction du méthyl(chloro)mercure(II) avec de l'oxyde d'argent(I), suivie d'une addition de phénol. Le motif dominant de la structure est une paire d'agrégats indépendants de MeHgOPh (Hg—C,O 2,05(2) Å, 2,06(1) Å (x2); C-Hg-O 176,6(5)°, 176,3(5)°) faiblement associés autour d'un centre de quasi-inversion par des interactions Hg⋯O (2,702(9) Å, 2,719(9) Å) qui permettent de former le dimère (Hg-O-HgN 106,0(4)°, 106,5(4)°; O-Hg-ON 73,0(3)°, 72,6(3)°) qui s'empile le long de l'axe cristallographique c (= 6,914(1) Å) à des distances de $c/2$. Les études spectroscopiques vibrationnelles sont insensibles aux interactions associatives.

Mots clés : mercure, méthylmercure, organomercure, structure, aryloxyde, phénolate.

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Introduction

The coordination chemistry of monoorganomercury(II) complexes has been reviewed (1, 2); for arylalkoxides and aryloxides, structural studies are limited to the early study of the 4-bromo-2-chlorophenoxo complex PhHgOC$_6$H$_3$ClBr (3, 4), although the structure of a trimethylsiloxo complex, MeHgOSiMe$_3$, has also been described (5). Vibrational spectroscopic data have been interpreted in terms of monomeric structures for MeHgOPh and PhHgOPh in both the solid state and in dichloromethane (**1** in Scheme 1), consistent with osmometric studies in dichloromethane (6). However, in the less polar solvent benzene, ebullioscopic studies indicate that PhHgOPh and relatives PhHgOR′ (R′ = Me, *i*-Pr, *s*-Bu, CMe$_2$Ph) are associated and consistent with a monomer (**1**) – dimer (**2**) equilibrium (7), and it has also been suggested that PhHgOPh can adopt both dimeric (**2**) and trimeric (**3**) forms (8). Vibrational spectra are also consistent with a dimeric structure in the solid state for PhHgOR′ (R′ = Me, Et) (6). The complex MeHgOSiMe$_3$ is monomeric in benzene (osmometry) (9), and in the solid state an incomplete X-ray structure determination (280 "observed" reflections, R = 0.21) indicated a tetrameric structure (**4**) with short Hg—O (2.11 Å) and long Hg⋯O

(2.75 Å) interactions (5). A weak intermolecular Hg⋯O interaction is also observed in PhHgOC$_6$H$_3$ClBr (2.85(2) Å), although the molecule is essentially a monomer with C-Hg-O 174(1)°, where this angle is opposite a weak intramolecular Hg⋯Cl interaction (3.03 Å) (3). Noting the additional weak interactions present in these structures and the marked tendency for unsymmetrical coordination geometries for monoorganomercury(II) complexes, geometries for **2**–**4** are drawn to illustrate this behaviour, and additional weak interactions could be anticipated for monomers (**1**) (Scheme 1). Archetypal examples of unsymmetrical geometry are illustrated by the 2,2′-bipyridine complex [MeHg(bpy)]NO$_3$, which has C-Hg-N 164(1)°, Hg—N 2.24(3) Å, Hg⋯N 2.43(3) Å (10); the D,L-penicillamine complex MeHgSCMe$_2$-CH(CO$_2$)NH$_2$HgMe, which has C-Hg-N 168.1°, Hg—N 2.216(5) Å, Hg⋯O 2.708(4) Å (11); and the closely related D,L-selenocysteine complex MeHgSeCH$_2$CH(CO$_2$)NH$_3$·H$_2$O, which has C-Hg-Se 177.8(11)°, with associated more distant approaches Hg⋯O 2.93(2) Å and Hg⋯Se 3.737(4) Å (12).

In view of the lack of structural characterization for fundamental aryloxo complexes, the propensity for organomercury(II) compounds to adopt unusual geometries for mercury, the various structures proposed on the basis of physical and spectroscopic studies (**1**–**3**), and the structure

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Scheme 1.

1   **2**   **3**   **4**
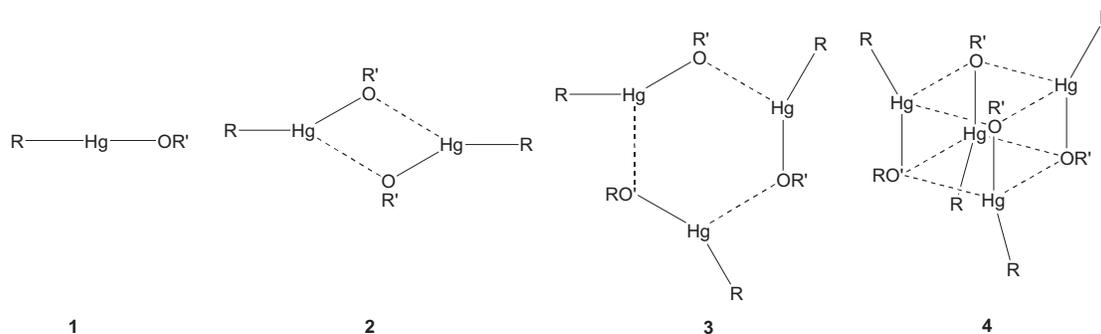
Table 1. Selected geometries for MeHgOPh.

Atoms	Parameter		Atoms	Parameter	
	$n = 1$	$n = 2$		$n = 1$	$n = 2$
Bond lengths (Å)					
Hg(n)—C(n)	2.046(16)	2.049(18)	Hg(n)—O(2)	2.702(9)	2.063(10)
Hg(n)—O(1)	2.060(11)	2.719(9)	C(n1)—O(n)	1.369(16)	1.364(16)
Bond angles (°)					
C(n)-Hg(n)-O(n)	176.6(5)	176.3(5)	Hg(1)-O(n)-Hg(2)	106.0(4)	106.5(4)
C(n)-Hg(n)-O(n')	109.4(5)	109.3(5)	C(11)-O(1)-Hg(n)	120.7(8)	123.5(8)
O(1)-Hg(n)-O(2)	73.0(3)	72.6(3)	C(21)-O(2)-Hg(n)	120.6(8)	121.4(8)

reported for the trimethylsiloxo complex (**4**), we have synthesized MeHgOPh and determined its structure in the solid state.

Results and discussion

Although the complex MeHgOPh was prepared by the reported method, the preparation is given in detail here in view of the brief description reported previously (13). Crystals were obtained from dichloromethane – light petroleum. Selected geometries are given in Table 1, and views of the structure are shown in Fig. 1.

The results of the low-temperature single crystal X-ray structure determination are consistent with the formulation of the complex, in terms of stoichiometry and connectivity, as neutral MeHgOPh. Two formula units, devoid of crystallographic symmetry, comprise the asymmetric unit of the structure. These may be viewed essentially as single molecules with almost linear C-Hg-O coordination (Hg—O 2.060(11) Å, 2.063(10) Å; Hg—C 2.046(16) Å, 2.049(18) Å; C-Hg-O 176.6(5)°, 176.3(5)°). The mercury environments lie side-by-side, quasi-inversion related (Fig. 1a), with long Hg···O interactions (2.702(9) Å, 2.719(9) Å), appreciably less than the van der Waals radii sum (O, 1.4 Å (14); Hg, ca. 1.73 Å (15)) that perturb the linearity of the C-Hg-O arrays. The Hg(μ-O)$_2$Hg arrays are quasi-planar (χ^2 523) with a fold angle across the Hg···Hg line of 17.4(6)° (Fig. 1b). The mercury atoms lie out of the associated C$_6$ ring planes by 0.17(3) Å and 0.20(2) Å, the Hg(n)-O(n)-C(n1)-C(n2) torsion angles being –8(2)° and –9(2)°. C(11, 21) lie out of the Hg$_2$O$_2$ "plane" by 0.22(2) Å and 0.32(2) Å. Despite these distortions, the quasi-dimeric arrays may be considered approximately planar and, as such, stack up the c axis of the almost orthogonal cell — Hg above O — these contacts be-

ing much longer and at the van der Waals limit (Hg(1)···O(1) (x, 1/2 – y, z – 1/2) 3.318(9) Å; Hg(2)···O(2) (x, 1/2 – y, z – 1/2) 3.368(10) Å) (Fig. 1c).

Although the structure determination reveals several interesting features in crystal chemistry, the structure of MeHgOPh conforms broadly to model **1** with the additional presence of weak intermolecular interactions, consistent with the monomeric behaviour exhibited in dichloromethane (6). Structural assignments for the solid state based on IR and Raman spectroscopic data (6), are supported by the structural determination, the spectroscopic data being insensitive to the weak intermolecular Hg···O interactions.

Experimental

Synthesis of MeHgOPh

Freshly precipitated silver(I) oxide (from an aqueous solution of silver(I) nitrate and sodium hydroxide) was collected and repeatedly washed and centrifuged until the pH of the solution was 7. An excess of Ag$_2$O was added to MeHgCl (6.28 g) in a small volume of water. The resulting aqueous solution was filtered, and phenol (2.35 g) was added. The white crystalline precipitate that formed was collected, washed with water, and dried over phosphorus pentoxide. The product was recrystallized from dichloromethane and then from dichloromethane – light petroleum (bp 40–60 °C) to give the pure complex (3.86 g, 50%). IR spectra are as reported (6).

X-ray data collection, structure determination, and refinement

Following earlier unsuccessful attempts at data acquisition at room temperature using a four-circle instrument (the ma-

Fig. 1. (*a*) The asymmetric unit of the structure of MeHgOPh projected down *c* and (*b*) oblique to the central plane; (*c*) Unit cell contents projected down *c*. 50% Probability amplitude displacement envelopes are shown for the non-hydrogen atoms, hydrogen atoms where shown having arbitrary radii of 0.1 Å.
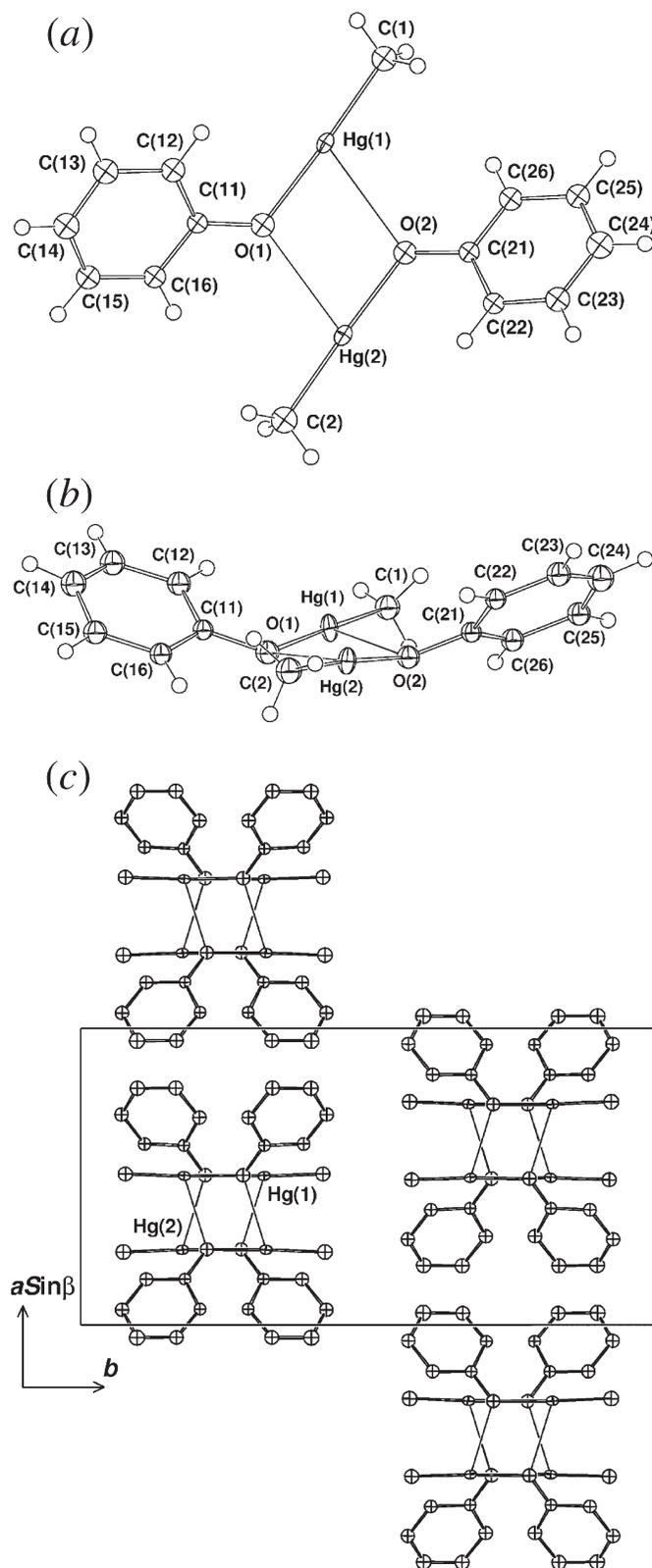
Table 2. Crystal data and structure refinement for MeHgOPh.

Empirical formula	$C_{14}H_{16}Hg_2O_2$
Formula mass	617.5
Crystal dimensions (mm^3)	$0.30 \times 0.07 \times 0.06$
Crystal system	Monoclinic
Space group	$P2_1/c$ (No. 14)
Z	4
a (Å)	10.340(2)
b (Å)	19.886(1)
c (Å)	6.914(1)
β (°)	91.200(4)
Collection ranges	$-13 \leq h \leq 13$;
	$-11 \leq k \leq 11$;
	$-8 \leq l \leq 8$
Temperature (K)	ca. 150
Volume (Å^3)	1421.4(4)
D_{calcd} (Mg m^{-3})	2.88$_5$
Radiation	Mo Kα (λ = 0.7107$_3$ Å)
Absorption coefficient (μ) (mm^{-1})	21.6
F(000)	1104
θ range for data collection (°)	1–27.5
Measured reflections	27 505
Independent reflections	3 196 (R_{int} = 0.072)
Data/restraints/parameters	2 345/(see text)/83
Maximum shift/error	9×10^{-4}
Goodness-of-fit	0.98
Final R indices ($I > 4\sigma(I)$)	R_1 = 0.064, wR_2 = 0.086
R indices (all data)	R_1 = 0.079, wR_2 = 0.096
Largest diff. peak and hole (e Å^{-3})	−6.1, 5.3(2)

terial being fine whiskers), a full sphere of low-temperature CCD area-detector diffractometer data were measured (Bruker AXS instrument), "empirical"–multiscan absorption correction (proprietary software) being applied ($T_{min/max}$ = 0.28) (Table 2). The full-matrix least-squares refinement would support meaningful anisotropic displacement parameter form refinement for the mercury atoms only (*x*, *y*, *z* $U_{iso})_H$, being included and constrained at estimated values (reflection weights: $(\sigma^2(F) + 0.005F^2)^{-1}$). Neutral atom complex scattering factors were employed within the Xtal 3.7 program system (16).[3]

Acknowledgements

References

1. J.L. Wardell. *In* Comprehensive organometallic chemistry. Vol. 1. *Edited by* G. Wilkinson, F.G.A. Stone, and E.W. Abel. Pergamon Press, Oxford. 1982. p. 863.
2. J.S. Casas, M.S. García-Tasende, and J. Sordo. Coord. Chem. Rev. **193–195**, 283 (1999).
3. L.G. Kuzʹmina, N.G. Bokii, Y.T. Struchkov, D.N. Kravtsov, and L.G. Golovchenko. Zh. Strukt. Khim. **14**, 508 (1973).
4. D.C. Bradley, R.C. Mehrotra, I.P. Rothwell, and A. Singh. Alkoxo and aryloxo derivatives of metals. Academic Press, San Diego. 2001.
5. G. Dittmar and E. Hellner. Angew. Chem. **81**, 707 (1969).
6. A.J. Canty and J.W. Devereux. Spectrochim. Acta, **36A**, 495 (1980).
7. A.J. Bloodworth. J. Chem. Soc. C, 2051 (1970).
8. G. Holan. Tetrahedron Lett. 1985 (1966).
9. H. Schmidbaur and F. Schindler. Angew. Chem. Int. Ed. Engl. **4**, 876 (1965).
10. A.J. Canty and B.M. Gatehouse. J. Chem. Soc. Dalton Trans. 2018 (1976).
11. Y.S. Wong, P.C. Chieh, and A.J. Carty. Can. J. Chem. **51**, 2597 (1973).
12. A.J. Carty, S.F. Malone, N.J. Taylor, and A.J. Canty. J. Inorg. Biochem. **18**, 291 (1983).
13. L.F. Sytsma and R.J. Kline. J. Organomet. Chem. **54**, 15 (1973).
14. L. Pauling. The nature of the chemical bond. 3rd ed. Cornell University Press, Ithaca, New York. 1960. p. 260.
15. A.J. Canty and G.B. Deacon. Inorg. Chim. Acta, **45**, L225 (1980).
16. S.R. Hall, D.J. du Boulay, and R. Olthof-Hazekamp. The XTAL 3.7 system [computer program]. University of Western Australia, Crawley, Australia. 2001.