Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1188). Services for accessing these data are described at the back of the journal.

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1-Bromomercurio-2-(2,5,8,11,14-pentaoxapentadecyl)benzene

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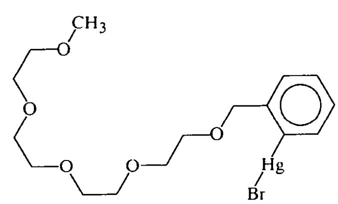
Abstract

The crystal structure of the title compound, [HgBr(C_{16}-$H_{25}O_5$)], shows a nearly-linear geometry at the Hg atom [C1—Hg—Br = 177.52 (13)°], and only weak interactions between the Hg atom and the O atoms in the open-chain polyether ligand. The three shortest Hg···O distances [2.862 (4), 2.949 (4) and 3.010 (4) Å], of which only one is intramolecular, are distinctly longer than in comparable ketones and carboxylates.

Comment

In recent years, we have investigated the influence of coordination number on the reactivity of organomagnesium and organomercury compounds. The coordination number of the metals can be increased by coordination to crown ethers or open-chain polyethers. The title compound, (I), is an open-chain analogue of [2-(bromomercurio)-1,3-xylene]-18-crown-5 (Markies *et al.*, 1993).



(I)

A view of the polyether complex, with our numbering scheme, is shown in Fig. 1. The distances Hg···O1 = 2.862 (4), Hg···O1^{i} = 2.949 (4) and Hg···O2^{i} = 3.010 (4) Å [symmetry code: (i) $x+\frac{1}{2}$, $1-y$, z] in the open-chain compound are even longer than the Hg···O distances of 2.754 (6), 2.855 (6) and 3.060 (6) Å in the crown ether complex, the latter set being all intramolecular. These distances are much longer than for the corresponding carboxylate and keto compounds (Fig. 2). The Hg···O interactions can therefore be considered as extremely weak. Another indication of the weakness of the interaction is the minimal deviation of the *R*—Hg—Br angle from linearity [177.52 (13)° in the open-chain and 175.0 (2)° in the crown ether compound]. That the interactions in the open-chain compound are weaker than in the crown ether is to be expected from entropy considerations (Inoue & Hakushi, 1985); it is also found in the crystal structures of similar Mg compounds (Markies *et al.*, 1994). In fact, the conformation of the polyether, with O—C—C—O torsion angles of −70.6 (6), −70.4 (6), 75.1 (6) and −70.6 (6)°, is approximately as expected for the parent polyether without the HgBr substituent, and is considered to be essentially undisturbed by the coordinated metal atom.

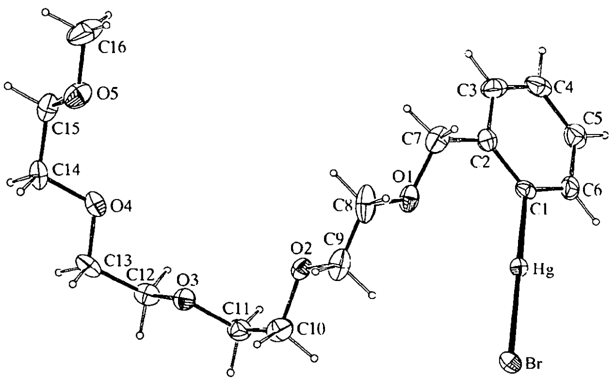


Fig. 1. Displacement ellipsoid plot (50% probability) of the title molecule.

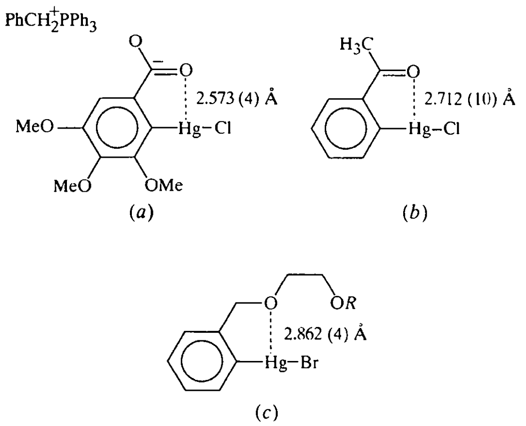


Fig. 2. Hg···O bond distances in (*a*) a carboxylate (Vicente *et al.*, 1992), (*b*) a ketone (Cooney *et al.*, 1987) and (*c*) a polyether (this study). The coordinated O atoms deviate from the plane defined by the phenyl ring by 0.270 Å in the carboxylate, 0.187 Å in the ketone and 0.907 (4) Å in the polyether.

Crystal structures of mercury salts HgX_2 (X = Br^-, CN^-, SCN^-) complexed by crown-5 ethers show weak bonding interactions with all five O atoms, in a distance range of 2.70–3.06 Å (Rebek *et al.*, 1985; Costero, Andreu *et al.*, 1996; Costero, Pitarch *et al.*, 1996; Weber, 1980; Bauer *et al.*, 1994). The Hg atom in these latter compounds is not fixed by a bond to a C atom of the crown ether; it can therefore adopt a central position with weak interactions to five O atoms. The title polyether compound should also be conformationally flexible enough to bind all five O atoms, but the enthalpy gain by weak binding is overcompensated by the loss of entropy, and only one intramolecular Hg···O interaction is found. The two intermolecular interactions noted above may also contribute to the packing energy of the crystal.

Experimental

The title compound was prepared according to a procedure described elsewhere (Markies, 1990).

Crystal data

[HgBr($C_{16}H_{25}O_5$)]	Mo $K\alpha$ radiation
M_r = 577.86	λ = 0.71073 Å
Orthorhombic	Cell parameters from 25 reflections
$Pca2_1$	θ = 9.88–13.96°
a = 8.544 (2) Å	μ = 10.274 mm^{-1}
b = 13.1640 (13) Å	T = 100 (2) K
c = 16.8094 (19) Å	Needle
V = 1890.6 (5) $Å^3$	0.97 × 0.25 × 0.14 mm
Z = 4	Colourless
D_x = 2.030 Mg m^{-3}	
D_m not measured	

Data collection

Enraf–Nonius CAD-4 diffractometer	R_{int} = 0.037
$\omega/2\theta$ scans	θ_{max} = 27.51°
Absorption correction: analytical (Alcock, 1970)	$h = 0 \rightarrow 11$
T_{min} = 0.071, T_{max} = 0.257	$k = -17 \rightarrow 17$
8467 measured reflections	$l = -21 \rightarrow 21$
4332 independent reflections	3 standard reflections
3830 reflections with $I > 2\sigma(I)$	frequency: 60 min
	intensity decay: 3%

Refinement

Refinement on F^2	$\Delta\rho_{max}$ = 0.969 e $Å^{-3}$
$R[F^2 > 2\sigma(F^2)]$ = 0.025	$\Delta\rho_{min}$ = −0.932 e $Å^{-3}$
$wR(F^2)$ = 0.051	Extinction correction: none
S = 0.996	Scattering factors from *International Tables for Crystallography* (Vol. C)
4332 reflections	Absolute structure: Flack (1983)
209 parameters	Flack parameter = 0.005 (7)
H atoms riding	
$w = 1/[\sigma^2(F_o^2) + (0.0273P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$	
$(\Delta/\sigma)_{max}$ = 0.015	

Table 1. *Selected geometric parameters (Å, °)*

Hg—C1	2.062 (5)	Hg···O1^i	2.949 (4)
Hg—Br	2.4428 (6)	Hg···O2^i	3.010 (4)
Hg···O1	2.862 (4)		
C1—Hg—Br	177.52 (13)	C2—C1—C6	119.5 (5)
C8—O1···Hg	123.7 (4)	C2—C1—Hg	122.5 (4)
C7—O1···Hg	95.7 (3)	C6—C1—Hg	118.0 (4)

O1···Hg—C1—C2	18.8 (4)	O1—C8—C9—O2	−70.6 (6)
O1···Hg—C1—C6	−159.9 (4)	O2—C10—C11—O3	−70.4 (6)
C3—C2—C7—O1	141.2 (5)	O3—C12—C13—O4	75.1 (6)
C1—C2—C7—O1	−39.1 (7)	O4—C14—C15—O5	−70.6 (6)

Symmetry code: (i) $\frac{1}{2}+x, 1-y, z$.

X-ray data were collected on a larger-than-usual needle using a sufficiently large collimator tube to ensure a homogeneous X-ray beam at the crystal. The adaptation of the collimator to the crystal size is possible here in view of the use of a β-filter as opposed to a graphite monochromator (Alexander & Smith, 1962).

Data collection: locally modified *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *SET*4 (de Boer & Duisenberg, 1984). Data reduction: *HELENA* (Spek, 1997). Program(s) used to solve structure: *DIRDIF*96 (Beurskens *et al.*, 1996). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *PLATON* (Spek, 1990). Software used to prepare material for publication: *PLATON*.

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Organization of the Cavity in a Bipyridyl Crown Ether Through Coordination with $PdCl_2$

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Abstract

In the crystal structure of dichloro[3,6,9,12,15,18-hexaoxa-24,27-diazatricyclo[24.4.0.0^{20,25}]triaconta-1(26),20,22,24,27,29-hexaene-N,N']palladium(II), [$PdCl_2$($C_{22}H_{30}N_2O_6$)], the Pd atom is tetracoordinated by the two pyridyl N atoms and two Cl atoms. The planes formed by atoms Pd1, N21, N31 and atoms Pd1, Cl1, Cl2 make an angle of 12.12 (9)° with one another. The twist of the two pyridyl rings of 31.59 (9)° is associated with the *ortho* substitution, and the complexation of $PdCl_2$ seems to alter the shape of the crown ether cavity, so that it is less suitable for complexing metal cations.

Comment

Allosteric effects represent an important mechanism for the regulation of the activity of important biomolecules. In this respect, much effort has been devoted to the development and study of simple synthetic models, *e.g.* bipyridyl crown ethers, that are able to mimic such a behaviour (Rebek, 1984).

Formation of transition metal complexes with bipyridyl crown ethers seems to pre-organize them in such a way as to selectively favour interaction with some specific alkali metal cations. In a different way, the pre-organization provided to the receptor (I) by interaction with the transition metal has been used as a molecular on–off switch for the uptake or release of $Hg(CF_3)_2$ (Rebek & Marshall, 1983), the very dramatic