Table 1 (cont.)

	x	y	z	U
F(6)	4382 (26)	1913 (15)	4902 (5)	207 (10)
P(8)	5236 (19)	3520 (8)	2686 (3)	200 (9)*
F(7)	4908 (33)	4222 (21)	2817 (6)	267 (15)
F(8)	4489 (26)	3704 (15)	2453 (5)	197 (10)
F(9)	5711 (29)	2847 (18)	2576 (6)	232 (12)
F(10)	6310 (30)	3982 (18)	2566 (6)	226 (12)
F(11)	4266 (34)	2987 (20)	2810 (6)	252 (14)
F(12)	5862 (47)	3373 (27)	2922 (10)	348 (24)

Table 2. Bond lengths (Å) and angles (°)

Au(1)–P(1)	2·281 (8)	Au(1)–S(1)	2·326 (7)
Au(2)–P(2)	2·270 (8)	Au(2)–S(1)	2·342 (7)
Au(3)–P(3)	2·259 (7)	Au(3)–S(1)	2·333 (7)
Au(4)–P(4)	2·284 (8)	Au(4)–S(2)	2·338 (7)
Au(5)–P(5)	2·262 (8)	Au(5)–S(2)	2·320 (7)
Au(6)–P(6)	2·257 (7)	Au(6)–S(2)	2·303 (7)
P(1)–Au(1)–S(1)	175·9 (3)	P(2)–Au(2)–S(1)	171·9 (3)
P(3)–Au(3)–S(1)	173·3 (3)	P(4)–Au(4)–S(2)	172·8 (3)
P(5)–Au(5)–S(2)	176·5 (3)	P(6)–Au(6)–S(2)	176·9 (3)
Au(1)–S(1)–Au(2)	87·7 (3)	Au(1)–S(1)–Au(3)	86·3 (3)
Au(2)–S(1)–Au(3)	83·3 (3)	Au(4)–S(2)–Au(5)	89·2 (3)
Au(4)–S(2)–Au(6)	82·9 (3)	Au(5)–S(2)–Au(6)	95·0 (3)

Au–P lengths fall in the expected range for two-coordinate Au, and the P–Au–S angles are all close to linear (maximum deviation 8·1°). The Au–S lengths vary from 2·303 (7) to 2·342 (7) Å; no other Au–sulphide bond lengths are available for comparison, although the dimeric organic sulphide derivative [AuSCH$_2$PEt$_2$]$_2$ has Au–S = 2·31 Å (Crane & Beall, 1978).

The cations are arranged in pairs with short contacts between the Au atoms [Au(1)···Au(5) 3·361 (3),

Au(2)···Au(4) 3·236 (3) Å] (Fig. 1). Such contacts are a common feature of the structural chemistry of Au^I, although no theoretical explanation for them has been proposed. It is also striking that the angles at S(1) are all rather less than 90°, associated with further short Au···Au distances. It is thus feasible that weak Au···Au interactions cause these distortions; a similar effect is seen in (Ph$_3$PAu)$_2$Cl$^+$ (Jones et al., 1980). However, the angles at S(2) show a different pattern, only Au(4)–S(2)–Au(6) being appreciably less than 90°. This leads to a more varied set of Au···Au distances, Au(5)···Au(6) being rather long and Au(4)···Au(6) short. The two cations also show appreciable differences in the orientation of the phenyl rings.

The PF$_6$ ions show high thermal motion, but do not appear to be disordered. The temperature factors of the cations are also somewhat high; both this and the rather high R may be attributed to the difficulty of performing accurate absorption corrections for a needle-shaped crystal with high μ.

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A Complex of 1,15-Bis(2-bromophenyl)-2,5,8,11,14-pentaoxapentadecane and Mercury Dibromide

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Abstract. C$_{22}$H$_{28}$Br$_2$O$_5$.HgBr$_2$, M_r = 892·7, C2/c, a = 31·805 (7), b = 7·954 (3), c = 23·826 (5) Å, β = 113·22 (4)°, Z = 8, d_c = 2·141 Mg m^{-3}, $\mu_{MoK\alpha}$ = 11·30 mm^{-1}; R_w = 0·066 for 3504 data [weight = $1/\sigma^2(F_o)$]. The ligand wraps around the cation in a nearly circular manner such that all its O atoms (in

addition to the Br ions) are coordinated to Hg^{2+}, whilst its terminal Br atoms are not involved in strong interactions.

Introduction. Rigid terminal groups containing donor atoms improve the coordination abilities of linear oligoethers towards alkali and alkaline-earth cations (Vögtle & Sieger, 1977). Because of its closed-shell configuration, Hg^{II} may be compared to alkali and alkaline-earth cations with respect to spherically symmetric e -acceptor properties. Structural details of complexes of $HgCl_2$ with 2,5,8,11,14-pentaoxapentadecane and 3,6,9,12,15-pentaoxaheptadecane have been reported (Iwamoto, 1973a,b). The present study was undertaken to investigate the influence of the 2-bromophenyl entity (as a rigid terminal group) on the complexation of Hg^{2+} by a linear oligoether.

Systematic absences on Weissenberg photographs indicated space group Cc or $C2/c$; based on the statistical distribution of E values, a Patterson map and the structure refinement, $C2/c$ was confirmed.

Cell dimensions were obtained by least squares from angle measurements of 25 strong reflexions between $2\theta = 20$ and $25°$ on an automated four-circle diffrac-

tometer with monochromated Mo $K\alpha$ radiation ($\lambda = 0.71069$ Å). A crystal $0.2 \times 0.3 \times 0.4$ mm grown from ethanol was used to measure 4842 unique reflexions ($7° \leq 2\theta \leq 50°$) by a profile-fitting procedure (Clegg, 1981). Data were corrected for Lp and crystal decay (ca 15%); application of an empirical absorption correction based on measurements of equivalent reflexions at different azimuthal angles reduced the merging R from 0.076 to 0.046 for 981 equivalent reflexions. 3504 data with $F > 4\sigma(F)$ were considered observed.

Hg was located from a Patterson map; the positions of the remaining non-hydrogen atoms were determined by subsequent difference syntheses. H atoms were positioned ideally (C—H = 0.96 Å) and assigned fixed thermal parameters 1.2 times the U values of the attached C atoms. During blocked-cascade least-squares refinement, anisotropic U's for the five heavy atoms were included, and a riding model was employed for H atoms. Final parameters of non-hydrogen atoms are given in Table 1, bond lengths and angles in Tables 2 and 3.*

Table 1. *Coordinates* ($\times 10^4$) *and isotropic temperature factors* ($\text{Å}^2 \times 10^3$)

	x	y	z	U
Hg	1597 (1)	1973 (1)	910 (1)	57 (1)*
Br(1)	1774 (1)	73 (3)	1747 (1)	110 (1)*
Br(2)	1342 (1)	3879 (3)	55 (1)	104 (1)*
Br(3)	−18 (1)	−424 (4)	1635 (1)	127 (1)*
Br(4)	1194 (1)	2537 (3)	3272 (1)	126 (2)*
C(1)	353 (6)	1346 (21)	923 (7)	66 (5)
C(2)	415 (6)	2852 (23)	668 (8)	75 (5)
C(3)	298 (7)	4388 (27)	784 (10)	99 (7)
C(4)	101 (8)	4467 (32)	1183 (10)	117 (8)
C(5)	28 (8)	3141 (30)	1462 (10)	112 (8)
C(6)	139 (7)	1470 (24)	1322 (9)	82 (6)
C(7)	471 (6)	−244 (21)	746 (8)	71 (5)
O(8)	720 (4)	−113 (14)	374 (5)	65 (3)
C(9)	860 (6)	−1699 (23)	197 (8)	78 (6)
C(10)	1157 (6)	−1445 (22)	−152 (8)	71 (5)
O(11)	1586 (4)	−926 (15)	256 (5)	76 (3)
C(12)	1891 (7)	−848 (27)	−49 (9)	95 (7)
C(13)	2339 (7)	−241 (24)	433 (9)	86 (6)
O(14)	2321 (4)	1344 (16)	606 (6)	83 (4)
C(15)	2742 (7)	2089 (27)	1012 (9)	103 (7)
C(16)	2657 (7)	3801 (24)	1160 (9)	91 (6)
O(17)	2389 (4)	3762 (15)	1513 (5)	75 (3)
C(18)	2302 (7)	5376 (23)	1700 (8)	83 (6)
C(19)	2064 (6)	5183 (24)	2136 (8)	80 (6)
O(20)	1614 (4)	4596 (14)	1805 (5)	72 (3)
C(21)	1401 (6)	3913 (23)	2181 (8)	74 (5)
C(22)	1261 (6)	5241 (22)	2519 (8)	64 (5)
C(23)	1232 (7)	6882 (26)	2336 (9)	89 (6)
C(24)	1085 (8)	8116 (33)	2652 (10)	117 (8)
C(25)	995 (7)	7609 (29)	3151 (10)	101 (7)
C(26)	1022 (7)	6032 (27)	3341 (10)	95 (7)
C(27)	1146 (6)	4844 (24)	3011 (8)	76 (5)

* Equivalent isotropic U calculated from anisotropic U.

Table 2. *Bond lengths* (Å)

Br(3)—C(6)	1.84 (2)	Br(4)—C(27)	1.92 (2)
C(1)—C(2)	1.39 (3)	C(1)—C(6)	1.37 (3)
C(1)—C(7)	1.43 (3)	C(2)—C(3)	1.34 (3)
C(3)—C(4)	1.33 (4)	C(4)—C(5)	1.32 (4)
C(5)—C(6)	1.45 (3)	C(7)—O(8)	1.41 (3)
C(9)—O(8)	1.45 (2)	C(10)—C(9)	1.50 (3)
C(10)—O(11)	1.39 (2)	C(12)—O(11)	1.42 (3)
C(12)—C(13)	1.52 (3)	C(13)—O(14)	1.34 (3)
C(15)—O(14)	1.43 (2)	C(15)—C(16)	1.46 (3)
C(16)—O(17)	1.42 (3)	C(18)—O(17)	1.42 (2)
C(18)—C(19)	1.51 (3)	C(19)—O(20)	1.41 (2)
C(21)—O(20)	1.43 (3)	C(21)—C(22)	1.50 (3)
C(22)—C(23)	1.37 (3)	C(22)—C(27)	1.40 (3)
C(23)—C(24)	1.42 (4)	C(24)—C(25)	1.39 (4)
C(25)—C(26)	1.33 (3)	C(26)—C(27)	1.38 (3)

Table 3. *Bond angles* (°)

C(2)—C(1)—C(6)	115.8 (18)	C(2)—C(1)—C(7)	122.2 (21)
C(6)—C(1)—C(7)	121.8 (19)	C(1)—C(2)—C(3)	126.6 (23)
C(2)—C(3)—C(4)	116.0 (23)	C(3)—C(4)—C(5)	123.4 (26)
C(4)—C(5)—C(6)	120.7 (27)	Br(3)—C(6)—C(1)	120.7 (16)
Br(3)—C(6)—C(5)	121.9 (20)	C(1)—C(6)—C(5)	117.3 (21)
C(1)—C(7)—O(8)	113.5 (17)	C(1)—O(8)—C(9)	115.5 (15)
O(8)—C(9)—C(10)	112.0 (16)	C(9)—C(10)—O(11)	108.2 (15)
C(10)—O(11)—C(12)	109.5 (15)	O(11)—C(12)—C(13)	104.6 (17)
C(12)—C(13)—O(14)	113.1 (17)	C(13)—O(14)—C(15)	117.2 (16)
O(14)—C(15)—C(16)	109.7 (18)	C(15)—C(16)—O(17)	109.5 (19)
C(16)—O(17)—C(18)	113.9 (16)	O(17)—C(18)—C(19)	109.6 (17)
C(18)—C(19)—O(20)	108.8 (15)	C(19)—O(20)—C(21)	113.8 (14)
O(20)—C(21)—C(22)	112.5 (16)	C(21)—C(22)—C(23)	120.1 (20)
C(21)—C(22)—C(27)	121.6 (17)	C(23)—C(22)—C(27)	118.3 (20)
C(22)—C(23)—C(24)	119.1 (23)	C(23)—C(24)—C(25)	118.3 (24)
C(24)—C(25)—C(26)	124.0 (26)	C(25)—C(26)—C(27)	116.7 (24)
Br(4)—C(27)—C(22)	118.3 (16)	Br(4)—C(27)—C(26)	118.1 (18)
C(22)—C(27)—C(26)	123.5 (20)		

Discussion. The main result of this investigation is the lack of influence of the rigid terminal donor groups on the complex formed. The present structure is nearly identical to those of complexes of $HgCl_2$ and 2,5,8,11,14-pentaoxapentadecane and 3,6,9,12,15-pentaoxaheptadecane (Iwamoto, 1973*a,b*). Fig. 1 shows a view of the structure in which the Hg^{2+} cation is ligated by both the anions and all the O atoms, but not by the terminal Br atoms of the ligand, though models indicate the possibility of at least one such coordinating Br without geometrical hindrance and strain.

Hg$\cdots$O distances range from 2·72 to 3·06 Å (Table 4), the longer distances probably being due to the bulky terminal groups. O$\cdots$Hg$\cdots$O angles are about 60° and indicate the hexagonal arrangement preferred by equatorially coordinating donor atoms in ligands with ethylene glycol entities (*e.g.* Saenger & Reddy, 1979).

The five O atoms and Hg^{2+} are approximately coplanar (within ±0·25 Å); nearly perpendicular to this plane, both the Br⁻ ions are arranged at distances slightly shorter than in $HgBr_2$ complexes with bridging anions (*e.g.* Bell, Goldstein, Jones & Nowell, 1980), thus completing the coordination bipyramid.
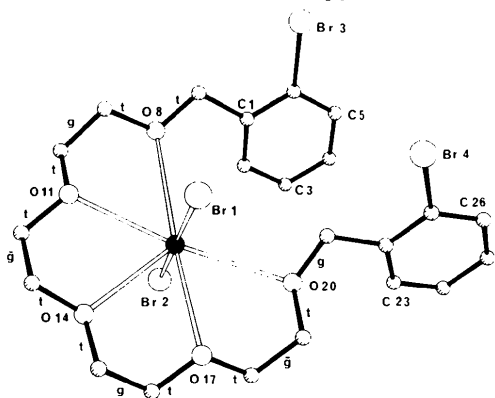

Fig. 1. A perspective view of the complex and the numbering scheme. Radii are arbitrary, *t* and *ḡ* indicate torsion angles *trans* or (−)*gauche*.

Table 4. *Coordination distances* (Å) *and angles* (°)

Hg–Br(1)	2·387 (3)	Hg–O(14)	2·718 (16)
Hg–Br(2)	2·409 (3)	Hg–O(17)	2·751 (11)
Hg–O(8)	3·059 (11)	Hg–O(20)	2·970 (12)
Hg–O(11)	2·776 (12)		
O(8)–Hg–O(11)	60·5 (4)	Br(1)–Hg–O(20)	85·0 (2)
O(11)–Hg–O(14)	61·4 (4)	Br(2)–Hg–O(8)	92·3 (2)
O(14)–Hg–O(17)	62·5 (4)	Br(2)–Hg–O(11)	97·0 (2)
O(17)–Hg–O(20)	60·6 (4)	Br(2)–Hg–O(14)	85·9 (3)
Br(1)–Hg–O(8)	83·2 (2)	Br(2)–Hg–O(17)	92·9 (2)
Br(1)–Hg–O(11)	83·7 (3)	Br(2)–Hg–O(20)	94·0 (2)
Br(1)–Hg–O(14)	99·3 (3)	Br(1)–Hg–Br(2)	174·4 (1)
Br(1)–Hg–O(17)	91·5 (3)		

Moreover, the conformation of the title ligand is comparable to that of 3,6,9,12,15-pentaoxaheptadecane in its $HgCl_2$ complex (Iwamoto, 1973*b*); along the chain all C—C torsion angles are *gauche* and C—O torsion angles are *trans*, with one exception at O(20)—C(21) which is *gauche* to avoid a collision of the phenyl groups. There are no short intermolecular contacts.

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