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Tetrabromo(1,4,7,10,13,16-hexathiacyclooctadecane)dimercury(II)

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Abstract. $[(HgBr_2)_2(C_{12}H_{24}S_6)]$, $M_r = 1081.48$, monoclinic, $P2_1/n$, $a = 11.756$ (3), $b = 12.683$ (2), $c = 8.448$ (2) Å, $\beta = 100.42$ (1)°, $V = 1238.8$ (5) Å^3, $Z = 2$, $D_x = 2.899$ Mg m^{-3}, $\mu = 19.26$ mm^{-1}, λ(Mo $K\alpha$) = 0.7107 Å, $F(000) = 984$, room temperature, $R = 0.048$, $wR = 0.058$ for 1126 unique reflections [$I > 4.5\sigma(I)$]. The hexathiacyclooctadecane ring acts as a binucleating agent, coordinating, facially, each Hg^{II} centre *via* two thia donors [Hg—S = 2.678 (5), 2.866 (5) Å]. The tetrahedron around Hg^{II} is completed by two terminal bromo ligands [Hg—Br = 2.481 (3), 2.540 (3) Å]. The shortest intermolecular contact of 3.427 (3) Å is Hg···Br2 and the compound is thus a one-dimensional polymer along the c axis and the effective coordination of Hg is five (trigonal bipyramid).

Introduction. Macrocyclic ligands have been widely studied and the ring size of polydentate crown thioethers is considered to be a fundamental parameter determining the stereochemistry of their metal complexes (Yoshida, Adachi, Ueda, Tanaka & Goto, 1990). Their metal-binding properties are also a consequence of the variety of their conformations.

Mercury is a polluting agent of considerable toxicity to living creatures. The mercury(II) halogenides are mutually distinct. Mercury(II) chloride crystallizes in an essentially molecular lattice with two short Hg—Cl distances of 2.284 (12) and 2.301 (14) Å, which average 2.291 (9) Å. Cl(1)—Hg—Cl(2) is found to be 178.9 (5)° (Subramanian & Seff, 1980). These distances are similar to the Hg—Cl bonds in gaseous $HgCl_2$ [2.28 (4) Å]. The other four distances are much longer: two are 3.38 and two 3.46 Å. The mercury(II) bromide and iodide crystallize in layer lattices. In $HgBr_2$ each Hg atom is surrounded by six Br atoms; two of them are close (2.48 Å) and the other four at a much longer distance (3.23 Å). There are regular HgI_4 tetrahedra in the crystals of red mercury(II) iodide with an Hg—I distance of 2.78 Å, which is appreciably longer than the Hg—I distance in the free molecule [2.57 (4) Å (Grdenić, 1965)].

In order to discover the coordination of the macrocyclic thioether 1,4,7,10,13,16-hexathiacyclooctadecane (18S6) to Hg we have determined the crystal structures of $(HgCl_2)_2$(18S6), $(HgBr_2)_2$(18S6), (HgI_2)(18S6) and $[Hg(18S6)](C_6H_2N_3O_7)_2$. We have found four different modes of 18S6 coordination to Hg (Herceg & Golič, 1981; Herceg, Matković-Čalogović, Matković & Sevdić, 1984; Herceg, Matković-Čalogović & Golič, 1989; Matković-Čalogović & Herceg, 1990; Herceg & Matković-Čalogović, 1991). We here present the crystal structure of $[(HgBr_2)_2$(18S6)].

Experimental. Colourless crystals were obtained from nitromethane by courtesy of Dr Drenka Sevdić, from 'Ruder Bošković' Institute.

All data were collected on a Philips PW1100 diffractometer (Mo $K\alpha$ radiation, graphite monochromator). The unit-cell parameters were obtained by least-squares refinement of 18 reflections, $12 < \theta < 15°$. Intensity data were collected within $2\theta_{max} < 60°$ ($-16 \le h \le 15$, $0 \le k \le 16$, $0 \le l \le 11$, in the $\theta/2\theta$ scan mode, scan speed 0.04° s^{-1} and scan width 1.4°. Three standard reflections ($40\bar{2}$, $33\bar{2}$, $23\bar{5}$) were monitored every 2 h and showed intensity variation of 7%. Intensities were corrected for decay, Lorentz, polarization and absorption effects (Harkema, 1979). Crystal dimensions (mm from centroid): (010) 0.060; (110), ($\bar{1}\bar{1}0$) 0.045; ($1\bar{1}0$), ($\bar{1}10$) 0.056; ($31\bar{4}$) 0.127; ($10\bar{1}$), ($\bar{1}01$) 0.110; min., max. transmission coefficients 0.138, 0.245. Out of 2098 measured reflections, 1896 unique ($R_{int} = 0.034$), 1126 with $I > 4.5\sigma(I)$ were used in the refinement. The structure was solved by Patterson and Fourier methods. H atoms were included in calculated positions (riding model, C—H 1.08 Å). Full-matrix least-squares refinement on F with anisotropic temperature factors for non-H atoms, overall isotropic temperature factor for H

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atoms (110 parameters) resulted in final $R = 0.048$, $wR = 0.058$, $w = 1/[\sigma^2(F) + 0.0010F^2]$, $S = 1.19$, max. Δ/σ in the last cycle 0.001, max. electron density in final $\Delta\rho$ map 1.33 e Å^{-3} (1.7 Å from Hg). The low-angle reflection 020 was omitted from the refinement in the last cycle. Scattering factors and corrections for anomalous dispersion were from *International Tables for X-ray Crystallography* (1974, Vol. IV). No extinction correction was made. Computing was carried out on an IBM PC/AT-compatible computer using the *CRYSRULER* package (Rizzoli, Sangermano, Calestani & Andreetti, 1987). Drawings of the structure have been prepared on a Philips digital A3 plotter PM 8153, using MicroVAX II and the *PLATON* and *PLUTON* programs (Spek, 1990).

Discussion. Atomic coordinates and equivalent isotropic thermal parameters are listed in Table 1.* Fig. 1 shows the numbering scheme. Selected bond lengths, bond angles, torsion angles and van der Waals contacts are listed in Table 2. The crystal packing is shown in Fig. 2. The compound crystallizes with imposed $\bar{1}$ symmetry and consists of two identically bound $HgBr_2$ units each coordinated, facially, to two S atoms of the macrocyclic ring and two S atoms remain uncoordinated.

The coordination around mercury is highly irregular and could be described as tetrahedral or trigonal bipyramidal. One Hg—Br distance is about the same length as the short Hg—Br bonds in crystalline $HgBr_2$ [2.481 (3) Å] and the other is somewhat longer [2.540 (3) Å] and comparable to the Hg—Br bond of 2.548 (4) Å found in the pyramidal $HgBr_3^-$ ion (Sandström, 1978). Similarly, there is a shorter and longer Hg—S bond, 2.678 (5) and 2.866 (5) Å, respectively. The angles within the tetrahedron vary from 79.2 (2)°, between two S atoms, to 141.55 (9)°, between two Br atoms. The irregularities of the Hg coordination polyhedron could be explained by steric effects and electronegativity differences between the S and Br ligands (Bent, 1961; Cheung & Sim, 1965). The shortest intermolecular contact in this structure is that between Hg in the asymmetric unit 1555 and Br2 in the asymmetric unit 3666 in Fig. 2. This contact of 3.427 (3) Å is just within the sum of the van der Waals radii for Br (1.95 Å; Pauling, 1960) and Hg, if 1.50 Å is taken as van der Waals radius of Hg (Grdenić, 1965). If instead the larger value of 1.72 Å is used for the latter radius (Brown, Massey & Wickens, 1978; Tiekink, 1986), the distance is shorter than the sum of the van der Waals radii. If this contact is taken into account, the effective coordination of Hg is five and the coordination polyhedron is a deformed trigonal bipyramid. The angle Br2(in 3666)···Hg—S4 is only 165.9 (1)° and the Hg atom is displaced from the equatorial Br1Br2S7 plane by

Table 1. *Atomic coordinates and equivalent isotropic thermal parameters* (Å^2) *with e.s.d.'s in parentheses*

$U_{eq} = (1/3)\sum_i\sum_j a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	U_{eq}
Hg	0.3364 (1)	0.5144 (1)	0.3447 (1)	0.0436 (3)
Br1	0.1747 (2)	0.4902 (2)	0.5042 (3)	0.0432 (8)
Br2	0.5109 (2)	0.6229 (2)	0.3368 (3)	0.0352 (6)
S1	0.4263 (4)	0.6769 (4)	−0.2496 (6)	0.038 (2)
C2	0.3603 (15)	0.5999 (16)	−0.1144 (23)	0.031 (7)
C3	0.2500 (17)	0.6524 (16)	−0.0804 (24)	0.039 (8)
S4	0.1790 (4)	0.5813 (4)	0.0630 (6)	0.028 (2)
C5	0.1417 (17)	0.4561 (14)	−0.0414 (24)	0.032 (7)
C6	0.1388 (16)	0.3665 (16)	0.0779 (27)	0.038 (7)
S7	0.2828 (4)	0.3291 (4)	0.1982 (6)	0.031 (2)
C8	0.3624 (16)	0.2962 (18)	0.0379 (25)	0.041 (7)
C9	0.4777 (16)	0.2411 (15)	0.1116 (28)	0.040 (8)

Table 2. *Bond lengths* (Å), *bond angles* (°), *selected torsion angles* (°) *and van der Waals contacts* (Å) *with e.s.d.'s in parentheses*

The asymmetric-unit numbers are explained in the caption to Fig. 2.

Hg—Br1	2.540 (3)	Hg—S4	2.866 (5)
Hg—Br2	2.481 (3)	Hg—S7	2.678 (5)

Br1—Hg—Br2	141.55 (9)	S4—Hg—S7	79.2 (2)
Br1—Hg—S4	92.5 (1)	Hg—S4—C3	113.1 (7)
Br1—Hg—S7	90.2 (1)	Hg—S4—C5	101.9 (6)
Br2—Hg—S4	103.1 (1)	Hg—S7—C6	98.2 (7)
Br2—Hg—S7	126.9 (1)	Hg—S7—C8	115.7 (7)

1 2 3 4	Bond length 2–3	Angle 1–2–3	Torsion angle 1–2–3–4
S1—C2—C3—S4	1.53 (3)	111.3 (13)	−178 (1)
C2—C3—S4—C5	1.83 (2)	114.4 (13)	−62 (2)
C3—S4—C5—C6	1.83 (2)	102.1 (9)	151 (1)
S4—C5—C6—S7	1.52 (3)	111.3 (13)	−69 (2)
C5—C6—S7—C8	1.87 (2)	114.9 (14)	−58 (2)
C6—S7—C8—C9	1.83 (2)	101.0 (10)	−169 (1)
S7—C8—C9—S1^i	1.55 (3)	109.3 (17)	−63 (2)
C8—C9—S1^i—C2^i	1.80 (2)	113.6 (14)	−81 (2)
C9—S1^i—C2^i—C3^i	1.78 (2)	101.3 (10)	−91 (1)

Symmetry code: (i) $1-x, 1-y, -z$.

Atom in the 1555 asymmetric unit	Contact atom	Asymmetric unit of the contact atom	Distance	Angle	
Hg	Br2	3666	3.427 (3)	S4—Hg···Br2	165.9 (1)
Br2	Hg	3666	3.427 (3)	Hg—Br2···Hg	90.88 (8)
Hg	S1	1556	3.975 (5)	S4—Hg···S1	126.4 (1)
				S7—Hg···S1	149.0 (1)
S1	Hg	1554	3.975 (5)		
Hg	Hg	3666	4.262 (2)	Br1—Hg···Hg	109.99 (6)
				S4—Hg···Hg	155.8 (1)
				S7—Hg···Hg	108.7 (1)
				Br2—Hg···Hg	53.53 (6)
Hg	S7	4555	4.224 (5)	S7—Hg···S7	138.0 (1)
S7	Hg	4545	4.224 (5)	Hg—S7···Hg	156.3 (2)
Br1	C9	2465	3.70 (2)		
C9	Br1	2564	3.70 (2)		
Br2	C6	4555	3.69 (2)		
C6	Br2	4545	3.69 (2)		
S4	S7	4555	3.718 (7)		
S7	S4	4545	3.718 (7)		

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55264 (11 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AB0268]

−0.16 Å towards S4. The angles Br2(in 3666)···Hg—X, X = Br1, Br2, S7 (all in 1555) are 81.84 (7), 89.12 (8) and 87.9 (1)°, respectively. For the other relevant angles see Table 2. As there is also a centrosymmetric contact, between Hg from the asymmetric unit 3666 and Br2 in 1555, a weak interaction between molecules exists and the compound could be considered as a one-dimensional polymer along the c axis. At the same time, Br2 is engaged in an intramolecular hydrogen bond C2—H21···Br2 of 3.91 (2) Å with an angle at H of 156. (2)°. The shortest Hg—non-bonded S1 (in 3665) intramolecular distance is 3.889 (5) Å. In the crystal structure of Hg_2NHBr_2, there are $HgBr_3^-$ groups with Hg—Br distances of 2.6 Å and two additional Br^- ions, above and below the $HgBr_3^-$ plane, at a distance of 3.08 Å, resulting in a fairly regular trigonal bipyramid (Brodersen, 1955).

Geometry of the 18S6 *ring*. The C—S distances (Marsh, 1955) involving bonded S atoms could be considered as equal, with some elongation of C6—S7, because the angle Hg—S7—C6 within the five-membered chelate ring is the smallest of all Hg—S—C angles and includes the shorter Hg—S bond. The mean value of the C—C distances is 1.53 Å which is in agreement with the 1.537 Å expected for Csp^3—Csp^3 bonds, but longer than usually found in macrocycles (Herceg, Matković, Sevdić, Matković-Čalogović & Nagl, 1984). The intramolecular C—S—C angles range from 101.0 (10) to 102.1 (9)°, with a mean value of 101.5°; the S—C—C angles range from 109.3 (17) to 111.3 (13)°, with a mean value of 110.6°; and the C—C—S angles range from 113.6 (14) to 114.9 (14)° with a mean value of 114.3°, Table 2. In the free 18S6 ring there is no difference between the S—C—C and the C—C—S angles (Wolf, Hartman, Storey, Foxman & Cooper, 1987).

Conformation. The attractive *gauche* effect at C—C—S—C bonds and the repulsive *gauche* effect at S—C—C—S bonds (Wolf, Hartman, Storey, Foxman & Cooper, 1987) are well pronounced in some thioethers, for instance in $HgI_2(C_{10}H_{20}S_4)$ which is isostructural with $HgBr_2(C_{10}H_{20}S_4)$ (Galešić, Herceg & Sevdić, 1986). In $(HgBr_2)_2$18S6, these effects do not always appear. There are twelve C—C—S—C (C—S—C—C) bonds in the 18S6 ring of the $HgBr_2$ compound: four are antiperiplanar and the others are synclinal [two with the value of ±91 (1)° are just on the limit between synclinal and anticlinal]. Two of the six remaining S—C—C—S bonds adopt antiperiplanar and four synclinal conformations. However, it seems that it is a quite relaxed form of the ring, Table 2 (Herceg, 1976).

The crystal packing is shown in Fig. 2, viewed along the crystallographic a axis. There is a possible hydrogen bond C6—H62···S1(in 4544) of 3.65 (2)° with an angle at H of 151.(2)°. Except for the already mentioned Hg···Br2 contact of 3.427 (3) Å all other contacts are of van der Waals type, Table 2. There is a shortest intermolecular Hg···Hg distance of 4.262 (2) Å through the centre of symmetry [at 2(*a*)], approximately in the *ac* plane, and the shortest Hg···Hg separation of 6.762 (2) Å is along the b axis. The intramolecular Hg···Hg separation is 7.547 (2) Å.

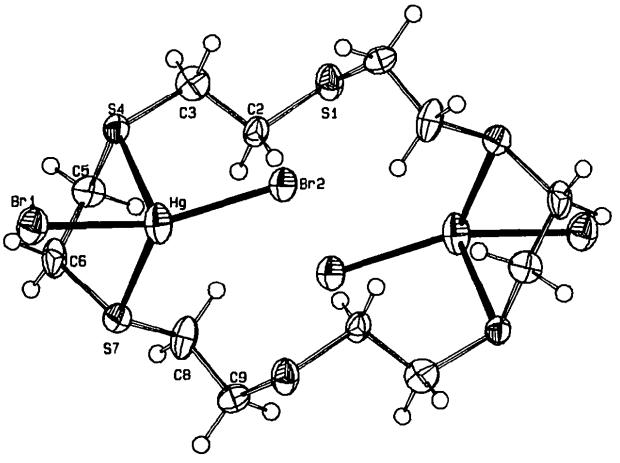

Fig. 1. View of the title compound showing the atom-numbering scheme.

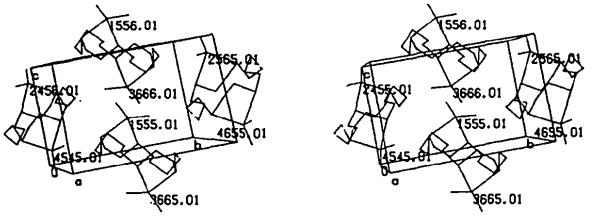

Fig. 2. Stereoview of the crystal structure. H atoms are omitted for clarity. The symmetry operations used are: (1) x, y, z; (2) $\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$; (3) $-x, -y, -z$; (4) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$. The input coordinates are designated by the code 1555. The code 3666 means that these coordinates have been transformed by the symmetry operation (3) and translated along the cell edges a, b, c for + 1.

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Structure of $[Ca(triethylene\ glycol)_2]Cl_2.4H_2O$

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Abstract. Bis{2,2′-[1,2-ethanediylbis(oxy)]bisethanol}-calcium dichloride tetrahydrate, $[Ca(C_6H_{14}O_4)_2]Cl_2.4H_2O$, $M_r = 483.40$, triclinic, $P\bar{1}$, $a = 8.471$ (1), $b = 10.157$ (1), $c = 14.821$ (3) Å, $\alpha = 102.81$ (1), $\beta = 97.74$ (1), $\gamma = 103.52$ (1)°, $V = 1185.4$ (3) Å^3, $Z = 2$, $D_x = 1.35$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71073 Å, $\mu = 5.32$ cm^{-1}, $F(000) = 516$, $T = 293$ K, final $R = 0.048$ for 2098 observed [$F_o \geq 5\sigma(F_o)$] reflections. The cation is 8-coordinate dodecahedral with the alcoholic O atoms in *B* sites [average Ca—O = 2.41 (1) Å] and the etheric O atoms in *A* sites [average Ca—O = 2.458 (9) Å]. The counter ions and water molecules are hydrogen bonded with the alcoholic ends of the glycol chains in a three-dimensional network.

Introduction. Lanthanide podates are reported to be less stable than the corresponding crown ether complexes owing to a size-related macrocycle effect (Bünzli & Pilloud, 1989; Barthelemy, Desreux & Massaux, 1986). Our efforts to study competitive crystallization of the hard lanthanide(III) ions between crown ethers and the related polyethylene glycols (PEG's) have always resulted in crystalline complexes of the acyclic PEG's (Rogers, Rollins, Henry, Murdoch, Etzenhouser, Huggins & Nuñez, 1991) or complexes consisting of a directly coordinated PEG and a hydrogen bonded crown ether (Rogers, Voss & Etzenhouser, 1988). There are some indications that the flexibility of the PEG and the added stability of hydrogen bonding from the terminal glycols may be responsible for the observed crystal structures.

This report continues our investigations of structural features which may lead to the preferential crystallization of PEG complexes. Competitive crystallization of $CaCl_2.2H_2O$ with 3-methylene-16-crown-5 and traces of triethylene glycol (EO3) resulted in isolation of the title complex.

Experimental. 0.1467 g of $CaCl_2.2H_2O$ was added to 5 mL of a 3:1 solution of CH_3CN:CH_3OH. To this was added 0.15 mL of a mixture of 3-methylene-16-crown-5 contaminated with triethylene glycol. The resulting solution was stirred at 333 K for 1 h followed by storage at 268 K for 20 h. Evaporation of the reaction solution initially gave a powder. Dissolution of the solid in a new aliquot of the solvent mixture followed by slow evaporation afforded diffraction-quality crystals. Analysis: calculated C 29.82, H 7.51; found for precipitate C 37.45, H 3.29; found for crystals C 31.99, H 5.29. A crystal of 0.13 × 0.13 × 0.40 mm was used for data collection on an Enraf–Nonius CAD-4 diffractometer, with graphite-monochromated Mo $K\alpha$ radiation. Cell constants were determined from setting angles of 25 reflections ($\theta > 19°$). Intensities were measured using ω–2θ scans, to $\theta_{max} = 50°$ and for h 0 to 10,

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