

Fig. 1. View of  $[\text{Pt}(\text{bpy})\text{Cl}_4]$  with the atom-numbering scheme. Thermal ellipsoids are drawn at the 50% probability level.

the equivalent Pd—Cl distances though the same relative *trans* effects on these distances are observed in each structure.

Least-squares-planes' calculations show that the two rings of the bipyridyl group are essentially planar [all deviations less than  $0.04$  (2) Å], are coplanar, meeting at an angle of  $2.2$  (7)°, and that no atoms of the ligand deviate by more than  $0.08$  (2) Å from the plane defined by Pt, Cl(3), Cl(4), N(1) and N(2).

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## A 1:1 Complex between 1,4,7,10,13,16-Hexaoxacyclooctadecane (18-Crown-6) and Mercury(II) Iodide

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**Abstract.**  $\text{C}_{12}\text{H}_{24}\text{O}_6 \cdot \text{HgI}_2$ ,  $M_r = 718.7$ , monoclinic,  $C2/m$ ,  $a = 13.049$  (5),  $b = 11.241$  (3),  $c = 9.285$  (2) Å,  $\beta = 134.89$  (3)°,  $V = 965$  Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 2.47$  g cm<sup>-3</sup>,  $\text{Cu K}\alpha$ ,  $\lambda = 1.54178$  Å,  $\mu = 410$  cm<sup>-1</sup>,  $F(000) = 660$ , room temperature,  $R = 0.036$  for 558 unique observed reflections with  $|F_o| > 3\sigma(|F_o|)$ . The complex has crystallographic  $2/m$  symmetry and approximate molecular  $D_{3d}$  symmetry. The structure is composed of linear  $\text{HgI}_2$  entities inserted normal to the mean plane of the macrocycle with the Hg atom positioned at its centre. The coordination of the Hg atom is hexagonal bipyramidal with axial Hg—I bond distances of  $2.622$  (1) Å and a mean equatorial Hg...O distance of  $2.86$  (2) Å. The accommodation of the large Hg atom within the macrocycle results in a significant

increase in the magnitude of the O—C—C—O torsional angles from the values normally observed in complexes of 18-crown-6 in which the ligands adopt the all-*gauche* conformation with pseudo  $D_{3d}$  symmetry.

**Introduction.** During our recent investigations (Allwood, Crosby, Pears, Stoddart & Williams, 1984) on the complexation of sulfonium cations by 18-crown-6 (18C6), we attempted to isolate a 2:1 crystalline complex between  $\text{MeSPh}_2^+\text{HgI}_3^-$  and 18C6 from MeOH. In fact, the first crystals we isolated corresponded to a 1:1 complex between  $\text{HgI}_2$  and 18C6, indicating that  $\text{MeSPh}_2^+\text{HgI}_3^-$  had disproportionated to  $\text{MeSPh}_2^+\text{I}^-$  and  $\text{HgI}_2$  under the conditions of the crystal-growing experiment. In view of the

interest which is currently being shown in the solid-state structures of [CdCl<sub>2</sub>.18C6] and [HgCl<sub>2</sub>.18C6] (Paige & Richardson, 1984) and their dibenzo-18-crown-6 (DB18C6) analogues (Kawasaki & Matsuura, 1984), in addition to the previously described (Malmsten, 1979) crystalline 1:1 complexes of CdI<sub>2</sub> and HgI<sub>2</sub> with 1,4,10,13-tetraoxa-7,16-diazacyclooctadecane (DA18C6), we now report on the fortuitous isolation and crystal structure of [HgI<sub>2</sub>.18C6].

**Experimental.** A solution of MeSPh<sub>2</sub>.HgI<sub>2</sub> (200 mg) in warm MeOH (15 ml) was added to a solution of 18C6 (34 mg) in MeOH (5 ml). The solution was allowed to stand at room temperature for 2 h and the resulting crystals initially isolated were found to be suitable for X-ray structural investigation. Crystal size 0.05 × 0.05 × 0.05 mm. Refined unit-cell parameters obtained by centring 18 reflections. Nicolet R3m diffractometer. 721 independent reflections ( $\theta \leq 50^\circ$ ) measured, Cu K $\alpha$  radiation (graphite monochromator),  $\omega$  scan; 558 [|F<sub>o</sub>| > 3 $\sigma$ (|F<sub>o</sub>|)] considered observed, index range h-14/10, k0/12, l0/10; two check reflections measured every 50 reflections, net count constant; Lorentz and polarization corrections, numerical absorption correction (max. and min. transmission factors, 0.30 and 0.10) for face-indexed crystal. Structure solved by heavy-atom method; non-hydrogen atoms refined anisotropically; positions of H atoms calculated (C-H 0.96 Å); H atoms assigned isotropic thermal parameters,  $U(H) = 1.2U_{eq}(C)$ , and allowed to ride on parent C atoms. An empirical extinction correction was applied [ $g = 0.0012(2)$ ]. Refinement using  $F$  magnitudes by block-cascade full-matrix least squares;  $R = 0.036$ ;  $wR = 0.039$  [ $w^{-1} = \sigma^2(F) + 0.0003F^2$ ];  $(\Delta/\sigma)_{max} = 0.002$ ; residual electron density in difference map within -1.0 and +0.82 e Å<sup>-3</sup>; atomic scattering factors and dispersion corrections from *International Tables for X-ray Crystallography* (1974). Computations carried out on an Eclipse S140 computer using the *SHELXTL* program system (Sheldrick, 1983).

**Discussion.** Table 1\* lists the fractional atomic coordinates of the non-hydrogen atoms, Table 2 the bond lengths and angles and the C-C and C-O torsional angles in 18C6.

The structure of [HgI<sub>2</sub>.18C6] is illustrated in Fig. 1, which also shows the atomic numbering scheme. Fig. 2† shows a space-filling representation of the complex.

\* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and a space-filling diagram have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42495 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

† A further space-filling diagram, highlighting the equatorial coordination of Hg by the six O atoms, has been deposited.

There are several examples of 18C6 (Paige & Richardson, 1984; Kawasaki & Matsuura, 1984), DA18C6 (Malmsten, 1979), and DB18C6 (Henrick, Matthews, Podejma & Tasker, 1982; Crowder, Henrick, Matthews & Podejma, 1983), and of the *cis-cisoid-cis* and *cis-transoid-cis* isomers of dicyclohexano-18-crown-6 (Hughes & Truter, 1983) forming complexes with guest molecules such as CdCl<sub>2</sub>, HgCl<sub>2</sub>, HgI<sub>2</sub>, and TlMe<sub>2</sub><sup>+</sup>, threaded through the centre of the

Table 1. Atom coordinates ( $\times 10^4$ ) and temperature factors ( $\text{\AA}^2 \times 10^3$ ) with *e.s.d.*'s in parentheses

	x	y	z	U <sub>eq</sub> *
Hg	0	0	0	39 (1)
I	-2758 (1)	0	-3399 (2)	55 (1)
O(1)	-486 (13)	0	2572 (18)	47 (9)
C(2)	-1247 (14)	1057 (13)	2204 (20)	56 (11)
C(3)	-435 (17)	2101 (14)	2501 (21)	63 (12)
O(4)	-632 (9)	2195 (7)	793 (13)	51 (7)
C(5)	146 (17)	3138 (12)	957 (24)	66 (12)

\* U<sub>eq</sub> is defined as one third of the trace of the orthogonalized U<sub>ij</sub> tensor.

Table 2. Bond lengths (Å), bond angles (°), and torsion angles (°)

Hg-O(1)	2.871 (21)	Hg-O(4)	2.858 (10)
Hg-I	2.622 (1)	O(4)-C(5)	1.401 (22)
O(1)-C(2)	1.426 (19)	C(3)-O(4)	1.420 (27)
C(2)-C(3)	1.471 (25)	C(5)-C(5')	1.531 (50)
O(4)-Hg-O(4 <sup>h</sup> )	119.4 (6)	O(4)-Hg-O(4')	60.6 (6)
O(1)-Hg-O(4)	119.2 (3)	I-Hg-O(1')	85.4 (2)
O(1)-Hg-O(4)	60.8 (3)	I-Hg-O(4')	95.2 (1)
I-Hg-O(1)	94.6 (2)	I-Hg-O(4)	84.8 (1)
I-Hg-I'	180.0	C(2)-O(1)-C(2 <sup>h</sup> )	112.9 (19)
O(1)-C(2)-C(3)	109.5 (16)	C(2)-C(3)-O(4)	108.1 (12)
C(3)-O(4)-C(5)	112.9 (12)	O(4)-C(5)-C(5')	107.8 (9)

C(2 <sup>h</sup> )-O(1)-C(2)-C(3)	-176.7 (10)
O(1)-C(2)-C(3)-O(4)	75.4 (15)
C(2)-C(3)-O(4)-C(5)	-177.6 (13)
C(3)-O(4)-C(5)-C(5')	179.6 (14)
O(4)-C(5)-C(5')-O(4)	-74.6 (15)

Symmetry code: (i) -x, y, -z; (ii) x, -y, z.

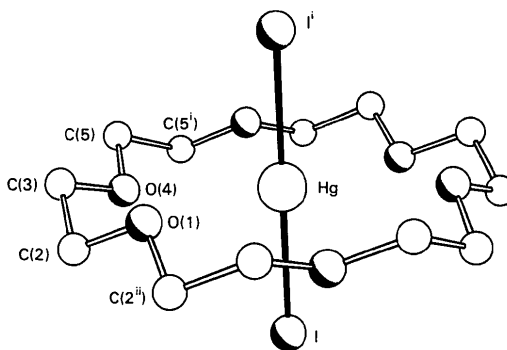


Fig. 1. Side view of the 1:1 complex and the atomic numbering scheme.

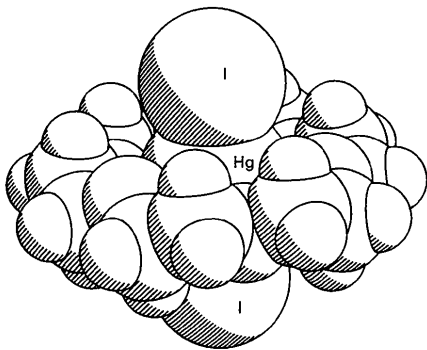


Fig. 2. Space-filling representation of  $[\text{HgI}_2 \cdot 18\text{C}6]$ .

macrocyclic ring, *i.e.* they have rotoxane-like structures. Of particular note are the closely related 18C6 complexes (Paige & Richardson, 1984; Kawasaki & Matsuura, 1984) with  $\text{CdCl}_2$  and  $\text{HgCl}_2$ , and the DA18C6 complex (Malmsten, 1979) with  $\text{HgI}_2$ , where the gross structural features of the 1:1 complexes are analogous to that of  $[\text{HgI}_2 \cdot 18\text{C}6]$ . The present structure provides another example of the relatively rare hexagonal-bipyramidal geometry. The Hg—I bond distances [2.622 (1) Å] are the same as those observed by Jeffrey & Vlasse (1967) in  $\text{HgI}_2$ , but significantly shorter than the value of 2.680 (1) Å reported by Malmsten (1979) for  $[\text{HgI}_2 \cdot \text{DA}18\text{C}6]$ . The Hg...O distances and the I—Hg...O angles (Table 2) do not depart significantly from those reported (Paige & Richardson, 1984) for  $[\text{HgCl}_2 \cdot 18\text{C}6]$ . A consequence of the accommodation of a large Hg atom at the centre of the 18C6 macrocycle is an increase in the magnitude of the mean O—C—C—O torsional angle [75 (2)°], *cf.* the 'normal' value of *ca* 65° (Goldberg, 1980).

Surprisingly, although the title complex as a whole has within statistical significance  $\bar{3}$  symmetry and

adopts a very similar packing arrangement to that reported by Paige & Richardson (1984) for  $[\text{HgCl}_2 \cdot 18\text{C}6]$  and  $[\text{CdCl}_2 \cdot 18\text{C}6]$ , the crystals are not rhombohedral. This may be a consequence of accommodating covalently larger I atoms in the structure in place of Cl atoms. In fact, the unit-cell parameters initially chosen by Paige & Richardson (1984) for a C-face-centred cell of  $a = 10.44$ ,  $b = 11.46$ ,  $c = 7.75$  Å, and  $\beta = 82.21^\circ$  are all different from the present C-face-centred cell.

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## Structures of Dibromo[*N,N'*-bis(2-pyridylmethylene)-1,3-propanediamine]copper(II) (1) and Bromo[*N,N'*-bis(2-pyridylmethylene)-1,4-butanediamine]copper(II) Bromide (2)

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**Abstract.** (1):  $[\text{CuBr}_2(\text{C}_{15}\text{H}_{16}\text{N}_4)]$ ,  $M_r = 475.7$ , monoclinic,  $C2/c$ ,  $a = 13.286$  (3),  $b = 9.723$  (3),  $c = 13.234$  (2) Å,  $\beta = 107.54$  (1)°,  $V = 1630.1$  (5) Å<sup>3</sup>,  $Z = 4$ ,  $D_m = 1.94$  (3),  $D_x = 1.94$  g cm<sup>-3</sup>,  $\lambda(\text{Mo K}\alpha) =$

0.7107 Å,  $\mu = 65.8$  cm<sup>-1</sup>,  $F(000) = 932$ ,  $T = 293$  K,  $R = 0.031$  for 1238 observed [ $I > 2\sigma(I)$ ] of 1898 unique reflections. (2):  $[\text{CuBr}(\text{C}_{16}\text{H}_{18}\text{N}_4)]\text{Br}$ ,  $M_r = 489.8$ , monoclinic,  $P2_1/c$ ,  $a = 12.142$  (3),  $b =$

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