Preferential Coordination of Mercury(II) to Oxygen over Sulfur Atoms in a Tropone-Attached Dithiocrown Ether

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Abstract

5,8,11,14-Tetraoxa-2,17-dithiabicyclo[16.4.1]tricosa-1(22),18,20-trien-23-one ($C_{17}H_{24}O_5S_2$) forms an endo-cyclic 1:1 complex with [HgCl$_2$]. The mercury(II) ion is surrounded by four ethereal O atoms and one S atom. The mesomeric effect lowers the basicity of the S atoms on the tropone ring making them less likely to act as ligating atoms.
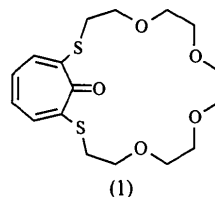
Comment

Currently, there is considerable interest in the complexation of HgCl$_2$ with macrocyclic ethers, since these molecules could be carriers of the Hg^{II} ion which is one of the most critical heavy-metal ions from an environmental viewpoint (Bacon & Kirch, 1985, 1987; Izatt, Bruening, Clark, Lamb & Christensen, 1986; Izatt, Jones, Lamb, Bradshaw & Christensen, 1986; Kasuga, Hirose, Takahashi & Hiratani, 1993). Troponoids have been thought to form complexes of similar stability with various metal ions, such as Zn^{II}, Cd^{II}, Hg^{II} and Cu^{II} (Asao & Kikuchi, 1972), and have received less attention as selective metal-ion binding materials. However, the recent findings of pronounced mercury selectivity in a series of dithiocrown tropone and heptafulvene derivatives (Takeshita, Mori & Hirayama 1989; Kubo, Mori & Takeshita, 1992, 1993; Mori, Kubo & Takeshita, 1994) led to recognition of their potential as host molecules. Meanwhile, Sibert, Lange, Stern, Hoffman & Barrett

(A)   (B)   (C)

(1994) claimed that an unusual feature of the HgCl$_2$ complex of 7,10,13,16-tetraoxa-1,4-dithiacyclooctadec-2-ene-2,3-dicarbonitrile, (A), was the coordination of Hg^{II} by only four O atoms.

In this regard, we recently demonstrated clear examples of preferential coordination of O over S atoms with the 8,8-dicyanoheptafulvene derivatives 23-dicyanomethylene-5,8,11,14,17-pentaoxa-2,20-dithiabicyclo[19.4.1]hexacosa-1(26),21,24-triene, (B), and 20-dicyanomethylene-5,8,11,14-tetraoxa-2,17-dithiabicyclo[16.4.1]tricosa-1(23),18,21-triene, (C) (Kubo, Kato, Mori & Takeshita, 1995).
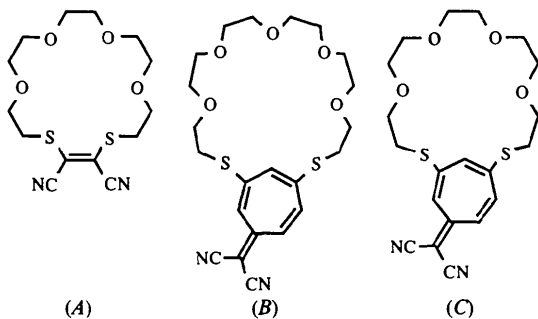
As a matter of efficiency in the transport of Hg^{II}, the dithiocrown derivatives condensed with a tropone system showed a dependence on the cavity size of the crown ethers (Mori *et al.*, 1994); among the previously synthesized sulfur-containing troponoid crown derivatives, 5,8,11,14-tetraoxa-2,17-dithiabicyclo[16.4.1]tricosa-1(22),18,20-trien-23-one, (1), was shown to be the most efficient mercurophile (Takeshita, Yin, Kubo & Mori, 1993). This prompted us to determine the structure of the Hg^{II} complex of (1) by an X-ray crystallographic analysis. Again the results showed a preferential coordination of O over S atoms.

(1)

The Hg^{II} ion is surrounded by one S and four O atoms of the crown ether in pentagonal bipyramidal coordination. The one remaining S atom, S2, is 5.250(4) Å from the Hg^{II} ion. Typical distances for Hg—S are 2.50–2.75 Å (Sibert *et al.*, 1994; Sato, Habata, Sato & Akabori, 1989; Alcock, Heeron & Moore, 1978; Dalley & Larson, 1981); thus, S2 is not coordinated. The coordination features of Hg^{II} in (1)–HgCl$_2$ are similar to those of the HgCl$_2$ complexes of acyclic polyethers such as tetraethylene glycol dimethyl ether (TGM) and tetraethylene glycol diethyl ether (TGE) (Iwamoto, 1973*a,b,c*).

The conformations of the ethereal moiety in the complex are S(*t*)C(*g*)C(*t*)O(*t*)C(*g*)C(*t*)O(*t*)C(*g*)C(*t*)O(*t*)C(*g*)-C(*t*)O(*t*)C(*t*)C(*g*)S, where *t* and *g* indicate *trans* and *gauche* forms, respectively. All the CH$_2$—O bonds are in *trans* conformations.

The Cl—Hg—Cl angle is 175.71(9)°, which is smaller by *ca* 3° than the reported angle [178.9(5)°] of HgCl$_2$ (Subramanian & Seff, 1980). The average value for the length of the Hg—Cl bond (2.299 Å) is similar to that of 2.291(9) Å for HgCl$_2$ (Subramanian & Seff, 1980). The angle between the least-squares plane defined by C1, C2 and C7, and the plane defined by C2, C3, C6 and C7 is 20.4(12)°. This diminished planarity
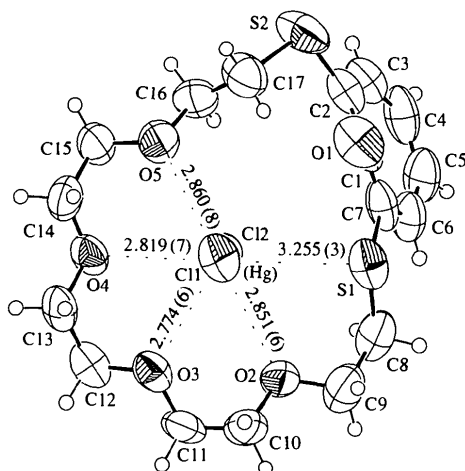
Fig. 1. Molecular structure showing 50% probability displacement ellipsoids. Heteroatoms are shown with shaded ellipsoids. Values shown are the contact distances (Å) between the Hg atom and heteroatoms shorter than 4.0 Å.

of the seven-membered conjugated system of (1)–HgCl$_2$ is a reflection of the decreased 6π-delocalization of the tropone system by complexation, and may be an additional factor for the liberation of the Hg^{II} ion upon acidification (Takeshita *et al.*, 1989; Kubo *et al.*, 1993).

The Hg···O distances range from 2.774 to 2.860 Å, and are similar to those found in the complexes TGM–HgCl$_2$ and TGE–HgCl$_2$ (2.736–3.021 Å) (Iwamoto, 1973*a,b,c*), but longer than those of HgCl$_2$–(18-crown-6) (Paige & Richardson, 1984) and HgCl$_2$–(dibenzo-18-crown-6) (Kawasaki & Matsuura, 1984). Interestingly, the distance between Hg^{II} and the carbonyl O atom in the tropone moiety in (1)–HgCl$_2$ is 4.009 (8) Å, which suggests no significant interactions with Hg^{II}; the comparable interatomic distances in the DMSO–HgCl$_2$ complex are 2.52 (1) or 2.56 (1) Å (Biscarini, Fusina, Nivellini, Mangia & Pelizzi, 1974).

Experimental

Synthesis of (1) has been reported (Kubo *et al.*, 1992). The single crystal of the HgCl$_2$ complex of (1) [(1)–HgCl$_2$], m.p. 481–482 K (in a sealed tube), was obtained by crystallization of an equimolar mixture of HgCl$_2$ and (1) from CH$_3$CN.

Crystal data

C$_{17}$H$_{24}$O$_5$S$_2$.[HgCl$_2$]
M_r = 644.00
Monoclinic
$P2_1/c$
a = 18.749 (4) Å
b = 8.025 (2) Å
c = 15.115 (3) Å
β = 95.84 (2)°
V = 2262.4 (9) Å^3
Z = 4
D_x = 1.891 Mg m^{-3}
D_m not measured

Cu $K\alpha$ radiation
λ = 1.54184 Å
Cell parameters from 25 reflections
θ = 22–42°
μ = 16.316 mm^{-1}
T = 296 K
sphere
0.16 mm (radius)
Yellow

Data collection

Enraf–Nonius FR590 diffractometer
ω–2θ scans
Absorption correction: spherical
T_{min} = 0.039, T_{max} = 0.129
8566 measured reflections
4290 independent reflections

3162 observed reflections
[$I > 2\sigma(I)$]
R_{int} = 0.1053
θ_{max} = 70.05°
h = −22 → 22
k = 0 → 9
l = −18 → 18
3 standard reflections
frequency: 120 min
intensity decay: 4.3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.0635
$wR(F^2)$ = 0.1909
S = 1.136
4289 reflections
244 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F_o^2) + (0.0768P)^2 + 3.0658P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 2.441 e Å^{-3}
$\Delta\rho_{min}$ = −2.519 e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters ($\mathring{A}^2$)*

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

	x	y	z	U_{eq}
Hg	0.70531 (2)	−0.00460 (4)	0.54937 (2)	0.0639 (2)
S1	0.81194 (13)	−0.0606 (5)	0.7307 (2)	0.0884 (7)
S2	0.9093 (2)	0.4460 (5)	0.5677 (3)	0.1217 (12)
O1	0.8473 (4)	0.2597 (11)	0.7086 (6)	0.107 (2)
O2	0.6972 (3)	−0.3091 (8)	0.6450 (4)	0.081 (2)
O3	0.5920 (3)	−0.2216 (8)	0.5059 (4)	0.079 (2)
O4	0.6231 (4)	0.0363 (9)	0.3840 (5)	0.077 (2)
O5	0.7229 (4)	0.2895 (10)	0.4470 (4)	0.091 (2)
C11	0.62837 (12)	0.1454 (3)	0.6277 (2)	0.0864 (7)
C12	0.78803 (12)	−0.1378 (4)	0.4718 (2)	0.0865 (6)
C1	0.8910 (5)	0.1697 (16)	0.6725 (7)	0.092 (3)
C2	0.9354 (5)	0.2503 (13)	0.6089 (6)	0.082 (2)
C3	0.9999 (6)	0.1878 (15)	0.5856 (7)	0.092 (3)
C4	1.0364 (6)	0.046 (2)	0.6085 (8)	0.100 (4)
C5	1.0144 (5)	−0.0916 (18)	0.6521 (7)	0.097 (3)
C6	0.9476 (5)	−0.1151 (16)	0.6832 (6)	0.088 (3)
C7	0.8939 (6)	−0.0056 (13)	0.6900 (7)	0.081 (3)
C8	0.8113 (6)	−0.2839 (15)	0.7256 (7)	0.098 (3)
C9	0.7366 (6)	−0.3465 (18)	0.7269 (8)	0.105 (4)
C10	0.6277 (5)	−0.3714 (14)	0.6365 (8)	0.093 (3)
C11	0.6019 (6)	−0.3837 (12)	0.5419 (8)	0.097 (3)
C12	0.5679 (6)	−0.2174 (14)	0.4122 (7)	0.090 (3)
C13	0.5552 (5)	−0.0425 (15)	0.3820 (7)	0.080 (3)
C14	0.6174 (6)	0.2058 (14)	0.3589 (6)	0.087 (3)
C15	0.6912 (5)	0.2774 (15)	0.3581 (6)	0.092 (3)
C16	0.7980 (6)	0.3275 (16)	0.4541 (7)	0.098 (3)
C17	0.8144 (6)	0.4215 (15)	0.5387 (9)	0.106 (3)

Table 2. *Selected geometric parameters (Å, °)*

Hg—Cl1	2.297 (2)	O5—C16	1.433 (11)
Hg—Cl2	2.301 (2)	C1—C7	1.431 (15)
S1—C7	1.769 (11)	C1—C2	1.482 (15)
S1—C8	1.794 (13)	C2—C3	1.387 (13)
S2—C2	1.742 (12)	C3—C4	1.35 (2)
S2—C17	1.800 (12)	C4—C5	1.37 (2)
O1—C1	1.258 (12)	C5—C6	1.395 (14)
O2—C10	1.389 (11)	C6—C7	1.348 (14)
O2—C9	1.409 (12)	C8—C9	1.49 (2)
O3—C11	1.415 (11)	C10—C11	1.465 (15)
O3—C12	1.441 (11)	C12—C13	1.49 (2)

O4—C14	1.414 (12)	C14—C15	1.499 (13)
O4—C13	1.418 (11)	C16—C17	1.49 (2)
O5—C15	1.416 (11)		
Cl1—Hg—Cl2	175.71 (9)	C4—C5—C6	126.5 (11)
C7—S1—C8	103.7 (5)	C7—C6—C5	129.8 (12)
C2—S2—C17	102.9 (5)	C6—C7—C1	129.9 (11)
C10—O2—C9	114.1 (7)	C6—C7—S1	123.1 (9)
C11—O3—C12	114.5 (8)	C1—C7—S1	106.9 (8)
C14—O4—C13	112.4 (8)	C9—C8—S1	109.8 (9)
C15—O5—C16	113.6 (7)	O2—C9—C8	109.1 (8)
O1—C1—C7	119.9 (11)	O2—C10—C11	109.1 (8)
O1—C1—C2	117.6 (11)	O3—C11—C10	109.3 (8)
C7—C1—C2	122.3 (10)	O3—C12—C13	110.4 (8)
C3—C2—C1	124.6 (10)	O4—C13—C12	107.4 (8)
C3—C2—S2	117.1 (9)	O4—C14—C15	109.1 (9)
C1—C2—S2	118.0 (7)	O5—C15—C14	108.5 (7)
C4—C3—C2	132.1 (11)	O5—C16—C17	106.7 (9)
C3—C4—C5	129.1 (10)	C16—C17—S2	112.1 (9)
C7—S1—C8—C9	−160.1 (8)	O3—C12—C13—O4	70.0 (11)
C10—O2—C9—C8	176.1 (10)	C13—O4—C14—C15	−177.0 (8)
S1—C8—C9—O2	71.2 (12)	C16—O5—C15—C14	169.3 (10)
C9—O2—C10—C11	−158.2 (10)	O4—C14—C15—O5	−70.1 (11)
C12—O3—C11—C10	178.9 (8)	C15—O5—C16—C17	150.6 (10)
O2—C10—C11—O3	−69.1 (11)	O5—C16—C17—S2	169.5 (8)
C11—O3—C12—C13	176.9 (8)	C2—S2—C17—C16	−76.7 (10)
C14—O4—C13—C12	−178.2 (8)		

All H atoms were located at ideal positions and were included in the refinement, but restrained to ride on the atom to which they are bonded. The isotropic displacement parameter of each H atom was held fixed at 1.2 times U_{eq} of the parent atom.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *Xtal_GX* (Hall & du Boulay, 1995). Software used to prepare material for publication: *SHELXL93*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: TA1067). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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cis-Dichlorobis(1,10-phenanthroline-N^1,N^{10})cadmium(II)

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Abstract

The title complex, $[CdCl_2(C_{12}H_8N_2)_2]$, exhibits slightly distorted octahedral geometry; the Cd atom is coordinated to four N atoms from two phenanthroline ligands and to two *cis* Cl atoms. The Cd—N bond lengths are in the range 2.387 (3)–2.486 (4) Å and the Cd—Cl distances are 2.505 (1) and 2.528 (1) Å. The Cl—Cd—Cl angle is 106.19 (5)° and the chelate ring N—Cd—N bond angles are 68.4 (1) and 68.5 (1)°.