Preferential Coordination of Mercury(II) Chloride to Ethereal Oxygens over Sulfurs in 23-Dicyanomethylene-5,8,11,14,17-pentaoxa-2,20-dithiabicyclo[19.4.1]hexacosa-1(26),21,24-triene and 20-Dicyanomethylene-5,8,11,14,-tetraoxa-2,17-dithiabicyclo[16.4.1]tricosa-1(23),18,21-triene

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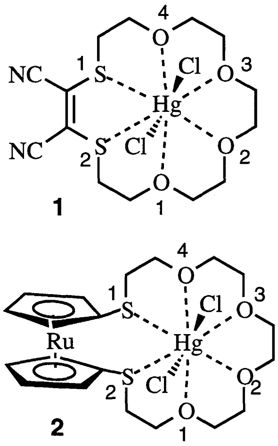
(Received April 27, 1995)

23-Dicyanomethylene-5,8,11,14,17-pentaoxa-2,20-dithiabicyclo[19.4.1]hexacosa-1(26),21,24-triene and $\mathrm{HgCl_2}$ formed a 1:1-complex in which Hg(II) was surrounded by only the five donor oxygens in a pentagonal bipyramidal coordination; the two sulfurs in the crown ring were free from the coordination. Analogously, in the $\mathrm{HgCl_2}$ complex of a lower homologue, 20-dicyanomethylene-5,8,11,14-tetraoxa-2,17-dithiabicyclo[16.4.1]tricosa-1(23),18,21-triene, four oxygen and one sulfur atoms were involved in the complexation, but one sulfur atom was free.

Macrocyclic ligands are of great interest since they can impose unusual coordination numbers and geometries upon complexations with metal salts.[1] Also they are models for metal ion transport through biomembranes.[2] The metallophilic properties of crown ethers having mixed donors of sulfur and oxygen atoms differ from the crown ethers with uniform sulfur or oxygen atoms.

Recently, Hoffman et al.[3] carried out X-ray structural analysis of the $\mathrm{HgCl_2}$ complex (**1**) of 1,4,7,10-tetraoxa-13,16-dithiacyclooctadec-14-ene-14,15-dicarbonitrile, in which Hg(II) was assumed to be coordinated by the four oxygen atoms. However, their claim that sulfurs are free from coordination was deduced on the basis of observed long interatomic distances ($d_{\text{Hg-S}}$), 3.396 and 3.336 Å, and may not be conclusive; the distances for O - Hg ($d_{\text{Hg-O}}$) of **1** fell in two categories, one was 2.681 and 2.657, and the other, 2.980 and 2.932. Should one assume the figure, 2.980, as a coordinated distance for Hg-O, the distances of Hg-S, 3.336 or 3.396, should be difficult to interpret as "not coordinated." In a rough approximation, the ratios of the $d_{\text{X-Y}}$ and the bond distance ($r_{\text{X-Y}}$) calculated from the covalent radii of two bonding atoms[4] are 1.32 and 1.35 for $d_{\text{Hg-S}}$:$r_{\text{Hg-S}}$, which are in a same category with one of those for $d_{\text{Hg-O}}$:$r_{\text{Hg-O}}$ in **1**, 1.34 and 1.32 which are shown in parentheses (Figure 1).



1
Hg-1-O=2.980 Å (1.34)
Hg-2-O=2.681 Å (1.21)
Hg-3-O=2.657 Å (1.20)
Hg-4-O=2.932 Å (1.32)
Hg-1-S=3.396 Å (1.35)
Hg-2-S=3.336 Å (1.32)

2
Hg-1-O=3.048 Å (1.37)
Hg-2-O=2.838 Å (1.27)
Hg-3-O=2.888 Å (1.30)
Hg-4-O=3.120 Å (1.40)
Hg-1-S=3.034 Å (1.20)
Hg-2-S=3.330 Å (1.32)

Figure 1. Interatomic distances of complexes **1**[3] and **2**.[5]

Indeed, Akabori et al.[5] already analyzed the crystal structure of the $\mathrm{HgCl_2}$ complex (**2**) of 4,7,10,13-tetraoxa-1,16-dithia-[16](1,1')ruthenocenophane to reveal a hexagonal bipyramidal structure with two kinds of interatomic distances for Hg-S, 3.034 and 3.330 Å, respectively. The latter was classified as "coordinated."

We herein present an ambiguous example of preferential coordination of Hg(II) ion to oxygen over sulfur atoms found in the $\mathrm{HgCl_2}$ complex (**3**) of 23-dicyanomethylene-5,8,11,14,17-pentaoxa-2,20-dithiabicyclo[19.4.1]hexacosa-1(26),21,24-triene; it has been the most effective mercurophilic dithiocrown ether ever investigated by us.[6,7,8]

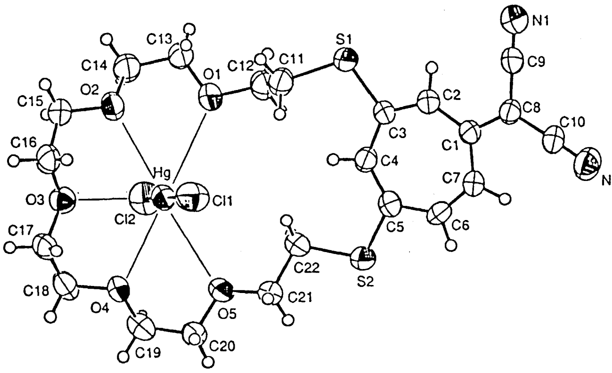
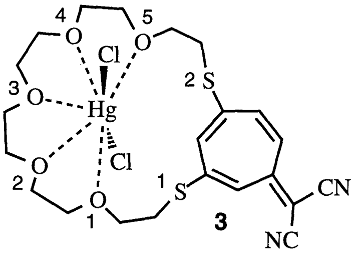


Figure 2. The ORTEP drawing of **3**.

The single crystal of **3** (M=736.10) obtained from $\mathrm{HgCl_2}$ and 23-dicyanomethylene-5,8,11,14,17-pentaoxa-2,20-dithiabicyclo[19.4.1]hexacosa-1(26),21,24-triene (1:1), red prism, mp 193-195 °C (sealed tube), by recrystallization from $\mathrm{CH_3CN}$, was triclinic with space group $P\bar{1}$, and had cell dimensions of a= 12.874(1), b=14.649(2), c=8.081(1) Å, α=101.56 (1), β= 107.27(1), γ=67.45(1), V=1337.6(3) Å^3, Z=2, and D_x=1.83 gcm^{-3}.

The ORTEP diagram (Figure 2) at the final stage of R= 0.074 and Rw=0.094 showed that the five oxygen atoms are endodentate, whereas the two sulfur atoms have the exo orientation. Thus, Hg(II) of **3** was surrounded by the five donor oxygen atoms in a pentagonal bipyramidal coordination (Figure 3). In this regard, coordination of pentaoxadithiocrown part in **3** to Hg (II) was clearer than the case of **1**;[3] two sulfur atoms did not coordinate to Hg(II) at all. Thus, the $d_{\text{Hg-O}}$ of **3**, 2.736-3.021 Å ($d_{\text{Hg-O}}$:$r_{\text{Hg-O}}$ = 1.23 to 1.36), which are similar to those of the $\mathrm{HgCl_2}$ complexes of open chain polyethers, i.e., tetraethylene glycol dimethyl ether (2.78–2.96 Å)[9] and 1,15-bis(2-bromophenyl)-2,5,8,11,14-pentaoxapentadecane (2.718-3.059 Å),[10] and are shorter than those of $\mathrm{HgCl_2}$•(18-crown-6)[11] and $\mathrm{HgCl_2}$•(dibenzo-18-crown-6).[12] The bond angles of four O-Hg-O were between 57 and 62°. The $d_{Hg\text{-}S}$ of **3** were 5.600 and 6.242, being clearly beyond the authentic $r_{Hg\text{-}S}$ (2.52 Å).[4]



3

Hg-1-O=3.021 Å (1.36)
Hg-2-O=2.861 Å (1.29)
Hg-3-O=2.736 Å (1.23)
Hg-4-O=2.787 Å (1.26)
Hg-5-O=2.970 Å (1.34)
Hg-1-S=6.242 Å (2.48)
Hg-2-S=5.600 Å (2.22)

Figure 3. Interatomic distances of complex **3**.

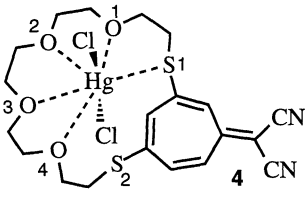
Other features of interest include the bond angle of Cl-Hg-Cl is 171.9°, which is smaller by 7° than the reported angle of $HgCl_2$, 178.9°,[13] and the average value for the bond length (2.295 Å) of Hg-Cl bond is similar to that (2.291(9) Å) of $HgCl_2$.[13]

The dicyanomethylene group of **3** is out of the crown ether ring, which has the conformation, S(g)C(t)C(g)O(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(t)S, where (t) and (g) denote trans and gauche linkages, respectively. One C-S bond was gauche placement, but the other was trans. Among ten C-O bonds, one C-O bond was gauche and others were trans, whereas two C-C bonds were trans and the other four bonds were gauche. The order of gauche preference[14] of C-S and C-O bonds is C-S>C-O even in the less symmetrical **3**.

The bond length of the exocyclic C=C (1.39(2) Å) of **3** is similar to those (1.389(3) and 1.392(5) Å) for 5- and 7-(dicyanomethylene)-2,3-dihydrocyclohepta-1,4-dithiane.[15] Delocalization of the n-electrons of the sulfur atoms made the exocyclic C=C bond shorter than that (1.422(13) Å) of 8,8-dicyanoheptafulvene.[16]

As a result, the decreased electron density of the Hg complex allowed to take the exodentate conformation of the sulfur atoms to become reluctant and only ethereal oxygens interacted.

It is noteworthy that in the Hg(II) complex (**4**) of a lower homologue, 20-dicyanomethylene-5,8,11,14-tetraoxa-2,17-dithiabicyclo[16.4.1]tricosa-1(23),18,21-triene, one sulfur and four oxygen atoms involved to form the similar pentagonal bipyramidal complex with $HgCl_2$. The structural features of **4**, red prisms, mp 171-172 °C, obtained from the X-ray analysis, are shown in Figure 4.

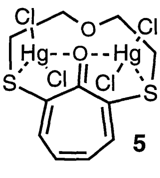


4

Hg-1-O=3.087 Å (1.39)
Hg-2-O=2.609 Å (1.18)
Hg-3-O=2.657 Å (1.23)
Hg-4-O=2.911 Å (1.31)
Hg-1-S=3.138 Å (1.25)
Hg-2-S=5.360 Å (2.13)

Figure 4. Interatomic distances of complex **4**.

Other than **3** and **4**, only the structure of a 2:1-Hg(II) complex (**5**) of 5-oxa-2,8-dithiabicyclo[7.4.1]tetradeca-1(13),9,11-trien-14-one was previously solved by X-ray analysis,[6] but it was a side-on complex with the tropone carbonyl and thioether sulfur atoms.



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Consequently, the side-on geometry should not be the primary reason of the facile reversible complexation to enable the transport of Hg(II) salts, a characteristic feature.

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