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Novel Structures of 1:1 Complexes of 1,4,7,10,13-Pentaoxa- and 1,13-Dioxa-4,7,10-trithia[13](1,1')ruthenocenophanes with $HgCl_2$

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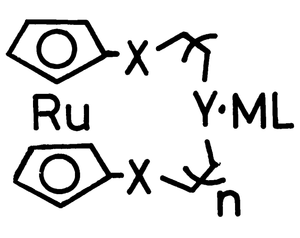
The structures of 1:1 complexes of 1,4,7,10,13-pentaoxa- and 1,13-dioxa-4,7,10-trithia[13](1,1')ruthenocenophanes with $HgCl_2$ have been determined by the single crystal X-ray diffraction method. The complexing forms of the two complexes are quite similar to each other. Only the Ru atom of the ruthenocene nucleus was coordinated to $HgCl_2$ with a slightly distorted trigonal-planar configuration. The distances between the Ru and the Hg atoms are 2.683(3) and 2.704(1) Å, respectively.

Many reserach groups have recently attempted to investigate modified crown ethers in order to develop a new functionality for them.[1)] In concert with this viewpoint, we have studied the preparation and structures of the complexes of metallocenocrown ethers with an interest in the electron-transfer interaction between the complexed cation and the metal atom of the metallocene nucleus. In a previous paper,[2)] we reported on the molecular structure of a 1:1 complex of 4,7,10,13-tetraoxa-1,16-dithia[16](1,1')ruthenocenophane with $HgCl_2$, in which the linear Cl-Hg-Cl moiety was found to be held perpendicularly in the central cavity of the macrocyclic moiety. The distance between the Ru atom and the Hg atom is longer than 3.6 Å, which is too long for direct Ru-Hg interaction. We have also previously reported[3)] on the complexes of polyoxa- and 1,n-dioxathia[n]ruthenocenophanes with $HgCl_2$ (or $AgNO_3$) (**2**-**4**) and a presence of the strong electron-transfer interaction between the Ru atom and the Hg



1, n=4, X=S, Y=O, ML=$HgCl_2$
2, n=3, X=S, Y=O, ML=$AgNO_3$
3, n=3, X=O, Y=O, ML=$HgCl_2$
4, n=3, X=O, Y=S, ML=$HgCl_2$

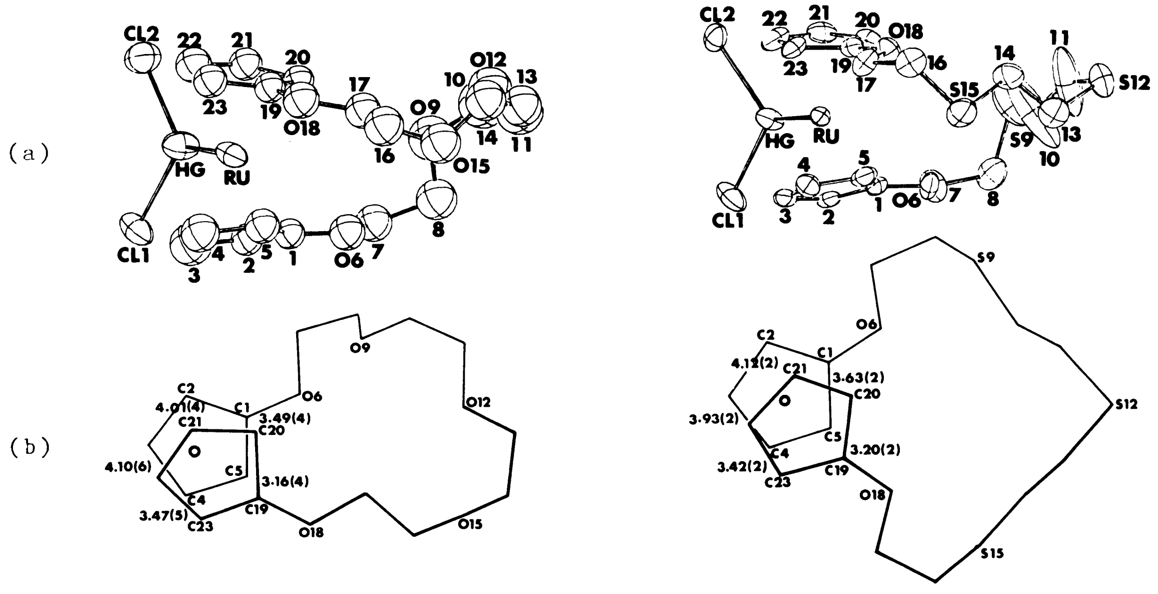
atom in **3** and **4** from the ^{1}H NMR and UV spectral data. The Ru-Hg interaction may be explained by two possibilities for the complexing manner: i) the Hg atom incorporated in the crown ether moiety has an interaction with Ru atom ; ii) the Hg atom is directly coordinated to the Ru atom from the opposite site of the macrocyclic ring. The result is very different from that of 1:1 silver complex **2** in which the Ag atom incorporated in the crown ether cavity of the host molecule did not interact with the Ru atom of the ruthenocene. In this paper, we report on the molecular structures of **3** and **4** in order to clarify the manner of the Ru-Hg interaction.

Complexes **2**, **3**, and **4** were prepared by the same manner as in the previous paper.$^{3)}$

Crystal data:**3**, $C_{18}H_{24}O_5RuHgCl_2$, Mw=693.0, triclinic, a=12.043(3), b=10.759(2), c=8.529(2) Å, α=98.76(2), β=101.22(2), γ=77.03(2)°, U=1049.5 Å^3, Z=2, Dc=2.19 g cm^{-3}, μ(MoKα)=84 cm^{-1}. **4**, $C_{18}H_{24}O_2S_3RuHgCl_2$, Mw=741.2, triclinic, a=17.100(3), b=8.986(1), c=8.618(2) Å, α=105.17(1), β=62.24(1), γ=100.54(1)°, U=1128.1 Å^3, Z=2, Dc=2.18 g cm^{-3}, μ(MoKα)=81 cm^{-1}.

The 3244 and 3394 independent reflections ($Fo \geq 2\sigma(Fo)$) for **3** and **4** were collected on a Rigaku AFC-5R diffractometer using MoKα radiation. The strucures were solved by the heavy atom method and refined by block-diagonal least-squares to final R values of 0.107 and 0.055 for **3** and **4**, respectively.

The molecular structures of **3** and **4** are illustrated in Fig. 1. The bond angles around Hg atom and bond lengths between metal-metal and metal-Cl are also listed in Table 1. The complexing forms of the two complexes are quite

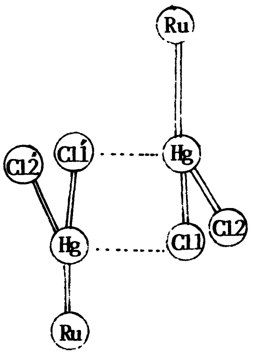


3 4

Fig. 1. (a) **ORTEP** drowings of the molecules with atomic numbering scheme. (b) Projections of the organic ligand moieties on the Cp ring containing the C(1) atom with the C----C distances (Å) between the rings. An open Circle denotes the Ru atom.

Table 1. Selected bond lengths and angles of **3** and **4**

			3		**4**	
1	2	3	1-2	1-2-3	1-2	1-2-3
Ru	Hg	Cl(1)	2.683(3)Å	126.3(2)°	2.704(1)Å	128.0(1)°
Ru	Hg	Cl(2)		128.1(2)		122.1(1)
Ru	Hg	Cl(1)'		99.4(2)		106.0(1)
Cl(1)	Hg	Cl(2)	2.528(9)	103.7(3)	2.430(5)	104.6(1)
Cl(1)'	Hg	Cl(1)	2.943(9)	89.9(3)	2.885(4)	99.2(2)
Cl(2)	Hg	Cl(1)'	2.451(9)	93.0(3)	2.574(4)	85.0(1)



similar to each other except for the conformation of the macrocyclic polyether moieties. In both complexes the Hg atom coordinated directly to the Ru atom of the ruthenocene nucleus from the opposite site of the crown ether moiety, with a slightly distorted trigonal-planar configuration. The Ru-Hg interatomic distances in **3** and **4** are 2.683(3) and 2.704(1) Å respectively, which essentially equals the sums (2.68 Å) of the covalent radii[4)] of Ru and Hg atoms. The results differ completely from that of **1** in which the Hg atom incorporated in the central cavity of the macrocyclic moiety forms a distorted hexagonal-bipyramidal geometry with the two chlorine atom coordinated axially and the Cl-Hg-Cl skeleton is almost linear with an angle of 172.7(2)°.[2)] Also, dibenzo-18-crown-6 react with $HgCl_2$ to give 1:1 adduct with an almost linear Cl-Hg-Cl skeleton with an angle of 176.9°, and the Hg atom is incorporated into the crown ether moiety perpendicular to the plane of O_6.[5)] In the ^1H NMR spectra of the metal free ligands, 1,13-dioxa-4,7,10-trithia- and 1,4,7,10,13-pentaoxa[13](1,1')ruthenocenophanes, the chemical shift differences between α- and β-protons of the Cp rings are only 0.41 and 0.38 ppm, respectively.[3)] Therefore, the two Cp rings are nearly parallel[6)] with each other and the direct attack of the Hg atom to the Ru atom may have disadvantages compared with the incorporation of the Hg atom into the crown ether part. Furthermore, CPK model inspections suggest that the cavity sizes of these ligands are enough to encapsule the Hg atom. Also, if the Hg atom is incorporated in the crown ether part of the [13]ruthenocenophanes, the Hg atom has to take a distorted pentagonal-bipyramidal geometry with two Cl atoms coordinated axially. However, the Hg atom in **3** and **4** is directly bonded to the Ru atom of the ruthenocene nucleus from the opposite site of crown ether moiety. The result suggests that, in the complexes **3** and **4**, the pentagonal-bipyramidal geometry of the Hg atom is unstable compared with the hexagonal-bipyramidal geometry such as in **1**, although some other reasons can not be ruled out. In the complexes (**3** and **4**), the sums of the three bond angles about each Hg atom are 358.1 and 354.7°, and the deviations of the Hg atom from the Cl(1)-Ru-Cl(2) plane are 0.201 and 0.340 Å, respectively. These values mean that the coordination of the Hg atom found in the present complexes is very close to trigonal, and that most probably those bonds are formed by sp^2 hybridization. This configuration of the Hg atom is very similar to those of $N(CH_3)_4HgBr_3$ 7) and $[(C_5H_5)_2Ru]_23HgCl_2$. 8) A slight distortion from sp^2 hybridization which would require an exactly planar configuration is due to the steric hindrance between the $HgCl_2$ unit and the two Cp rings and the interaction with the adjacent molecule as described below. Furthermore, one Cl atom of the complex, which is the atom with the longer distance in the two Hg-Cl bonds, is linked by weak bond to the Hg atom of the adjacent complex. These distances are 2.943(9) and 2.885(4) Å for **3** and **4** which are about 0.35 Å shorter than the sum of the van der Waals radii 4) of Hg and Cl atoms. These results indicate that complexes (**3** and **4**) consist of a dimer by the Hg-Cl' bond in the crystals.

In addition, X-ray analysis of the silver complex **2** was carried out. However, we were unfortunately not able to obtain satisfactory results because of the decomposition of the sample during X-ray measurement.

More detailed structural studies on the mercury complexes of many other metallocenocrown ethers are in progress.

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