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PREPARATION OF DIBENZO-18-CROWN-6 COMPLEXES OF CADMIUM(II) AND MERCURY(II), $[MX_2(dbc)]$, AND MOLECULAR STRUCTURE OF $[HgCl_2(dbc)]$

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$[MX_2(dbc)]$ complexes (M= Cd and Hg, X= Cl, Br, I, CN, and SCN) were prepared by heating an equimolar mixture of MX_2 and dibenzo-18-crown-6 (dbc) in acetonitrile or toluene. A linear Cl-Hg-Cl moiety was found to be held perpendicularly in a quasi-planar ring of O_6 from the X-ray cryatal structure analysis.

In mercury(II) chloride, the Cl-Hg bonds show marked covalent character with a linear Cl-Hg-Cl skeleton.[1)] In the solid state, the mercury atom was coordinated by two chloride ions with short Hg-Cl distances and four chloride ions with long ones. This molecule is isoelectronic with dimethylthallium(III) ion, which forms complexes with some macrocyclic crown-ethers.[2 - 5)] Pedersen, however, reported that cadmium(II) and mercury(II) chlorides do not form complexes with dibenzo-18-crown-6 in CH_3OH.[6)] Dalley and Larson reported a mercury(II) chloride complex of dithia-18-crown-6, $[HgCl_2(C_{12}H_{24}O_4S_2)]\cdot HgCl_2$. In this complex, however, only two sulfur atoms of the crown-ether coordinate to one of the mercury atom, forming a distorted tetrahedral geometry and the other $HgCl_2$ unit is free from coordination of the crown-ether.[7)]

In this paper we will report the preparation of cadmium(II) and mercury(II) complexes of dibenzo-18-crown-6 (dbc) and their IR, Raman, and ^1H NMR spectra. The molecular structure of $[HgCl_2(dbc)]$ will also be reported.

The $[HgCl_2(dbc)]$ complex, for example, was obtained by heating an equimolar mixture of mercury(II) chloride and dbc in CH_3CN until the solid was dissolved and by distilling off some portion of solvent. The other complexes were prepared

$$MX_2 \quad + \quad dbc \quad \xrightarrow[\text{sol.}]{\Delta} \quad [MX_2(bdc)]$$

M= Cd	X= Cl(**1**), Br(**2**), and I(**3**)	sol.= CH_3OH/CH_3CN(1:9)
Hg	Cl(**4**), Br(**5**), and SCN(**6**)	CH_3CN
	CN(**7**)	$CH_3CN/CH_3C_6H_5$(1:9)
	I(**8**)	$CH_3C_6H_5$

essentially by the same method.[8)] The complexes obtained are colorless and soluble in polar solvents such as CH_3CN, CH_2Cl_2, and $CHCl_3$. The mercury complexes are non-electrolytes in CH_3CN.[9)] The IR spectra of these complexes in the NaCl region are quite similar to that of [K(dbc)]NCS,[6)] i.e., a strong band at about 1000 cm^{-1} observed in free dbc shifted to about 950 cm^{-1} and four medium bands at 1070 - 1030 cm^{-1} were replaced by a single strong band at 1060 cm^{-1} in the complexes. In the SCN complex, an additional strong band was observed at 2132 cm^{-1} and weak one at 700 cm^{-1}, suggesting coordination of the sulfur atom of the SCN group to the mercury atom. In the low frequency region of the vibrational spectra of the mercury complexes, a ν_{asym}(X-Hg-X) band was observed in the IR spectra and a ν_{sym}(X-Hg-X) one in the Raman spectra. Frequencies of these bands are shown in Table 1. The bands observed in the complexes shift to lower frequency as compared with those of gaseous HgX_2.[10)] Considering the selection rule of the vibrational spectra, the X-Hg-X skeleton in these complexes may also have a linear geometry.

Table 1. Relevant IR and Raman data of $[HgX_2(dbc)]$ in the solid state(in cm^{-1})[a)]

X	ν_{asym}(X-Hg-X) (IR)	ν_{sym}(X-Hg-X) (Raman)
Cl	353 (413)	305 (355)
Br	273 (293)	192 (220)
I	b) (237)	141 (155)
CN	422	386
SCN	299	268

a) Values in parentheses are those of HgX_2 in the gaseous state(Ref. 10).

b) Below 200 cm^{-1}.

In the ^1H NMR spectra, the proton signals of the methylene groups of the complexes, $[MX_2(dbc)]$, and free dbc appeared at the similar position in $CDCl_3$. The profile of the signals of the complexes, however, was a little different from that of free dbc. In **1**, **2**, **3**, and **8**, two kinds of the methylene signals coalesced into almost single signal. The methylene signals of a mixture of $[MX_2(dbc)]$ and free dbc in $CDCl_3$ at an ambient temperature were found to be a superposition of each signal and did not show any indication of exchange of dbc even at 50 °C. The exchange reaction shown below, therefore,

$$[MX_2(dbc)] \quad + \quad dbc^* \quad \underset{CDCl_3}{\overset{slow}{\rightleftharpoons}} \quad [MX_2(dbc^*)] \quad + \quad dbc$$

is slow on the NMR time scale. The ^1H NMR spectrum measured immediately after dissolving a 1 : 1 mixture of $HgBr_2$ and dbc in CH_3CN was found to be the same as that of $[HgBr_2(dbc)]$. The rate of complexation, therefore, is fast at ambient temperature. The above observations suggest that a linear X-Hg-X skeleton is

$$HgBr_2 \quad + \quad dbc \quad \xrightarrow[CH_3CN]{fast} \quad [HgBr_2(dbc)]$$

held strongly in the crown-ether ring.

The crystal structure analysis of **4** was performed to confirm the above assumption. Crystal data: $C_{20}H_{24}O_6Cl_2Hg$, tetragonal, I4, a= 24.390(15), c= 7.705(9) Å, U= 4583.2 $Å^3$, Z= 8, Dc= 1.83, μ(Mo Kα)= 71.2 cm^{-1}.
The X-ray diffraction data were collected for needle-shaped crystal on a Rigaku automated four-circle diffractometer with graphite monochromated Mo kα radiation. A total of 2408 independent reflections were collected up to 2θ= 50° by ω-2θ scan method, in which 1744 were non-zero reflections. No absorption corrections were made. The crystal structure was solved by the usual heavy atom method. Anisotropic temperature factors were used for heavy atoms in the refinement by the block-diagonal least squares method. In the electron density map, there exist small positional disorders in the methylene and benzene groups. The final R factor is 0.100. A stereoview of structure of **4** is depicted in Fig. 1. As expected from spectroscopic analyses, **4** contains an almost linear Cl-Hg-Cl skeleton with an angle of 176.90(70)° which is perpendicular to the plane of O_6. The Hg atom displaced from the O_6 plane(rms= 0.11) by 0.10 Å toward Cl(1). The Hg-Cl(1) and Hg-Cl(2) distances are 2.323(20)

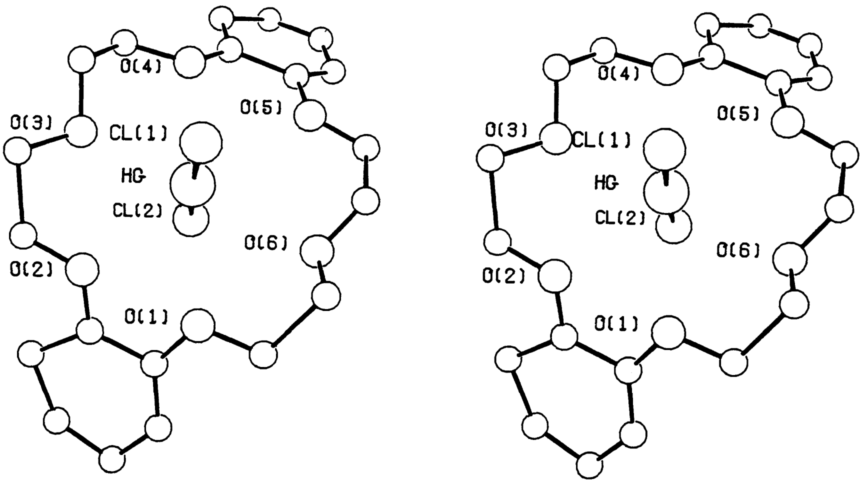

Fig. 1. A stereoview of molecular structure of **4**.

and 2.395(17) Å, respectively. Similar values were reported for $[(HgCl_2)_3(DMSO)_2]$ (2.309 and 2.320 Å).$^{11)}$ These values are slightly longer than those of crystalline $HgCl_2$(2.29 Å).$^{12)}$ The crown-ether adopts a syn conformation as in $[Tl(CH_3)_2(dbc)]$pic (pic= picrate).$^{3)}$ The least squares planes of the two phenyl groups incline at 40 and 44°, respectively, to the O_6 plane. In this conformation all oxygen atoms direct one of their lone pairs to the central mercury atom. The mean distance of the six Hg-O bonds is 2.79 Å. This value is comparable to that of $[Tl(CH_3)_2(dbc)]$pic (2.76 Å).$^{3)}$

All the crystallographic computations were performed at the crystallographic Research Center of Osaka University.

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8) Elemental analyses of C, H, N of all complexes prepared agreed to the calculated values of MX_2(dbc) within 0.3% except **8**, in which observed value of C is greater than calculated one by 0.65%. **1**, yield 88%, mp >270 °C. **2**, yield 86%, mp > 270 °C (decomp). **3**, yield 94%, mp ≈270 °C(decomp). **4**, yield 89%, mp 260 - 261 °C. **5**, yield 69%, mp 229 - 231 °C. **6**, yield 60%, mp 263 - 265 °C. **7**, yield 80%, mp ≈225 °C(decomp). **8**, yield 67%, mp 173 - 174 °C.

9) The molar conductances of the complexes at 1×10^{-3} mol dm^{-3} in CH_3CN at 25 °C were 0.3, 0.3. 1.2, 0.3, and 0.5 $\times 10^{-4}$ S m^2 mol^{-1} for **4**, **5**, **6**, **7**, and **8**, respectively.

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