The Structure of Diaquatetrakis(thiocyanato)cobalt(II)mercury(II)-*N*-Methyl-2-pyrrolidone(1/2), $CoHg(SCN)_4(H_2O)_2 \cdot 2(C_3H_6CONCH_3)$

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Synopsis. The crystal and molecular structure of the title complex was determined using the single-crystal X-ray diffraction method. A crystal of $CoHgC_{14}H_{22}N_6O_4S_4$, F.W. 726.15, is tetragonal with a space group $P\bar{4}$, a=12.082(3), c=8.097(2) Å, U=1182.0(5) Å^3, Z=2, D_x=2.04 Mg m^{-3}, and μ(Mo $K\alpha$)=7.72 mm^{-1}. Tetrahedral mercury(II) coordinated with four sulfur atoms and octahedral cobalt(II) coordinated with four nitrogen atoms of SCN^- (equatorially) and two oxygen atoms of H_2O (axially) are linked by thiocyanate bridges to form planar networks parallel to (001). The planes are connected by *N*-methyl-2-pyrrolidone (mpd) molecules through the hydrogen bonds with two coordinated water molecules at both side networks. The structure resembles that of the *N,N*-dimethylacetamide (dma) adduct, $CoHg(SCN)_4(H_2O)_2 \cdot 2dma$. These are new types of inclusion compounds.

Cobalt(II), mercury(II), thiocyanate (**1**),[1] and its Lewis-base adducts[2—5] are known to exist in a variety of polymeric structures. Among them, the previously reported *N,N*-dimethylacetamide (dma) adduct, $CoHg(SCN)_4(H_2O)_2 \cdot 2dma$ (**2**),[5] was regarded as a kind of inclusion compound because dma molecules are maintained between the metal–thiocyanate networks by only the hydrogen bonds to the two ligating water molecules of both planes. The dma molecules are not easily removed, even when they are left standing for a long time in the air.

During the course of our further investigation we synthesized the *N*-methyl-2-pyrrolidone (mpd) adduct shown in the title (**3**). The structure has been determined by an X-ray diffraction analysis using its single crystal.

Experimental

Single-Crystal X-Ray Analysis. Crystals of **3** were obtained as follows: **1** (1.0 g, 2.0 mmol) was dissolved into 20 cm^3 of mpd. To the blue solution, an equal volume of water was added; the color of the solution turned red. After the solution was left standing overnight, precipitated **3** (red-brown in color) was separated. The yield was 1.1 g (74%). Anal. ($CoHgC_{14}H_{22}N_6O_4S_4$) Co, C, H, N.

The crystal was shaped into a sphere (ϕ=0.22 mm). Reflections within the range $3° < 2\theta < 70°$ were studied with a Rigaku AFC-6A automated four-cirle diffractometer using graphite-monochromated Mo $K\alpha$ radiation and the ω—2θ scan technique (scan speed 4° min^{-1}, scan width, 1.35+0.5 tanθ°). The intensities were corrected for Lorentz and polarization factors as well as for absorption. Of the 3082 independent reflections collected, 1751 reflections with $|F_o| > 3\sigma(|F_o|)$ were used for a structure determination. All the calculations were carried out on a HITAC M-280H computer at the Computer Center of the University of Tokyo using the local version of UNICS.[6] The scattering factors were taken from Ref. 7. The final R value[8] for all non-hydrogen atoms (applying the anisotropic temperature parameters) was 0.052. (The R value was 0.053 for the structure with an inverse chirality.)

Results and Discussion

Figures 1 and 2 show projections of the structures of **3** and **2**[5,a] (along the c axis) together with the numbering scheme of the atoms. Perspective drawings around the mpd bridge are given in Fig. 3. The select-

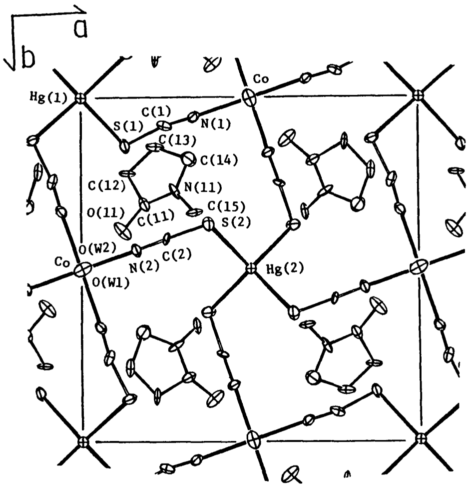

Fig. 1. The projection of the unit cell of **3** along c-axis.

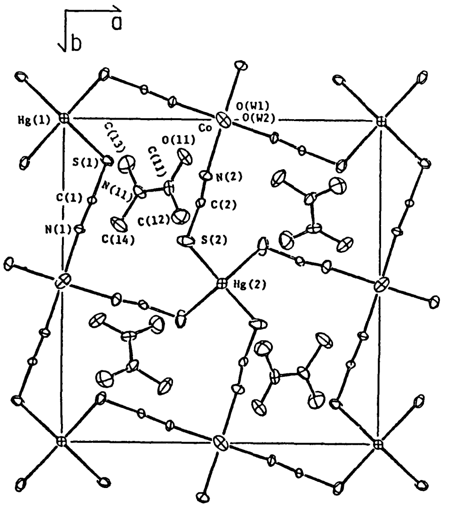

Fig. 2. The projection of the unit cell of **2** along c-axis.[5)]

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[a] For the convenience to compare the respective structures of **2** and **3**, the numbering of some atoms in **2** shown in Ref. **5** is modified.

Table 1. Selected Bond Lengths and Bond Angles with Estimated Standard Deviations in Parentheses

Bond length	l/Å	Bond length	l/Å	Bond length	l/Å
Hg(1)-S(1)	2.535(3)	Co-O(W1)	2.110(9)	C(1)-N(1)	1.115(16)
Hg(2)-S(2)	2.536(4)	Co-O(W2)	2.107(9)	C(2)-N(2)	1.196(14)
Co-N(1)	2.151(10)	S(1)-C(1)	1.634(12)	O(W1)···O(11)	2.694(13)
Co-N(2)	2.068(9)	S(2)-C(2)	1.665(11)	O(W2$^{\mathrm{i}}$)···O(11)	2.799(13)
Bond angle	**ϕ/°**	**Bond angle**	**ϕ/°**	**Bond angle**	**ϕ/°**
S(1)-Hg(1)-S(1$^{\mathrm{vi}}$)	100.7(1)	N(1$^{\mathrm{vi}}$)-Co-N(2)	90.3(4)	Co-N(2)-C(2)	164.0(9)
S(1)-Hg(1)-S(1$^{\mathrm{ii}}$)	128.8(1)	N(2)-Co-O(W1)	88.7(4)	S(1)-C(1)-N(1)	170.0(11)
S(2)-Hg(2)-S(2$^{\mathrm{iii}}$)	105.5(1)	N(2)-Co-O(W2)	91.3(4)	S(2)-C(2)-N(2)	178.0(10)
S(2)-Hg(2)-S(2$^{\mathrm{iv}}$)	117.6(1)	Hg-S(1)-C(1)	101.8(2)	O(W1)···O(11)···O(W2$^{\mathrm{i}}$)	89.9(4)
N(1$^{\mathrm{vi}}$)-Co-N(1$^{\mathrm{iii}}$)	174.1(4)	Hg(2)-S(2)-C(2)	100.4(2)	O(11)···O(W1)···O(11$^{\mathrm{v}}$)	92.3(4)
N(2)-Co-N(2$^{\mathrm{v}}$)	177.4(4)	Co-N(1$^{\mathrm{vi}}$)-C(1$^{\mathrm{vi}}$)	170.8(9)	O(11)···O(W2$^{\mathrm{i}}$)···O(11$^{\mathrm{v}}$)	87.9(4)

Key to the symmetry operations: i, x, y, $1+z$; ii, $-x$, $-y$, z,; iii, y, $1-x$, $-z$; iv, $1-x$, $1-y$, z; v, $-x$, $1-y$, z; vi, $-y$, x, $-z$

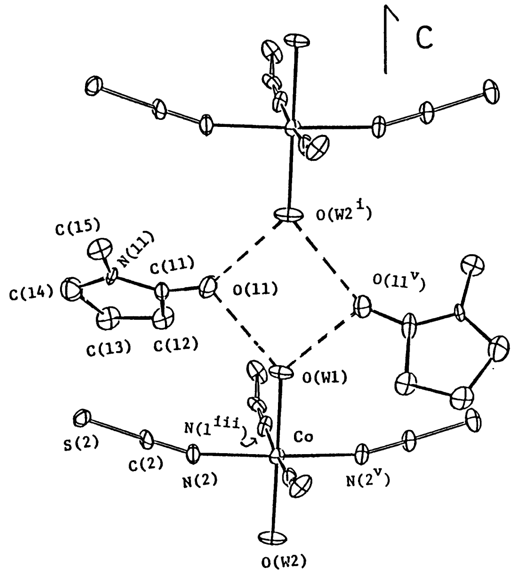

Fig. 3. A perspective drawing of the complex around a cobalt atom and the hydrogen bridging.

ed interatomic distances and bond angles are shown in Table 1.[9] The general feature of the thiocyanate network, as well as the hydrogen-bond bridging, is quite similar to that of **2**. The Hg(1) and Hg(2) atoms are tetrahedrally coordinated by four thiocyanate sulfur atoms, while the cobalt(II) atom is coordinated octahedrally with four thiocyanate nitrogen atoms (equatorially) and two water oxygen atoms (axially). The mpd molecules of **3** are maintained between two thiocyanate networks by only the hydrogen bonds. Thus, we can add **3** as the second member of the **2**-type inclusion compound. The interatomic distances and bond angles of the thiocyanate network, as well as those of the hydrogen-bridging part, are about the same as the corresponding values in **2**, respectively.

The volume of a unit cell of **3** is larger than that of **2** by 13 Å^3.[5] This is because an mpd molecule is larger than a dma molecule. Comparing Figs. 1 and 2, the corresponding position of the carbonyl oxygen atoms of dma and mpd in **2** and **3** are about the same; however, the positions of the other atoms are different, probably to pack dma or mpd molecules into the spaces most effectively. The angles around O(11), the carbonyl oxygen atom, in **2** and **3** are different from each other: O(W1)···O(11)-C(11), O(W1)···O(11)···O(W2$^{\mathrm{i}}$), and O(W2$^{\mathrm{i}}$)···O(11)-C(11) are 122.2(9), 89,9(4), and 147.3(10) in **3**, and are 138.9(9), 86.1(4), and 127.7(7)° in **2**,[5] respectively. (The key to the symmetry operation; i,x,y, $1+z$.) The Lewis base molecules in **2** or **3** are considered to occupy this space in order to pack the cage of the thiocyanate network well.

Our attempts to obtain the same type of complexes using *N*,*N*-diethylacetamide, *N*,*N*-dimethylpropionamide, *N*-ethyl-2-pyrrolidone, *N*,*N*-dimethylformamide, and *N*-methylformamide as the guests have not yet been successful. To be a guest of this type complex, of course, the formation of the effective hydrogen bonds to bridge it to the network-oxygen atoms is indispensable. Also, there may be some restrictions regarding the shape and the size of the guest molecule to be included into the vacancy of a host.

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8) $R=\sum||F_o|-|F_c||/\sum|F_o|$

9) The final atomic and thermal parameters, the final F_o-F_c table and additional data of bond lengths and bond angles are deposited as Document No. 8621 at the Office of the editor of Bull. Chem. Soc. Jpn.