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Synthesis, Properties, and Crystal and Molecular Structure of Diaquatetrakis(thiocyanato)cobalt(II)mercury(II)-2-pyrrolidone (1/2), $[CoHg(SCN)_4(H_2O)_2]\cdot 2C_4H_7NO$

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Synopsis. The title inclusion compound, which has a new-type "double decker" host skeleton, has been obtained, and its crystal and molecular structure has been determined by the X-ray diffraction technique using its single crystal. 2-Pyrrolidone molecules are not directly coordinated to any metal atoms, but are hydrogen-bonded with coordinated water-oxygen atoms in the two-dimensional polymer planes of $[CoHg(SCN)_4(H_2O)_2]_n$. In the complex polymer, each pair of adjacent Hg(4S(SCN) four-coordinated in a tetrahedral geometry) and Co(4N(SCN), 2O(water, trans) six-coordinated in an octahedral geometry) atoms are bridged with a thiocyanate (SCN) ion. Such two types of networks are spread approximately parallel to the (010) plane at 1/4 and 3/4 heights, and the included Lewis base molecule layers are also doubled. Compared with the previously reported single-layer host skeleton of $[CoHg(SCN)_4(H_2O)_2]\cdot 2L$ (L=Lewis base), the present one is short in its inter-complex layer distance, in spite of the analogous size of the included molecule. The crystallographic data are: orthorhombic, space group $P2_1nb$, $a=12.004(4)$, $b=15.330(5)$, $c=11.985(4)$ Å, and $Z=4$. The final R value was 0.054.

Previously, the present authors[1,2] have reported about the crystal structures of some adducts of tetrakis(thiocyanato) cobalt(II)mercury(II), $CoHg(SCN)_4$ (**1**), with the general formula of $CoHg(SCN)_4(H_2O)_2\cdot 2L$ (L=*N,N*-dimethylacetamide (dma), (**2**)[1] or *N*-methyl-2-pyrrolidone (mpd) (**3**).[2] These complexes were found to be a new type of inclusion compound in which the Lewis bases were not coordinated to any metal atoms directly, but were kept between the two-dimensional polymeric planar networks only by the hydrogen bondings. The cage structure of **2** and **3** are almost the same.

In this line of research, the title complex was obtained. From the preliminary test, its crystal system and the unit cell size were found to be different from those of **2** and **3**. Expecting to find a new type of structure of the inclusion compound, we have investigated the crystal and molecular structures of this complex by means of the X-ray diffraction method, using its single-crystal.

Experimental

Synthesis of Diaquatetrakis(thiocyanato)cobalt(II)mercury(II)-2-pyrrolidone(1/2), $CoHg(SCN)_4(H_2O)_2\cdot 2pd$ (4). The crystalline powder of **1** (1.0 g, 2.0 mmol) was dissolved into 2-pyrrolidone (pd) (10 cm^3), and 20 cm^3 of water was added to the solution. The mixture was left standing for several days; thereby the red-brown crystals of **4** were deposited. They were filtered off and dried over silica gel. Yield: 0.8 g, 57%. Anal. Found: Co, 8.22; C, 20.75; H, 2.76; N, 12.33%. Calcd for $CoHgC_{12}H_{18}N_6O_4S_4$: Co, 8.44; C, 20.65; H, 2.60; N, 12.04%.

X-Ray Structure Analysis. A crystal of **4** with the dimensions of $0.3\times0.3\times0.12$ mm^3 was used for the intensity measurement. Crystallographic data: $CoHgC_{12}H_{18}N_6O_4S_4$ *F.W.*=698.10, orthorhombic, with the space group of $P2_1nb$, $a=12.004(4)$, $b=15.330(5)$, $c=11.985(4)$ Å, $U=2205.5(11)$ Å^3, $Z=4$, $D_m=2.07(3)$ Mg m^{-3}, $D_x=2.07$ Mg m^{-3}, $\mu(\text{Mo } K\alpha)=8.28$ mm^{-1}. Reflections within a range of $3°<2\theta<60°$ were collected on a Rigaku AFC-6A automated four-circle X-ray diffractometer, with graphite-monochromated Mo $K\alpha$ radiation, the ω–2θ scan technique was employed (scan speed, 4° min^{-1} in θ; scan width, $1.12+0.5\tan\theta°$). Of the 3564 independent reflections measured, 1841 $|F_o|>3\sigma(|F_o|)$ reflections were used for the structure determination. The intensities were corrected for the Lorentz and polarization factors as well as for the absorption. The last correction was made using a numerical Gaussian integration.[3] The structure was solved by the heavy atom method. The final R value obtained by applying the anisotropic temperature parameters was 0.054.[4] As the R value for the structure with an inversed chirality was 0.059, the value was not adopted.

All the calculations were carried out on a HITAC M-680H computer apparatus at the Computer Center of the University of Tokyo, using the local version of the UNICS program system.[5] The atomic scattering factors were taken from Ref. 6.

Other Measurements. The infrared absorption spectra were obtained by means of a Hitachi EPI-G3 grating infrared spectrophotometer using mineral oil and hexachloro-1,3-butadiene mull. The magnetic moment of the solid sample was measured at 20 °C using a Gouy balance.

Results and Discussion

The selected bond-lengths and bond angles, and also some interatomic distances, are shown in Table 1.[7] A perspective drawing of the complex around a cobalt atom, together with the hydrogen bondings between the neighboring cobalt atoms along the b-axis, is shown in Fig. 1. The projection of the structure along the b-axis is shown in Fig. 2.

Each mercury atom is coordinated tetrahedrally to four SCN sulfur atoms. The cobalt atom is six-coordinated and is in an octahedral geometry, where four SCN nitrogen atoms are ligated equatorially, and two water oxygen atoms, axially, approximately from the b-axis directions. The bond lengths of Hg–S, Co–O, and Co–N (on the average, 2.536, 2.089, and 2.12 Å respectively) are not much different from the respective sums of Shannon's ionic radii: Hg–S, 2.80; Co–O, 2.00; and Co–N, 2.11 Å.[8] Both of the bond angles, Co–N–C (169° on the average) and N–C–S (177° on the average) deviate a little from 180°.

As is shown in Fig. 1, both kinds of pd molecules

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-S(1^{i})	2.551(7)	Co-N(1)	2.138(16)	S(1)-C(1)	1.64(2)
Hg-S(2^{ii})	2.514(7)	Co-N(2)	2.08(2)	S(2)-C(2)	1.66(2)
Hg-S(3)	2.548(7)	Co-N(3)	2.11(2)	S(3)-C(3)	1.62(2)
Hg-S(4^{iii})	2.529(7)	Co-N(4)	2.149(18)	S(4)-C(4)	1.66(3)
Co-O(W1)	2.085(11)	O(W1)···O(11)	2.71(2)	C(1)-N(1)	1.15(3)
Co-O(W2)	2.093(11)	O(W1)···O(21)	2.72(2)	C(2)-N(2)	1.16(3)
C(11)-O(11)	1.22(3)	O(W2^{iv})···O(21)	2.64(2)	C(3)-N(3)	1.13(3)
C(21)-O(21)	1.26(3)	O(W2^{iv})···O(21)	2.68(2)	C(4)-N(4)	1.11(3)
Boud angle	ϕ/°	Bond angle	ϕ/°	Bond angle	ϕ/°
S(1^{i})-Hg-S(2^{ii})	101.9(2)	N(1)-Co-N(2)	92.7(8)	N(1)-Co-O(W1)	88.0(5)
S(1^{i})-Hg-S(3)	121.3(2)	N(1)-Co-N(3)	175.0(7)	N(1)-Co-O(W2)	87.7(5)
S(2^{ii})-Hg-S(3)	104.8(2)	N(2)-Co-N(3)	89.7(8)	N(2)-Co-O(W1)	93.8(7)
S(3)-Hg-S(4^{iii})	102.5(2)	N(1)-Co-N(4)	87.6(7)	O(W1)-Co-O(W2)	175.7(5)
Hg-S(1^{i})-C(1^{i})	99.2(8)	Co-N(1)-C(1)	167.6(16)	S(1)-C(1)-N(1)	176.8(19)
Hg-S(2^{ii})-C(2^{ii})	97.3(9)	Co-N(2)-C(2)	172(2)	S(2)-C(2)-N(2)	174(2)
Co-O(W1)···O(11)	136.0(10)	O(11)···O(W1)···O(21)	91.7(6)	O(W1)···O(11)···O(W2^{iv})	87.7(8)
Co-O(W1)···O(21)	126.9(10)	O(11)···O(W2^{iv})···O(21)	94.0(6)	O(W1)···O(21)···O(W2^{iv})	86.6(7)

Key to the symmetry operations: i, $-1+x, y, z$; ii, $-0.5+x$, $0.5-y$, $-0.5+z$; iii, $-0.5+x$, $0.5-y$, $0.5+z$; iv, x, $0.5+y$, $0.5-z$; v, x, $-0.5+y$, $0.5-z$.

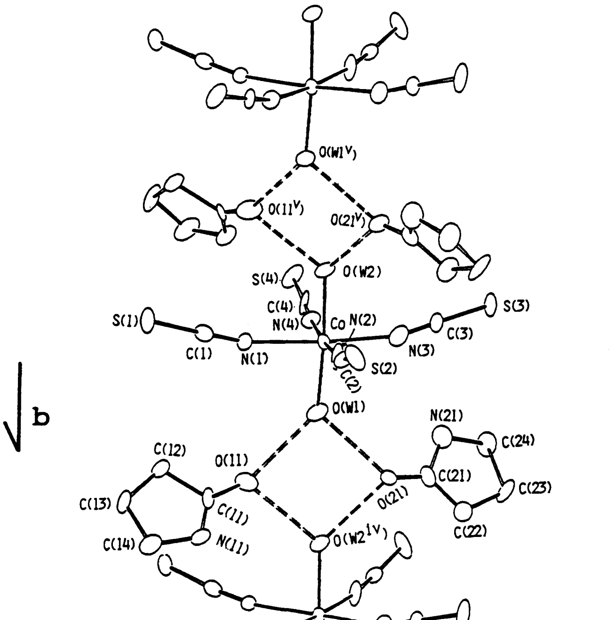

Fig. 1. The perspective drawing of the complex around a cobalt atom and the included Lewis bases.

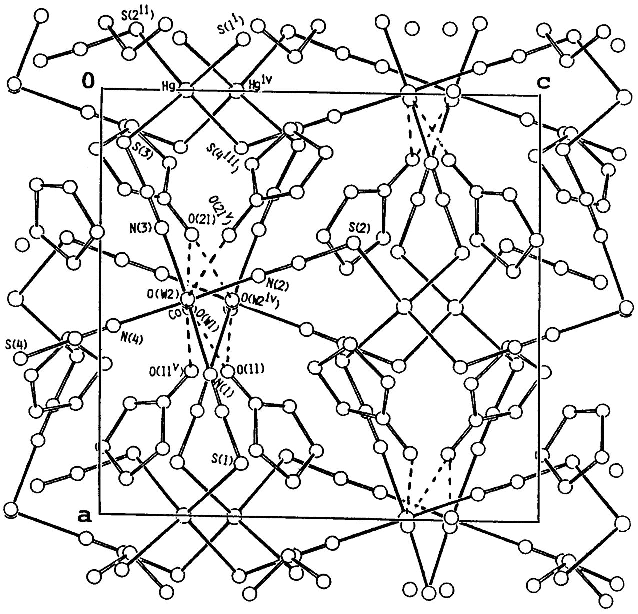

Fig. 2. The projection of the unit cell of the complex to the (010) plane.

are linked by hydrogen-bondings to the water oxygen atoms, which are ligated to the cobalt atoms. As is shown in Fig. 2, two mercury(II), two cobalt(II), and four SCN ions make a sixteen-membered ring which organizes the unit of the two-dimensional network of the polymeric complex and which is about the same as those of **2** and **3**.

The 1/4 of the ac face of the unit cell of **4** is 35.97 Å^2, while those of **2** and **3** (1/4 of the ab face) are 36.75 and 36.17 Å^2 respectively. Therefore, the areas of this sixteen-membered rings (exactly, the projections to the average plane) are approximately the same.

However, the crystal structures **2** or **3**, and **4** are very different with each other. In the cases of **2** and **3**, the network of the complex as well as the base molecule layer spread parallel to the ab-plane, and the separation of the plane corresponds with the c-axis length: 7.985 Å in **2** and 8.097 Å in **3** respectively. On the other hand, there are two such networks in the **4**

Table 2. Infrared Absorption Data of **1**, mpd, **3**, pd, and **4** (in σ/cm^{-1})

1[1]	mpd[9]	**3**	pd[9]	**4**	Tentative Assignment
		3360 (s)		3290 (s)	ν(O-H)
			3240 (w)	3400 (w)	ν(N-H)
	2895 (m)	2950 (m)	2940 (m)	2980 (m)	ν(C-H)
2150 (s)		2140 (s)		2140 (s)	ν(CN)
		1650 (m)		1655 (m)	δ(HOH)
	1682 (s)	1640 (s)	1687 (s)	1640 (s)	ν(CO)
720 (s)		730 (m)		720 (m)	ν(CS)
470 (s)		460 (s)		470 (m)	δ(SCN)
447 (s)		440 (s)		445 (m)	δ(SCN)

1, $CoHg(SCN)_4$; **3**, $CoHg(SCN)_4(H_2O)_2\cdot 2$mpd; **4**, $CoHg(SCN)_4(H_2O)_2\cdot 2$pd.

complex, approximately 1/4 and 3/4 in height respectively, parallel to the (010) plane. Therefore, the separation of the network plane is a half of the b-axis length, 7.665 Å, which is much shorter than those of **2** and **3**. On both network layers, the respective metal atomic positions deviated only a little, approximately in the c-axis direction, from each other. However, the positions of the pd molecules in the two intervals are very different. Each pd molecule exists in a interval space where the top and bottom walls are concave, while the space between the convexed walls is vacant. Thus, the filled and empty intervals are laid alternately, perpendicular to the plane. This is probably the main cause of the shorter inter-layer distance of this complex.

If we define the cage volumes of this type of inclusion compound by the unit-cell volume divided by the number of the included base molecule, they are 292 and 296 Å^3 in the cases of **2** and **3** respectively. On the other hand, the volume of the **4** complex is 2205.5/8=276 Å^3, which is smaller than the former two, showing the more compact packing in this complex.

Some infrared spectral data are shown in Table 2. When the wavenumbers of the peaks of **4** are compared with those of the free-ligand molecules,[9] its ν(C=O) peak is found to be red-shifted by 40—50 cm^{-1}. Such a red shift has also been observed in the spectra of **3** as well as **2**,[1] and it is considered to be due to the strong hydrogen bonds between the Lewis-base molecule and the ligating water molecules. The hydrogen bondings are manifested by the ν(O-H) at high frequencies, too.[10] The ν(N-H) of **4** is shifted from 3240 (free pd) to 3400 cm^{-1} as a result of the release from mutual hydrogen bondings in the free ligand molecules.[11] The wavenumbers of the bands caused by the SCN ions of **1**, **2**,[1] **3**, and **4** are not very different from one another.

The magnetic moment of **4** is about 5.05 BM at 20 °C, about the same as that of **3**, 4.98 BM (1 BM=9.274078(36)×10^{-24} JT^{-1}). These are typical values for the cobalt(II) ion in the octahedral geometry.

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