The Synthesis, and the Crystal and Molecular Structure of [Diaquatetrakis-(thiocyanato)cobalt(II)mercury(II)]-*N,N*-Dimethylacetamide (1/2), $CoHg(SCN)_4(H_2O)_2 \cdot 2\{CH_3CON(CH_3)_2\}$

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The new complex indicated in the title was synthesized and its crystal and molecular structures were determined by the use of a single-crystal X-ray diffraction method. The crystal is tetragonal, with the space group $P\bar{4}$, and the cell constants are $a=12.124(5)$ and $c=7.985(2)$ Å. The structure was solved using the heavy-atom method, and the final R value was 0.039. Two kinds of crystallographically independent mercury atoms in the unit cell are tetra-coordinated and they are in the tetrahedral geometry, where four sulfur atoms of the thiocyanate ions are ligated, respectively. The cobalt atom is hexa-coordinated, and is in an octahedral geometry, where four nitrogen atoms of the thiocyanate ions are coordinated equatorially, and two water oxygen atoms axially. Thiocyanate ions span mercury and cobalt atoms to form two-dimensional networks parallel to the (001) plane. The planar polymeric complexes are linked to the c-axis direction, through hydrogen bonds between coordinated water molecules and *N,N*-dimethylacetamide.

The tetrakis(thiocyanato)cobalt(II)mercury(II), $CoHg(SCN)_4$ (**1**), has a so called "diamond-like" three-dimensional polymeric structure,[1] and to study such complexes is attractive. Some of the Lewis-base adducts of **1** were synthesized,[2,3] and the structure of some adducts, $CoHg(SCN)_4L_2$ (where L=pyridine (**2**),[4] *N,N*-dimethylformamide (**3**),[5] and triphenylphosphine (**4**)[6]), as well as $CoHg(SCN)_4(tu)_4$ (**5**) (where tu=thiourea)[7] were already elucidated. Complexes **2** and **3** have a three-dimensional polymeric structure, where both of the base ligands are coordinated as an unidentate, taking *trans* positions in **2** and *cis* positions in **3**. Compex **4** has a one-dimensional "ladder-like" structure, where each dimer ring is linked to their neighbors on both sides by a pair of weak Hg–S bonds, respectively. Complex **5** consists of discrete anionic and cationic complexes, $[Hg(tu)_4]^{2+}$ and $[Co(SCN)_4]^{2-}$, and no bridging exists between them.

In this research we could obtain a new type Lewis-base adduct, indicated in the title (**6**), which includes two moles of water and two moles of *N,N*-dimethylacetamide (DMA) per one mole of the core complex **1**. The cobalt(II) atom in this complex was expected to be in an octahedral configuration since the complex is reddish-brown in color. However, no more details regarding its structure were clarified by the spectroscopic method. Although the structure of the *N,N*-dimethylformamide adduct, **3**, was already known, this complex has not only DMA molecules but also water molecules. It is of the $CoHg(SCN)_4L_2L'_2$ type. Consequently, we have determined its structure using an X-ray diffraction technique with its single crystal.

Experimental

*Synthesis of Diaquatetrakis(thiocyanato)cobalt(II)mercury(II)–DMA (1/2) **6**.* To a finely powdered **1** (1.00 g, 2.0 mmol), was added about 10 cm^3 of a mixed solvent of DMA and water (1:1=v/v). This mixture was warmed and stirred until **1** was dissolved. The solution, which was reddish violet in color, was left standing at about 15 °C over night. The deposited crystals were separated, washed with mixed solvent and water and dried by pressing between filter paper sheets. The yield was 1.28 g (85—91%). The crystals used for the X-ray structure analysis were obtained from a more dilute solution of the mixed solvent after being left standing for several days. Anal. Found: Co, 8.35; C, 20.41; H, 3.19; N, 12.26%. Calcd for $CoHgC_{12}H_{22}N_6O_4S_4$: Co, 8.39; C, 20.53; H, 3.16; N, 11.97%.

Intensity-data Collection. A parallelepiped crystal with the dimensions of 0.28×0.22×0.11 mm^3 along the unit cell axes was used for the intensity measurement. Crystallographic data are: $CoHgC_{12}H_{22}N_6O_4S_4$, F.W.=702.13, tetragonal, space group $P\bar{4}$, $Z=4$, $a=12.124(5)$, $c=7.958(2)$ Å, $U=1169.4(8)$ Å^3, $D_m=1.99(3)$, $D_x=1.99$ Mg m^{-3}, μ(Mo $K\alpha$)=7.80 mm^{-1}. Reflections within a range of $3°<2\theta<70°$ were collected on a Rigaku Denki 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 2θ; scan width, $\Delta\omega=1.05+0.5\tan\theta$°). The crystal was stable during the measurement process. Of the 5597 reflections measured in a quartant of the reciprocal space, 1081 independent reflections with $|F_o|>3\sigma(|F_o|)$ were used for the structure determination. The intensities were corrected for the Lorentz and polarization factors as well as for the absorption. The latter correction was made using numerical Gaussian integration.[8]

Structure Determination. The structure was solved by the heavy-atom method. The positions of the mercury(II) and cobalt(II) atoms were deduced from a three-dimensional Patterson map, while the other non-hydrogen atoms were located by means of succesive Fourier syntheses. Their positions and thermal parameters (firstly isotropic and finally anisotropic) were refined by a block-diagonal least squares method. At the final refinement step, shifts of all the parameters were less than $\sigma/3$'s. The final R value[9] (applying anisotropic temperature parameters) was 0.039. The R value was 0.041 for the structure with an inverse chirality. We carried also out a refinement using an alternate space group P4, where two kinds of cobalt atoms are on four-fold axes and mercury atoms lie on two-fold axes. However, the $CoHg(SCN)_4$ skeleton was almost equivalent to that of $P\bar{4}$. The main difference lies in the orientation of the DMA mole-

cules. As unreasonably short contacts occured between the DMA molecules in this ordered structure, an orientational disorder of the DMA molecules was introduced into the refinement. This disorder shows favor to a hydrogen-bond formation regarding all coordinated water molecules. The refinement converged R=0.065 and no improvement was attained in the R value. From these points, the space group P4 is thought to be less probable.

Although the space group P4/m is also possible, it was apparent that an adoption of this group implies that no ordered arrangement could be realized for almost all the atoms. Consequently, the space group was considered unacceptable.

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 the UNICS program system.[10] The atomic-scattering factors were taken from the tables.[11]

Other Measurements. The magnetic moment of the solid sample was measured at 20 °C using a Gouy balance. The infrared absorption spectra were obtained by means of a JASCO A202 grating infrared spectrophotometer using Nujol and hexachloro-1,3-butadiene mull. The visible diffuse reflectance spectrum of the solid complex was measured by means of a Hitachi 124 spectrophotometer using MgO as the reference.

Results and Discussion

The final atomic parameters of the non-hydrogen atoms are listed in Table 1, while the selected bond lengths, bond angles, and some of the short interatomic distances that were assumed to be hydrogen bonds are tabulated in Table 2.[12] In Figs 1 and 2, perspective drawings of the complex around a mercury atom Hg (1), and that around a cobalt atom, together with the hydrogen-bond bridging between the neighboring cobalt atoms along the c-axis, respectively, are given. The numbering scheme is also shown in the figures. The geometry atound the Hg (2) atom is nearly the same that around the Hg(1) atom. The projection of the structure along the c-axis is shown in Fig. 3.

Each mercury atom is coordinated tetrahedrally to four thiocyanate ions, and lies on a four-fold improper rotation axis. The tetrahedron around Hg (2) is almost regular. However, that around Hg (1) is a little deformed. The Hg-S bond lengths are normal and are nearly equal to the sum of both the atomic radii, r_{Hg}=1.48 and r_S=1.04 Å.[13a] The angles Hg-S-C, 102.4(4) and 98.5(5)°, are a little larger than those in related complexes such as **1**, **2**, and **3**.

The cobalt atom is hexa-coordinated and is in a octahedral geometry, where four nitrogen atoms of

TABLE 1. FINAL ATOMIC COORDINATES ($\times 10^4$) AND EQUIVALENT ISOTROPIC TEMPERATURE FACTORS OF NON-HYDROGEN ATOMS, WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Atom	x	y	z	B_{eq}/Å^2 [a]
Hg(1)	0	0	0	2.48
Hg(2)	5000	5000	0	2.48
Co	5000	0	487(2)	1.95
O(W1)	5000	0	3154(13)	3.12
O(W2)	5000	0	−2154(14)	3.78
S(1)	1370(3)	1259(3)	−1447(6)	3.85
S(2)	3860(4)	3724(3)	1798(6)	4.88
N(1)	534(8)	3390(7)	−591(16)	2.87
N(2)	4469(8)	1708(8)	637(16)	3.09
C(1)	910(8)	2509(7)	−925(14)	1.91
C(2)	4307(9)	2547(8)	1051(19)	2.81
C(11)	3685(15)	2981(13)	6730(25)	5.51
C(12)	3309(9)	2107(12)	5565(19)	3.40
C(13)	1980(15)	1375(14)	3606(26)	5.64
C(14)	1764(14)	3248(15)	4756(27)	6.16
N(11)	2399(9)	2224(11)	4689(21)	4.09
O(11)	3800(8)	1129(9)	5418(12)	4.18

a) The isotropic temperature factors were computed using the following expression: $B_{eq}=4/3(B_{11}a^2+B_{22}b^2+B_{33}c^2)$. The B_{ij}'s are defined by: $\exp[-(h^2B_{11}+k^2B_{22}+l^2B_{33}+2hlB_{13}+2hkB_{12}+2klB_{23})]$.

TABLE 2. SELECTED BOND LENGTHS AND BOND ANGLES, WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Bond length	l/Å	Bond length	l/Å
Hg(1)-S(1)	2.533(4)	Hg(2)-S(2)	2.520
Co-N(2)	2.171(10)	Co-N(1^{ii})	2.058(9)
Co-O(W1)	2.123(10)	Co-O(W2)	2.101(11)
N(1)-C(1)	1.191(13)	C(1)-S(1)	1.668(10)
N(2)-C(2)	1.088(15)	C(2)-S(2)	1.639(12)
O(W1)···O(11)	2.690(13)	O(W2)···O(11^{iii})	2.779(14)
C(12)-O(11)	1.332(17)	C(12)-N(11)	1.313(19)
C(11)-C(12)	1.48(3)	C(13)-N(11)	1.44(3)
C(14)-N(11)	1.46(2)		

Bond angle	ϕ/°	Bond angle	ϕ/°
S(1)-Hg(1)-S(1^{i})	125.92(12)	S(1)-Hg(1)-S(1^{ii})	101.93(11)
S(2)-Hg(2)-S(2^{vi})	108.81(14)	S(2)-Hg(2)-S(2^{vii})	110.80(15)
N(1^{ii})-Co-N(1^{vi})	175.4(4)	N(2)-Co-N(2^{v})	173.7(4)
N(2)-Co-N(1^{vi})	88.8(4)	N(2)-Co-N(1^{ii})	90.9(4)
N(2)-Co-O(W1)	86.9(4)	N(2)-Co-O(W2)	93.2(4)
N(1^{ii})-Co-O(W1)	87.7(4)	Hg(1)-S(1)-C(1)	102.4(4)
Hg(2)-S(2)-C(2)	98.5(5)	S(1)-C(1)-N(1)	176.8(9)
S(2)-C(2)-N(2)	170.0(12)	Co-N(2)-C(2)	164.2(10)
Co-N(1^{ii})-C(1^{ii})	168.4(8)	C(11)-C(12)-O(11)	123.7(13)
C(11)-C(12)-N(11)	121.0(14)	O(11)-C(12)-N(11)	115.2(13)
C(12)-N(11)-C(13)	122.6(13)	C(12)-N(11)-C(14)	121.0(14)
C(13)-N(11)-C(14)	116.4(14)		
O(W1)···O(11)···O(W2^{iv})	86.1(4)		
O(11)···O(W1)···O(11^{v})	95.9(5)		
O(11)···O(W2^{iv})···O(11^{v})	91.9(5)		

Key to the symmetry operations: i, $-x$, $-y$, z; ii, y, $-x$, $-z$; iii, 1.0$-x$, $-y$, $-1.0+z$; iv, x, y, 1.0+z; v, 1.0$-x$, $-y$, z; vi, 1.0$-y$, x, $-z$; vii, 1.0$-x$, 1.0$-y$, z.

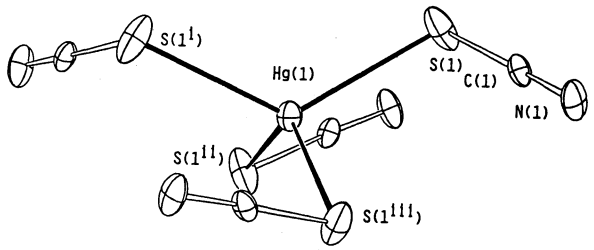

Fig. 1. A perspective drawing of the complex around a mercury(II) atom (Hg(I)), with the numbering scheme.

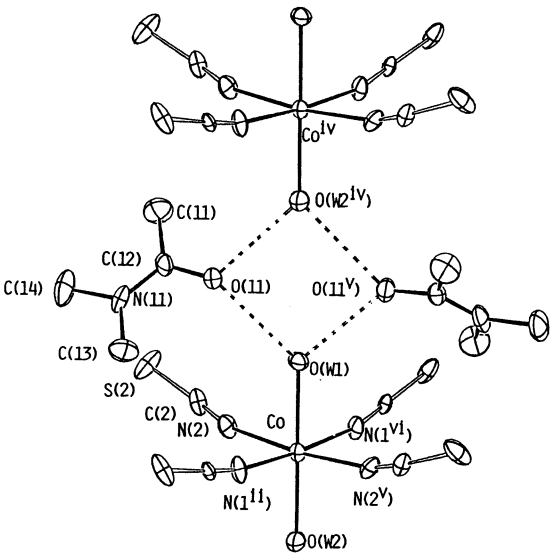

Fig. 2. A perspective drawing of the complex around a cobalt(II) atom and the hydrogen-bond bridging to the next metal atom, with the numbering scheme.

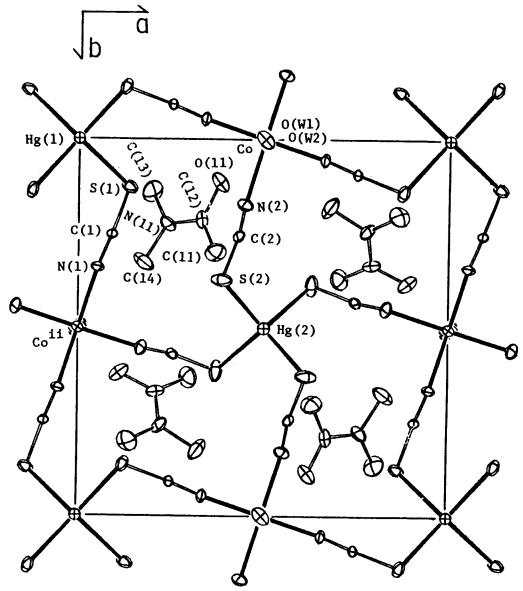

Fig. 3. The crystal packing diagram of the complex.

the thiocyanate ions are ligated equatorially and two water oxygen atoms axially along the c-axis directions. The cobalt atom as well as two oxygen atoms lie on the two-fold axis. All Co–N and Co–O bond lengths are normal, considering the respective atomic radii: r_{Co}=1.32, r_N=0.70, and r_O=0.66 Å.[13a]

The Co–N–C angles are 164.2(10) and 168.4(8)°, and are far from linear. In many isothiocyanato complexes, the M–N–C angles are approximately 180°; and in some related compounds such as **1** and **3**, the angles are not much different from 180°.[1,5] However, more deformed angles in this complex are found in **2** and **4** (about 165°).[4,6] Therefore, the angles in this complex are not exceptional. The N–C–S angles, 176.8(9) and 170.0(12)°, are a little less than 180°. Such a deformation was scarcely found in the common thiocyanato complexes, including **1**—**4**. In Cd(ben)$(SCN)_2$ (where ben=bis(2-aminoethyl)amine) the angles are 167.8(9) and 170.8(10)°,[14] and in $Hg(SCN)_2[(C_6H_5)_3P]$ one of them is 164.2°.[15] Therefore, the relatively large deviations of the bond angles in this complex are thought to be due to a crystal packing effect. Consequently, the bridgings in this complex may be deformed and stressed.

As shown in Table 2, the bond lengths and angles of the DMA molecule are normal except for C(12)–O(11). The length 1.332(17) Å is longer than the values observed in the carbonyl group of common organic compounds, 1.20—1.22 Å.[16] This fact is probably due to hydrogen bondings which are described later. The bond length (C(12)–N(11), 1.313(19) Å) almost corresponds with Pauling's double-bonding C=N distance, 1.29 Å.[13b] Such a short C–N bond is also found in many amide molecules.

The crystal consists of layers parallel to the (001) plane. In a layer, the cobalt atoms slightly deviate (by 0.387 Å) above or below the plane on which the mercury atoms are situated. The cobalt and mercury atoms are bridged by thiocyanate ions to form a two-dimensional network. No bridging ligand exists between the network. The cobalt atoms are linked along the [001] direction through hydrogen bonds between the coordinated water and the DMA oxygen atoms; the hydrogen bonds are shown in Fig. 2. The angles, O(11)···O(W1)···$O(11^V)$ and O(11)···$O(W2^{IV})$···$O(11^V)$ are 95.9(5) and 91.9(5)°, which are smaller than the H–O–H angles of water molecule, 104.5°.

When **6** in a powder state was kept in an organic solvent such as benzene or acetone at 15°C, it turned blue in color within one day. The residual solid found to be **1**. Thus, the DMA and water molecules in **6** could be easily removed. From this, the bonds of the additional molecules, DMA and water, in **6** are thought not to be stable.

The infrared absorption spectra of complex **6**, as well as **1** and DMA were measured and compared with each other. Some of the results are shown in Table 3. The corresponding absorption maximum wave numbers of the main peaks of the free DMA, such as 1508, 1400, 1265, 1190, 1018, and 592 cm^{-1}, are also found in the spectrum of **6**. As shown in the table, the ν(C=O) peaks of **6** are red shifted by 40 cm^{-1}, probably due to the strong hydrogen bonds to the oxygen atom of DMA in **6**. The peaks concerned with the thiocyanate ion appear almost at the same region in the spectra of **1** and **6**, as shown in the table. The ν(O–H)peaks of **6** appear at 3360 and 3250 cm^{-1}, which are near to those of the ν_1 and ν_3 peaks of free water in the solid state (3400 and 3220 cm^{-1}).[17] Therefore, the splitting is likely to be due to the strong hydrogen bonds of the water molecules in **6**.

The magnetic moment of **6** is about 4.83 BM (1 BM=9.274078(36)$\times 10^{-24}$ J T^{-1}) at 20°C. Its visible

Table 3. Infrared absorption spectral data of **1**, **6**, and DNA (in ν/CM^{-1})

6	1	DMA	Tentative assignment
3360(s) 3250(s)			ν(OH)
2970(m) 2930(m)		2940(s)	ν(CH)
2150(s)	2150(s)		ν(CN)
1648(m)			δ(HOH)
1600(s)		1640(s)	ν(CO)
720(s) 462(m) 440(m)	720(s) 470(s) 447(s)		ν(CS) δ(SCN)

1, $CoHg(SCN)_4$; 6, $CoHg(SCN)_4(H_2O)_2 \cdot 2DMA$; DMA, *N,N*-dimethylacetamide.

reflectance spectrum shows the main peak of the d-d band at 517 nm with an intense shoulder at about 485 nm. These values are almost the same as those of the related adducts, such as **2** or **3**.[2] These facts are explained by the octahedral geometry around the cobalt atom in this complex as shown by the result of the X-ray structure analysis mentioned above.

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