Crystal and Molecular Structure of Cobalt(II)mercury(II) Thiocyanate Adducts Having a New Layer Structure

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N-Methyl-2-piperidone adduct and dimethyl sulfoxide adduct of cobalt(II)mercury(II) thiocyanate were synthesized and their crystal and molecular structures were determined by the single-crystal X-ray diffraction technique. The former adduct is triclinic with a space group $P\bar{1}$, a=8.488(3), b=17.206(7), c=8.466(3) Å, α=103.72(1)°, β=90.00(1)°, γ=100.85(1)°, Z=2, while the latter adduct is orthorhombic with a space group $P2_12_12_1$, a=8.418(3), b=27.389(10), c=8.407(3) Å, Z=4, and the final R values obtained were 0.059 and 0.066, respectively. In these adducts each mercury atom is in the tetrahedral geometry, coordinated with four sulfur atoms of the thiocyanate (SCN) ions, and each cobalt atom is in the octahedral geometry, coordinated with four nitrogen atoms of SCN ions and two oxygen atoms of the Lewis-base molecules which occupy the trans-positions. Each pair of different kinds of metal atoms are bridged by an SCN ion forming a 16-membered ring of $Co_2Hg_2(SCN)_4$; these are linked, forming a two-dimensional network. The Lewis-base ligands are extended perpendicular to the plane on both sides. The complex layers are piled up in parallel, and there are no chemical or hydrogen bondings between the layers. This is a new type of the structure for $CoHg(SCN)_4L_2$ (L=Lewis base) type adducts.

The cobalt(II)mercury(II) thiocyanate (**1**) was found to have a diamond-like three-dimensional polymeric structure,[1] in which both kinds of the metal atoms are in the tetrahedral geometry. Each metal atom is linked with four metal atoms of another kind by one thiocyanate ion (SCN), respectively.

Previously, the present authors studied and determined the crystal and molecular structures of various Lewis base adducts of **1**.[2-6] According to our results, as well as other references, adducts with formula $CoHg(SCN)_4L_2$ (L=*N*,*N*-dimethylformamide (dmf),[7] *N*-methylformamide (mfa),[3] and pyridine (py)[8]) always have three-dimensional polymeric structures. On the other hand, complexes with formula $CoHg(SCN)_4(H_2O)_2\cdot 2L$ (L=*N*,*N*-dimethylacetamide (dma),[4] *N*-methyl-2-pyrrolidone (mpd)[5] and 2-pyrrolidone (pd)[6]) have a layer-type network structure of $[CoHg(SCN)_4(H_2O)_2]_n$: the Lewis-base molecules are not directly coordinated to any metal atoms, but are only hydrogen-bonded to the coordinated water, taking positions between the layers.

Along this line of research, we have continued to search for adducts with other linkage structures; we found two adducts of the type $CoHg(SCN)_4L_2$ in their crystalline states (L=*N*-methyl-2-piperidone (mpp) and dimethyl sulfoxide (dmso)). The former is a new compound, while the latter had already been reported by Makhija,[9] However, neither of their structures had been reported. Consequently, their crystal and molecular structures were determined by the X-ray diffraction method using their single crystals.

Experimental

Synthesis of the Adducts. (1) Bis(*N*-methyl-2-piperidone)-tetrakis(thiocyanato)cobalt(II)mercury(II) (**2**). A crystalline powder of **1** (1.0 g, 2.0 mmol) was dissolved into mpp (10 cm^3), and 20 cm^3 of water was added to the solution. It was left standing for several days and crystals of **2** were deposited. The pink crystals were filtered off and dried over silica gel. Yield: 0.5 g, 36%. Found: Co, 8.30; C, 26.24; H, 3.21; N, 11.55%. Calcd for $CoHgC_{16}H_{22}N_6O_2S_4$: Co, 8.21; C, 26.76; H, 3.09; N, 11.70%.

(2) Bis(dimethyl sulfoxide)tetrakis(thiocyanato)cobalt(II)-mercury(II) (**3**). Although this adduct had already been synthesized by Makhija from the tetrahydrofuran adduct of **1**,[9] we could obtain **3** more easily by the following method. A crystalline powder of **1** (1.0 g, 2.0 mmol) was dissolved into dmso(10 cm^3), and 12 cm^3 of water was added to the solution. It was left standing overnight and crystals of **3** were deposited. The pink-red crystals were filtered off and dried over silica gel. Yield: 0.8 g, 62%. Found: Co, 9.10; C, 14.66; H, 1.84; N, 8.61%. Calcd for $CoHgC_8H_{12}N_4O_2S_6$: Co, 9.09; C, 14.83; H, 1.87; N, 8.64%.

Intensity Data Collection. Crystals of **2** (dimensions 0.2×0.2×0.2 mm^3), and of **3** (spherical, with ϕ=0.21 mm) were used for intensity data measurements.

Crystallographic data are as follows: **2**, $CoHgC_{16}H_{22}N_6O_2S_4$, $F.W.$=718.17, triclinic, with the space group of $P\bar{1}$, a=8.488(3), b=17.206(7), c=8.466(3) Å, α=103.72(1)°, β=90.00(1)°, γ=100.85(1)°, U=1178.4(6) $Å^3$, Z=2, D_m=2.03(3) g cm^{-3}, D_c=2.03 g cm^{-3}, μ(Mo $K\alpha$)=7.74 mm^{-1}.

3, $CoHgC_8H_{12}N_4O_2S_6$, $F.W.$=648.12, orthorhombic with the space group of $P2_12_12_1$, a=8.418(3), b=27.389(7), c=8.407(3) Å, U=1938.3(10) $Å^3$, Z=4, D_m=2.22(3) g cm^{-3}, D_c=2.22 g cm^{-3}, μ(Mo $K\alpha$)=9.57 mm^{-1}.

Reflections within the ranges of $3°<2\theta<55°$ for **2** and $3°<2\theta<60°$ for **3** were collected on a Rigaku AFC-6A automated four-circle X-ray diffractometer with graphite-monochromated Mo $K\alpha$ radiation (λ=0.71073 Å). The ω-2θ scan technique was employed (scan speed, 4° min^{-1}; scan width, $1.21+0.5\tan\theta°$ for **2** and $1.25+0.5\tan\theta°$ for **3**).

For **2**, of the 5435 independent reflections measured, 4051 $|F_o|>3\sigma(|F_o|)$ reflections were used for a structure determinaion; for **3**, of the 3271 independent reflections measured, 1953 $|F_o|>3\sigma(|F_o|)$ reflections were used. The intensities were corrected for Lorentz and polarization factors, as well as for absorption using numerical Gaussian integration.[10]

Structure Determination. The structures were solved by the heavy-atom method. The positions of the mercury and

cobalt atoms were deduced from a three-dimensional Patterson map, while the other non-hydrogen atoms were located by means of succesive Fourier syntheses. Their positional and thermal parameters (first isotropic and finally anisotropic) were refined by a block-diagonal least-squares method. The final R values obtained, applyng their anisotropic temperature parameters, were 0.059 for **2** and 0.066 for **3**.[11] (In the case of **3**, since it does not have a center of symmetry, the structure of the reversed chirality was also examined. However, since its R value was 0.069, the structure was not adopted.)

All calculations were carried out on a HITAC M-680H computer apparatus at the Computer Center of the University of Tokyo using a local version of the UNICS program system.[12] The atomic scattering factors were taken from Ref. 13.

Other Measurements. The magnetic moments of their solid samples were measured at 20 °C using a Gouy balance. The infrared absorption spectra were obtained by means of a JASCO IR810 grating infrared spectrophotometer using mineral oil and hexachloro-1,3-butadiene mull.

Results and Discussion

The final atomic parameters of the non-hydrogen atoms are listed in Tables 1 and 2, while the selected bond lengths and bond angles are shown in Tables 3 and 4, respectively.[14] Perspective drawings of both complexes around the mercury and the cobalt atoms are given in Figs. 1 and 2, together with the numbering scheme of the atoms.

Although the crystal systems as well as the space groups of **2** and **3** are different from each other (triclinic, $P\bar{1}$ for **2**, and orthorhombic, $P2_12_12_1$ for **3**), their molecular structures resemble each other. In both adducts each mercury atom is coordinated with four SCN sulfur atoms and is in a tetrahedral geometry.

Table 1. Final Atomic Coordinates ($\times 10^3$) and Equivalent Isotropic Temperature Factors (B_{eq}/Å^2) of **2** with Estimated Standard Deviations in Parentheses

Atom	x	y	z	B_{eq}/Å^2 a)
Hg	108.96(5)	251.32(3)	414.83(5)	2.9_6
Co	604.1(2)	251.1(1)	953.9(2)	2.0_3
S(1)	408.2(3)	313.4(2)	442.8(3)	3.2_9
S(2)	71.1(3)	173.2(2)	116.2(3)	3.0_0
S(3)	1062.6(4)	177.8(2)	641.8(4)	4.0_1
S(4)	903.0(4)	342.3(2)	443.1(3)	3.6_8
N(1)	492.9(10)	251.2(6)	700.9(10)	2.8_6
N(2)	379.2(11)	232.4(6)	25.5(11)	3.1_2
N(3)	827.2(10)	254.7(6)	805.5(11)	3.2_7
N(4)	728.3(11)	267.8(6)	150.7(11)	3.1_2
C(1)	455.3(11)	274.9(6)	594.8(12)	2.2_7
C(2)	254.2(13)	208.5(6)	62.4(12)	2.3_9
C(3)	922.6(11)	225.0(7)	736.2(12)	2.4_9
C(4)	799.7(12)	297.4(7)	269.3(12)	2.5_4
O(11)	602.6(10)	126.2(5)	872.4(11)	3.8_2
O(21)	616.2(10)	377.0(5)	1001.8(11)	3.7_5
N(11)	595.8(12)	−5.4(6)	766.7(12)	3.3_8
N(21)	729.1(11)	505.8(6)	1107.7(12)	3.1_8
C(11)	522.0(14)	58.5(7)	805.4(13)	2.9_1
C(12)	346.6(15)	47.2(9)	765.5(18)	4.5_4
C(13)	265(2)	−38.6(14)	686(4)	11.6_8
C(14)	346(3)	−98.2(11)	647(4)	10.8_5
C(15)	517(2)	−90.3(8)	687.7(19)	5.3_8
C(16)	773.9(16)	8.8(9)	795(2)	5.4_2
C(21)	684.9(12)	443.6(7)	979.2(13)	2.7_8
C(22)	712.6(19)	453.6(9)	810.3(16)	4.7_4
C(23)	769(3)	544.4(14)	806(2)	10.4_6
C(24)	862(3)	593.3(11)	935(3)	7.7_3
C(25)	806.4(18)	589.3(8)	1100.3(19)	4.7_3
C(26)	709.9(19)	495.3(9)	1273.2(14)	4.6_2

a) The isotropic temperature factors were computed using the following expressions: $B_{eq}=4/3(B_{11}a^2+B_{22}b^2+B_{33}c^2)$. The Bij's are defined by: $T=\exp[-(h^2B_{11}+k^2B_{22}+l^2B_{33}+2hlB_{13}+2hkB_{12}+2klB_{23})]$.

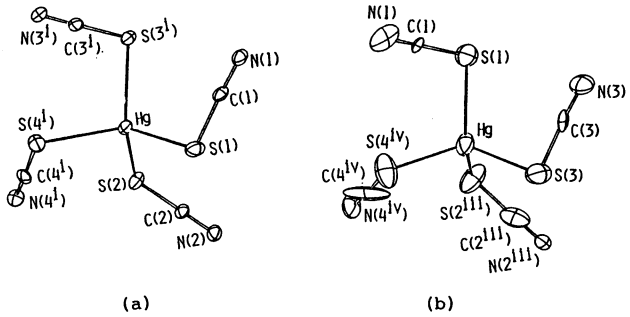

Fig. 1. The perspective drawing of the complex around a mercury atom and the included Lewis bases. (a) $CoHg(SCN)_4(mpp)_2$: (b) $CoHg(SCN)_4(dmso)_2$. Key to the symmetry operations, see Ref. 15.

Table 2. Final Atomic Coordinates ($\times 10^3$) and Equivalent Isotropic Temperature Factors (B_{eq}/Å^2) of **3** with Estimated Standard Deviations in Parentheses

Atom	x	y	z	B_{eq}/Å^2 a)
Hg	261.26(8)	624.31(4)	6.20(9)	3.3_8
Co	763.3(3)	625.2(1)	498.4(3)	2.4_0
S(1)	266.5(8)	577.0(3)	266.0(7)	4.8_5
S(2)	287.7(10)	574.6(3)	754.2(7)	4.9_2
S(3)	501.9(8)	681.0(3)	18.9(9)	4.8_0
S(4)	996.6(7)	667.5(3)	994.4(8)	4.1_3
N(1)	−10(2)	616.6(8)	393(2)	3.5_5
N(2)	537(2)	626.8(8)	613(2)	3.6_5
N(3)	652(2)	637.9(7)	276.5(19)	2.8_0
N(4)	871(2)	622.1(8)	730(2)	4.4_5
C(1)	106(3)	601.4(9)	337(2)	2.9_2
C(2)	439(3)	604.6(9)	676(5)	6.7_4
C(3)	595(3)	655.0(9)	176(3)	3.7_8
C(4)	924(2)	642.2(8)	835.5(19)	2.0_5
O(11)	792.5(16)	700.6(5)	497.5(19)	3.3_3
O(21)	738.1(18)	549.3(6)	465(2)	4.3_6
S(11)	653.6(6)	734.2(2)	502.3(10)	3.5_8
S(21)	739.7(8)	517.0(2)	614.3(8)	3.8_4
C(11)	652(4)	771.4(14)	688(4)	7.3_7
C(12)	705(4)	779.2(11)	368(3)	5.9_3
C(21)	603(4)	471.6(10)	565(4)	6.8_6
C(22)	923(3)	482.3(15)	630(3)	6.6_6

a) The isotropic temperature factors were computed using the following expressions: $B_{eq}=4/3(B_{11}a^2+B_{22}b^2+B_{33}c^2)$. The Bij's are defined by: $T=\exp[-(h^2B_{11}+k^2B_{22}+l^2B_{33}+2hlB_{13}+2hkB_{12}+2klB_{23})]$.

Table 3. Selected Bond Lengths and Bond Angles of **2** with Estimated Standard Deviations in Parentheses

Bond length	*l*/Å	Bond length	*l*/Å
Hg-S(1)	2.551(3)	Hg-S(2)	2.554(3)
Hg-S(3^{i})	2.533(4)	Hg-S(4^{i})	2.533(4)
Co-N(1)	2.111(10)	Co-N(2^{ii})	2.095(10)
Co-N(3)	2.140(9)	Co-N(4^{ii})	2.122(10)
Co-O(11)	2.087(9)	Co-O(21)	2.093(8)
S(1)-C(1)	1.660(13)	C(1)-N(1)	1.140(17)
S(2)-C(2)	1.664(11)	C(2)-N(2)	1.135(14)
S(3)-C(3)	1.663(11)	C(3)-N(3)	1.129(14)
S(4)-C(4)	1.654(11)	C(4)-N(4)	1.130(14)
O(11)-C(11)	1.238(12)	O(21)-C(21)	1.241(14)
Bond angle	***φ*/°**	**Bond angle**	***φ*/°**
S(1)-Hg-S(2)	102.66(9)	S(1)-Hg-S(3^{i})	104.59(11)
S(1)-Hg-S(4^{i})	120.28(10)	S(2)-Hg-S(3^{i})	121.22(11)
S(2)-Hg-S(4^{i})	103.22(11)	S(3^{i})-Hg-S(4^{i})	106.05(13)
N(1)-Co-N(2^{ii})	90.3(4)	N(1)-Co-N(4^{ii})	172.3(4)
N(1)-Co-N(3)	88.2(4)	N(2^{ii})-Co-N(3)	173.0(4)
N(2^{ii})-Co-N(4^{ii})	92.6(4)	N(1)-Co-O(11)	96.7(4)
N(1)-Co-O(21)	89.8(4)	O(11)-Co-O(21)	173.5(3)
Hg-S(1)-C(1)	97.6(5)	Hg-S(2)-C(2)	96.6(4)
Hg-S(3^{i})-C(3^{i})	98.5(4)	Hg-S(4^{i})-C(4^{i})	97.8(4)
Co-N(1)-C(1)	159.5(9)	Co-N(3)-C(3)	152.8(9)
Co-N(2^{ii})-C(2^{ii})	167.6(9)	Co-N(4^{ii})-C(4^{ii})	162.0(10)
Co-O(11)-C(11)	143.2(8)	Co-O(21)-C(21)	143.0(8)
S(1)-C(1)-N(1)	177.2(12)	S(3)-C(3)-N(3)	176.6(10)
S(2)-C(2)-N(2)	179.8(10)	S(4)-C(4)-N(4)	178.9(10)

Key to the symmetry operations: See Ref. 15.

Table 4. Selected Bond Lengths and Bond Angles of **3** with Estimated Standard Deviations in Parentheses

Bond length	*l*/Å	Bond length	*l*/Å
Hg-S(1)	2.540(7)	Hg-S(2^{iii})	2.528(7)
Hg-S(3)	2.554(7)	Hg-S(4^{iv})	2.525(6)
Co-N(1^{v})	2.123(18)	Co-N(2)	2.136(18)
Co-N(3)	2.115(17)	Co-N(4)	2.15(2)
Co-O(11)	2.080(13)	Co-O(21)	2.110(16)
S(1)-C(1)	1.63(2)	C(1)-N(1)	1.15(3)
S(2)-C(2)	1.65(3)	C(2)-N(2)	1.15(4)
S(3)-C(3)	1.70(3)	C(3)-N(3)	1.08(3)
S(4)-C(4)	1.62(2)	C(4)-N(4)	1.14(3)
O(11)-S(11)	1.488(14)	O(21)-S(21)	1.534(18)
Bond angle	***φ*/°**	**Bond angle**	***φ*/°**
S(1)-Hg-S(2^{iii})	116.4(2)	S(1)-Hg-S(3)	105.1(2)
S(1)-Hg-S(4^{iv})	106.8(2)	S(3)-Hg-S(4^{iv})	114.6(2)
N(1^{v})-Co-N(2)	174.5(7)	N(1^{v})-Co-N(3)	92.6(7)
N(1^{v})-Co-N(4)	89.7(8)	N(1^{v})-Co-O(11)	90.1(6)
N(2)-Co-N(3)	90.0(7)	N(2)-Co-N(4)	88.3(7)
N(1^{v})-Co-O(21)	85.7(7)	O(11)-Co-O(21)	172.1(6)
Hg-S(1)-C(1)	95.3(9)	Hg-S(3)-C(3)	98.4(9)
Hg-S(2^{iii})-C(2^{iii})	97.8(10)	Hg-S(4^{iv})-C(4^{iv})	99.3(7)
Co-N(1^{v})-C(1^{v})	165.1	Co-N(4)-C(4)	148.9(19)
Co-N(2)-C(2)	146.5(2)	Co-N(3)-C(3)	163.4(2)
Co-O(11)-S(11)	121.4(8)	Co-O(21)-S(21)	117.3(9)
S(1)-C(1)-N(1)	177(2)	S(4)-C(4)-N(4)	176.0(19)
S(2)-C(2)-N(2)	175(2)	S(3)-C(3)-N(3)	179(2)

Key to the symmetry operations: See Ref. 15.

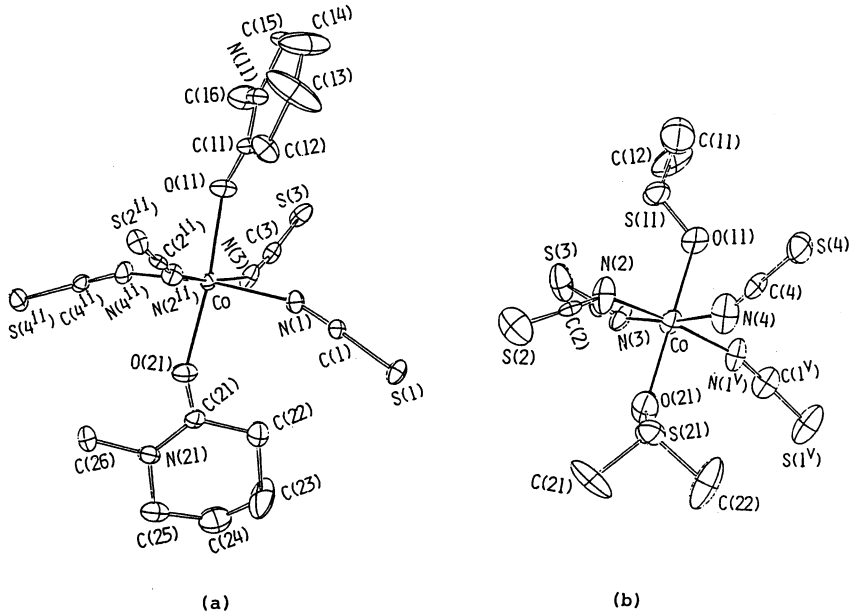

Fig. 2. The perspective drawing of the complex around a cobalt atom and the included Lewis bases. (a) $CoHg(SCN)_4(mpp)_2$: (b) $CoHg(SCN)_4(dmso)_2$. Key to the symmetry operations, see Ref. 15.

The average Hg-S lengths are 2.542 Å (maximum 2.554 and minimum 2.533 Å) for **2** and 2.537 Å (maximum 2.554 and minimum 2.525 Å) for **3**. The average bond angles around the mercury atoms of these complexes are not much different from the typical tetrahedral angles: the deviations are in the same grade as the other several mercury thiocyanates already reported.[1,16-18]

In **2** and **3**, the cobalt atom is hexa-coordinated and is in an octahedral geometry; both of the oxygen atoms of the Lewis base molecules are coordinated axially, while four SCN nitrogen atoms are coordinated equa-

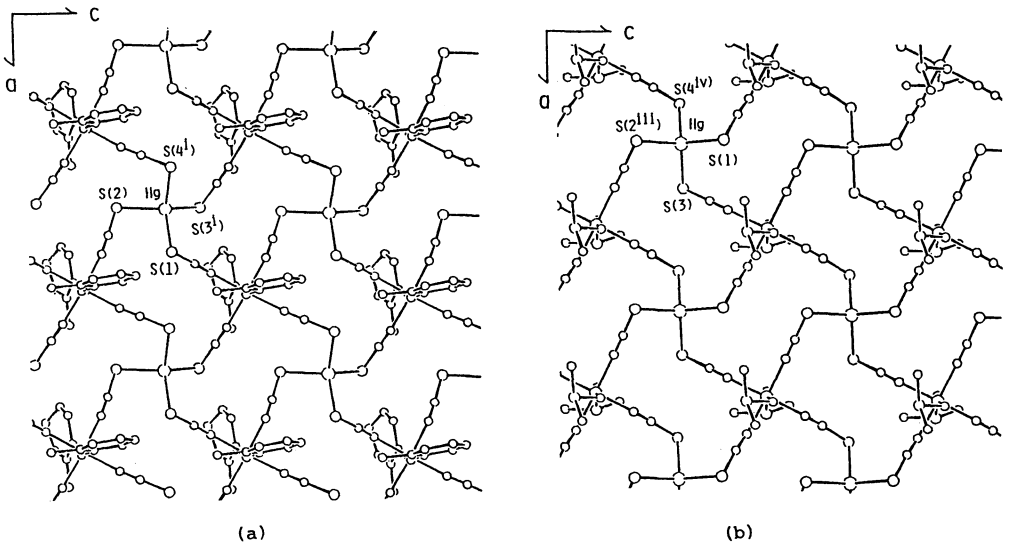

Fig. 3. The perspective drawing of the complex layer parallel to the (0 1 0) plane. (a) $CoHg(SCN)_4(mpp)_2$: (b) $CoHg(SCN)_4(dmso)_2$. Key to the symmetry operations, see Ref. 15.

torially. The average Co-N and Co-O bond lengths are 2.117 and 2.090 Å for **2** and 2.131 and 2.095 Å for **3**, respectively. They are about the same as the Co-N[19-21] and Co-O[22-24] lengths of the common octahedral cobalt(II) complexes. The average bond angles, N-Co-O and N-Co-N (between vicinal nitrogen atoms), are 90.0° and 90.2° for **2** and 90.1° and 90.2° for **3**, respectively. The angles O-Co-O are a little distorted from 180°, i.e. 173.5(3)° for **2** and 172.1(6)° for **3**, respectively. In total, the octahedral geometry of the cobalt core is not much deformed from the ideal form. The bond angles of Co-N-C, on the average, are 160.5° for **2** and 156.0° for **3**, respectively, being much deviated from 180°. Such large distortions of the angles are probably due to a steric hindrance to form the planar complex networks in the crystal.

Each pair of mercury and cobalt atoms is bridged by one SCN ion (where the sulfur atom is ligated to the mercury and the nitrogen atom to the cobalt atom). As is shown in Fig. 3, in both adducts, two mercury(II), two cobalt(II), and four SCN ions make a sixteen-membered ring which organizes the unit of a two-dimensional network. They resemble the $[CoHg(SCN)_4(H_2O)_2]_n$ network found in the $CoHg(SCN)_4(H_2O)_2 \cdot 2L$ type inclusion compounds previously reported,[4-6] although in these new complexes, Lewis base molecules are coordinated directly to the cobalt(II) atoms in place of the water molecules. As shown in Fig. 4, the complex network layers are piled up in the b-axis direction, and no chemical or hydrogen-bond bridgings exist between the layers: the interlayer space is occupied by the Lewis base molecules (mpp in **2**, dmso in **3**), which are coordinated to the cobalt(II) atoms of both side layers, respectively.

The respective complex layers found in **2** and **3** are almost in the same type structure. The y-coordinates

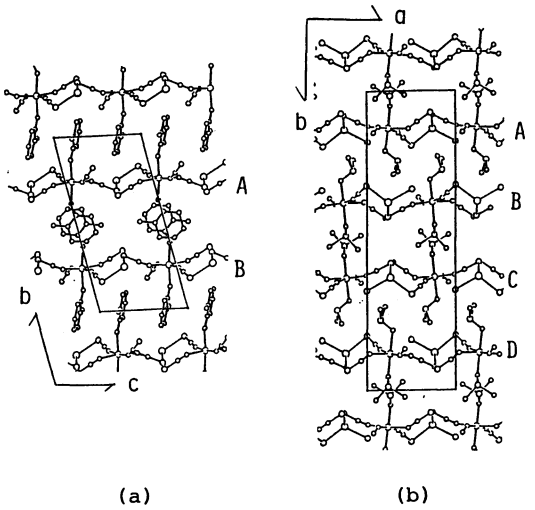

Fig. 4. The projection of the unit cell of the complex to the (1 0 0) plane (a) and to the (0 0 1) plane (b). (a) $CoHg(SCN)_4(mpp)_2$: (b) $CoHg(SCN)_4(dmso)_2$.

of all the (Co and Hg) metal atoms of one unit, sixteen-membered ring is approximately the same; the ring is regarded as being nearly in a plane, although four SCN sulfur atoms (and to a less extent the SCN carbon atoms) are located above or below the plane of the four metal atoms. The side-by-side SCN ions coordinated to one cobalt atom are extended above and beneath the respective positions of their sulfur atoms, which are above or beneath the complex plane, making a tetrahedral geometry around the mercury atom which is on the plane.

On the other hand, in $[CoHg(SCN)_4(H_2O)_2] \cdot 2L$ type complexes, cobalt atoms exist in positions slightly above and below the mercury network plane, alternately, since all four SCN ions coordinated to one

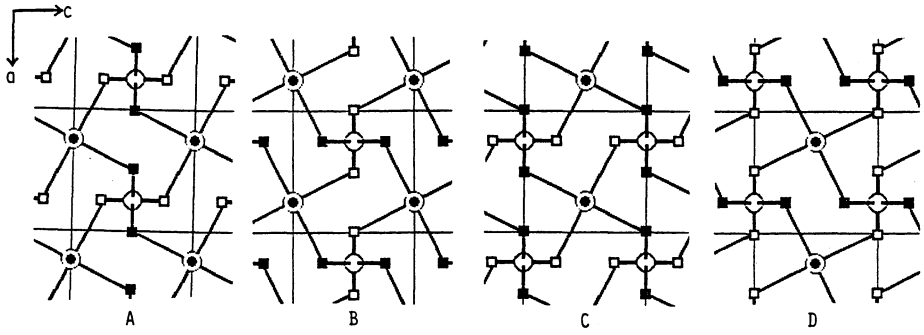

Fig. 5. Projection along b-axis of the network layers of the complex **3**. Approximate metal *y*-coordinates are: A, 0.12; B, 0.38; C, 0.62; D, 0.88. ○: Hg, ◉: Co, ■; S (above the layer plane), □: S (below the layer plane) atoms, respectively.

Table 5. Infrared Absorption Data of **1**, mpp, **2**, dmso, and **3** (in σ/cm^{-1})

1[1]	mpp[24]	**2**	dmso[25]	**3**	Tentative assignment
2150(s)		2145(s)		2145(s)	ν(CN)
	1675(s)	1610(s)			ν(CO)
			1055(s)	995(s)	ν(SO)
720(s)		725(m)		725(m)	ν(CS)
470(s)		460(s)		460(m)	δ(SCN)
447(s)		440(s)		440(s)	δ(SCN)

1, $CoHg(SCN)_4$; **2**, $CoHg(SCN)_4(mpp)_2$; **3**, $CoHg(SCN)_4(dmso)_2$.

cobalt atom are extended upward or downward. The stress around the cobalt atom may be less than that of the title complexes. (The angles of Co-C-N of the $[CoHg(SCN)_4(H_2O)_2]\cdot 2L$ type complexes are about 165—170°:[4-6] the distortions from 180° are less than the title complexes.)

The unit rings are linked two-dimensionally. In each network plane, there are two types of unit rings, I and II, which are alternately laid side by side along the [1, 0, 1] and [1, 0, −1] axes. Rings I and II are about the same in form: the latter has an arrangement of atoms which rotates unit I by 90° around an axis perpendicular to the ring plane.

In **2**, since the unit cell has a center of symmetry and Z=2, two kinds of layers, A and the reversed one B, are in a unit cell, they appear alternately along the b-axis in the crystal. As shown in Table 1, since the *y*-coordinates of the cobalt and mercury atoms are approximately the same, 0.25, all the interlayer separations (b-axis length $\times 0.5 \sin\alpha \sin\gamma$) are about the same, 8.21 Å. In the crystal, the same kind of metal atoms of all layers are laid in a zigzag pattern along the b-axis. As shown in Fig. 4, the respective planes of the mpp rings coordinated to the cobalt atoms of the layers above and below line up, one after another, and are arranged in the a- or c-axis direction.

Although the structure of the layers in **3** is not much different from that of **2**, some of their detailed bond lengths and bond angles are a little different from each other. Since the space group of **3** is $P2_12_12_1$, (Fig. 4), there are four such parallel complex layers in one unit cell along the b-axis; however, only one layer is crystallographically independent. As shown in Table 2, since the *y*-coordinates of the cobalt(II) and mercury(II) atoms of **3** are approximately the same, 0.62, the metal atomic *y*-coordinates of the four layers, A—D, are about, 0.12(A), 0.38(B), 0.62(C), and 0.88(D), respectively. Therefore, all interlayer separations are about the same in distances, about one-fourth of the b-axis length, 6.847 Å; they are piled up in the order D′, A, B, C, D, A″,⋯. Since the *x*- and *z*-coordinates of the cobalt and mercury atoms are approximately 0.25, 0 and 0.75, 0.50 (exactly, 0.26126, 0.00620 and 0.7633, 0.4984), the mercury and cobalt atoms of the A-layer have approximately the same *x*- and -coordinates as the cobalt and mercury atoms of the C-layer, respectively; the same relation for the metal coordinates are also found between those in the B and D layers. The positions of the metal atoms, together with the bridging SCN ions of the respective layers of **3**, are schematically shown in Fig. 5 by the projections to the ac-plane. The dmso ligands coordinated to the cobalt atoms are extended approximately perpendicular to the complex layer. The positions above and below the cobalt atom of one layer are approximately at the center of the sixteen-membered rings of the next complex layers on both sides. Therefore, no other atoms take positions very near the dmso molecules.

The positions of half of the SCN sulfur atoms overlap with the sulfur atom positions of one-side next complex layer respectively; the other half overlap with those of the other side next layer. Each pair of over-

lapping sulfur atoms of the side-by-side planes deviate above or below the network in order to decrease their interatomic distances to a value smaller than the separation of the complex layers.

Thus, these $CoHg(SCN)_4L_2$ type mixed complexes have a new characteristic layer structure, which is reported here for the first time.

Some infrared spectral data are shown in Table 5. When the wavenumbers of the peaks of **2** and **3** are compared with those of the free-ligand molecules, mpp[25] and dmso,[26] its ν(C=O) peak in **2** and ν(S=O) peak in **3** are found to be red-shifted by 60—70 cm^{-1}. Such red shifts are larger than those which have also been observed in the spectra of some amide adducts of previously reported $[CoHg(SCN)_4(H_2O)_2]\cdot 2L$ types.[4-6] This fact is due to the direct coordinate bonds of the Lewis base molecule to the cobalt atom. The wave numbers of the bands caused by the SCN ions of **1**, **2** and **3** are not very different from one another.

The magnetic moment of **2** is about 5.10 BM, and that of **3**, about 4.99 BM at 20 °C (1 BM=9.274078(36)$\times 10^{-24}$ $J\,T^{-1}$). These values are typical for the cobalt(II) ion in the octahedral geometry.

References

1) J. W. Jeffery and K. M. Rose, *Acta Crystallogr., Sect. B*, **24**, 653 (1968).

2) H. Kinoshita, M. Shimoi, and A. Ouchi, *Bull. Chem. Soc. Jpn.*, **58**, 1304 (1985).

3) H. Kinoshita and A. Ouchi, *Bull. Chem. Soc. Jpn.*, **59**, 3495 (1986).

4) H. Kinoshita, M. Shimoi, A. Ouchi, and S. Sato, *Bull. Chem. Soc. Jpn.*, **58**, 2782 (1985).

5) H. Kinoshita, M. Shimoi, and A. Ouchi, *Bull. Chem. Soc. Jpn.*, **59**, 1253 (1986).

6) H. Kinoshita and A. Ouchi, *Bull. Chem. Soc. Jpn.*, **60**, 1933 (1987).

7) M. R. Udupa and B. Krebs, *Inorg. Chim. Acta*, **42**, 37 (1980).

8) A. L. Beauchamp, L. Pazdernik, and R. Rivest, *Acta Crystallogr., Sect. B*, **32**, 650 (1976).

9) R. Makhija and R. Rivest, *J. Inorg. Nucl. Chem.*, **39**, 683 (1977).

10) W. R. Busing and H. A. Levy, *Acta Crystallogr.*, **10**, 180 (1957).

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

12) "The Universal Crystallographic Computation Program-System (UNICS)," ed by T. Sakurai, Crystallographic Society of Japan, Tokyo (1967).

13) "International Tables for X-Ray Crystallography," Kynoch Press, Birmingham (1974), Vol. IV, pp. 72, 150.

14) The final atomic and thermal parameters, and the final F_o-F_c tables are deposited as Document No. 8782 at the Office of the editor of Bull Chem. Soc. Jpn.

15) Key to the symmetry operations: for **2**, i, $-1+x,y,z$; ii, $x,y,1+z$; for **3**, iii, $x,y,-1+z$; iv, $-1+x,y,-1+z$; v, $1+x,y,z$.

16) R. C. Makhija, A. L. Beauchamp, and R. Rivest, *J. Chem. Soc., Dalton Trans.*, **1973**, 2447

17) R. C. Makhija, A. L. Beauchamp, and R. Rivest, *J. Chem. Soc., Chem. Commun.*, **1972**, 1043.

18) D. Grdenic, *Quart. Rev.*, **19**, 303 (1965).

19) H. Hartl and S. Steidl, *Z. Naturforsh.*, **B32**, 6 (1977).

20) B. Buss, P. G. Jones, R. Mews, M. Noltemeyer, and G. M. Sheldrick, *Acta Crystallogr., Sect. B*, **36**, 141 (1980).

21) H. Hartl and I. Brudgam, *Acta Crystallogr., Sect. B*, **36**, 162 (1980).

22) H. Lynton and P. Y. Siew, *Can. J. Chem.*, **51**, 227 (1973).

23) J. A. Bertrand and T. C. Hightower, *Inorg. Chem.*, **12**, 206 (1973).

24) A. Vegas, *Acta Crystallogr., Sect. B*, **37**, 1916 (1981).

25) S. E. Krikorian, T. A. Andrea, and M. Mahpour, *Spectrochim. Acta*, **32A**, 1447 (1976).

26) W. F. Currier, and J. H. Weber, *Inorg. Chem.*, **6**, 1539 (1967).