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Synthesis, and Crystal and Molecular Structure of Bis(*N*-methylformamide)tetrakis(thiocyanato)cobalt(II)mercury(II), $CoHg(SCN)_4(HCONHCH_3)_2$

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The title complex was synthesized and its crystal and molecular structures were determined by the single-crystal X-ray diffraction technique. The crystal is orthorhombic with a space group $P2_1nb$, $a=14.953(4)$, $b=15.955(4)$, $c=7.6838(9)$ Å. The structure was solved by means of the heavy-atom method and the final R value was 0.059. The mercury atom is in the tetrahedral geometry, coordinated with four sulfur atoms of the thiocyanate (SCN) ions, and the cobalt atom is in the octahedral geometry, coordinated with four nitrogen atoms of SCN ion and two oxygen atoms of *N*-methylformamide which occupy the *cis* positions. Each pair of different kinds of metal atoms is bridged by an SCN ion and are in a three-dimensional network. Twenty-four membered rings of $Co_3Hg_3(SCN)_6$, where the metal atoms are arranged hexagonally in a chair-form, are condensed two-dimensionally approximately parallel to the (1 0 0) plane. All mercury atoms on one plane are bridged by SCN ions to the cobalt atoms of the polymeric plane next to the [1 0 0] direction, while the cobalt atoms are linked by SCN ions to the mercury atoms on the next plane of the opposite side. The mfa ligands take their positions in the vacancy of the network.

The cobalt(II) mercury(II) thiocyanate (**1**) was found to have a diamond-like three-dimensional polymeric structure,[1] where both kinds of the metal atoms are in the tetrahedral geometry, and each pair of the different kind of metal atoms are bridged by one thiocyanate (SCN) ion. In **1**, a twenty-four membered ring containing three mercury and three cobalt atoms and six thiocyanate ions is formed as the unit where the six metal atoms are in a chair-form hexagonal arrangement. The units are condensed and linked three-dimensionally in a crystal comprising a diamond-like structure.

The pyridine (py) and *N,N*-dimethylformamide (dmf) adducts of **1**, $CoHg(SCN)_4py_2$ (**2**),[2] and $CoHg(SCN)_4dmf_2$ (**3**),[3] were obtained and their structures were elucidated; they are in the respective characteristic three-dimensional polymeric structures. Since the types of the networks of **1**, **2**, and **3** are different from each other, it is expected that if another kind of the Lewis-base adduct of **1** is obtained, it may have a different type of the three-dimensional network structure. Previously, the present authors studied and determined the crystal structures of some adducts of **1**.[4–6] Among them, relatively bulky amide molecules, such as *N,N*-dimethylacetamide (dma)[5] and *N*-methyl-2-pyrrolidone (mpd),[6] were shown to form a kind of inclusion compound of the type $CoHg(SCN)_4(H_2O)_2\cdot 2L$ (where L=dma or mpd).

Along this line of research, the title complex has been synthesized, where the added Lewis base, *N*-methylformamide (mfa) is smaller in size than dma or mpd (and even py or dmf). Its crystal and molecular structure has been determined by the X-ray diffraction method using its single-crystal.

Experimental

Synthesis of Bis(*N*-methylformamide)tetrakis(thiocyanato)cobalt(II)mercury(II) (4). A crystalline powder of **1** (1.0 g, 2.0 mmol) was dissolved into mfa (20 cm^3), and 3 cm^3 of water was added to the solution. It was left standing for several days and crystals of **4** were deposited. The red-violet crystals were filtered off and dried over silica-gel. Yield: 0.65 g, 54%. Found: Co, 9.63; C, 15.45; H, 1.57; N, 14.00%. Calcd for $CoHgC_8N_6O_2S_4$: Co, 9.66; C, 15.75; H, 1.65; N, 13.78%.

Intensity-Data Collection. A crystal shaped into a sphere[a] ($\phi=0.21$ mm) was used for the intensity data measurement. Crystallographic data are: $CoHgC_8H_{10}N_6O_2S_4$ F.W.=609.99, orthorhombic, with the space group of $P2_1nb$, $a=14.953(4)$, $b=15.955(4)$, $c=7.6838(9)$ Å, $U=1833.2(7)$ Å^3, $Z=4$, $D_m=2.21(3)$ Mg m^{-3}, $D_x=2.21$ Mg m^{-3}, $\mu(\text{Mo }K\alpha)=9.94$ 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 2θ; scan width, $1.12+0.5\tan\theta°(\theta)$). Of the 3072 independent reflections measured, 1707 $|F_o|>3\sigma(|F_o|)$ reflections were used for the structure determinaion. The intensities were corrected for Lorentz and polarization factors as well as for absorption. The latter correction was made using a numerical Gaussian integration.[7]

Structure Determination. The structure was 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.

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[a] The crystal was shaped by rolling it on the fine particle sand-paper while pressing very weakly.

During the final refinement step, the shift of the all the parameters was less than σ/3's. At the step, two spots remained at positions about 2.1 Å from the mercury atom on the differential synthesis map. A calculation of the structure analysis was repeated using new intensity data obtained from another crystal, but the spot remained, although the intensity of the both spots were about 3 electrons Å^{-3}. As these spots were about 2.1 Å from the thiocyanate nitrogen atoms, their positions were too near to be thought of as those of the coordinated water oxygen atoms. Actually, the infrared spectra of the complex, as well as the element analysis did not show the existence of water in the crystal. The adopted space group was also found to be the correct one from Weissenberg and oscillation photographs. Therefore, the spots are now thought to be due to a termination effect owing to the large mercury atom; such a phenomenon was sometimes found around a heavy atom. The final R value obtained by applying anisotropic temperature parameters was 0.059.[8] As the R value for structure with an inversed chirality was 0.064, the structure was not adopted.

All calculations were carried out on a HITAC M-280H computer apparatus at the Computer Center of the University of Tokyo using a local version of the UNICS program system.[9] The atomic scattering factors were taken from Ref. 10.

Other Measurement. The magnetic moment of the solid sample was measured at 20 °C using a Gouy balance.

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

Atom	x	y	z	B_{eq}/Å^2 a)
Hg	500.0	435.4(1)	548.3(1)	3.27
Co	306.6(2)	127.9(2)	477.7(3)	2.31
S(1)	332.0(4)	440.4(4)	528.0(9)	3.82
S(2)	550.3(5)	302.8(4)	701.3(11)	4.64
S(3)	568.4(4)	548.7(4)	749.4(9)	3.49
S(4)	554.5(5)	458.5(5)	239.5(10)	4.93
N(1)	304.6(13)	552.3(11)	797(2)	2.96
N(2)	407.6(14)	205.6(11)	587(3)	3.19
N(3)	708.0(13)	447.0(13)	859(3)	3.74
N(4)	405.1(11)	552.6(12)	130(3)	3.12
C(1)	316.1(15)	507.1(13)	690(3)	2.51
C(2)	463.8(15)	244.0(12)	630(3)	2.82
C(3)	651.3(15)	488.4(13)	814(3)	2.66
C(4)	464.2(14)	515.8(13)	174(3)	2.40
O(11)	212.3(11)	206.0(11)	595(2)	3.67
O(21)	308.1(13)	210.5(9)	260.3(19)	3.34
N(11)	120.2(15)	317.8(11)	613(3)	3.98
N(21)	303(2)	242.7(19)	−30(3)	6.07
C(11)	185.9(17)	273.3(14)	541(4)	3.42
C(12)	74(3)	296(2)	760(6)	9.73
C(21)	299(2)	184.5(16)	104(3)	5.22
C(22)	317(4)	328(2)	5(5)	7.82

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 B_{ij}'s are defined by: $T=\exp[-(h^2B_{11}+k^2B_{22}+l^2B_{33}+2hlB_{13}+2hkB_{12}+2klB_{23})]$.

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 interatomic distances are shown in Table 2.[11] Perspective drawings of the complex around the mercury and the cobalt atoms are given in Figs. 1 and 2, together with the numbering

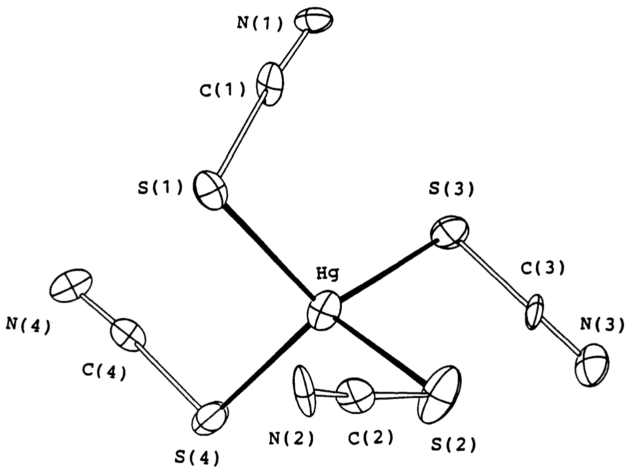

Fig. 1. The perspective drawing of the complex around a mercury atom.

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

Bond length	l/Å	Bond length	l/Å
Hg-S(1)	2.518(6)	Hg-S(2)	2.535(7)
Hg-S(3)	2.588(7)	Hg-S(4)	2.537(9)
Co-N(1^{i})	2.113(19)	Co-N(2)	2.13(2)
Co-N(3^{ii})	2.11(2)	Co-N(4^{iii})	2.073(19)
Co-O(11)	2.087(17)	Co-O(21)	2.128(16)
S(1)-C(1)	1.66(2)	C(1)-N(1)	1.11(3)
S(2)-C(2)	1.69(2)	C(2)-N(2)	1.09(3)
O(11)-C(11)	1.22(3)	O(21)-C(21)	1.28(3)
C(11)-N(11)	1.33(3)	C(21)-N(21)	1.38(4)
Hg···Co	5.722(3)	Hg···Co^{i}	5.573(3)
Hg···Co^{ii}	5.738(3)	Hg···Co^{iii}	5.842(3)
Bond angle	**ϕ/°**	**Bond angle**	**ϕ/°**
S(1)-Hg-S(2)	110.5(2)	S(1)-Hg-S(3)	114.2(2)
S(1)-Hg-S(4)	105.0(2)	S(2)-Hg-S(3)	100.9(2)
N(1^{i})-Co-N(2)	91.1(8)	N(2)-Co-N(3^{ii})	177.5(8)
N(2)-Co-N(4^{iii})	89.4(8)	N(2)-Co-O(11)	87.8(7)
N(2)-Co-O(21)	86.6(7)	O(11)-Co-O(21)	88.7(6)
Hg-S(1)-C(1)	96.7(8)	Hg-S(2)-C(2)	94.9(8)
Co-N(1^{i})-C(1^{i})	168.3(19)	Co-N(2)-C(2)	173.6(19)
Co-O(11)-C(11)	126.9(16)	Co-O(21)-C(21)	122.5(16)
S(1)-C(1)-N(1)	179(2)	S(2)-C(2)-N(2)	179(2)

Key to the symmetry operations: i, x, $-0.5+y$, $1.5-z$; ii, $-0.5+x$, $0.5-y$, $-0.5+z$; iii, x, $-0.5+y$, $0.5-z$

scheme of the atoms. A crystal-packing diagram of the unit cell is shown in Fig. 3.

Each mercury atom is coordinated with four thiocyanate sulfur atoms and has a tetrahedral geometry. The average Hg-S length is 2.545 Å (maximum Hg-S(3), 2.588(7) and minimum Hg-S(1), 2.518(6) Å) which is about the same as the sum of the Pauling's radii, 2.52 Å (r_{Hg}=1.48, r_{S}=1.04 Å).[12] The average angles of S-Hg-S and Hg-S-C are 109.5 and 95.5°, respectively. These bond lengths and angles about the mercury atoms of these complexes are normal compared with several mercury thiocyanates whose structures are crystallographycally known.[1,13–15]

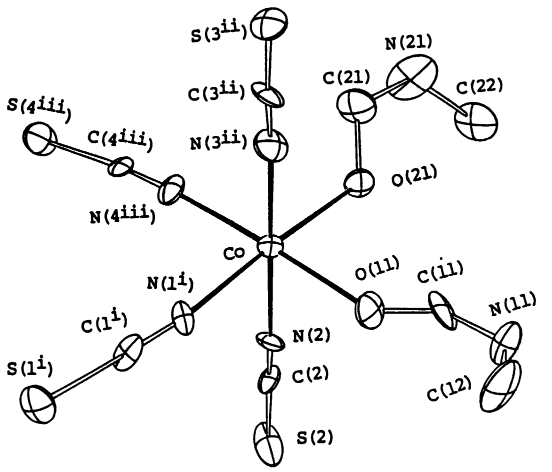

Fig. 2. The perspective drawing of the complex around a cobalt atom.

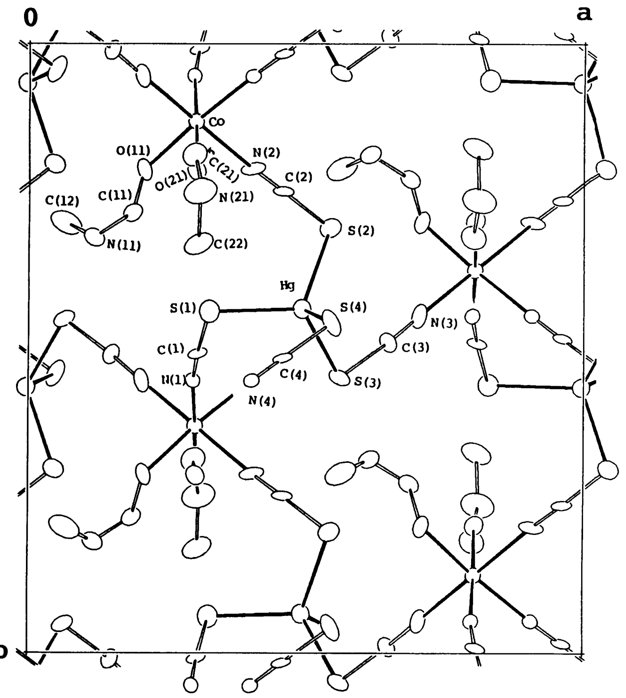

Fig. 3. The projection of the unit cell of the complex to the (0 0 1) plane.

The cobalt atom is hexa-coordinated and is in an octahedral geometry, where two amide oxygen atoms are ligated in a *cis*-orientation, and four thiocyanate nitrogen atoms are bonded to the rest positions. The average Co-N and Co-O bond-lengths are 2.104, and 2.108 Å, respectively. Although they are a little longer than the respective sums of the Pauling radii, 2.02 and 1.98 Å (where r_{Co}=1.32, r_{N}=0.70, r_{O}=0.66 Å), such Co-O[16–18] and Co-N[19–21] lengths are found in many octahedral cobalt(II) complexes. The bond angles N-Co-N′ are; N(2)-Co-N(3^{ii})=177.5(8)°, and the other five angles are 90.15° on the average. Including the bond angles around the cobalt atoms, such as O-Co-N and O-Co-O, it was thought that the octahedral geometry of the cobalt core is not much deformed from the ideal one. The bond angle Co-N-C is 172° on the average (maximum Co-N(4^{iii}),

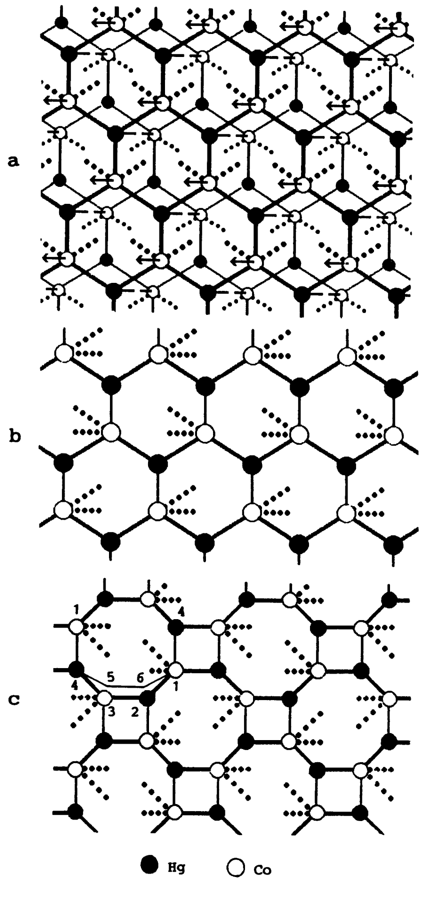

Fig. 4. The schematic presentation of the projection of the metal atomic arrangements of the complexes. a: $\mathrm{CoHg(SCN)_4(mfa)_2}$ projected to (1 0 0) plane, b: $\mathrm{CoHg(SCN)_4(mfa)_2}$ projected to (0 0 1) plane, c: $\mathrm{CoHg(SCN)_4(dmf)_2}$ projected to an appropriate plane.

Each solid line indicates the thiocyanato bridge. The broader lines show respective polymeric planes parallel(a) or perpendicular(b and c) to the projected plane. The dotted lines indicate the Lewis base molecules.

174(2); minimum Co–N(1^{i})–C(1^{i}), 168(2)°), being deformed only slightly from 180°.

Each pair of mercury and cobalt atoms are bridged by a thiocyanate ion (where the sulfur atom is ligated to the mercury and the nitrogen atom to the cobalt atom).

The projection of the metal atoms of **4** onto the (1 0 0) plane is shown schematically in Fig 4-a, where each bridging thiocyanate ion between the metal atoms is abbreviated as a straight line, in place of the real one which is broken at the sulfur atom position in about right angle. As shown in the figure, there are two kinds of two-dimensional networks (shown by broad and narrow lines) piled up alternatively. Both of them consist of condensed twenty-four membered rings where each three mercury and cobalt atoms are arrayed hexagonally in a chair form, and their average plane is parallel to (1 0 0). The dotted lines indicate mfa molecules. Each mercury atom in the plane is bridged by a thiocyanate ion to the cobalt atoms on the parallel next polymer plane on one side, (shown by the broken line), while each cobalt atom is linked to the mercury atom on the plane of the other side (shown by the arrow), respectively. All such inter-layer bridging SCN ions are the S(3)–C(3)–N(3) types.

As shown in Fig. 4-b, which is a schematic presentation of the projection of the network to the (0 0 1) plane, there are other kinds of twenty-four membered rings represented by the hexagons of their metal atomic positions. However, projections of the hexagons are not very deformed. They are very different from the exact chair forms since the up and down deviations of the respective metal atomic positions from the average plane are irregular. Thus the three-dimensional network of complex **4** is regarded as consisting of a unit cage surrounded by two chair forms (up and down face parallel to (1 0 0) plane), and three deformed (side ones) twenty-four membered rings. The cages are arranged three-dimensionally and mfa ligands take positions in them.

A type of cage consisting of twenty-four membered rings was also found in **1**,¹⁾ but all the hexagons of the metal-atom positions of all the rings were in the chair form. The metal atoms were arrayed like the carbon atoms in a diamond crystal.

According to Udupa's data of **3**,[3)] two dmf oxygen atoms are ligated to a cobalt atom in a cis orientation, but its bridging structure is much different from that of **4** (written as follows). As schematically shown in Fig. 4-c, which is the projection to an appropriate plane, there are the same types of the twenty-four membered ring units; the hexagons indicating the metal-atom positions are condensed and linked to form a planar-type polymer which are spread perpendicular to the paper plane (one such hexagon is shown schematically as 1—6 in the figure). All the hexagons are in a boat form; the concave and convex types are arrayed alternatively. Their planar networks are shown by the broad lines in the figure. The metal atoms at the head and tail (1 and 4) positions of one hexagon unit are also bridged to the respective different kind of metal atoms at the 4 or 1 positions of another ring on a parallel next plane by the thiocyanate ions, while the other four metal atoms (2,3,5, and 6 position ones) are linked to the respective other kind of metal atoms on the next parallel plane of the opposite side. Thus, in **3** there are two kinds of cages (large and small ones) and as shown in the figure the side wall of the large one consists of two thirty-two membered rings (including, each, four mercury and cobalt atoms as well as eitht thiocyanate ions). Thus, the crystal of **3** has the vacant small cages other than the large cages to accomodate large dmf ligands in them; it is expected to have a less compact structure than that of **4**; the density of **3** and **4** are 2.01[3)] and 2.21, respectively.

According to Beauchamp,[2)] in **2**, two py nitrogen atoms are axially ligated to a cobalt atom, and four thiocyanate nitrogen atoms equatorially; its unit cage comprises two thirty-two membered rings ($\mathrm{Co_4Hg_4(SCN)_8}$) and four sixteen-membered rings ($\mathrm{Co_2Hg_2(SCN)_4}$) and the shape of the unit cage is much different from that of **1** or **4**.

From these comparisons of the framework, in **4** the mfa ligand can be included into the network of **1** with a relatively minor modification of the network, although the diamond-like structure of **1** is lost.

On the other hand, as py and dmf consist of six and five non-hydrogen atoms, respectively, they are relatively large in size compared with mfa which has only four non-hydrogen atoms. Therefore, the frameworks of **2** and **3** are too much different from those of **1** and **4** to take in these additional ligands.

The magnetic moment of **4** is about 5.02 BM (1 BM=$9.274078(36)\times10^{-24}\ \mathrm{JT^{-1}}$) at 20 °C. The value is almost the same as that of the related adducts, such as **2** or **3**, and which is the typical value for cobalt(II) complexes in an octahedral geometry.

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