The Synthesis and the Crystal and Molecular Structure of Tris(*N*-ethyl-2-pyrrolidone)tetrakis(thiocyanato)cobalt(II)mercury(II), $[CoHg(SCN)_4(C_6H_{11}NO)_3]$

Hisashi KINOSHITA* and Akira OUCHI†
Department of Chemistry, Faculty of Liberal Arts, Shizuoka University, Ohya, Shizuoka 422
†Department of Chemistry, College of Arts and Sciences, The University of Tokyo, Komaba, Meguro-ku, Tokyo 153
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Synopsis. The title complex, which has a new-type layer structure, has been obtained, and its crystal and molecular structure has been determined by the X-ray diffraction technique. The crystallographic data are: monoclinic, space group $P2_1/n$, a=18.264(7), b=16.223(7), c=10.623(5) Å, β=92.77(5)° and Z=4. The final R value was 0.059. The cobalt atoms are in an octahedral geometry, ligated by three thiocyanato(SCN) nitrogen atoms and three oxygen atoms (*N*-methyl-2-pyrrolidone) in a meridional configuration; these cobalt atoms are cross-linked to adjacent mercury atoms by SCN ions, forming a characteristic layer structure which consists of twenty-four-membered rings of the $[Co_3Hg_3(SCN)_6]$ unit. The mercury atoms are in the tetrahedral geometry, ligated by four sulfur atoms of SCN ions, three bridging and one unidentate. The complex layers in parallel are piled up in the a-axis direction, and there are no bridgings or hydrogen bondings between them.

Previously, the present authors[1-3] have reported the crystal structures of some Lewis base adducts of tetrakis(thiocyanato)cobalt(II)mercury(II), $CoHg(SCN)_4$ (**1**), with the general formula of $CoHg(SCN)_4L_2$ (L= *N*-methyl-2-piperidone(mpp) (**2**)[1] or dimethyl sulfoxide(dmso) (**3**)[1]) and of $CoHg(SCN)_4(H_2O)_2\cdot 2L$ (L= *N*,*N*-dimethylacetamide(dma) (**4**)[2] or *N*-methyl-2-pyrrolidone(mpd) (**5**)[3]). These complexes were found to have two-dimensional planar networks consisting of sixteen-membered rings of the $Co_2Hg_2(SCN)_4$ unit. By continuing this line of research using *N*-ethyl-2-pyrrolidone(abbr.; epd) as the Lewis base, the title complex was obtained. From the preliminary test, its chemical composition ($CoHg(SCN)_4L_3$), its crystal system, and its unit cell size were found to be different from those of **2**—**5**. Therefore, we have investigated the crystal and molecular structure of this complex by means of the X-ray diffraction method.

Experimental

Synthesis of Tris(*N*-ethyl-2-pyrrolidone)tetrakis(thiocyanato)cobalt(II)mercury(II) (6). The crystalline powder of **1** (1.0 g, 2.0 mmol) was dissolved into epd (10 cm³), and 10 cm³ of tetrahydrofuran was added to the solution. The mixture was then left standing for several days; thereby red-purple crystals of **6** were deposited. They were filtered off and dried over silica gel. Yield: 0.6 g, 28%. Found: Co, 7.07; C, 31.68; H, 3.81; N, 11.82%. Calcd for $CoHgC_{22}H_{33}N_7O_3S_4$: Co, 7.09; C, 31.79; H, 4.00; N, 11.79%.

X-Ray Structure Analysis. A crystal of **6**, red-purple in color and in the shape of a parallelepiped (0.3×0.3×0.2 mm³), was used for the intensity measurement. Crystallographic data: $CoHgC_{22}H_{33}N_7O_3S_4$ $F.W.$=831.33, monoclinic, with the space group of $P2_1/n$, a=18.264(7), b=16.223(7), c=10.623(5) Å, β=92.77(5) ,U=3144.0(9) Å³, Z=4, D_m=1.75(3) g cm⁻³, D_x=1.76 g cm⁻³, μ(Mo $K\alpha$)=5.75 mm⁻¹. Reflections within the range of $3°<2\theta<60°$ were collected on a Rigaku AFC-6A automated four-circle X-ray diffractometer with graphite-monochromatd Mo $K\alpha$ radiation (λ=0.71073 Å): the ω—2θ scan technique was employed (scan speed, 4° min⁻¹ (θ); scan width, 1.12+0.5 tan θ(θ/°)). Of the 3841 independent reflections measured, 3023 $|F_o|>3\sigma(|F_o|)$ 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.[4] The structure was solved by the heavy atom method. The positional and thermal parameters were refined by the block-diagonal least-squares method. Hydrogen atoms were not included in the structure factor calculation. The final R value obtained by applying the anisotropic temperature parameters was 0.059.[5]

All the calculations were carried out on a HITAC M-682H computer apparatus at the Computer Center of the University of Tokyo, using the local version of the UNICS program system.[6] The atomic scattering factors were taken from Ref. 7.

Results and Discussion

The selected bond lengths and bond angles, and also some interatomic distances, are shown in Table 1.[8] A perspective drawing of the complex around a cobalt atom is sown Fig. 1. The projection of the structure along the a axis is shown in Fig. 2.

Each mercury atom is coordinated tetrahedrally by four SCN sulfur atoms. The cobalt atom is six-coordinated and is in an octahedral geometry, where three SCN nitrogen atoms and three carbonyl-oxygen atoms of the *N*-ethyl-2-pyrrolidone molecule are ligated in a meridional configuration. Therefore, one of the four SCN ions, which are ligated to each mercury atom with their sulfur atom, has a free nitrogen terminal. The bond lengths of Co–O and Co–N (on the average, 2.080 and 2.131 Å respectively) are not very different from the respective sums of Shannon's ionic radii (Co–O: 2.00, and Co–N: 2.11 Å).[9] The Hg–S bond lengths (2.531 Å, on the average) are shorter than the sum of the Shannon ionic radii, 2.80 Å; especially, the bond length Hg–S(4) of the unidentate SCN ion, 2.455(7) Å, is a little shorter than the other three Hg–S bonds.

The bond angles, Co–N–C (160.5° on the average), deviate a little from 180°, while the N–C–S angles (177° on the average) are almost 180°. In this complex, three mercury(II), three cobalt(II), and six SCN ions make a twenty-four-membered ring unit which forms a two-dimensional polymeric network which is quite different from those of **2**, **3**, **4**, and **5**. In

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

Bond length	l/Å	Bond length	l/Å
Hg-S(1)	2.562(5)	Hg-S(2)	2.550(5)
Hg-S(3)	2.557(5)	Hg-S(4)	2.455(7)
Co-N(1)	2.137(16)	Co-N(2^{i})	2.125(12)
Co-N(3^{ii})	2.130(15)	Co-O(11)	2.064(10)
Co-O(21)	2.096(10)	Co-O(31)	2.081(10)
S(1)-C(1)	1.660(18)	C(1)-N(1)	1.12(2)
S(2)-C(2)	1.631(15)	C(2)-N(2)	1.146(19)
S(3)-C(3)	1.612(18)	C(3)-N(3)	1.15(2)
S(4)-C(4)	1.66(2)	C(4)-N(4)	1.14(3)
O(11)-C(11)	1.230(17)	O(21)-C(21)	1.25(2)
O(31)-C(31)	1.256(19)		
Bond angle	**ϕ/°**	**Bond angle**	**ϕ/°**
S(1)-Hg-S(2)	105.84(16)	S(1)-Hg-S(3)	104.49(15)
S(1)-Hg-S(4)	113.78(19)	S(2)-Hg-S(3)	102.04(15)
N(1)-Co-N(2^{i})	87.8(5)	N(1)-Co-N(3^{ii})	175.4(6)
N(1)-Co-O(11)	90.0(5)	N(1)-Co-O(21)	83.9(5)
N(1)-Co-O(31)	94.7(5)	O(11)-Co-O(21)	94.7(4)
O(11)-Co-O(31)	90.8(4)	O(21)-Co-O(31)	174.3(4)
Hg-S(1)-C(1)	95.7(6)	Hg-S(2)-C(2)	96.4(6)
Hg-S(3)-C(3)	98.3(6)	Hg-S(4)-C(4)	97.0(7)
Co-N(1)-C(1)	161.9(15)	Co-N(2^{i})-C(2^{i})	154.4(11)
Co-N(3^{ii})-C(3^{ii})	165.2(14)	S(1)-C(1)-N(1)	179.2(17)
S(2)-C(2)-N(2)	175.8(14)	S(3)-C(3)-N(3)	178.8(18)
S(4)-C(4)-N(4)	175.4(19)	Co-O(11)-C(11)	139.6(9)
Co-O(21)-C(21)	136.9(10)	Co-O(31)-C(31)	137.7(10)

a) Key to the symmetry operations: i, 1.5−x, 0.5+y, 0.5−z; ii, x, y, −1+z.

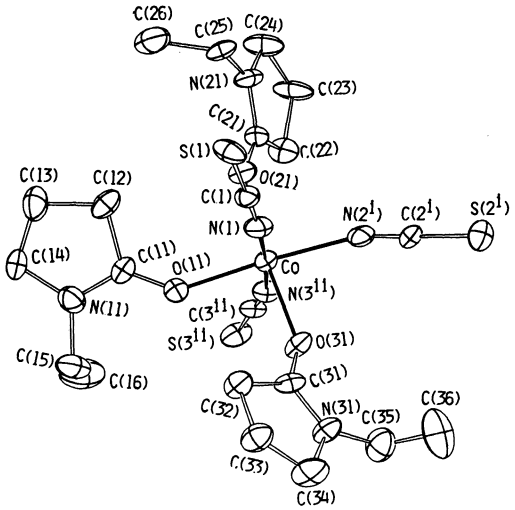

Fig. 1. The perspective drawing of the complex around a cobalt atom.

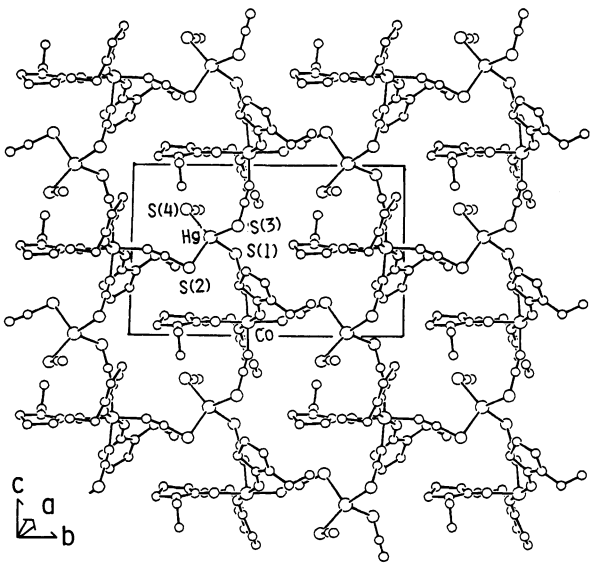

Fig. 2. The projection of the unit cell of the complex to the (100) plane.

the latter four complexes, the planar networks are composed of sixteen-membered ring units, including two mercury, two cobalt and four SCN^- ions.[1,2] Therefore, the present complex was found to have a new type of layer structure. In a unit cell there are two layers which spread out parallel to the (1 0 0) plane. The interlayer distance is 9.12 Å, which is much longer than those of **2** and **3**, where the distances are 8.21 and 6.85 Å respectively.[1] The ethyl group of epd may cause the steric hindrance, resulting in the bulky structure with the relatively small specific gravity of 1.76 g cm^{-3}; the specific gravities of **2**, **3**, **4**, and **5** are 2.03, 2.22, 1.99, and 2.04 g cm^{-3} respectively.

Regarding the metal atoms only, this complex layer has an obvious structural feature; it is of the so-called "graphite" type, consisting of the six-membered ring

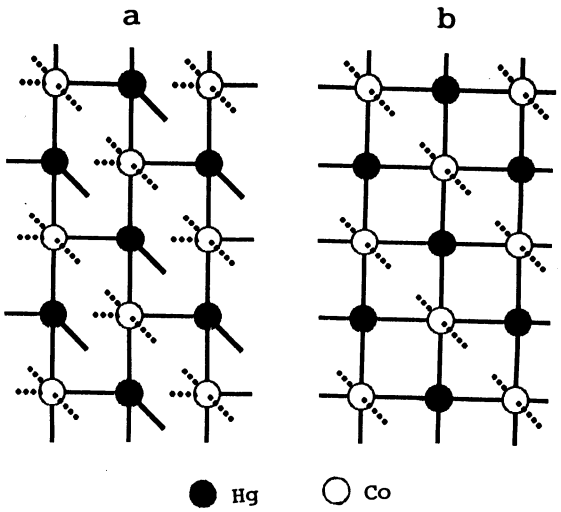

Fig. 3. The schematic presentation of the projection of the metal atomic arrangements of the complexes. a. $CoHg(SCN)_4(epd)_3$ projected to (100) plane. b. $CoHg(SCN)_4L_2$-type[1] or $CoHg(SCN)_4(H_2O)_2 \cdot L$-type[2,3] complexes projected to an appropriate plane. Each solid line indicates the thiocyanate ion. The dotted lines indicate the Lewis base (or water) molecules.

unit shown in Fig. 3(a), which is deduced from the "diamond" type structure of $CoHg(SCN)_4$, the starting material. On the other hand, in all of the layer structures of **2—5**, the units of the positions of the metal atoms are the four-membered ring units of Co_2Hg_2, as is shown in Fig. 3(b).

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5) $R=\Sigma||F_o|-|F_c||/\Sigma|F_o|$

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