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Crystal and Molecular Structure of Mercury(II) Tetrathiocyanatobis(dimethylformamide)cobaltate(II)

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The crystal and molecular structure of mercury(II) tetrathiocyanatobis(dimethylformamide)cobaltate(II) $Hg(SCN)_4Co(DMF)_2$ was determined from three-dimensional X-ray data collected by counter methods. The pink prismatic crystals are monoclinic, space group $P2_1/n$. The unit cell dimensions are a = *9.163(2),* b = *14.057(3),* c = *16.276(3) Å, β = 92.88(3)° and Z = 4. The structure was solved by direct methods from 3298 reflections and refined by least-squares methods to R = 0.053.*

The structure is polymeric with the four sulphur atoms of the thiocyanate groups tetrahedrally coordinated around the mercury atom. The average Hg–S bond length is 2.525 Å. The linear thiocyanate groups have a mean angle of 96.5° to the Hg–S bonds. The dimethylformamide molecules are bonded to the cobalt atom in cis *configuration through the oxygen atoms with average Co–O distance of 2.114 Å and an O–Co–O angle of 88.2°. Octahedral six-coordination around cobalt is completed by the thiocyanate N atoms of four $Hg(SCN)_4$ units with mean Co–N bond lengths of 2.113 Å.*

Introduction

The thiocyanate ion is an ambidentate ligand, capable of bonding through S, N or both towards metal ions, and extensive studies have been made on metal–thiocyanate complexes [*e.g.* 1–3]. Recently Makhija and coworkers [4–6] have investigated mercury(II) tetrathiocyanatometallate(II) complexes with Lewis bases by spectroscopic techniques. The crystal structure analysis of $Hg(SCN)_4Cu(en)_2$ has revealed [7] that Hg is in a tetrahedral arrangement of thiocyanate S atoms, and Cu is six-coordinated with the two bidentate ethylenediamine molecules and two of the thiocyanate groups, all bonded through the N atoms, as the nearest neighbours. In this paper we report the preparation and the crystal and molecular structure of mercury(II) tetrathiocyanatobis(dimethylformamide)cobaltate(II), $Hg(SCN)_4Co(DMF)_2$. The aim of this study is to establish the stereochemistry of Hg and Co and the bonding properties of the SCN groups in the complex.

Experimental

Preparation of $Hg(SCN)_4Co(DMF)_2$

To a hot solution of mercury(II) chloride containing 3.4 g of $HgCl_2$ in 50 ml of water 10 ml of an aqueous solution containing 3.5 g of $CoSO_4 \cdot 7H_2O$ and 3.8 g of NH_4SCN were added. The resultant solution was stirred, and the precipitated blue complex was filtered. The dried $HgCo(SCN)_4$ complex was dissolved in a minimum amount of hot dimethylformamide when a pink solution was obtained, which on cooling gave a pink crystalline product. Analysis: found, C 19.31, H 2.54, N 12.78, S 19.52, calcd. for $C_{10}H_{14}N_6O_2S_4HgCo$, C 18.82; H 2.22, N 13.17, S 20.10%.

Crystal Data

Preliminary Weissenberg and precession photographs revealed that the crystals are monoclinic. The systematic absences observed from the photographs, 0k0, k = 2n + 1, h0l, h + l = 2n + 1, suggested the space group $P2_1/n$ (C_{2h}^5, No. 14). The unit cell parameters, refined by least-squares from diffractometer coordinates of 15 high-order reflections, are *a* = 9.163(2), *b* = 14.057(3), *c* = 16.276(3) Å, β = 92.88(3)°, V = 2094 $Å^3$. The measured density by the flotation method, d_m = 2.02(2) g cm^{-3} is in agreement with the calculated value of d_c = 2.023 g cm^{-3} for four formula units of the complex per unit cell.

X-ray Data Collection

The X-ray intensity data for a crystal of approximate dimensions 0.10 × 0.09 × 0.25 mm^3 were collected at 22 °C on a Syntex $P2_1$ four-circle diffrac-

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TABLE I. Coordinates of the Atoms in the Structure of Mercury(II) Tetrathiocyanatobis(dimethylformamide)cobaltate(II).[a]

	x	y	z
Hg	−0.01529(6)	0.20361(4)	0.41839(3)
Co	0.48133(20)	0.34989(13)	0.24660(11)
S1	−0.01590(40)	0.22898(32)	0.26657(23)
S2	0.17788(43)	0.08312(28)	0.45931(24)
S3	−0.26809(38)	0.15707(29)	0.45906(23)
S4	0.06562(43)	0.34717(27)	0.50645(24)
O1	0.6871(10)	0.4218(7)	0.2499(6)
O2	0.4137(11)	0.4462(7)	0.3348(6)
N1	0.2731(14)	0.2840(9)	0.2539(8)
N2	0.0927(12)	−0.0543(8)	0.3451(7)
N3	−0.4223(13)	0.2623(9)	0.3390(7)
N4	0.0425(14)	0.2449(9)	0.6526(7)
N5	0.9009(12)	0.4653(9)	0.1988(9)
N6	0.4389(12)	0.5774(9)	0.4141(7)
C1	0.1570(16)	0.2585(10)	0.2588(8)
C2	0.1259(14)	0.0025(10)	0.3918(8)
C3	−0.3617(14)	0.2173(10)	0.3876(8)
C4	0.0537(13)	0.2860(10)	0.5952(9)
C5	0.7685(15)	0.4238(11)	0.1933(9)
C6	0.9999(24)	0.4569(16)	0.1323(16)
C7	0.9497(27)	0.5067(33)	0.2780(29)
C8	0.4860(18)	0.5128(14)	0.3634(9)
C9	0.5346(22)	0.6557(17)	0.4484(13)
C10	0.2889(35)	0.5733(28)	0.4391(26)

[a] Estimated standard deviations are given in all tables in units of the least significant digits.

tometer using graphite monochromated MoKα radiation (Kα_1 = 0.70926 Å, Kα_2 = 0.71354 Å, ω–2θ scan, scintillation counter, take-off angle 6°). The sampling interval in 2θ for each reflection was 1.0° below the calculated MoKα_1 maximum to 1.0° above the calculated MoKα_2 maximum. The scan rate was in the range 2–15° min^{-1} in 2θ, depending on the intensity of the reflection. Background measurements with the total time for background counts being equal to the scan time were made at the start and end of each scan with the counter stationary. A standard reflection was measured for every 50 reflections.

A complete set of 4612 unique reflections was measured up to $(\sin\theta)/\lambda = 0.64$ Å^{-1}, of which 3298 reflections were accepted as statistically above the background on the basis of $I > 1.96\ \sigma(I)$. The linear absorption coefficient was calculated to be 86.9 cm^{-1}; an empirical absorption correction was made on the basis of ψ scans of 12 reflections. The data reduction was done applying Lorentz and polarization corrections including a Wilson plot.

Solution and Refinement of the Structure

The correct solution for the structure was achieved by direct methods using the MULTAN programme system [8] and from the Patterson map. An E map calculated with phases having the best figures of merit revealed the positions of most of the non-hydrogen atoms. The remaining non-hydrogen atoms were found in the difference Fourier maps after isotropic refinement of the heavy atoms. The

TABLE II. Anisotropic Temperature Factors.[a]

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Hg	3.36(2)	3.98(3)	3.05(2)	0.91(3)	0.02(2)	0.14(3)
Co	3.07(8)	3.72(9)	3.06(8)	0.30(7)	0.08(7)	0.92(7)
S1	3.51(17)	7.05(27)	3.45(17)	−0.81(17)	−0.45(14)	0.76(16)
S2	4.80(20)	4.16(20)	5.13(20)	2.22(17)	−2.66(16)	−1.89(16)
S3	3.21(16)	4.78(20)	4.63(19)	−0.01(15)	−0.39(14)	2.09(16)
S4	4.72(19)	3.48(18)	4.80(20)	−1.14(16)	0.18(16)	0.25(16)
O1	3.3(4)	4.7(5)	4.4(5)	0.2(4)	0.6(4)	−0.3(4)
O2	4.7(5)	4.7(6)	4.0(5)	0.0(5)	1.2(4)	−0.3(4)
N1	4.9(7)	6.0(8)	4.2(6)	0.2(7)	0.8(5)	2.1(6)
N2	3.6(6)	3.4(6)	5.0(6)	0.6(5)	−0.1(5)	−1.2(5)
N3	4.2(6)	5.2(7)	2.8(5)	0.6(5)	−0.3(5)	0.6(5)
N4	6.0(7)	4.1(6)	2.3(5)	1.0(6)	0.8(5)	0.3(5)
N5	2.4(5)	4.3(7)	7.2(8)	−0.6(5)	0.6(6)	0.4(6)
N6	3.5(6)	5.2(7)	3.5(6)	0.5(5)	0.8(5)	−0.6(5)
C1	4.0(7)	4.2(7)	2.7(6)	0.7(6)	1.5(5)	1.7(5)
C2	3.2(6)	3.7(7)	3.3(7)	0.5(6)	−1.7(5)	−0.6(6)
C3	3.3(6)	3.7(7)	3.4(6)	−0.3(6)	0.0(5)	0.4(6)
C4	2.4(6)	3.2(7)	5.3(8)	0.1(5)	0.5(5)	−1.3(7)
C5	2.9(7)	4.6(8)	4.3(7)	1.5(6)	0.3(6)	1.0(7)
C6	3.9(8)	10.9(19)	7.5(12)	1.5(12)	1.7(8)	4.0(13)
C7	5.0(17)	11.0(27)	13.7(30)	−3.7(18)	0.6(22)	−6.2(24)

(continued on facing page)

TABLE II. *(continued)*

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
C8	4.2(8)	6.5(10)	2.6(6)	1.4(8)	0.5(6)	0.6(7)
C9	4.7(9)	8.3(12)	6.3(11)	−0.8(10)	−0.3(8)	−3.2(10)
C10	4.7(11)	7.9(17)	9.6(23)	−1.2(11)	1.7(13)	−4.1(13)

[a] The temperature factors are defined as $\exp[-\frac{1}{4}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

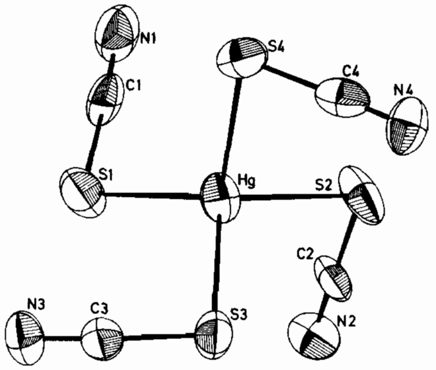

Fig. 1. ORTEP plot of the Hg(SCN)$_4$ units in the polymeric structure of mercury(II) tetrathiocyanatobis(dimethylformamide)cobaltate(II) with atomic designations (50% probability ellipsoids).

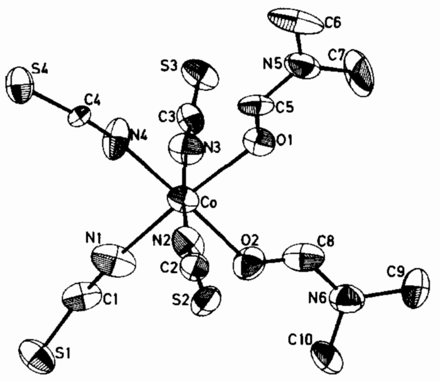

Fig. 2. Co(NCS)$_4$(DMF)$_2$ coordination polyhedron in the polymeric Hg(SCN)$_4$Co(DMF)$_2$ structure with atomic designations (ORTEP plot, 50% probability ellipsoids).

TABLE III. Bond Distances and Bond Angles in the Structure of Mercury(II) Tetrathiocyanatobis(dimethylformamide)cobaltate(II).

Distances (Å)		Angles (°)	
Hg Coordination			
Hg–S1	2.496(4)	S1–Hg–S2	109.0(1)
Hg–S2	2.515(4)	S1–Hg–S3	109.9(1)
Hg–S3	2.527(4)	S1–Hg–S4	115.3(1)
Hg–S4	2.563(4)	S2–Hg–S3	113.5(1)
		S2–Hg–S4	101.7(1)
		S3–Hg–S4	107.5(1)
Co Coordination			
Co–O1	2.138(9)	O1–Co–O2	88.2(4)
Co–O2	2.089(10)	O1–Co–N1	174.8(4)
Co–N1	2.130(13)	O1–Co–N2	88.1(4)
Co–N2	2.098(12)	O1–Co–N3	85.5(4)
Co–N3	2.104(12)	O1–Co–N4	92.9(4)
Co–N4	2.125(12)	O2–Co–N1	86.9(5)
		O2–Co–N2	88.6(4)
		O2–Co–N3	90.9(4)
		O2–Co–N4	177.1(4)
		N1–Co–N2	97.5(5)
		N1–Co–N3	92.9(5)
		N1–Co–N4	92.1(5)
		N2–Co–N3	173.6(5)
		N2–Co–N4	88.7(5)
		N3–Co–N4	91.8(5)
Thiocyanate Ions			
C1–S1	1.649(15)	Hg–S1–C1	99.1(5)
C1–N1	1.129(18)	Hg–S2–C2	96.4(5)
C2–S2	1.633(14)	Hg–S3–C3	97.7(5)
C2–N2	1.133(18)	Hg–S4–C4	92.8(5)
C3–S3	1.645(14)	S1–C1–N1	176.0(14)
C3–N3	1.135(18)	S2–C2–N2	178.6(13)
C4–S4	1.689(15)	S3–C3–N3	176.9(13)
C4–N4	1.108(19)	S4–C4–N4	178.1(13)
		C1–N1–Co	172.8(12)
		C2–N2–Co	174.8(11)
		C3–N3–Co	175.5(11)
		C4–N4–Co	166.7(12)
Dimethylformamide Molecules			
C5–O1	1.21(2)	C5–O1–Co	124.5(9)
C5–N5	1.35(2)	N5–C5–O1	123.1(14)

(continued overleaf)

atomic scattering factors for Hg, Co, S, O, N and C were taken from the International Tables [9]. The positions of the atoms were calculated (one H per CH$_3$ group was located from the ΔF map) and not refined. Full-matrix least-squares refinement with anisotropic temperature factors for all the non-hydrogen atoms and fixed coordinates and isotropic temperature factors (5 Å^2) for all the hydrogen atoms converged to residuals of $R_1 = 0.053$, $R_2 =$

TABLE III. *(continued)*

Distances (A)		Angles (°)	
C6–N5	1.45(3)	C5–N5–C6	120.7(14)
C7–N5	1.46(5)	C5–N5–C7	117.7(19)
C8–O2	1.23(2)	C8–O2–Co	125.7(10)
C8–N6	1.31(2)	N6–C8–O2	125.4(15)
C9–N6	1.50(3)	C8–N6–C9	122.5(14)
C10–N6	1.45(4)	C8–N6–C10	119.6(19)

0.051, where $R_1 = \Sigma(\|F_o| - |F_c\|)/\Sigma|F_o|$ and $R_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o^2]^{1/2}$. The weighting scheme was based on the counting statistics. The final difference Fourier map had no significant features.

The final coordinates and thermal parameters of the atoms are given in Tables I and II. Tables of the calculated and observed structure factors and of the H coordinates are available from the Editor.

Results and Discussion

The structure consists of a polymeric network of $[Hg(SCN)_4Co(DMF)_2]$ units linked by Hg–SCN–Co bridges. A view of the $Hg(SCN)_4$ and $Co(NCS)_4$-$(DMF)_2$ segments are shown in Figs. 1 and 2.

The four sulphur atoms of the thiocyanate groups are arranged tetrahedrally about the Hg atom. On the other hand, each cobalt atom is strongly bonded to two DMF molecules in a *cis* configuration. Additional interactions with four nitrogen atoms of neighbouring thiocyanate groups complete an octahedral six-coordination around cobalt. Thus, the thiocyanate groups act as bridges between Hg and Co resulting in a polymeric structure similar to the one observed in $HgCo(SCN)_4$ [10].

The interatomic bond distances and bond angles are given in Table III. The tetrahedral Hg–S bond lengths vary from 2.496 to 2.563 Å with a mean value of 2.525 Å which is in good agreement with the sum of the tetrahedral bond radii of 2.52 Å [11]. In several mercury(II) thiocyanates whose structures are crystallographically known [7, 10, 12–15] the Hg–S bond lengths fall in the range 2.45–2.58 Å, suggesting the observed values in the present complex being normal. The tetrahedral angle varies from 101.7 to 115.3° which could be favourably compared to those found in $HgCo(SCN)_4$ [10] and $Hg(SCN)_4Cu(en)_2$ [7].

Typical octahedral Co–O bond lengths fall in the range 1.83–2.21 Å [16–22] with a mean value of 2.09 Å [23]. The values of 2.09(1) (Co–O2) and 2.14(1) Å (Co–O1) observed in the present complex are close to this average and suggest strong interaction between Co and the DMF molecules. In several N-ligated octahedral Co(II) complexes, the Co–N bond lengths lie in the range 1.97–2.41 Å [16, 18, 24–29] with an average value of 2.16 Å [23]. In the present complex, the Co–N distances vary from 2.10(1) to 2.13(1) Å with a mean value of 2.11 Å. The bond angles and the bond distances show the CoN_4O_2 octahedron to be only slightly distorted.

The thiocyanate groups make an angle with the Hg-S bonds, (Hg–S–C 92.8 to 99.1°) and do not follow the tetrahedral arrangement of the S atoms around Hg. Similar observations were also made in the structures of $HgCo(SCN)_4$ [10] and $Hg(SCN)_4$-$Cu(en)_2$ [7]. The S, C and N atoms lie in a straight line within experimental error in $HgCo(SCN)_4$ whereas the SCN group is bent at the carbon atom up to 20° in $Hg(SCN)_4Cu(en)_2$. In the present case, the maximum kink at the C atom is 4° (N1–C1–S1 176.0°) suggesting that the SCN group is almost linear. However, the C–N–Co angles vary from 167 to 176° which indicates that the S–C–N–Co strings are significantly non-linear. The C–N and S–C bond distances (mean values 1.126 and 1.654 Å) are comparable to those found in several other thiocyanate complexes [*e.g.* 7, 10, 15, 30], suggesting, as expected, appreciable weight of the resonance form $S{=}C{=}N^-$.

The dimethylformamide molecules are essentially planar. The least-squares planes consisting of atoms O1, C5, N5, C6, C7 and O2, C8, N6, C9, C10 are $-0.3822x + 0.8600y - 0.3380z - 1.4095 = 0$ and $-0.2486x + 0.5725y - 0.7813z + 1.5314 = 0$ respectively, where x, y and z are related to the monoclinic axes. The maximum deviations from the planes are 0.07 Å for C6 and 0.01 Å for C9. The angles Co–O1–C5 (124.5°) and Co–O2–C8 (125.7°) do not deviate much from those expected for sp^2-hybridized oxygen.

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