

Bispyridine Adduct of Cobalt(II) Mercury(II) Tetrathiocyanate

BY ANDRÉ L. BEAUCHAMP, LEROY PAZDERNIK* AND ROLAND RIVEST

Département de Chimie, Université de Montréal, Case Postale 6210, Montréal, Canada H3C 3V1

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Abstract. Monoclinic, $C2/c$, $a=11.459$ (6), $b=13.293$ (7), $c=14.498$ (7) Å, $\beta=105.65$ (3)°, $Z=4$ $C_{14}H_{10}CoHgN_6S_4$ formula units per cell, $D_c=2.030$, $D_o=2.02$ (1) g cm⁻³. The crystal consists of an infinite three-dimensional framework of HgS₄ tetrahedra and *trans*-CoN₄ (pyridine)₂ octahedra connected *via* bridging SCN groups.

Introduction. The addition compound CoHg(SCN)₄.2 pyridine was first prepared by Makhija, Pazdernik & Rivest (1973). The crystals used in the present study were obtained as follows: ethanol solutions of Co(SCN)₂ and excess Hg(SCN)₂ were mixed and the mixture was filtered to obtain a solution of the pink complex CoHg(SCN)₄.2ethanol. Crystals of the pyridine adduct were grown by vapour diffusion of pyridine into the pink solution.

The systematic absences noted on precession photographs (hkl , $h+k \neq 2n$ and $h0l$, $l \neq 2n$) are consistent with space groups Cc and $C2/c$. The centrosymmetric $C2/c$ was assumed first and this choice was subsequently found to be correct by successful refinement of the structure. Refinement in Cc failed to converge.

The crystal used for diffractometer work was bounded by the forms $\{110\}$ and $\{11\bar{1}\}$, with a distance of 0.85 mm between each pair of parallel faces. The cell parameters were determined by least-squares refinement of the setting angles 2θ , Ω and χ of 12 Mo $K\alpha$ peaks automatically centred in the counter aperture of a Picker FACS-1 diffractometer [$\lambda(\text{Mo } K\alpha)=0.71069$ Å, graphite monochromator]. Intensities of 1451 unique

hkl and $hk\bar{l}$ reflexions with $h+k=2n$ within a sphere $2\theta \leq 46^\circ$ were measured with the FACS-1 diffractometer using the $\theta/2\theta$ scan technique. The scan rate was 1° (2 θ) min⁻¹ and the 2θ range was 1.70° plus a correction for α_1, α_2 separation. Stationary background counts ($B1$ and $B2$) of 20 s each were taken at the limits of the scan. Three standard reflexions (008, $\bar{7}14$ and 0,10,0) were measured every 25 reflexions and showed maximum fluctuations of $\mp 3\%$ during data collection.

Net intensities I were calculated from $I=I_t - T(B1 + B2)/40$, where I_t is the total intensity and T is the scan time. The standard deviations $\sigma_i = [I_t + T^2(B1 + B2)/1600 + (0.03 I)^2]^{1/2}$ were calculated and a total of 321 reflexions with $I/\sigma_i < 2.5$ were assigned zero weight. Since the crystal approximated a sphere (same distance between each pair of parallel faces), no absorption correction was made ($\mu=85.1$ cm⁻¹). Lp corrections were applied and the set of 1130 nonzero reflexions was used to determine the structure.

The structure was solved by the conventional heavy-atom method and refined by full-matrix least-squares calculations. The function minimized was $\sum w(|F_o| - |F_c|)^2$. From the Patterson map, Hg and Co were found to occupy special positions 4(*e*) and 4(*c*), respectively, in the $C2/c$ unit cell. The S, C and N atoms were then located on a Fourier map. Isotropic refinement of all nonhydrogen atoms using unit weights converged to $R = \sum ||F_o| - |F_c|| / \sum |F_o| = 0.068$ (=0.081 including reflexions with zero weights). The H atoms were visible on the Fourier map calculated at that stage. They were placed at ideal positions (C-H distance=0.95 Å) with isotropic temperature factors $B=6.0$ Å². The H parameters were not refined, but the shifts on the C coordinates were applied to those of the corresponding H

* Present address: Département de Chimie, Université du Québec à Trois-Rivières, Trois-Rivières, Québec, Canada.

Table 1. Fractional coordinates ($\times 10^4$) and anisotropic temperature factors ($\times 10^3$, $\times 10^4$ for Hg and Co)

	<i>x</i>	<i>y</i>	<i>z</i>	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Hg	0	501	2500	706 (5)	544 (4)	637 (4)	0	229 (3)	0
Co	2500	2500	0	555 (11)	467 (11)	511 (11)	31 (9)	144 (9)	-9 (9)
S(1)	1440 (2)	-676 (2)	1955 (2)	72 (2)	82 (2)	54 (2)	13 (2)	-26 (1)	10 (1)
S(2)	1038 (3)	1530 (3)	3956 (2)	59 (2)	93 (2)	110 (3)	-9 (2)	25 (2)	-41 (2)
N(1)	2006 (8)	-1759 (6)	3678 (6)	78 (6)	62 (6)	61 (6)	2 (5)	18 (5)	15 (5)
N(2)	-1025 (8)	1830 (6)	4596 (6)	59 (6)	60 (6)	71 (6)	9 (5)	21 (5)	-3 (4)
N(11)	3668 (8)	1286 (6)	637 (5)	63 (6)	53 (6)	61 (5)	9 (5)	18 (4)	5 (4)
C(1)	1774 (8)	-1325 (7)	2971 (7)	54 (6)	51 (6)	62 (7)	1 (5)	20 (5)	-10 (5)
C(2)	-183 (10)	1698 (7)	4331 (7)	59 (7)	46 (6)	59 (7)	-3 (6)	-1 (5)	-9 (5)
C(12)	4830 (10)	1427 (9)	1146 (7)	69 (8)	77 (8)	69 (7)	12 (7)	28 (6)	10 (6)
C(13)	5610 (10)	667 (12)	1526 (8)	73 (8)	120 (12)	70 (8)	26 (9)	26 (6)	25 (8)
C(14)	5203 (14)	-301 (11)	1368 (10)	93 (10)	95 (11)	98 (10)	39 (9)	43 (8)	32 (8)
C(15)	4040 (12)	-473 (9)	863 (9)	101 (10)	62 (7)	103 (9)	21 (8)	66 (8)	34 (8)
C(16)	3297 (9)	329 (8)	498 (7)	82 (8)	50 (8)	70 (7)	8 (6)	33 (6)	5 (5)

atoms. The real and imaginary contributions to anomalous dispersion for Hg, Co and S were included in the structure factor calculations. In the last cycles of refinement, weights $w=1/\sigma_F^2$, where $\sigma_F^2=0.25\sigma_I^2/LpI$, were applied to each reflexion. Anisotropic refinement of all nonhydrogen atoms converged to $R=0.038$ ($=0.055$ including zero-weight reflexions) and $R_w=[\sum w(|F_o|-|F_c|)^2/\sum w|F_o|^2]^{1/2}=0.037$. The error on an observation of unit weight was 1.48. On the final ΔF map, a peak of $0.7 \text{ e } \text{\AA}^{-3}$ was found at 1.1 \AA from Hg. All the remaining peaks were lower than $\pm 0.25 \text{ e } \text{\AA}^{-3}$. The refined parameters are listed in Table 1.*

The form factors originated from Stewart, Davidson & Simpson (1965) for H and from Cromer & Waber (1965) for the other atoms. The anomalous dispersion coefficients were taken from Cromer (1965). The computer programs used are listed elsewhere (Terzis, Beauchamp & Rivest, 1973).

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31383 (11 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. *Interatomic distances (Å) and bond angles (°)*

Hg—S(1)	2.551 (3)	S(1)—Hg—S(2) ⁱ	105.8 (1)
Hg—S(2)	2.527 (3)	S(1)—Hg—S(1) ⁱ	104.3 (1)
Co—N(1) ⁱⁱ	2.091 (8)	S(2)—Hg—S(2) ⁱ	114.5 (1)
Co—N(2) ⁱ	2.126 (9)	S(1)—Hg—S(2)	113.1 (1)
Co—N(11)	2.140 (8)	N(1) ⁱⁱ —Co—N(2) ⁱ	91.0 (3)
S(1)—C(1)	1.660 (10)	N(1) ⁱⁱⁱ —Co—N(2) ^{iv}	89.0 (3)
S(2)—C(2)	1.648 (11)	N(11)—Co—N(1) ⁱⁱ	91.4 (3)
C(1)—N(1)	1.144 (13)	N(11)—Co—N(1) ⁱⁱⁱ	88.6 (3)
C(2)—N(2)	1.145 (14)	N(11)—Co—N(2) ⁱ	90.9 (3)
N(11)—C(12)	1.35 (1)	N(11)—Co—N(2) ^{iv}	89.1 (3)
C(12)—C(13)	1.36 (2)	Hg—S(1)—C(1)	93.3 (3)
C(13)—C(14)	1.37 (2)	Hg—S(2)—C(2)	95.6 (3)
C(14)—C(15)	1.36 (2)	Co ^v —N(1)—C(1)	177.0 (8)
C(15)—C(16)	1.37 (2)	Co ⁱ —N(2)—C(2)	164.0 (8)
C(16)—N(11)	1.34 (1)	S(1)—C(1)—N(1)	179.0 (9)
		S(2)—C(2)—N(2)	178.8 (9)
		C(12)—N(11)—C(16)	116.1 (9)
		N(11)—C(12)—C(13)	124.1 (11)
		C(12)—C(13)—C(14)	118.3 (12)
		C(13)—C(14)—C(15)	119.4 (13)
		C(14)—C(15)—C(16)	119.4 (12)
		C(15)—C(16)—N(11)	122.7 (10)
		Co—N(11)—C(12)	122.8 (7)
		Co—N(11)—C(16)	121.0 (7)

(i) $\bar{x}, y, \frac{1}{2}-z$; (ii) $x, \bar{y}, -\frac{1}{2}+z$; (iii) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$;
 (iv) $\frac{1}{2}+x, \frac{1}{2}-y, -\frac{1}{2}+z$; (v) $x, \bar{y}, \frac{1}{2}+z$.

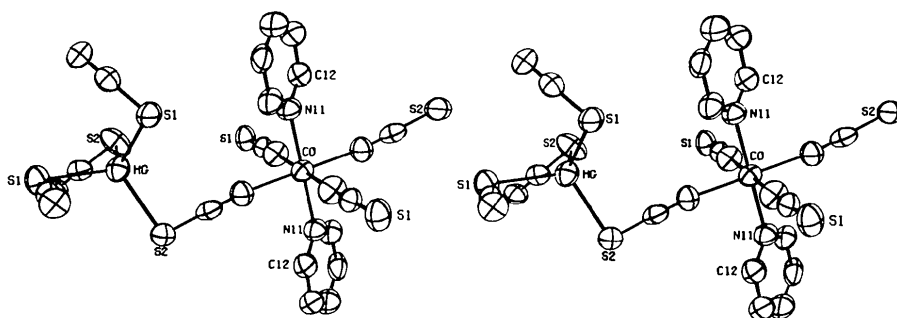


Fig. 1. Stereoscopic projection showing the environment of Hg and Co in the structure. The ellipsoids correspond to 50% probability.

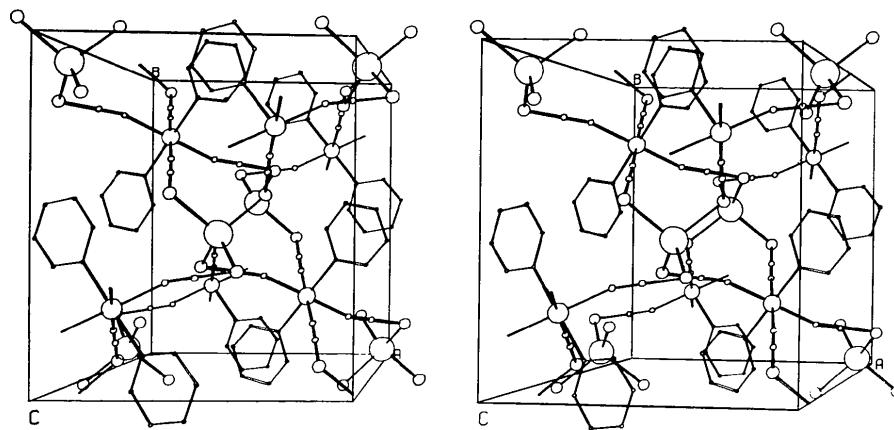


Fig. 2. Stereoscopic view of the unit cell. The atoms can be identified by comparison with Fig. 1. Hg, Co and S are represented by spheres of decreasing size.

Description of the structure and discussion. The environment of the metal atoms is shown in Fig. 1. Interatomic distances and bond angles are given in Table 2. Earlier conclusions (Makhija, Pazdernik & Rivest, 1973) based on magnetic measurements, infrared and ultra violet-visible spectra are confirmed by the present work. Thiocyanate groups, acting as bridging bidentate ligands, are attached to Hg *via* S and to Co *via* N. The pyridine N is also coordinated to Co making it hexacoordinate.

Hg lies on a crystallographic twofold axis and is tetrahedrally coordinated by four S atoms. The Hg-S distances (2.527 and 2.551 Å) are normal for four-coordinate Hg (Makhija, Beauchamp & Rivest, 1973). The S-Hg-S angles (104.3–114.5°) differ significantly from 109.5°, but such small differences have little chemical meaning.

Co is found on a centre of symmetry of the unit cell. It is octahedrally surrounded by six N atoms, *i.e.* two pairs from thiocyanate groups at 2.091 and 2.126 Å respectively, and one more pair at 2.140 Å from pyridine molecules at positions *trans* to each other. The Co-N₆ octahedron is virtually undistorted (N-Co-N = 88.6–91.4°). The Co-N bond lengths agree with values from the literature for six-coordinate compounds. The Co-pyridine distances are 2.12 and 2.14 Å for Co(SCN)₂Py₂ (Porai-Koshits & Tishchenko, 1960) and CoCl₂Py₂ (Dunitz, 1957) respectively. Longer distances (2.17–2.20 Å) in other compounds (Elder, 1968; Kusaj, Tomlonovic, Murtha, Lintvedt & Glick, 1973) are probably due to bulkier ligands in the equatorial plane. The Co-NCS bonds lengths are similar to those of Co(SCN)₂Py₂ (2.09 Å) (Porai-Koshits & Tishchenko, 1960).

The pyridine ligand shows the expected geometry. It is planar within 0.5σ (0.006 Å) and the plane approximately bisects equatorial N-Co-N angles. Intramolecular repulsions between pyridine H atoms and coordinated SCN groups are at a minimum in this orientation. Co is 0.10 Å from the plane of the pyridine ring.

The thiocyanate groups are linear within experimental errors and the S-C and C-N bond lengths are normal. A bend at S (Hg-S-C 93.3 and 95.6°) is observed as usual. Ideally, the Co-N-C angles should be 180°, as found for CoHg(SCN)₄ (Jefferey & Rose, 1968), although considerable departure from linearity is quite common (*e.g.*, 158° in Co(SCN)₂Py₂) (Porai-Koshits & Tishchenko, 1960). In the present compound, a significant bend is found for Co-N(2)-C(2) (164.0°). Presumably, the total bonding interaction is less for Co-N(2), which is manifest in Co-N(2) (2.126 Å) being longer than Co-N(1) (2.091 Å).

The unit cell is shown in Fig. 2. It consists of an infinite three-dimensional arrangement of HgS₄ tetra-

hedra and CoN₄(pyridine)₂ octahedra connected by bridging thiocyanate groups. Each HgS₄ tetrahedron is attached to four different CoN₄(pyridine)₂ units; in turn, each of the latter groups is connected to four different HgS₄ units and so on. The octahedra are so oriented that pyridine molecules on neighbouring octahedra are approximately parallel at normal van der Waals distances (~3.5 Å).

Similar patterns of SCN-connected metal atoms have been found in CoHg(SCN)₄ (where Co is tetrahedrally coordinated) (Jefferey & Rose, 1968) and in NiHg(SCN)₄(H₂O)₂ (where Ni has a *trans*-octahedral coordination) (Kuo-Chan & Porai-Koshits, 1960). These and other patterns have been discussed by Porai-Koshits (1963). The Ni compound is remarkably similar to the present Co complex, which, in turn, is isomorphous with ZnHg(SCN)₄(pyridine)₂ (Makhija *et al.*, 1973).

It appears that MHg(SCN)₄ frameworks of the type observed here act as host structures in which various ligands can be held. This would be consistent with the easy preparation of other CoHg(SCN)₂L₂ compounds where L = dioxan, tetrahydrofuran and aniline (Makhija *et al.*, 1973). It is noteworthy that bulky ligands like phenanthroline, triphenylphosphine, *etc.*, yielded compounds with different stoichiometries and/or properties. The present framework seems to be particularly well suited for smaller ligands.

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