Cu(1)—O(5)	2.424 (4)	C(9)—C(13)	1.525 (6)
O(1)—C(9)	1.400 (5)	C(9)—C(14)	1.562 (6)
O(2)—C(14)	1.224 (5)	C(10)—C(11)	1.395 (6)
O(3)—C(14)	1.272 (5)	C(11)—C(12)	1.459 (7)
O(4)—C(26)	1.214 (7)	C(12)—C(13)	1.392 (6)
N(1)—C(15)	1.322 (6)	Cu(1)···Cu(1^i)	3.007 (4)
N(1)—C(22)	1.367 (5)		
O(1)—Cu(1)—O(1^i)	76.9 (1)	C(26)—N(2)—C(24)	122.0 (6)
O(1)—Cu(1)—O(3)	83.3 (1)	O(1)—C(9)—C(10)	115.0 (4)
O(1)—Cu(1)—N(1)	166.6 (2)	O(1)—C(9)—C(14)	107.4 (3)
O(1^i)—Cu(1)—O(3)	159.2 (1)	C(10)—C(9)—C(13)	101.6 (3)
O(1^i)—Cu(1)—N(1)	98.9 (1)	C(1)—C(10)—C(11)	121.2 (4)
O(3)—Cu(1)—N(1)	98.9 (1)	C(11)—C(10)—C(9)	110.5 (4)
O(5)—Cu(1)—O(1)	98.4 (1)	C(4)—C(11)—C(10)	120.5 (5)
O(5)—Cu(1)—O(1^i)	99.9 (1)	C(10)—C(11)—C(12)	108.6 (4)
O(5)—Cu(1)—O(3)	89.3 (1)	C(5)—C(12)—C(13)	120.5 (5)
O(5)—Cu(1)—N(1)	94.9 (1)	C(5)—C(12)—C(11)	130.3 (4)
Cu(1)—O(1)—Cu(1^i)	103.1 (1)	C(8)—C(13)—C(12)	120.5 (4)
C(9)—O(1)—Cu(1)	116.9 (2)	C(8)—C(13)—C(9)	129.3 (4)
C(9)—O(1)—Cu(1^i)	139.6 (2)	O(2)—C(14)—O(3)	124.9 (4)
C(14)—O(3)—Cu(1)	115.3 (3)	O(3)—C(14)—C(9)	116.1 (4)
C(15)—N(1)—C(22)	118.8 (4)	N(1)—C(15)—C(16)	122.8 (4)
C(15)—N(1)—Cu(1)	119.8 (3)	N(1)—C(22)—C(21)	120.8 (4)
C(22)—N(1)—Cu(1)	121.3 (3)	O(4)—C(26)—N(2)	126.1 (6)
C(26)—N(2)—C(25)	120.6 (5)		

Symmetry code: (i) $1-x, 1-y, 1-z$.

Table 3. *Hydrogen-bonding geometry (Å, °)*

D—H···A	H···A	D···A	D—H···A
O(5)—H(23)···O(4)	1.885	2.811 (6)	167.1
O(6)—H(26)···O(2^i)	1.813	2.720 (6)	160.4
O(5)—H(24)···O(6)	1.996	2.838 (6)	146.8

Symmetry code: (i) $\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$.

The data were corrected for Lorentz–polarization effects. Difference Fourier maps revealed maxima in positions consistent with the expected locations of all H atoms. In the final round of calculations, the H atoms of the quinoline and α-hydroxylated acid ligands were positioned on geometrical grounds. All calculations were performed using *TEXSAN* (Molecular Structure Corporation, 1989).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: KH1048). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Tetraethylammonium Tris(pyridine-2-thiolato-*S*,*N*)cobalt(II), $(Et_4N)[Co(2\text{-}S\text{-}C_5H_4N)_3]$

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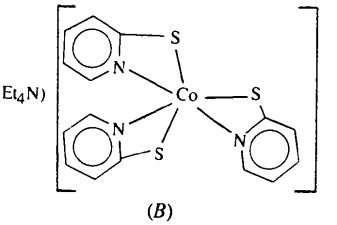
Abstract

$Na[Co(CO)_4]$ was reacted with pyridine-2-thiol (PyS) in tetrahydrofuran to give the title complex, $(C_8H_{20}N)[Co(C_5H_4NS)_3]$, in which the three S atoms and the three N atoms of the PyS ligands coordinate to the central Co^{II} atom, forming three four-membered chelate rings with S—Co—N angles of 66°. The geometry around the Co^{II} atom is distorted octahedral. The average Co—S and Co—N bond distances are 2.568 and 2.108 Å, respectively.

Comment

Since low-valence cobalt was discovered to be a good hydrosulfurization catalyst, the study of the reactions of cobalt in low oxidation states, *e.g.* $[Co_2(CO)_8]$ and $[Co(CO)_4]^-$, with different types of organic and inorganic sulfur-containing compounds, has attracted increased attention from chemists (Doedens & Dahl, 1966). Most of the research work, however, has focused on monodentate or bidentate organic sulfur compounds, with only a few mixed bidentate organic sulfur compounds being studied. Pyridine-2-thiol (PyS) is known as either a monodentate ligand, which binds to the metal atom through the S atom (one-electron donor), or as a mixed bidentate ligand, which binds through both the S and the N atom (three-electron donor). While studying the reaction of $Na[Co(CO)_4]$ with PyS, we obtained a new type of cobalt–sulfur product with mixed-valence Co^I and Co^{III} atoms, $[Co_5(\mu_3\text{-}S)_3(\mu\text{-}CO)_2(PyS)_7]$, (*A*), and a Co^{II} compound, $(Et_4N)[Co(PyS)_3]$, (*B*). We report here the synthesis and crystal structure of compound (*B*).



(*B*)

Compound (*B*) is composed of an Et_4N^+ cation and a $[Co(PyS)_3]^-$ anion. The coordination polyhedron around the Co atom is a highly distorted octahedron, composed of three S and three N atoms of the PyS ligands. The three PyS ligands and the Co atom form three four-membered *S,N*-chelate rings with S—Co—N angles of 66.4 (2)° (the standard deviations of averages were taken as the larger of the individual standard deviations). The Co^{II}—S bond distances in compound (*B*) fall in the narrow range 2.552 (1)–2.585 (1) Å, which are considerably longer than the Co^{II}—S bond lengths in $[Co_2(PhS)_4]$ (2.222–2.269 Å) (Power & Shoner, 1991), $[Co_2\{(o\text{-}SCH_2)_2C_6H_4\}_3\}]^{2-}$ (2.271–2.310 Å) and $[Co_2(SC_3H_7)_5]$ (2.210–2.346 Å) (Henkel & Weissgraber, 1992). The Co^{II}—N bond distances [2.094 (3)–2.135 (3) Å] in compound (*B*), however, are close to the Co^{II}—N bond lengths found in the $[Co(bpy)]^{2+}$ cation (2.13 Å) (Adams, Dei, Rheingold & Hendrickson, 1993). This effect might be caused by the formation of the four-membered chelate rings which produce the additional strain. On the other hand, the Co^{II}—S bond distances in compound (*B*) just fall in the range of Fe^{II}—S and Ni^{II}—S bond distances in the comparative compounds $[Fe(PyS)_3]$ (2.568–2.589 Å) (Rosenfield, Swedberg, Arora & Mascharak, 1986) and $[Ni(PyS)_3]$ (2.518–2.541 Å) (Rosenfield, Berends, Gelmini, Stephan & Mascharak, 1987). This is obviously in accordance with the order of electrophilic reactivity: $Fe^{II} < Co^{II} < Ni^{II}$.

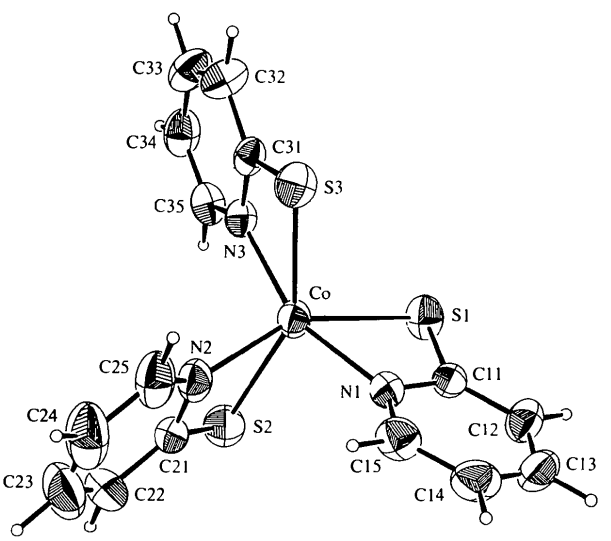


Fig. 1. An *ORTEP* drawing (Johnson, 1965) of the $[Co(2\text{-}S\text{-}C_5H_4N)_3]$ anion showing 50% probability displacement ellipsoids. H atoms are omitted for clarity.

Experimental

A mixture of $[Co_2(CO)_8]$ and NaOH was stirred in tetrahydrofuran at room temperature and then filtered. To the filtrate were added Et_4NCl and PySH. The resulting reaction mixture was stirred at 313 K for 2 h resulting in a brown–yellow solution containing a white solid. The solid was filtered off and the filtrate evaporated under vacuum to remove part of the solvent. EtOH was added and the resulting solution was cooled at 277 K for several days. A dark brown crystalline product, (*A*), was isolated by filtration. A little air was added to the filtrate and a red–brown crystalline product, (*B*), was obtained the next day.

Crystal data

$(C_8H_{20}N)[Co(C_5H_4NS)_3]$
$M_r = 519.66$
Monoclinic
$P2_1/c$
$a = 15.223\ (6)$ Å
$b = 9.321\ (3)$ Å
$c = 18.792\ (6)$ Å
$\beta = 104.77\ (2)°$
$V = 2578.4$ Å^3
$Z = 4$
$D_x = 1.34$ Mg m^{-3}
Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 20 reflections
$\theta = 5–10°$
$\mu = 0.91$ mm^{-1}
$T = 260$ K
Plate
0.40 × 0.30 × 0.30 mm
Brown

Data collection

MSC Rigaku diffractometer
$\omega/2\theta$ scans
Absorption correction:
ψ scans (North, Phillips & Mathews, 1968)
$T_{min} = 0.92$, $T_{max} = 1.00$
5036 measured reflections
4840 independent reflections
3290 observed reflections [$I > 3\sigma(I)$]
$R_{int} = 0.019$
$\theta_{max} = 25°$
$h = 0 \rightarrow 18$
$k = 0 \rightarrow 11$
$l = -22 \rightarrow 21$
3 standard reflections monitored every 250 reflections
intensity decay: 0.8%

Refinement

Refinement on F
$R = 0.038$
$wR = 0.054$
$S = 1.43$
4840 reflections
280 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F_o^2) + (0.020F_o)^2 + 1.0]$
$(\Delta/\sigma)_{max} = 0.16$
$\Delta\rho_{max} = 0.35\ (7)$ e Å^{-3}
$\Delta\rho_{min} = -0.10\ (7)$ e Å^{-3}
Atomic scattering factors from Cromer & Waber (1974) and *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$B_{eq} = (4/3)\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j$.

	x	*y*	*z*	B_{eq}
Co	0.74957 (3)	0.05791 (6)	0.14480 (3)	2.97 (1)
S(1)	0.83261 (7)	−0.1416 (1)	0.09395 (6)	3.68 (2)
S(2)	0.77890 (9)	−0.0345 (1)	0.27662 (6)	4.53 (3)
S(3)	0.71880 (7)	0.2598 (1)	0.04728 (6)	3.72 (2)
N(1)	0.6626 (2)	−0.1017 (3)	0.0877 (2)	2.96 (7)
N(2)	0.6542 (2)	0.1346 (4)	0.2018 (2)	3.51 (7)
N(3)	0.8509 (2)	0.2155 (3)	0.1628 (2)	2.90 (7)
N(4)	0.8007 (2)	0.5094 (3)	0.3570 (2)	2.80 (6)
C(11)	0.7201 (3)	−0.1947 (4)	0.0674 (2)	2.79 (8)
C(12)	0.6864 (3)	−0.3189 (4)	0.0287 (2)	3.81 (9)
C(13)	0.5951 (3)	−0.3451 (5)	0.0106 (3)	4.5 (1)
C(14)	0.5369 (3)	−0.2483 (6)	0.0293 (2)	4.4 (1)
C(15)	0.5729 (3)	−0.1279 (5)	0.0685 (2)	3.92 (9)
C(21)	0.6833 (3)	0.0676 (5)	0.2685 (2)	3.76 (9)

C(22)	0.6351 (4)	0.0894 (6)	0.3219 (3)	5.7 (1)
C(23)	0.5600 (3)	0.1759 (7)	0.3064 (3)	6.8 (1)
C(24)	0.5311 (3)	0.2412 (7)	0.2393 (3)	6.4 (1)
C(25)	0.5802 (3)	0.2192 (5)	0.1884 (3)	4.7 (1)
C(31)	0.8226 (2)	0.3056 (4)	0.1050 (2)	2.92 (8)
C(32)	0.8771 (3)	0.4225 (5)	0.0966 (3)	4.3 (1)
C(33)	0.9567 (3)	0.4468 (5)	0.1489 (3)	4.8 (1)
C(34)	0.9841 (3)	0.3563 (5)	0.2084 (3)	4.3 (1)
C(35)	0.9299 (3)	0.2415 (5)	0.2127 (2)	3.52 (9)
C(41)	0.8245 (3)	0.3892 (5)	0.4128 (2)	3.56 (9)
C(42)	0.8948 (3)	0.2836 (5)	0.4022 (3)	4.9 (1)
C(43)	0.7365 (3)	0.6111 (5)	0.3813 (2)	3.70 (9)
C(44)	0.6479 (3)	0.5461 (6)	0.3858 (3)	4.8 (1)
C(45)	0.7563 (3)	0.4456 (5)	0.2819 (2)	3.62 (9)
C(46)	0.7211 (4)	0.5511 (6)	0.2206 (2)	5.1 (1)
C(47)	0.8844 (3)	0.5924 (5)	0.3519 (2)	4.1 (1)
C(48)	0.9413 (3)	0.6495 (6)	0.4232 (3)	5.7 (1)

Table 2. *Selected geometric parameters (Å, °)*

Co—S(1)	2.566 (1)	N(4)—C(47)	1.514 (5)
Co—S(2)	2.552 (1)	C(11)—C(12)	1.394 (6)
Co—S(3)	2.585 (1)	C(12)—C(13)	1.366 (7)
Co—N(1)	2.096 (3)	C(13)—C(14)	1.371 (7)
Co—N(2)	2.135 (3)	C(14)—C(15)	1.377 (7)
Co—N(3)	2.094 (3)	C(21)—C(22)	1.401 (6)
S(1)—C(11)	1.730 (4)	C(22)—C(23)	1.367 (9)
S(2)—C(21)	1.713 (5)	C(23)—C(24)	1.368 (8)
S(3)—C(31)	1.727 (4)	C(24)—C(25)	1.372 (7)
N(1)—C(11)	1.354 (5)	C(31)—C(32)	1.401 (6)
N(1)—C(15)	1.342 (5)	C(32)—C(33)	1.370 (7)
N(2)—C(21)	1.369 (6)	C(33)—C(34)	1.378 (7)
N(2)—C(25)	1.345 (6)	C(34)—C(35)	1.367 (6)
N(3)—C(31)	1.354 (5)	C(41)—C(42)	1.503 (6)
N(3)—C(35)	1.345 (5)	C(43)—C(44)	1.501 (7)
N(4)—C(41)	1.515 (5)	C(45)—C(46)	1.506 (7)
N(4)—C(43)	1.514 (5)	C(47)—C(48)	1.495 (7)
N(4)—C(45)	1.520 (6)		
S(1)—Co—S(2)	97.82 (4)	C(41)—N(4)—C(47)	111.4 (3)
S(1)—Co—S(3)	106.32 (4)	C(43)—N(4)—C(45)	110.9 (3)
S(1)—Co—N(1)	66.54 (9)	C(43)—N(4)—C(47)	108.5 (3)
S(1)—Co—N(2)	153.1 (2)	C(45)—N(4)—C(47)	108.9 (4)
S(1)—Co—N(3)	98.98 (9)	S(1)—C(11)—N(1)	113.5 (3)
S(2)—Co—S(3)	152.75 (5)	S(1)—C(11)—C(12)	126.4 (3)
S(2)—Co—N(1)	100.9 (1)	N(1)—C(11)—C(12)	120.0 (4)
S(2)—Co—N(2)	66.4 (2)	C(11)—C(12)—C(13)	119.6 (4)
S(2)—Co—N(3)	98.0 (1)	C(12)—C(13)—C(14)	120.1 (4)
S(3)—Co—N(1)	100.2 (1)	C(13)—C(14)—C(15)	118.5 (4)
S(3)—Co—N(2)	95.1 (2)	N(1)—C(15)—C(14)	122.1 (4)
S(3)—Co—N(3)	66.2 (1)	S(2)—C(21)—N(2)	113.8 (4)
N(1)—Co—N(2)	94.2 (1)	S(2)—C(21)—C(22)	127.3 (4)
N(1)—Co—N(3)	157.5 (1)	N(2)—C(21)—C(22)	119.0 (5)
N(2)—Co—N(3)	104.5 (1)	C(21)—C(22)—C(23)	119.7 (5)
Co—S(1)—C(11)	76.7 (1)	C(22)—C(23)—C(24)	120.9 (6)
Co—S(2)—C(21)	78.0 (2)	C(23)—C(24)—C(25)	118.1 (6)
Co—S(3)—C(31)	76.3 (1)	N(2)—C(25)—C(24)	122.4 (5)
Co—N(1)—C(11)	103.2 (2)	S(3)—C(31)—N(3)	113.8 (3)
Co—N(1)—C(15)	137.2 (3)	S(3)—C(31)—C(32)	126.5 (4)
C(11)—N(1)—C(15)	119.6 (4)	N(3)—C(31)—C(32)	119.8 (4)
Co—N(2)—C(21)	101.8 (3)	C(31)—C(32)—C(33)	119.3 (4)
Co—N(2)—C(25)	138.3 (3)	C(32)—C(33)—C(34)	120.7 (4)
C(21)—N(2)—C(25)	119.9 (4)	C(33)—C(34)—C(35)	117.7 (4)
Co—N(3)—C(31)	103.6 (3)	N(3)—C(35)—C(34)	123.1 (4)
Co—N(3)—C(35)	136.9 (3)	N(4)—C(41)—C(42)	116.4 (4)
C(31)—N(3)—C(35)	119.5 (4)	N(4)—C(43)—C(44)	115.0 (4)
C(41)—N(4)—C(43)	108.2 (4)	N(4)—C(45)—C(46)	116.2 (4)
C(41)—N(4)—C(45)	108.9 (13)	N(4)—C(47)—C(48)	115.5 (4)

The sample for analysis was mounted on a glass fibre in a random orientation. The structure was solved by direct methods. A total of four atoms were located from an *E* map, the remaining atoms being located in the succeeding difference Fourier syntheses. H atoms were located and added to the structure-factor calculations, but their positions were not refined. Calculations were performed on a Compaq computer using the *MolEN* package (Fair, 1990).

The financial support of NNSFC and CPNKPFR is gratefully acknowledged.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AS1185). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1996). C**52**, 632–634

A Bis(6-methyl-2-pyridylmethyl) Thioether (DMPT) Copper(II) Complex, $[Cu(OSO_2CF_3)_2(C_{14}H_{16}N_2S)].CH_2Cl_2$

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Abstract

The X-ray crystal structure determination of the title copper derivative, [bis(6-methyl-2-pyridylmethyl) sulfide-*N*,*N*′,*S*]bis(trifluoromethylsulfonato-*O*)copper(II) dichloromethane solvate, shows that this compound contains monomeric $[Cu(DMPT)(OSO_2CF_3)_2]$ molecules in which the Cu^{II} ion is surrounded by a tridentate DMPT