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Tris(4,6-dimethylpyrimidine-2-thiolato-*N*,*S*)cobalt(III) Monohydrate: a Complex with Three Stable Four-Membered *N*,*S*-Chelate Rings

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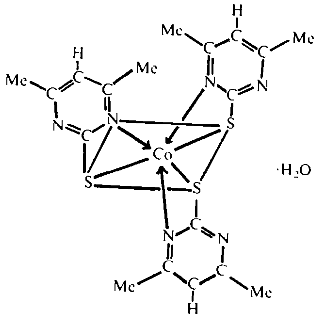
(*Received* 28 *March* 1993; *accepted* 20 *October* 1993)

Abstract

In the title compound, [Co($C_6H_7N_2S$)$_3$].H_2O, the Co^{III} ion is surrounded by three thiolate S atoms [Co—S 2.247 (2), 2.260 (2), 2.271 (2) Å] and three azomethine N atoms [Co—N 1.976 (4), 1.956 (5), 1.991 (5) Å] which define a *fac*-octahedral geometry that is highly distorted owing to the presence of three four-membered *N*,*S*-chelate rings. All three bidentate ligands are planar to within ±0.06 Å and display bond lengths and angles very close to expected values. Intermolecular hydrogen bonding between the water O atom and an uncoordinated pyrimidine N atom stabilizes the molecular packing.

Comment

4,6-Dimethylpyrimidine-2-thiol (4,6Me$_2$Pm2SH) and its derivatives possess antibacterial and antiviral properties (Coutts & Casy, 1975). Its IR spectrum as a ligand in the title complex (I) exhibits no N–H stretch in the 3500–3200 cm^{-1} region. A single crystal X-ray diffraction study was undertaken in order to characterize the compound fully and to compare its structural features with those of the acetone solvate of the same complex (Cartwright, Goodgame, Jeeves, Langguth & Skapski, 1977; Cartwright, Langguth & Skapski, 1979) and to study the bonding within the molecule.



(I)

Fig. 1 shows an *ORTEP*II (Johnson, 1976) view of the molecule with atomic numbering scheme. The structure consists of discrete [Co($C_6H_7N_2S$)$_3$] molecules with approximate C_3 point symmety, together with one strongly bound water molecule of crystallization per complex. The three bidentate 4,6Me$_2$Pm2SH ligands are planar to within ±0.06 Å and are chemically identical though crystallographically distinct. They are mutually perpendicular [88.2 (1), 94.2 (1) and 99.5 (1)°] to each other. The Co^{III} ion lies nearly in the plane of each ligand with deviations of 0.014 (1), −0.065 (1) and −0.242 (1) Å

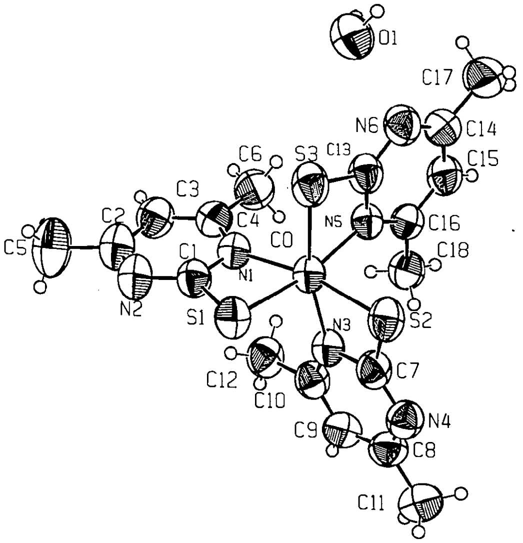


Fig. 1. *ORTEP* (Johnson, 1976) drawing of Co(4,6Me$_2$Pm2S)$_3$.H_2O showing the atom-numbering scheme. For non-H atoms, 50% probability ellipsoids are shown; H atoms are represented by spheres of a arbitrary size.

from the three ligand planes. The thiolate S and azomethine N atoms are coordinated to Co^{III} to form a *fac*-octahedral geometry which is highly distorted owing to the small bite angles of the ligands. The bond lengths and bond angles in the ligands are very close to those in related complexes (see Table 2). Out of three four-membered chelate rings, only one (Co, S1, C1 N1) is strictly planar; the other two deviate significantly from planarity [maximum deviations: C7 −0.020 (7), C13 −0.069 (6) Å].

The Co—S [2.247 (2)–2.271 (2) Å] and Co—N [1.956 (5)–1.991 (5) Å] distances are in agreement with those reported for the acetone solvate of the same complex and other Co^{III} complexes (Onan, Davies, El-sayad & El-toukhy, 1986). The Co—N5 distance [1.991 (5) Å], *trans* to Co—S1 [2.247 (2) Å], is longer than the normal Co^{III}—N bond of *ca* 1.9 Å (Kime & Ibers, 1969). Unequal distribution of strain in the metal coordination polyhedron, resulting from the steric conditions for complex formation, is evident from some distorted angles and may influence both resonance and the bond lengths.

There is one molecule of water of crystallization [U_{eq}(O1) = 0.091 (2) Å^2]. The water H atoms were not freely refined, but the O···N distance [O1—H2···N4($2-x, y+\frac{1}{2}, 2-z$)] of 2.969 (7) Å is consistent with the existence of an intermolecular hydrogen bond. The close contacts N(6)···O(1) [3.083 (8) Å] and S(3)···O(1) [3.411 (7) Å] may indicate the presence of a very weak bifurcated intramolecular hydrogen bond. A stereographic view of the unit-cell contents is presented in Fig. 2. The absence of short intermolecular contacts suggests that packing forces are unlikely to influence the geometry of the molecule to an appreciable extent.

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

$U_{eq} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	U_{eq}
Co	0.95836 (1)	0.20640	0.61948 (1)	0.0587 (2)
S1	0.7434 (2)	0.1230 (1)	0.5666 (2)	0.0716 (5)
S2	1.0487 (2)	0.1455 (1)	0.8458 (2)	0.0733 (4)
S3	0.8076 (2)	0.3008 (1)	0.7383 (2)	0.0762 (5)
N1	0.8539 (5)	0.2364 (3)	0.4114 (5)	0.0628 (13)
N2	0.6172 (7)	0.1756 (4)	0.2805 (6)	0.0802 (18)
N3	1.1220 (6)	0.1265 (3)	0.5643 (5)	0.0626 (13)
N4	1.2781 (7)	0.0410 (3)	0.7421 (6)	0.0719 (16)
N5	1.1089 (5)	0.2977 (3)	0.6736 (5)	0.0614 (14)
N6	1.0433 (6)	0.4106 (4)	0.8317 (7)	0.0762 (19)
C1	0.7306 (7)	0.1822 (4)	0.3993 (6)	0.0654 (15)
C2	0.6283 (8)	0.2255 (5)	0.1640 (8)	0.086 (3)
C3	0.7488 (9)	0.2849 (5)	0.1677 (8)	0.084 (2)
C4	0.8637 (7)	0.2907 (4)	0.2949 (7)	0.0712 (18)
C5	0.5056 (13)	0.2161 (10)	0.0225 (10)	0.124 (4)
C6	0.9954 (10)	0.3517 (5)	0.3054 (10)	0.089 (2)
C7	1.1660 (8)	0.0971 (4)	0.7096 (7)	0.0656 (17)
C8	1.3534 (8)	0.0104 (4)	0.6201 (9)	0.076 (2)
C9	1.3144 (9)	0.0358 (4)	0.4674 (8)	0.078 (2)
C10	1.1950 (8)	0.0944 (4)	0.4404 (7)	0.0680 (18)
C11	1.4793 (11)	−0.0529 (5)	0.6528 (12)	0.096 (3)
C12	1.1488 (10)	0.1263 (5)	0.2791 (7)	0.083 (2)
C13	1.0032 (7)	0.3435 (4)	0.7514 (7)	0.0663 (17)
C14	1.2061 (9)	0.4318 (4)	0.8346 (9)	0.077 (2)
C15	1.3217 (8)	0.3879 (4)	0.7565 (9)	0.0736 (19)
C16	1.2716 (7)	0.3197 (4)	0.6746 (7)	0.0631 (16)
C17	1.2558 (10)	0.5044 (5)	0.9280 (13)	0.105 (3)
C18	1.3859 (7)	0.2694 (4)	0.5871 (9)	0.077 (2)
O1	0.7028 (7)	0.4666 (4)	0.9407 (6)	0.0911 (18)

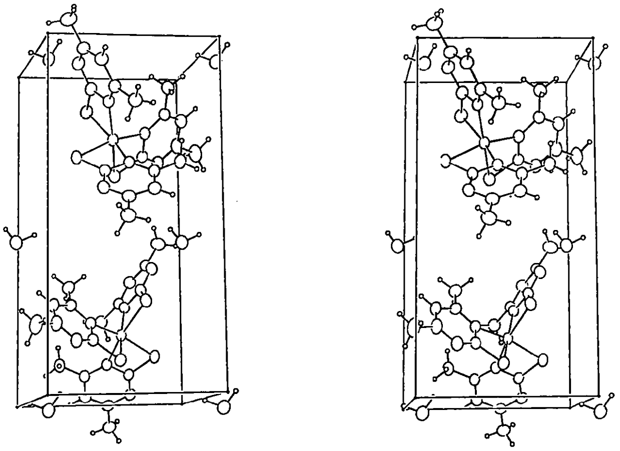
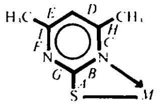


Fig. 2. A stereographic packing diagram showing the contents of one unit cell of the title compound. The origin is in the lower-left-hand corner, *a* is directed into the page, *b* vertically upwards and *c* horizontally.

Table 2. *Comparison of mean bond lengths* (Å) *in* 4,6Me$_2$Pm2S *and* Pm2S *metal complexes*



	A	*B*	*C*	*D*	*E*	*F*	*G*	*H*	*I*
[Co($C_6H_7N_2S$)$_3$].H_2O^{a}	1.732 (8)	1.350 (7)	1.352 (3)	1.3384 (5)	1.387 (3)	1.331 (23)	1.331 (16)	1.484 (13)	1.498 (16)
[Co($C_6H_7N_2S$)$_3$].(CH_3)$_2$CO^b	1.728 (8)	1.357 (7)	1.347 (7)	1.390 (4)	1.376 (6)	1.347 (6)	1.327 (7)	1.488 (10)	1.503 (9)
[Mo$_2$($C_6H_7N_2S$)$_4$].2CH_2Cl_2^{c}	1.71 (45)	1.38 (1)	1.36 (2)	1.40 (3)	1.39 (4)	1.34 (3)	1.33 (2)	1.50 (2)	1.54 (4)
[(C_6H_5)$_4$P][Ni($C_4H_3N_2S$)$_3$].CH_3CN^{d}	1.705 (9)	1.349 (5)	1.329 (5)	1.385 (8)	1.336 (6)	1.330 (4)	1.360 (5)		
[N(C_4H_9)$_4$][Tc($C_4H_3N_2S$)Cl_4]^e	1.713 (8)	1.360 (10)	1.368 (10)	1.393 (12)	1.373 (13)	1.357 (11)	1.33 (10)		
[N(CH_3)$_4$][Fe($C_4H_3N_2S$)$_3$]^f	1.726 (6)	1.357 (8)	1.336 (7)	1.37 (1)	1.37 (1)	1.346 (8)	1.333 (8)		
[Mo($C_4H_3N_2S$)$_4$].CH_2Cl_2^{f}	1.723 (10)	1.349 (10)	1.347 (9)	1.370 (15)	1.369 (11)	1.333 (20)	1.329 (4)		
[Hg(CH_3)($C_5H_6N_3S$)]^g	1.78 (1)	1.36 (2)	1.31 (2)	1.44 (2)	1.42 (2)	1.35 (2)	1.31 (2)		

References: (*a*) present study; (*b*) Cartwright, Goodgame, Jeeves, Langguth & Skapski (1977); (*c*) Cotton, Niswander & Sekutowski (1979); (*d*) Rosenfield, Berends, Gelmini, Stephan & Masharak (1987); (*e*) Bush *et al.* (1987); (*f*) Latham *et al.* (1986); (*g*) Stuart, Nassimbeni, Hutton & Koch (1980).

Experimental

4-6-Dimethylpyrimidine-2-thiol hydrochloride (4,6Me$_2$Pm2-SH.HCl) was obtained by condensation of acetylacetone and thiourea in the presence of HCl. A hot solution of the ligand (0.004 mol) and anhydrous sodium acetate (2 g) in ethanol (20 ml) was filtered into an alcoholic solution (5 ml) of $CoCl_2.6H_2O$ and refluxed for 6 h. The resulting mixture was allowed to stand overnight at 300 K after which a black crystalline product was collected at the filter, washed and dried *in vacuo* over silica gel to give the product. Crystals were obtained by the slow evaporation of a solution in alcohol at room temperature. Elemental analysis for C, H, N and Co found 43.6, 4.5, 17.1 and 11.9%, respectively (calculated for $CoC_{18}H_{23}N_6OS_3$: 43.7, 4.7, 16.9 and 11.9%, respectively).

Crystal data

$[Co(C_6H_7N_2S)_3].H_2O$
$M_r = 494.53$
Monoclinic
$P2_1$
$a = 8.014$ (2) Å
$b = 16.840$ (3) Å
$c = 8.501$ (1) Å
$\beta = 93.53$ (1)°
$V = 1145.1$ (4) Å^3
$Z = 2$
$D_x = 1.434$ Mg m^{-3}
$D_m = 1.45$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 11.2$–$12.8°$
$\mu = 1.03$ mm^{-1}
$T = 293$ K
Plate
0.25 × 0.18 × 0.12 mm
Deep blue

Data collection

CAD-4 diffractometer
ω–2θ scans
Absorption correction: none
2453 measured reflections
2083 independent reflections
2015 observed reflections [$I > 3\sigma(I)$]
$R_{\rm int} = 0.031$

$\theta_{\rm max} = 29°$
$h = 0 \rightarrow 6$
$k = 0 \rightarrow 20$
$l = -10 \rightarrow 10$
3 standard reflections
frequency: 60 min
intensity variation: not significant

Refinement

Refinement on F
$R = 0.053$
$wR = 0.048$
$S = 1.365$
2015 reflections
262 parameters
$w = 1/[\sigma^2(F_o) + 0.0015F_o^2]$
$(\Delta/\sigma)_{\rm max} = 0.21$
$\Delta\rho_{\rm max} = 0.55$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.42$ e Å^{-3}

Extinction correction: $F' = F(1-xF^2/\sin\theta)$
Extinction coefficient: $x = 0.094$ (4)
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Electronic transitions [(A_{1g}–T_{1g}) at 15600 cm^{-1} and (A_{1g}–T_{2g}) at 20000 cm^{-1}] suggest octahedral coordination around Co$^{\rm III}$ (Lever, 1984; Onan, Davies, El-sayed & El-toukhy, 1986). The approximate position of the Co atom was obtained from a Patterson function and the positions of the remaining non-H atoms from successive weighted Fourier syntheses. Anisotropic displacement parameters were adjusted for C, N, S and Co atoms; H atoms were included in calculated positions, riding on their bonded C atoms, and kept fixed during refinement with $U = 0.08$ Å^2. Water H atoms were located in a difference map; their positions were kept fixed. Least-squares refinement of the enantiomer gave $R = 0.061$. The thermal motion of the molecule is strongly anisotropic with U_{22} larger than the other components for most of the atoms. Anomalous-dispersion corrections for Co were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). All computations were carried out using the Cyber computer of the Regional Computer Centre, Calcutta. The programs used were *XRAYARC* (Vickery, Bright & Mallinson, 1971) for Patterson systhesis, *NORMAL*, *EXFFT* and *SEARCH* sequences of *MULTAN*78 (Main *et al.*, 1978) for the weighted Fourier syntheses and *SHELX*76 (Sheldrick, 1976) for the refinement.

The author thanks Dr Michael A. Bruck, Department of Chemistry, University of Arizona, Tucson, for the collection of diffractometer data and also for the preparation of figures, Professors Siddhartha Ray and Saktiprosad Ghosh, IACS, Jadavpur, Calcutta, and Dr Md. M. Hossion, Department of Chemistry, University of Burdwan, for their valuable suggestions and discussions. Financial assistance from the University Grants Commission, New Delhi, is also gratefully acknowledged.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and least-squares-planes data have been deposited with the IUCr (Reference: MU0310). 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. (1994). C**50**, 1199–1201

Ferrocenyltriphenylsilane

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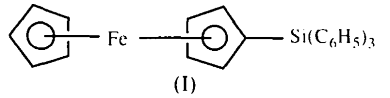
(*Received* 1 *June* 1993; *accepted* 17 *December* 1993)

Abstract

The Fe atom of the title compound, 1-(triphenylsilyl)ferrocene, $[Fe(C_5H_5)\{C_5H_4Si(C_6H_5)_3\}]$, is symmetrically bonded to the two cyclopentadienyl ligands in an η^5 fashion and the two rings are within 2° of being parallel. The C atoms of the two cyclopentadienyl rings are within 1° of being eclipsed and the internal ring angle at the triphenylsilyl-substituted C atom is 2° smaller than other internal ring angles. The triphenylsilyl group occupies a steric volume similar to that of the ferrocenyl group.

Comment

The cyclopentadienyl ligand has played a central role in the development of organometallic chemistry. Recently, cyclopentadienyl ligands incorporating bulky substituents have received considerable attention as a means of modifying the reactivity of organometallic compounds (Janiak & Schumann, 1991). The present study was undertaken to assess the utility of the triphenylsilyl group as a bulky cyclopentadienyl substituent. The title compound, $[Fe(\eta^5\text{-}C_5H_5)\{C_5H_4Si(C_6H_5)_3\}]$, (I), was prepared from ferrocene as described by Benkeser, Goggin & Schroll (1954) and was recrystallized from hot heptane.



(I)

The atomic labeling scheme and a view down the Si(01)—C(01) bond vector are shown as *ORTEP*II (Johnson, 1971) diagrams in Figs. 1 and 2, respectively. The Fe atom is sandwiched between and is essentially equidistant from the two cyclopentadienyl rings, at an average perpendicular distance to the ring mean planes of 1.645 Å. Both cyclopentadienyl rings are planar to within 0.006 Å and are within 2° of being parallel. The ring C atoms are essentially eclipsed (rotation angle of < 1°).

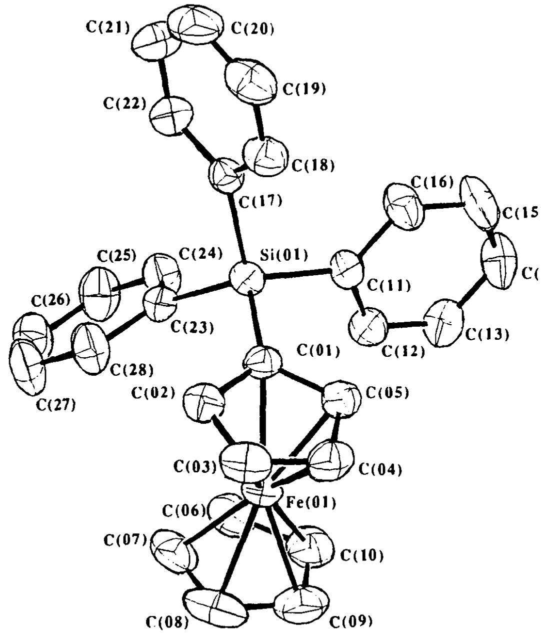


Fig. 1. An *ORTEP*II (Johnson, 1971) drawing of 1-(triphenylsilyl)ferrocene showing the atomic numbering scheme and displacement ellipsoids at 50% probability.

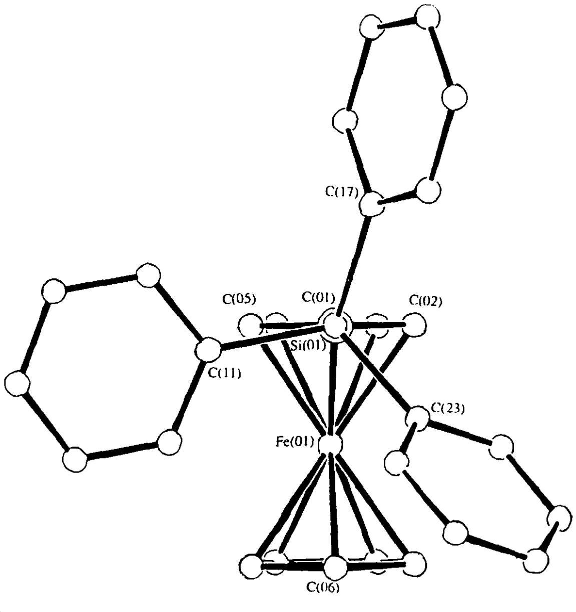


Fig. 2. An *ORTEP*II (Johnson, 1971) drawing of 1-(triphenylsilyl)ferrocene showing a view down the Si(01)—C(01) bond vector.