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fac-Tris(6-methyl-2-mercaptopyridinato)-cobalt(III) at 150 K

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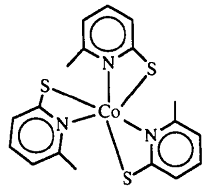
Abstract

The title compound, tris(6-methylpyridine-2-thiolato-*N*,*S*)cobalt(III), $[Co(C_6H_6NS)_3]$, has been isolated and characterized as the *fac* isomer. However, several closely related cobalt and iron complexes which have been characterized previously all adopt the *mer* configuration.

Comment

Recent results from this laboratory have revealed the remarkable capacity of 6-substituted 2-pyridonate ligands to stabilize a structurally diverse array of polyoxo complexes of the later first-row transition metals, for example $[Fe_{17}O_{15}(OH)_6(chp)_{12}(phen)_8(OMe)_3]$ (Parsons, Solan & Winpenny, 1995), $[Ni_{12}(O_2CMe)_{12}(H_2O)_6(thf)_6]$ (Blake, Grant, Parsons, Rawson & Winpenny, 1994) and $[Co_{13}(chp)_{20}(phth)_2(OH)_2]$ (Brechin, Harris, Parsons & Winpenny, 1996) (ch is 6-chloro-2-pyridonate, phen is phenanthroline, thf is tetrahydrofuran and phth is phthalate). The synthesis and structural characterization of a chalcogenide-bridged complex containing 146 metal atoms (Krautscheid, Fenske, Baum & Semmelmann, 1993) encouraged us to extend our results in the coordination chemistry of 2-pyridone to the analogous sulfur system 2-mercaptopyridine. As part of this work we have prepared and isolated the complex *fac*-tris(6-methyl-2-mercaptopyridinato)cobalt(III), (1), and determined its crystal structure at 150 K.



(1)

The crystal structure of (1) consists of discrete distorted octahedral complexes containing three chelating mercaptopyridinate ligands (Fig. 1). Five tris(2-mercaptopyridinate) complexes of first-row transition metals have been structurally characterized previously [FeL_3^- (Rosenfield, Swedberg, Arora & Mascharak, 1986), NiL_3^- (Rosenfield, Berends, Gelmini, Stephan & Mascharak, 1987), CoL_3 and CoL'_3 (Block, Kang, Ofori-Okai & Zubieta, 1991), and VL_3^- (Henkel, Krebs & Schmidt, 1992), where L is 2-mercaptopyridinate and L' is 6-trimethylsilyl-2-mercaptopyridinate]. All have a similar distorted octahedral arrangement at the metal centre imposed by the narrow bite angle of the ligand (65–73°). The *M*—N and *M*—S bond lengths [shown for (1) in Table 2] are determined mostly by the oxidation state of the metal, with the *M*—S distances spanning 2.52–2.58 Å for the divalent V, Fe and Ni systems, and 2.22–2.31 Å for the trivalent cobalt complexes; the ranges for the *M*—N bond lengths are 2.13–2.18 and 1.90–1.99 Å, respectively. Longer metal–ligand bonds are associated with smaller bite angles at the metal centre and approximately linear correlations can be established between these three parameters when taken in pairs.

Burdett (1976) has suggested that low-spin d^6 complexes of general formula MA_3B_3 will preferentially

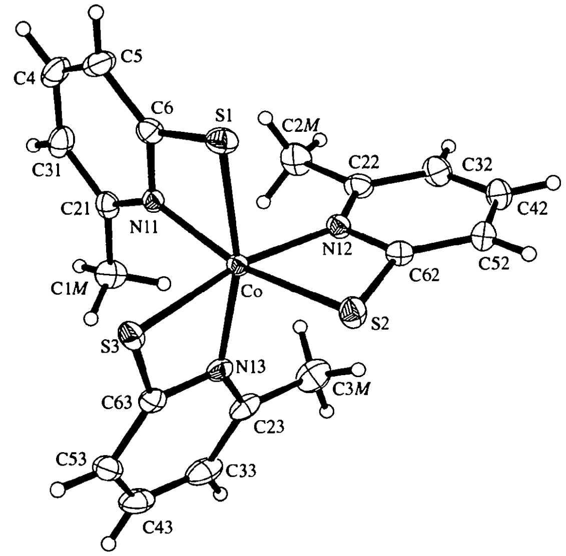


Fig. 1. A view of (1) with the atom-numbering scheme. Displacement ellipsoids enclose 50% probability surfaces.

adopt the *fac* configuration. The structure of (1) is consistent with this, with the complex adopting approximate threefold symmetry (Fig. 1). By contrast, both the d^6 iron and cobalt systems previously examined adopt the *mer* configuration (only the vanadium system is *fac*). Rosenfield *et al.* (1986) originally invoked steric arguments to explain this anomaly, although the present observation of the *fac* isomer suggests that other influences must also apply. It seems probable that deviations from Burdett's (1976) analysis, which was developed on the assumption of ideal octahedral geometry, must be expected in highly distorted coordination environments, such as those in (1) and its analogues.

Experimental

The title compound, (1), was prepared by the action of sodium 6-methyl-2-mercaptopyridinate on $Co(NO_3)_2.6H_2O$ in methanol. Crystals were grown by diffusion of diethyl ether into a tetrahydrofuran solution at 277 K.

Crystal data

$[Co(C_6H_6NS)_3]$
$M_r = 431.46$
Monoclinic
$P2_1/n$
$a = 8.648\ (3)$ Å
$b = 14.383\ (6)$ Å
$c = 15.173\ (6)$ Å
$\beta = 99.77\ (5)°$
$V = 1859.9\ (12)$ Å^3
$Z = 4$
$D_x = 1.541$ Mg m^{-3}
D_m not measured
Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 44 reflections
$\theta = 15–16°$
$\mu = 1.265$ mm^{-1}
$T = 150.0\ (2)$ K
Block
0.50 × 0.40 × 0.40 mm
Black

Data collection

Stoe Stadi-4 diffractometer equipped with an Oxford Cryosystems variable temperature device (Cosier & Glazer, 1986)
ω–θ scans
Absorption correction: ψ scans (North, Phillips & Mathews, 1968)
$T_{min} = 0.488$, $T_{max} = 0.607$
3272 measured reflections
3272 independent reflections
2828 reflections with $I > 2\sigma(I)$
$\theta_{max} = 25.04°$
$h = -10 \rightarrow 10$
$k = 0 \rightarrow 17$
$l = 0 \rightarrow 18$
3 standard reflections
frequency: 60 min
intensity decay: <2%

Refinement

Refinement on F^2
$R(F) = 0.0288$
$wR(F^2) = 0.0729$
$S = 1.055$
3267 reflections
230 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0408P)^2 + 0.9186P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.39$ e Å^{-3}
$\Delta\rho_{min} = -0.32$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0020 (4)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Co—N13	1.975 (2)	Co—S2	2.2696 (9)
Co—N12	1.976 (2)	C61—S1	1.735 (3)
Co—N11	1.994 (2)	C62—S2	1.740 (2)
Co—S1	2.2588 (12)	C63—S3	1.738 (3)
Co—S3	2.2607 (10)		
N13—Co—N12	102.61 (8)	N11—Co—S3	90.74 (6)
N13—Co—N11	99.14 (8)	S1—Co—S3	93.80 (4)
N12—Co—N11	101.03 (8)	N13—Co—S2	94.84 (6)
N13—Co—S1	164.65 (6)	N12—Co—S2	72.77 (6)
N12—Co—S1	91.94 (7)	N11—Co—S2	165.70 (6)
N11—Co—S1	72.93 (6)	S1—Co—S2	94.12 (4)
N13—Co—S3	72.85 (6)	S3—Co—S2	96.28 (4)
N12—Co—S3	167.99 (6)		

H atoms were placed in calculated positions; those on the phenyl rings were allowed to ride on their parent C atoms with $U_{iso}(H) = 1.2U_{eq}(C)$, while the methyl groups were treated as rotating rigid groups with $U_{iso}(H) = 1.5U_{eq}(C)$.

Data collection: *DIF*4 (Stoe & Cie, 1990*a*). Cell refinement: *DIF*4. Data reduction: *REDU*4 (Stoe & Cie, 1990*b*). Program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994). Program(s) used to refine structure: *SHELXTL/PC* (Sheldrick, 1995). Molecular graphics: *SHELXTL/PC*. Software used to prepare material for publication: *SHELXTL/PC*.

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Lists of structure factors, anisotropic displacement parameters, atomic coordinates and complete geometry have been deposited with the IUCr (Reference: MU1291). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Tetraaquabis(*p*-nitrosalicylato) Complexes of Zinc(II) and Cobalt(II)

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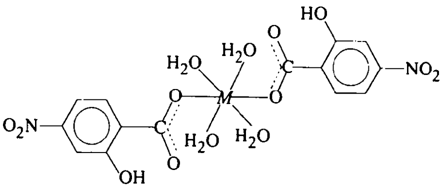
Abstract

In the title compounds having the general formula $[M(C_7H_4NO_5)_2(H_2O)_4]$, where $M = Zn^{II}$, Co^{II} and Ni^{II}, the coordination polyhedron around the metal atom is a slightly distorted octahedron involving one carboxy O atom from each *p*-nitrosalicylato ligand and the O atoms of the four water molecules. The mean $M—O_{water}$ and $M—O_{carboxyl}$ distances are 2.126 (1) and 2.047 (1) Å, respectively, for the zinc complex, and 2.118 (1) and 2.052 (1) Å, respectively, for the cobalt complex. Centrosymmetric monomers are cross-linked *via* intermolecular hydrogen bonds.

Comment

The structures of metal complexes having different benzoic acid substituents have been the subject of much interest in our laboratory. The coordination properties and geometric parameters are available from the crystal structure studies of poly[bis(*p*-nitrosalicylato-*O*:*O*′)-disilver(I)-O^3:*Ag*′;*Ag*:$O^{3\prime}$] (Tahir, Ülkü & Movsumov, 1996*a*), cerium 3,5-dinitrobenzoate dihydrate (Tahir, Ülkü & Movsumov, 1996*c*) and monoaquabis(*p*-nitrosalicylato)lead(II) (Tahir, Ülkü & Movsumov, 1996*d*). Reports on zinc(II) benzoate (Guseinov, Musaev, Usubaliev, Amiraslanov & Mamedov, 1984), zinc(II) *p*-nitrobenzoate (Guseinov, Musaev, Amiraslanov, Usubaliev & Mamedov, 1983), bis(*p*-nitrobenzoato)tetraaquacobalt(II) dihydrate (Nadzhafov, Shnulin & Mamedov, 1981) and tetraaquabis(salicylato)cobalt(II) (Gupta & Mahanta, 1978) also contain structural details of a similar group of complexes. As a continuation of our investigations, we synthesized three new isomorphous metal complexes of general formula $[M(C_7H_4NO_5)_2(H_2O)_4]$, where $M = Zn^{II}$, Co^{II} and Ni^{II}. We report here the structural parameters in detail for the cobalt(II), (I), and zinc(II), (II), complexes.



(I) M = Co
(II) M = Zn

The structures consists of centrosymmetric monomers with the metal atom occupying the two inversion centers at 0,0,0 and $0,\frac{1}{2},\frac{1}{2}$ of the monoclinic unit cell. Slightly distorted octahedral coordination around the metal atom involves one carboxyl O atom from each *p*-nitrosalicylato ligand and the O atoms of four water molecules. The $M—O_{water}$ distances within the basal plane of the octahedron have values between 2.086 (2)–2.151 (1) Å and 2.096 (1)–2.156 (1) Å for the Co and Zn complexes, respectively, and are longer than the $M—O_{carboxyl}$ bonds of 2.052 (1) and 2.047 (1) Å found in the respective complexes. In the related octahedral complex tetraaquabis(3,5-dinitrobenzoato-*O*)cobalt(II) tetrahydrate (Tahir, Ülkü & Movsumov, 1996*b*), the $Co—O_{water}$ distances are shorter than the $Co—O_{carboxyl}$ distances. As can be seen from Table 3, the second carboxyl O atom of the ligand which is not coordinated to the metal atom, is involved in intermolecular hydrogen bonding with a hydroxyl group on one side and a coordinated water molecule on the other. Intermolecular hydrogen bonding between the water molecules of the coordination sphere as well as between the water molecules and the nitro O atoms constitute a three-dimensional hydrogen-bonding network in the crystal.

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