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Tris(2-sulfidopyridine *N*-oxide-*O*,*S*)-chromium(III) Acetone Solvate (1/1)

TING-BIN WEN,[a] JI-CHENG SHI,[a] QIU-TIAN LIU,[a] BEI-SHENG KANG,[a] BO-MU WU[b] AND THOMAS C. W. MAK[b]

[a]*State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Stucture of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, People's Republic of China, and* [b]*Department of Chemistry, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong*

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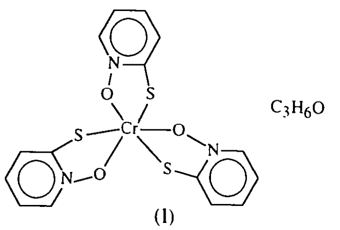
Abstract

The title compound, $[Cr(C_5H_4NOS)_3].(CH_3)_2CO$, contains a $Cr^{III}(mpo)_3$ unit (Hmpo = 2-mercaptopyridine-*N*-oxide) and $(CH_3)_2CO$. Each mpo^- ligand chelates to the Cr atom *via* one O and one S atom with an average bite angle of 83.3 (1)°, forming a distorted octahedral O_3S_3 coordination environment of the Cr atom. The average Cr—S and Cr—O bond distances are 2.363 (1) and 1.986 (2) Å, respectively.

Comment

Transition metal thiolato complexes are important analogues of metallo-enzymes and their study is a topic of current interest. In our investigation of transition metal complexes with bidentate sulfur–oxygen ligands, such as *o*-mercaptophenol (mpH_2) (Kang *et al.*, 1990), 2-mercaptopyridinol ($mppH_2$) (Chen, Weng & Kang, 1991) and 2-mercaptopyridine *N*-oxide (Hmpo) (Chen, Hu, Wu, Weng & Kang, 1991), numerous complexes of V, Fe, Co, Ni and Mn have been prepared. We now extend our studies to chromium, whose thiolate chemistry has hitherto been essentially unexplored, and report the structure of the title compound, (I).



(I)

The structure of the $Cr(mpo)_3$ unit of the title compound (Fig. 1) is quite similar to that of $Cr(mtb)_3$ (mtb = *N*-methylthiobenzohydroxamate) and the average Cr—S and Cr—O bond distances [2.363 (1) and 1.986 (2) Å, respectively] agree well with those of $Cr(mtb)_3$ [2.367 (8), 1.976 (6) Å; Freyberg, Abu-Dari & Raymond, 1979]. The coordination about the Cr atom is distorted from regular octahedral, with an average bite angle of 83.3 (1)° due to the limited bite distance (average 2.903 Å) of the ligand. The distortion of the CrO_3S_3 octahedral core is characterized by an average *trans* angle of 170.2 (1)°. The average S—C and O—N distances are within the range found for other mpo^- lig-

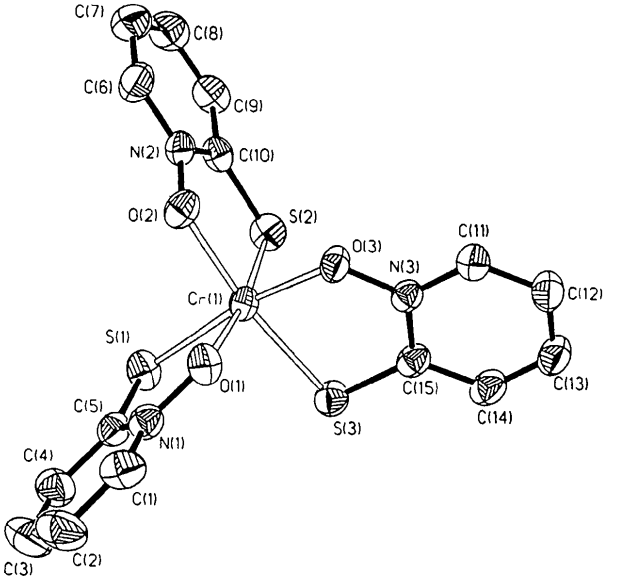


Fig. 1. Crystal structure of $Cr(mpo)_3$ showing 50% probability displacement ellipsoids. H atoms are omitted for clarity.

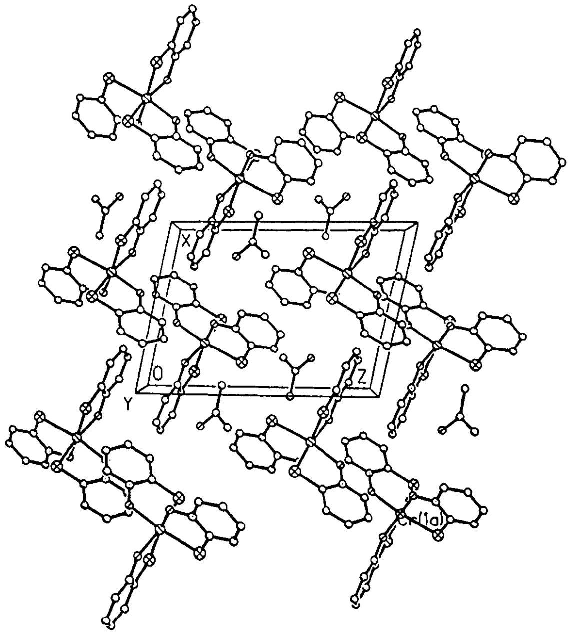


Fig. 2. Packing diagram of the molecules in the crystal. Note the solvent molecule in the cell.

ated complexes (Hu *et al.*, 1991; Hu, Chen, Dai, Weng & Kang, 1993). The mean Cr—S—C and Cr—O—N angles [96.9 (1) and 119.8 (1)°, respectively] show that the bonding orbitals of the S donor atom are mainly of *p* character, while those of the O donor atom are sp^2 hybridized (Chen, Hu, Wu, Weng & Kang, 1991; Higes-Rolando, Perez-Florindo, Valazuela-Calahorro, Martin-Ramos & Romero-Garzon, 1994).

Within the crystal lattice, the stacked molecules are inversion related (Fig. 2). The shortest Cr···Cr distance is 6.7010 (7) Å. The shortest intermolecular contact between pyridine rings (for non-H atoms) is 3.390 Å between N(3) and $C(12^{i})$. The approaches between adjacent parallel ring atoms in the stack, such as $N(3)\cdots C(13^{i})$ 3.544, $C(11)\cdots C(14^{i})$ 3.539, $N(2)\cdots C(8^{ii})$ 3.480, $C(6)\cdots C(9^{ii})$ 3.512, $N(1)\cdots C(3^{iii})$ 3.715 and $C(2)\cdots C(4^{iii})$ 3.681 Å (e.s.d.s ≃ 0.005 Å), are of van der Waals magnitude (Pauling, 1960) [symmetry codes: (i) $-x, -y, -z$; (ii) $1-x, 1-y, 1-z$; (iii) $1-x, -y, -z$].

Experimental

Crystals of the title compound were obtained from the reaction of $CrCl_3.6H_2O$ with mpoNa (1:3 molar ratio) in $DMF/CH_3CN/(CH_3)_2CO$ solvent (2:1:1 *v*/*v*/*v*) at room temperature.

Crystal data

$[Cr(C_5H_4NOS)_3].C_3H_6O$
$M_r = 488.5$
Triclinic
$P\overline{1}$
$a = 9.330 (1)$ Å
$b = 9.339 (1)$ Å
$c = 12.805 (1)$ Å
$\alpha = 82.51 (1)°$
$\beta = 77.38 (1)°$
$\gamma = 84.75 (1)°$
$V = 1077.2 (5)$ Å^3
$Z = 2$
$D_x = 1.506$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 40 reflections
$\theta = 3.5–22.5°$
$\mu = 0.851$ mm^{-1}
$T = 293$ K
Prism
0.55 × 0.40 × 0.30 mm
Black–green

Data collection

Rigaku *R*-axis diffractometer
Collection method: image plate (see below)
Absorption correction: none
3897 measured reflections
3897 independent reflections

3225 observed reflections $[F > 8\sigma(F)]$
$\theta_{max} = 27°$
$h = -11 \rightarrow 11$
$k = -11 \rightarrow 0$
$l = -16 \rightarrow 15$

Refinement

Refinement on *F*
$R = 0.044$
$wR = 0.058$
$S = 1.11$
3225 reflections

Extinction correction: $F^* = F[1 + (0.002\chi \times F^2/\sin 2\theta)]^{-1/4}$
Extinction coefficient: $\chi = 0.0012 (3)$

263 parameters
H atoms: see below
$w = 1/[\sigma^2(F) + 0.00001(F)^2]$
$(\Delta/\sigma)_{max} = 0.011$
$\Delta\rho_{max} = 0.52$ e Å^{-3}
$\Delta\rho_{min} = -0.34$ e Å^{-3}

Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

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

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

	x	*y*	*z*	U_{eq}
Cr(1)	0.28392 (6)	0.36461 (4)	0.22978 (4)	0.0447 (1)
S(1)	0.43425 (10)	0.15659 (8)	0.27460 (8)	0.0596 (2)
S(2)	0.16515 (10)	0.38445 (9)	0.40965 (8)	0.0611 (2)
S(3)	0.10054 (10)	0.21935 (7)	0.20725 (8)	0.0598 (2)
O(1)	0.4113 (2)	0.3558 (2)	0.0848 (2)	0.053 (1)
O(2)	0.4087 (2)	0.5129 (2)	0.2557 (2)	0.054 (1)
O(3)	0.1615 (2)	0.5240 (2)	0.1671 (2)	0.051 (1)
N(1)	0.5092 (2)	0.2430 (2)	0.0642 (2)	0.049 (1)
C(1)	0.5837 (3)	0.2411 (2)	−0.0385 (2)	0.064 (1)
C(2)	0.6853 (3)	0.1302 (3)	−0.0659 (3)	0.084 (1)
C(3)	0.7121 (3)	0.0208 (3)	0.0137 (3)	0.084 (1)
C(4)	0.6375 (3)	0.0262 (2)	0.1170 (3)	0.069 (1)
C(5)	0.5308 (3)	0.1395 (2)	0.1465 (2)	0.050 (1)
N(2)	0.3823 (2)	0.5617 (2)	0.3535 (2)	0.050 (1)
C(6)	0.4717 (3)	0.6637 (3)	0.3658 (3)	0.067 (1)
C(7)	0.4551 (3)	0.7149 (3)	0.4634 (3)	0.082 (1)
C(8)	0.3479 (3)	0.6644 (3)	0.5479 (3)	0.082 (1)
C(9)	0.2555 (3)	0.5630 (3)	0.5341 (2)	0.069 (1)
C(10)	0.2729 (3)	0.5099 (2)	0.4345 (2)	0.053 (1)
N(3)	0.0291 (2)	0.4972 (2)	0.1515 (2)	0.044 (1)
C(11)	−0.0538 (3)	0.6123 (2)	0.1154 (2)	0.054 (1)
C(12)	−0.1880 (3)	0.5951 (3)	0.0971 (2)	0.065 (1)
C(13)	−0.2427 (3)	0.4600 (3)	0.1155 (3)	0.068 (1)
C(14)	−0.1573 (3)	0.3435 (3)	0.1509 (2)	0.063 (1)
C(15)	−0.0173 (3)	0.3595 (2)	0.1685 (2)	0.049 (1)
C(18)	−0.1848 (3)	−0.0161 (3)	0.4128 (3)	0.125 (1)
C(16)	−0.1089 (3)	−0.1305 (3)	0.3502 (3)	0.113 (1)
C(17)	0.0445 (3)	−0.1764 (3)	0.3497 (3)	0.112 (1)
O(4)	−0.1906 (3)	−0.1914 (3)	0.2956 (3)	0.164 (1)

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

Cr(1)—S(1)	2.373 (1)	S(1)—C(5)	1.710 (3)
Cr(1)—S(2)	2.351 (1)	S(2)—C(10)	1.713 (3)
Cr(1)—S(3)	2.365 (1)	S(3)—C(15)	1.725 (2)
Cr(1)—O(1)	1.981 (2)	O(1)—N(1)	1.344 (3)
Cr(1)—O(2)	1.992 (2)	O(2)—N(2)	1.352 (3)
Cr(1)—O(3)	1.986 (2)	O(3)—N(3)	1.344 (3)
S(1)—Cr(1)—S(2)	93.8 (1)	S(2)—Cr(1)—O(3)	95.3 (1)
S(1)—Cr(1)—S(3)	91.3 (1)	S(3)—Cr(1)—O(3)	83.5 (1)
S(2)—Cr(1)—S(3)	91.2 (1)	O(1)—Cr(1)—O(3)	88.8 (1)
S(1)—Cr(1)—O(1)	82.9 (1)	O(2)—Cr(1)—O(3)	88.4 (1)
S(2)—Cr(1)—O(1)	171.2 (1)	Cr(1)—S(1)—C(5)	96.6 (1)
S(3)—Cr(1)—O(1)	97.0 (1)	Cr(1)—S(2)—C(10)	97.4 (1)
S(1)—Cr(1)—O(2)	97.6 (1)	Cr(1)—S(3)—C(15)	96.7 (1)
S(2)—Cr(1)—O(2)	83.4 (1)	Cr(1)—O(1)—N(1)	120.7 (1)
S(3)—Cr(1)—O(2)	169.8 (1)	Cr(1)—O(2)—N(2)	119.4 (1)
O(1)—Cr(1)—O(2)	89.0 (1)	Cr(1)—O(3)—N(3)	119.4 (1)
S(1)—Cr(1)—O(3)	169.6 (1)		

Diffraction intensities were collected on a Rigaku *R*-axis image-plate diffractometer (Sato, Yamamoto, Zmada, Katsube, Tanaka & Higashi, 1992) by taking oscillation photographs (total oscillation range, φ = 0–180°; 20 frames in total; oscillation angle, $\Delta\varphi = 9°$ per frame; exposure time = 10 min per frame). The structure was solved by Patterson methods and refined by full-matrix least-squares methods. H atoms were fixed at ideal positions with common isotropic displacement parameters (U_{iso} = 0.08 Å^2). Atoms O(4), C(16), C(17) and C(18) represent the acetone solvent molecule.

Data collection: Rigaku *R*-axis diffractometer software (Sato *et al.*, 1992). Cell refinement: Rigaku *R*-axis diffractometer software. Data reduction: *SHELXTL-Plus* (Sheldrick, 1987). Program(s) used to solve structure: *SHELXTL-Plus*. Program(s) used to refine structure: *SHELXTL-Plus*. Molecular graphics: *ORTEP*II (Johnson, 1976).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BM1038). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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