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Key indicators

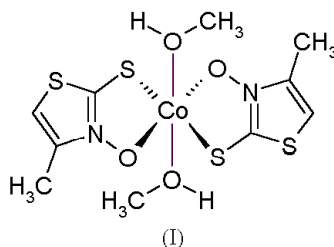
Single-crystal X-ray study
T = 180 K
Mean $\sigma(\text{C}-\text{C}) = 0.005 \text{ \AA}$
R factor = 0.034
wR factor = 0.078
Data-to-parameter ratio = 13.8For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.Bis[3-hydroxy-4-methyl-2(3*H*)-thiazolethiolato-*S*²,*O*]-bis(methanol-*O*)cobalt(II)

The structure of the title compound, $[\text{Co}(\text{C}_4\text{H}_4\text{N}-\text{OS}_2)_2(\text{CH}_4\text{O})_2]$, has been determined at 180 (2) K. The molecule possesses $\bar{1}$ point symmetry with the Co^{II} atom adopting a Jahn–Teller-distorted octahedral geometry. The molecules are linked into chains by $\text{O}-\text{H}\cdots\text{O}$ hydrogen-bond interactions involving the H atom of the coordinated methanol molecules.

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Comment

Cyclic thiohydroxamic acids, such as 1-hydroxy-2(1*H*)-pyridinethione (pyrithione, HPT), find extensive use as fungicides (Paulus, 1993). It has been suggested that their mode of action is based predominantly on chelate complex formation (Albert, 1973). 3-Hydroxy-4-methyl-2(3*H*)-thiazolethione (methylthiazolethione, HMTT) contains a chelating unit similar to that in pyrithione and might, therefore, be expected to exhibit similar antimicrobial properties. We are currently studying the solid-state chemistry of cyclic thiohydroxamic acids (Bond & Jones, 2000) and their complexes with first-row d-block elements, and report here the crystal structure of the chelate complex $\text{Co}(\text{MTT})_2(\text{methanol})_2$, (I) (Fig. 1).



In (I), Co1 occupies a centre of symmetry and adopts octahedral coordination *via* two bidentate MTT ligands and two methanol molecules. The $\text{Co1}-\text{S1}$ distance [2.4590 (7) \AA] is significantly greater than the $\text{Co}-\text{S}$ distances in comparable complexes [see, for example, Kang *et al.* (1993); $\text{Co}-\text{S}_{\text{ave}} = 2.377$ (5) \AA]; this may be attributed to a tetragonal Jahn–Teller distortion about the Co^{II} atom (d^7). The $\text{C1}-\text{S1}$ and $\text{N1}-\text{O1}$ bond distances [1.699 (3) \AA and 1.352 (3) \AA , respectively] suggest that these bonds retain some multiple-bond character [*cf.* $\text{C}-\text{S}_{\text{ave}} = 1.773$ (9) \AA and $\text{N}-\text{O}_{\text{ave}} = 1.396$ (12) \AA ; Allen *et al.*, 1987].

The H atom of the coordinated methanol molecule is involved in a hydrogen-bond interaction with the O atom of an MTT ligand in an adjacent molecule [$\text{H1}\cdots\text{O1}^i = 1.96$ (4) \AA and $\text{O2}-\text{H1}\cdots\text{O1}^i = 171$ (4) $^\circ$; symmetry code: (i) $1-x, 1-y, -z$], giving rise to extended chains running parallel to the *a* direction (Fig. 2). These chains pack in a herring-bone-type

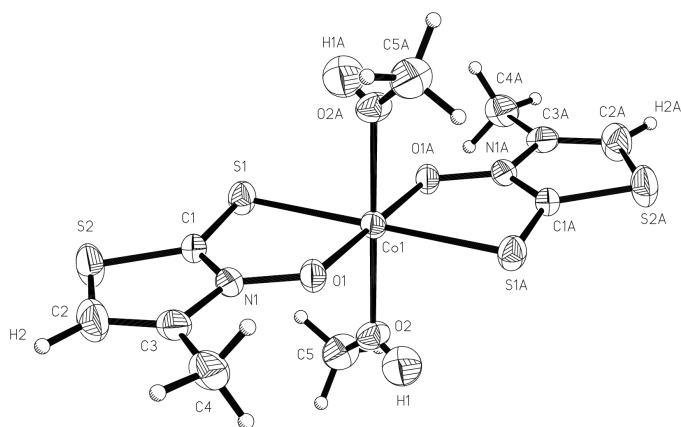


Figure 1
The molecular unit in (I) showing displacement ellipsoids at the 50% probability level (XP; Sheldrick, 1993).

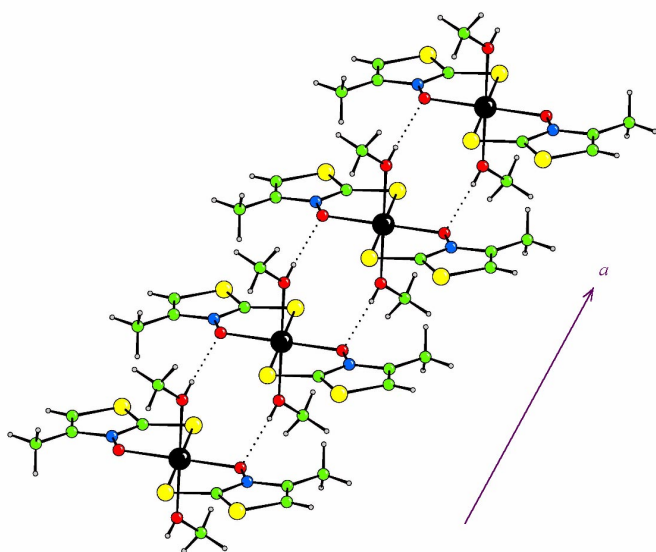


Figure 2
Chains of (I) linked via O—H...O interactions (CAMERON; Watkin *et al.*, 1996).

arrangement (Fig. 3). The vinylic atom H2 may be expected to be sufficiently acidic to become involved in a hydrogen-bond interaction. H2 makes its closest approach to an S atom in an MTT molecule of an adjacent chain [$\text{H2} \cdots \text{S1}^{\text{ii}} = 2.82 \text{ \AA}$ and $\text{C2} - \text{H2} \cdots \text{S1}^{\text{ii}} = 163.3^\circ$; symmetry code: (ii) $1 + x, \frac{1}{2} - y, \frac{1}{2} + z$]. The approximately linear geometry of this interaction may be indicative of a C—H...S-type hydrogen bond.

Experimental

HMTT was obtained from the Aldrich Chemical Co. and was recrystallized from CH_2Cl_2 . The sodium salt hydrate $\text{Na}(\text{MTT}) \cdot x\text{H}_2\text{O}$ was prepared by addition of 1 mol equivalent of NaOH to a suspension of HMTT in water, followed by evaporation of the solvent. The cobalt(II) complex was prepared initially as a monohydrate $\text{Co}(\text{MTT})_2 \cdot \text{H}_2\text{O}$ by combination of aqueous solutions of CoCl_2 and $\text{Na}(\text{MTT})$ in a 1:2 molar ratio at room temperature. The resulting pink precipitate was removed by filtration under gravity and dried in air at room temperature. Single crystals of (I) were grown by

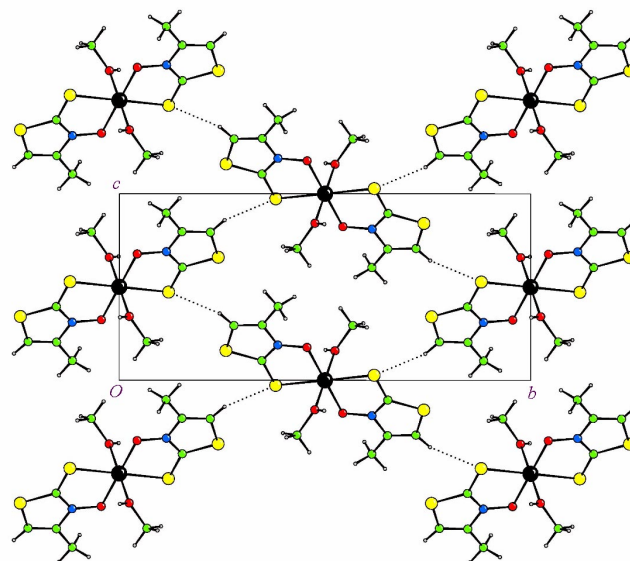


Figure 3
Projection on to (100) showing chains of (I) packed in a herring-bone-type arrangement. Close H...S contacts are indicated by dotted lines (CAMERON; Watkin *et al.*, 1996).

slow evaporation of a solution of $\text{Co}(\text{MTT})_2 \cdot \text{H}_2\text{O}$ in methanol at room temperature.

Crystal data

$[\text{Co}(\text{C}_4\text{H}_4\text{NOS}_2)_2(\text{CH}_4\text{O})_2]$
 $M_r = 415.42$
 Monoclinic, $P2_1/c$
 $a = 5.0414 (4) \text{ \AA}$
 $b = 18.878 (2) \text{ \AA}$
 $c = 8.6814 (11) \text{ \AA}$
 $\beta = 99.349 (7)^\circ$
 $V = 815.23 (16) \text{ \AA}^3$
 $Z = 2$

$D_x = 1.692 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation
 Cell parameters from 9582 reflections
 $\theta = 2.9\text{--}25.0^\circ$
 $\mu = 1.58 \text{ mm}^{-1}$
 $T = 180 (2) \text{ K}$
 Plate, red
 $0.13 \times 0.08 \times 0.02 \text{ mm}$

Data collection

Nonius KappaCCD diffractometer
 Thin-slice ω and φ scans
 2478 measured reflections
 1424 independent reflections
 1087 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.029$
 $\theta_{\text{max}} = 25.0^\circ$
 $h = -5 \rightarrow 5$
 $k = -20 \rightarrow 22$
 $l = -10 \rightarrow 10$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.034$
 $wR(F^2) = 0.078$
 $S = 1.01$
 1424 reflections
 103 parameters

H atoms treated by a mixture of independent and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0359P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.017$
 $\Delta\rho_{\text{max}} = 0.31 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.42 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (\AA).

Co1—O1	2.0459 (17)	S2—C2	1.725 (3)
Co1—O2	2.121 (2)	O1—N1	1.352 (3)
Co1—S1	2.4590 (7)	N1—C1	1.339 (3)
S1—C1	1.699 (3)	N1—C3	1.400 (3)
S2—C1	1.717 (3)	C2—C3	1.336 (4)

Table 2

Hydrogen-bonding geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$O2-H1 \cdots O1^i$	0.75 (4)	1.96 (4)	2.696 (3)	171 (4)

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

All H atoms except H1 were placed geometrically and allowed to ride during subsequent refinement. H1 was located in a difference Fourier map and refined freely with an isotropic displacement parameter.

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *HKL SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *HKL DENZO* and *SCALEPACK* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); software used to prepare material for publication: *SHELXL97*.

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