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Key indicators

Single-crystal X-ray study

$T = 293\text{ K}$

Mean $\sigma(\text{C}-\text{C}) = 0.011\text{ \AA}$

R factor = 0.061

wR factor = 0.139

Data-to-parameter ratio = 19.0

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

A new polymorph of *fac*-tris(4,6-dimethylpyrimidine-2-thiolato- κ^2N,S)cobalt(III) monohydrate

A new polymorph of the title compound, $[\text{Co}(\text{C}_6\text{H}_7\text{N}_2\text{S})_3]\cdot\text{H}_2\text{O}$, was obtained by slow evaporation of the compound from tetrahydrofuran. The structure is almost exactly the same as that of the first polymorph [Seth (1994). *Acta Cryst. C* **50**, 1196–1199]. The packing arrangement and position of the water molecule differ in the two forms.

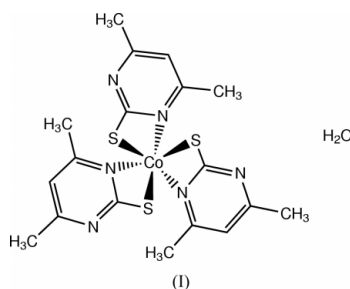
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Comment

As part of our systematic work on the coordination mode of the potential ambidentate ligand 4,6-dimethylpyrimidine-2(1*H*)-thione (4,6-Me₂pymSH) (Lang *et al.*, 2002; Fernandes *et al.*, 2002; Oliveira *et al.*, 2002), we studied the reaction of the ligand with cobalt(II) acetate tetrahydrate. Aerobic oxidation with slow evaporation of tetrahydrofuran produced crystals of the blue Co^{III} title compound, (I), in the non-centrosymmetric orthorhombic space group $Pca2_1$ (Fig. 1). Seth (1994) reported the first polymorph of the title compound in the non-centrosymmetric monoclinic space group $P2_1$; racemic twinning was not reported.



The $\text{Co}(4,6\text{-Me}_2\text{pymS})_3$ molecule of (I) shows almost the same, strongly distorted, *fac*-octahedral geometry, due to the small bite angle of the three bidentate 4,6-Me₂pymS ligands, as that reported in the earlier polymorph. The planes formed by each of the three ligands are mutually perpendicular, with angles of 85.82 (12), 87.35 (12) and 86.19 (13)° between them. The Co atom is situated 0.1322 Å from the point defined by the intersection of the three planes. The bond distances and angles within the ligands are close to those reported for similar compounds.

The difference between the two polymorphs lies in the packing and the position of the solvent water molecule. The packing diagram of the title compound is shown in Fig. 2. In the unit cell of the first polymorph, the water molecule forms a hydrogen bond to only one pyrimidine N atom, with an O...N distance of 2.969 (7) Å. In the new polymorph, the water molecule bridges between two neighbouring Co(4,6-

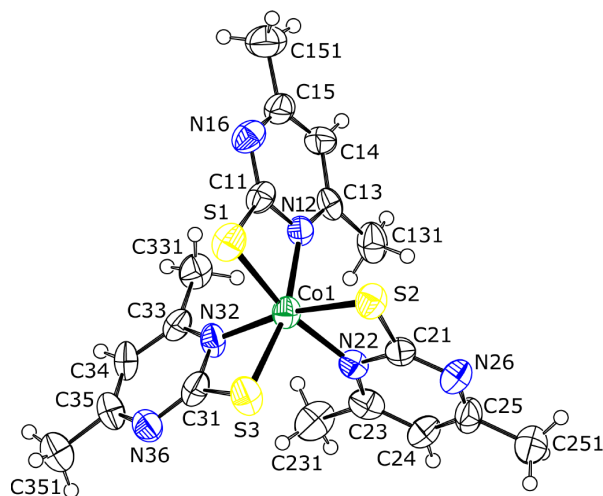


Figure 1
View of (I) without the water molecule, with the atomic labelling scheme. Displacement ellipsoids are drawn at the 50% probability level.

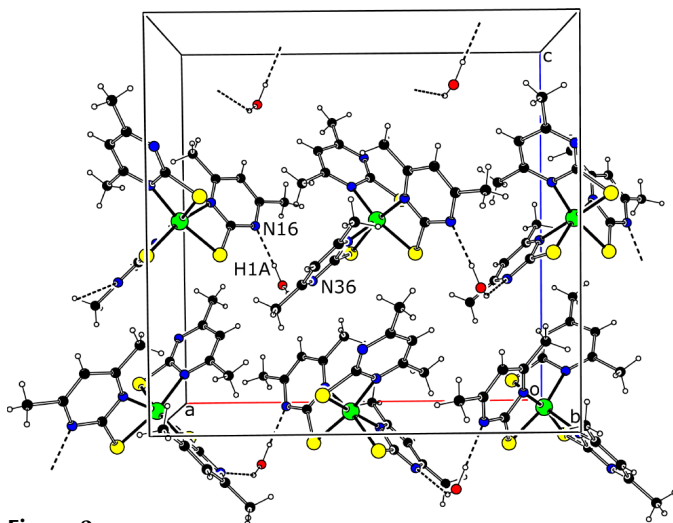


Figure 2
The crystal packing of the title compound.

Me_2pymS)₃ molecules, forming hydrogen bonding to two different N atoms, as shown in Table 2. Comparing the volume of the asymmetric units, the first polymorph occupies a slightly larger volume, 572.6 (1) Å³, than the new polymorph, 564.8 (1) Å³, implying a greater packing efficiency in the latter.

Experimental

The compound 4,6-dimethylpyrimidine-2(1*H*)-thione (4,6- Me_2pymSH) was prepared according to a literature method (Nigam *et al.*, 1983). The title complex was synthesized by the following procedure: 0.42 g (3 mmol) of 4,6- Me_2pymSH was dissolved in 20 ml of THF (freshly distilled) in a Schlenk tube kept under an N₂ atmosphere. To this solution, 0.25 g (1 mmol) of $[\text{Co}(\text{O}_2\text{CCH}_3)_2]\cdot 4\text{H}_2\text{O}$ dissolved in 10 ml of THF was added over 10 min, and the mixture was stirred for about 2 h. Slow evaporation of the solvent in air led to the appearance of a blue microcrystalline solid. Yield: ~96% (0.45 g). Elemental analysis: calculated for C₁₈H₂₃CoN₆S₃: C 43.71, H 4.68, N 16.99%; found: C 43.69, H 4.64, N 17.1%. FAB MS: *m/z* 476.0 (14%, *M*), *m/z*

337.0 (32%, {Co[4,6- Me_2pymS]₂}), *m/z* 198.0 (15%, {Co[4,6- Me_2pymS]}).

Crystal data

[Co(C₆H₇N₂S)₃] \cdot H₂O
M_r = 494.56
Orthorhombic, *Pca*2₁
a = 16.969 (2) Å
b = 8.0436 (11) Å
c = 16.552 (2) Å
V = 2259.2 (5) Å³
Z = 4
D_x = 1.454 Mg m⁻³

Mo *K*α radiation
Cell parameters from 3091 reflections
 θ = 5.5–54.7°
 μ = 1.06 mm⁻¹
T = 293 (2) K
Block, blue
0.19 × 0.17 × 0.17 mm

Data collection

Bruker SMART area-detector diffractometer
 φ and ω scans
Absorption correction: multi-scan (*SADABS*, Sheldrick, 1996)
T_{min} = 0.824, *T_{max}* = 0.841
12629 measured reflections

5124 independent reflections
2380 reflections with *I* > 2σ(*I*)
R_{int} = 0.103
 θ_{max} = 28.1°
h = −22 → 22
k = −10 → 5
l = −21 → 21

Refinement

Refinement on *F*²
 $R[F > 2\sigma(F_o^2)] = 0.0482$
where $P = (F_o^2 + 2F_c^2)/3$
(Δ/σ)_{max} = 0.001

$\Delta\rho_{\text{max}} = 0.76 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.33 \text{ e \AA}^{-3}$
Absolute structure: Flack (1983)
Flack parameter = 0.03 (3)

Table 1

Selected geometric parameters (Å, °).

Co1—N12	1.970 (6)	Co1—S2	2.250 (2)
Co1—N32	1.975 (6)	Co1—S1	2.251 (2)
Co1—N22	1.982 (6)	Co1—S3	2.259 (2)
N12—Co1—N32	99.8 (2)	N32—Co1—S1	91.30 (19)
N12—Co1—N22	102.8 (2)	S2—Co1—S1	94.71 (8)
N32—Co1—N22	101.9 (3)	N32—Co1—S3	72.53 (18)
N12—Co1—S2	91.73 (17)	N22—Co1—S3	90.86 (17)
N22—Co1—S2	72.63 (18)	S2—Co1—S3	96.77 (8)
N12—Co1—S1	72.69 (18)	S1—Co1—S3	94.92 (9)

Table 2

Hydrogen-bonding geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O1—H1A...N16 ⁱ	0.98	2.02	2.990 (8)	168
O1—H1A...S1 ⁱ	0.98	3.17	3.654 (6)	112
O1—H1B...N36 ⁱⁱ	0.72	2.52	3.088 (8)	137

Symmetry codes: (i) 1 − *x*, 1 − *y*, $\frac{1}{2}$ + *z*; (ii) $\frac{1}{2}$ − *x*, *y*, $\frac{1}{2}$ + *z*.

The intensities of the measured reflections were, in general, weak, leading to a slightly high value of *R_{int}*. The H atoms of the methyl groups were refined as riding atoms with ideal tetrahedral geometry [*d*(C—H) = 0.96 Å], allowed to rotate to fit the electron density; the isotropic displacement parameters were fixed to be 50% larger than those of the atoms to which the H atoms were bonded. The aromatic H atoms were constrained to ideal trigonal planar geometry [*d*(C—H) = 0.93 Å]; their isotropic displacement parameters were set to be 20% larger than the those of the atoms to which the H atoms were bonded. The water H atoms were located in a difference Fourier map and refined as riding atoms, with isotropic displacement parameters 50% larger than that of the parent O atom. A total of 2326 Friedel pairs were measured.

Data collection: *SMART* (Bruker, 1997); cell refinement: *SMART*; data reduction: *SAINTE* (Bruker, 1997); program(s) used to solve

structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

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