

## Tris(1,1,5,5-tetramethyl-2-thiobiuretato)cobalt(III)

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## Key indicators

Single-crystal X-ray study  
T = 150 K  
Mean  $\sigma(\text{N}-\text{C}) = 0.003 \text{ \AA}$   
R factor = 0.033  
wR factor = 0.070  
Data-to-parameter ratio = 25.2For details of how these key indicators were  
automatically derived from the article, see  
<http://journals.iucr.org/e>.

At 150 K, the title compound,  $[\text{Co}(\text{C}_6\text{H}_{12}\text{N}_3\text{OS})_3]$ , comprises an octahedral cobalt(III) ion with three anionic bidentate 1,1,5,5-tetramethyl-2-thiobiuretate ligands. Within the first coordination sphere of the cobalt ion, the disposition of the three S atoms is *fac*.

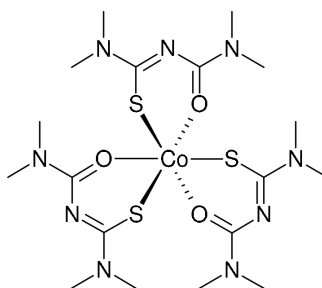
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## Comment

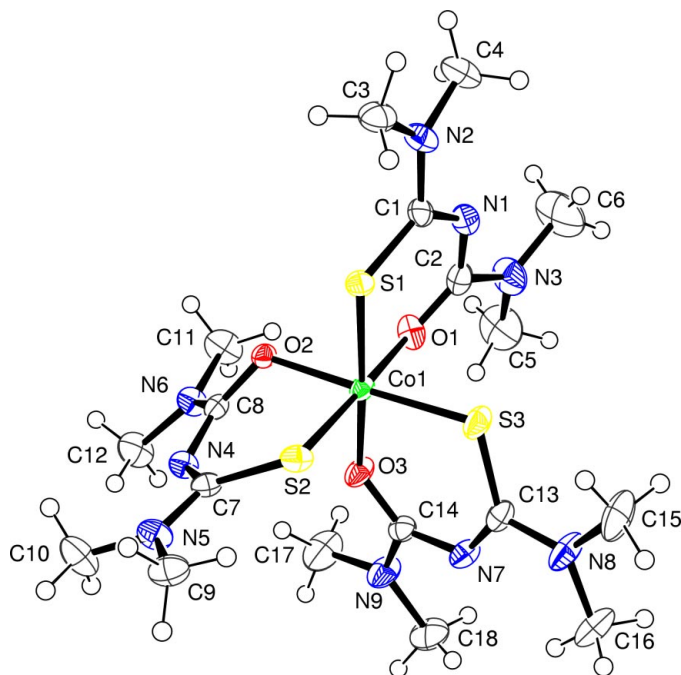
The title compound, (I), is the neutral homoleptic cobalt(III) complex of the anionic bidentate 1,1,5,5-tetramethyl-2-thiobiuretate ligand. The cobalt(III) ion is octahedral (Table 1) with an  $\text{S}_3\text{O}_3$  donor set. The sets of three S and three O atoms are each mutually *fac*, and their respective planes are almost parallel with a dihedral angle of  $1.73(4)^\circ$ . Within each of the three thiobiuretate ligands, the four atoms of the urea or thiourea groups are close to being coplanar, with the greatest deviation from the least-squares plane of  $0.0231(16) \text{ \AA}$  for atom C8. However, overall, the three thiobiuretate ligands all show significant deviations from planarity due to twisting about the central N atom; the dihedral angles between the three pairs of urea and thiourea least-squares planes are  $18.28(6)$ ,  $21.49(6)$  and  $7.78(6)^\circ$ . In all three ligands, the pattern of bond distances indicates that the formal negative charge is predominately localized on the S atom. The relatively long C–S and short C–O average bond lengths of  $1.745(4)$  and  $1.265(3) \text{ \AA}$  are consistent with mostly single- and double-bond character, respectively, and this bond localization is also reflected in the average C–N bond distances to the central N atom:  $1.318(3) \text{ \AA}$  in the (iso)thiourea group and  $1.349(2) \text{ \AA}$  in the urea group. In contrast, all the C–NMe<sub>2</sub> bond lengths are similar, with an average of  $1.353(2) \text{ \AA}$ .



(I)

## Experimental

The title compound, (I), was prepared by a variation of the method of Koenig *et al.* (1987). Dimethylcarbonyl chloride (1.08 g, 10 mmol)



**Figure 1**  
View of the molecule of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are represented by circles of arbitrary size.

and potassium thiocyanate (0.97 g, 10 mmol) in acetonitrile (40 ml) were heated at reflux for 2 h. The solution was allowed to cool to room temperature and excess 40% aqueous dimethylamine (3.4 ml, 30 mmol) was added with stirring, followed after 15 min by cobalt(II) acetate tetrahydrate (0.87 g, 3.5 mmol) and water (5 ml). After stirring for a further 15 min, the crude product was obtained as a green powder by precipitation with methanol (200 ml), isolation by filtration and washing sequentially with water, methanol and diethyl ether. Suitable crystals were grown by recrystallization from dichloromethane/methanol (yield 1.18 g, 61%). Spectroscopic analysis, IR (KBr disk,  $\nu$   $\text{cm}^{-1}$ ): 2916 (w), 1533 (s), 1473 (s), 1387 (s), 1355 (s), 1269 (w), 1198 (w), 1115 (m), 1027 (m), 729 (m), 461 (w);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , p.p.m.): 3.34 (br s, 9H), 3.14 (br s, 9H), 3.01 (s, 18H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , p.p.m.): 173.4, 165.6, 39.7 (2 peaks), 37.5, 36.1; analysis calculated for  $\text{C}_{18}\text{H}_{36}\text{CoN}_9\text{O}_3\text{S}_3$ : C 37.17, H 6.24, N 21.67, S 16.54%; found: C 36.90, H 6.34, N 21.49, S 16.24%.

#### Crystal data

$[\text{Co}(\text{C}_6\text{H}_{12}\text{N}_3\text{OS})_3]$   
 $M_r = 581.67$   
Monoclinic,  $P2_1/c$   
 $a = 13.1635$  (11) Å  
 $b = 12.1355$  (7) Å  
 $c = 18.0309$  (16) Å  
 $\beta = 106.665$  (7)°  
 $V = 2759.4$  (4) Å<sup>3</sup>  
 $Z = 4$

$D_x = 1.400$  Mg  $\text{m}^{-3}$   
Mo  $K\alpha$  radiation  
Cell parameters from 17 726 reflections  
 $\theta = 2.8$ – $30^\circ$   
 $\mu = 0.89$   $\text{mm}^{-1}$   
 $T = 150$  (2) K  
Plate, green  
 $0.55 \times 0.45 \times 0.10$  mm

#### Data collection

Stoe IPDS-II area-detector diffractometer  
 $\varphi$  and  $\omega$  scans  
Absorption correction: numerical (*X-SHAPE*; Stoe & Cie, 2001)  
 $T_{\min} = 0.533$ ,  $T_{\max} = 0.820$   
28 286 measured reflections

8038 independent reflections  
5023 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.060$   
 $\theta_{\max} = 30.0^\circ$   
 $h = -18 \rightarrow 18$   
 $k = -14 \rightarrow 17$   
 $l = -25 \rightarrow 25$

#### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.033$   
 $wR(F^2) = 0.070$   
 $S = 0.80$   
8038 reflections  
319 parameters

H-atom parameters constrained  
 $w = 1/[\sigma^2(F_o^2) + (0.0316P)^2]$   
where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.002$   
 $\Delta\rho_{\max} = 0.38$  e Å<sup>-3</sup>  
 $\Delta\rho_{\min} = -0.53$  e Å<sup>-3</sup>

**Table 1**

Selected geometric parameters (Å, °).

Co1—O1	1.9387 (13)	N1—C1	1.324 (2)
Co1—O2	1.9538 (11)	N1—C2	1.348 (3)
Co1—O3	1.9101 (12)	N2—C1	1.358 (2)
Co1—S1	2.2072 (5)	N3—C2	1.358 (2)
Co1—S2	2.2133 (6)	N4—C7	1.320 (2)
Co1—S3	2.2008 (5)	N4—C8	1.349 (2)
S1—C1	1.7358 (19)	N5—C7	1.351 (2)
S2—C7	1.7530 (18)	N6—C8	1.348 (2)
S3—C13	1.7455 (19)	N7—C13	1.311 (2)
O1—C2	1.262 (2)	N7—C14	1.349 (2)
O2—C8	1.272 (2)	N8—C13	1.355 (2)
O3—C14	1.261 (2)	N9—C14	1.350 (2)
S1—Co1—S2	88.196 (19)	O3—Co1—S1	176.93 (4)
S3—Co1—S1	87.97 (2)	C1—S1—Co1	107.22 (7)
S3—Co1—S2	90.40 (2)	C7—S2—Co1	105.50 (6)
O1—Co1—O2	86.80 (5)	C13—S3—Co1	107.50 (6)
O3—Co1—O1	85.72 (6)	C2—O1—Co1	127.72 (13)
O3—Co1—O2	86.54 (5)	C8—O2—Co1	119.05 (10)
O1—Co1—S1	93.47 (4)	C14—O3—Co1	131.79 (12)
O2—Co1—S2	90.50 (4)	C1—N1—C2	123.39 (16)
O3—Co1—S3	95.02 (4)	C7—N4—C8	122.94 (15)
O1—Co1—S2	176.83 (4)	C13—N7—C14	125.12 (16)
O2—Co1—S3	178.17 (4)		

All H atoms were initially located in a difference Fourier map. They were then constrained to an ideal geometry, with a C—H distance of 0.98 Å and  $U_{\text{iso}}(\text{H})$  values set at  $1.2U_{\text{eq}}(\text{C})$ , but each methyl group was allowed to rotate freely about its X—C bond.

Data collection: *X-AREA* (Stoe & Cie, 2001); cell refinement: *X-AREA*; data reduction: *X-RED* (Stoe & Cie, 2001); program(s) used to solve structure: *X-STEP32* (Stoe & Cie, 2001) and *WinGX* (Farrugia, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX*.

#### References

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