

Tris(*O*-methyl dithiocarbonato)cobalt(III)

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## Key indicators

Single-crystal X-ray study  
 $T = 296$  K  
Mean  $\sigma(\text{O}-\text{C}) = 0.004$  Å  
 $R$  factor = 0.029  
 $wR$  factor = 0.036  
Data-to-parameter ratio = 18.0For details of how these key indicators were  
automatically derived from the article, see  
<http://journals.iucr.org/e>.

In the title complex,  $[\text{Co}(\text{C}_2\text{H}_3\text{OS}_2)_3]$ , the Co atom is coordinated by six S atoms in a distorted octahedral arrangement. The six Co–S bond distances are in the range 2.262 (1)–2.275 (1) Å, with an average of 2.270 (2) Å.

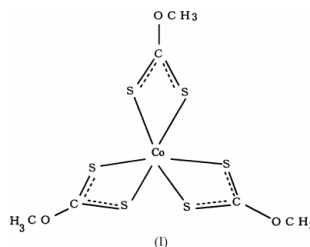
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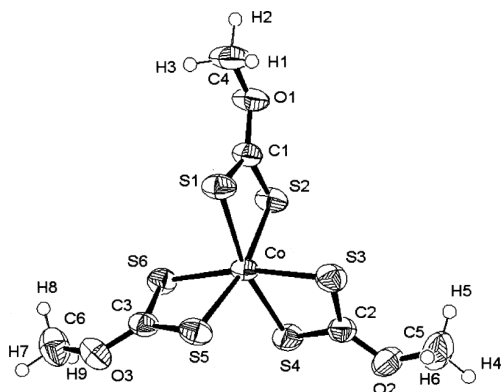
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## Comment

As part of a study of metal xanthates and dialkyl dithiophosphates (Ito, 2002*a,b,c*), the crystal and molecular structure of the title complex, (I), has been determined. A displacement ellipsoid plot of (I) is shown in Fig. 1. The average Co–S distance of 2.270 (2) Å is 0.052 (7) Å shorter than that in tris(*O,O'*-dimethyldithiophosphato)cobalt(III), (II), (McConnell & Schwartz, 1972), which shows that the Co–S bonds in (I) are stronger than those in (II). On the other hand, distortions of the S atoms around the Co atom from an octahedral coordination in (I) are larger than those in (II). For example, average S–Co–S chelate angles in (I) and (II) are 76.7 (1)° and 84.1 (1)°, respectively. A similar trend was found between chromium methylxanthate, (III) (Ito, 2002*c*), and chromium dimethyldithiophosphate (Ito, 2002*b*).



The structure of (I) is isostructural with those of chromium methylxanthate (III) and iron methylxanthate (IV) (Ito, 2002*a*). The structures of the xanthate ligands in the three complexes are very similar. Average S–C, S<sub>2</sub>C–O and O–CH<sub>3</sub> bond distances of 1.684 (3), 1.316 (3) and 1.450 (5) Å, respectively, in (I) are in agreement with the corresponding distances in (III) and (IV), within standard uncertainties. Significant differences between the three structures are found in the metal–S distances. The average Co–S, Fe–S and Cr–S distances are 2.270 (2), 2.307 (3) and 2.397 (2) Å, respectively. The components along the Co–S bonds of the anisotropic displacement parameters of the six S atoms are systematically larger than those of the Co atom by an average  $\Delta U$  of 0.0027 (4) Å<sup>2</sup>. Similar differences were also observed for the chromium and iron analogues, (III) and (IV), with average  $\Delta U$ 's for (III) and (IV) of 0.0017 (7) and 0.0026 (4) Å<sup>2</sup>, respectively.



**Figure 1**  
ORTEP (Burnett & Johnson, 1996) drawing of the title cobalt methylxanthate complex. Displacement ellipsoids are drawn at the 50% probability level.

## Experimental

Sodium methylxanthate (0.5 g) and hexaamminecobalt(III) chloride (1.0 g) were each dissolved in 30 ml pure water, and a powder of (I) was precipitated by combining the two solutions. Recrystallization from an ether solution at 278 K gave black plate-shaped crystals of (I).

### Crystal data

$[\text{Co}(\text{C}_2\text{H}_3\text{OS}_2)_3]$	$D_x = 1.803 \text{ Mg m}^{-3}$
$M_r = 380.48$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 25 reflections
$a = 9.552 (1) \text{ \AA}$	$\theta = 16.2\text{--}16.5^\circ$
$b = 13.461 (1) \text{ \AA}$	$\mu = 2.10 \text{ mm}^{-1}$
$c = 11.357 (1) \text{ \AA}$	$T = 296.1 \text{ K}$
$\beta = 106.235 (7)^\circ$	Plate, black
$V = 1402.1 (2) \text{ \AA}^3$	$0.60 \times 0.40 \times 0.25 \text{ mm}$
$Z = 4$	

### Data collection

Rigaku AFC-5S diffractometer	$R_{\text{int}} = 0.013$
$\omega$ - $2\theta$ scans	$\theta_{\text{max}} = 27.5^\circ$
Absorption correction: $\psi$ scan	$h = 0 \rightarrow 12$
(North <i>et al.</i> , 1968)	$k = 0 \rightarrow 17$
$T_{\text{min}} = 0.379$ , $T_{\text{max}} = 0.591$	$l = -14 \rightarrow 14$
3550 measured reflections	3 standard reflections
3224 independent reflections	every 150 reflections
2629 reflections with $I > 3\sigma(I)$	intensity decay: 0.6%

### Refinement

Refinement on $F$	$w = 1/\sigma^2(F_o)$
$R = 0.029$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$wR = 0.036$	$\Delta\rho_{\text{max}} = 0.41 \text{ e \AA}^{-3}$
$S = 1.66$	$\Delta\rho_{\text{min}} = -0.58 \text{ e \AA}^{-3}$
2629 reflections	Extinction correction: Larson
146 parameters	(1970)
H-atom parameters constrained	Extinction coefficient: 125.9 (9)

**Table 1**

Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ).

Co—S1	2.2746 (7)	S4—C2	1.690 (3)
Co—S2	2.2688 (7)	S5—C3	1.686 (3)
Co—S3	2.2623 (8)	S6—C3	1.683 (3)
Co—S4	2.2731 (7)	O1—C1	1.321 (3)
Co—S5	2.2742 (7)	O1—C4	1.446 (3)
Co—S6	2.2668 (7)	O2—C2	1.310 (3)
S1—C1	1.682 (3)	O2—C5	1.459 (4)
S2—C1	1.684 (3)	O3—C3	1.317 (3)
S3—C2	1.682 (3)	O3—C6	1.446 (3)
S1—Co—S2	76.69 (3)	S2—Co—S6	94.29 (3)
S1—Co—S3	93.40 (3)	S3—Co—S4	76.71 (3)
S1—Co—S4	166.57 (3)	S3—Co—S5	95.05 (3)
S1—Co—S5	94.38 (3)	S3—Co—S6	167.74 (3)
S1—Co—S6	96.20 (3)	S4—Co—S5	95.52 (3)
S2—Co—S3	95.33 (3)	S4—Co—S6	94.90 (3)
S2—Co—S4	94.97 (3)	S5—Co—S6	76.66 (3)
S2—Co—S5	166.68 (3)		

H atoms were placed in geometrically calculated positions (C—H 0.95  $\text{\AA}$ ) and allowed to ride on their parent atoms, with  $U_{\text{iso}}$  parameters equal to 1.2 times  $U_{\text{eq}}$  of the parent atom.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *CrystalStructure* (Molecular Structure Corporation & Rigaku, 2002); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *CrystalStructure*; molecular graphics: *ORTEP* (Burnett & Johnson, 1996); software used to prepare material for publication: *CrystalStructure*.

## References

- Altomare, A., Cascarano, G., Giacovazzo, C., Guagliardi, A., Burla, M. C., Polidori, G. & Camalli, M. (1994). *J. Appl. Cryst.* **27**, 435.
- Burnett, M. N. & Johnson, C. K. (1996). *ORTEP*. Report ORNL-6895. Oak Ridge National Laboratory, Tennessee, USA.
- Ito, T. (2002a). *Acta Cryst.* **E58**, m265–m266.
- Ito, T. (2002b). *Acta Cryst.* **E58**, m449–m450.
- Ito, T. (2002c). *Acta Cryst.* **E58**, m517–m518.
- Larson, A. C. (1970). *Crystallographic Computing*, edited by F. R. Ahmed, S. R. Hall & C. P. Huber, pp. 291–294. Copenhagen: Munksgaard.
- McConnell, J. F. & Schwartz, A. (1972). *Acta Cryst.* **B28**, 1546–1550.
- Molecular Structure Corporation (1988). *MSC/AFC Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
- Molecular Structure Corporation & Rigaku (2002). *CrystalStructure*. Version 3.00. MSC, 9009 New Trails Drive The Woodlands, TX 77381–5209, USA, and Rigaku Corporation, Akishima, Tokyo 196–8666, Japan.
- North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–359.