Tetsuzo Ito

Department of Applied Chemistry, Kanagawa Institute of Technology, Atsugi, Kanagawa 243-0292, Japan

Correspondence e-mail: ito@chem.kanagawa-it.ac.jp

Key indicators

Single-crystal X-ray study
$T = 295$ K
Mean σ(O–C) = 0.004 Å
R factor = 0.026
wR factor = 0.034
Data-to-parameter ratio = 17.0

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

Iron methylxanthate

The title complex, tris(O-methyldithiocarbonato)iron(III), [Fe(S$_2$COCH$_3$)$_3$], has an approximate threefold rotation axis passing through the Fe atom. The Fe atom is coordinated by six S atoms in a distorted octahedral arrangement. The six Fe—S distances range from 2.299 (1) to 2.319 (1) Å, with an average of 2.307 (3) Å, showing that the Fe atom is in a low-spin state with short Fe—S distances.
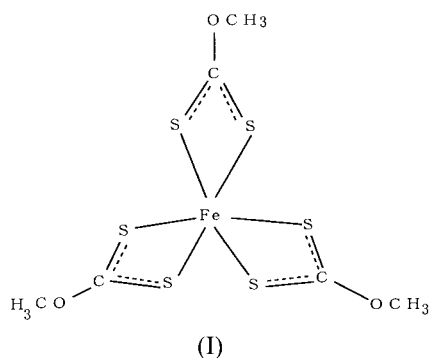
Comment

As part of the study of metal xanthates, M(S$_2$COR)$_n$, where M = metal and R = alkyl, we report here the crystal and molecular structure of iron methylxanthate [abbreviated here as Fe(MeX)$_3$], (I).

(I)

An *ORTEP*II drawing (Johnson, 1976) of Fe(MeX)$_3$ with the atomic numbering scheme is shown in Fig. 1. Related tris(dithiocarbamato)iron(III) complexes, [Fe(S$_2$CNR_2)$_3$], are known to show a spin equilibrium in the solid state, and the Fe—S distance varies between about 2.30 Å in the low-spin state and about 2.45 Å in the high-spin state (Chandrasekhar & Bürgi, 1984). The average Fe—S distance of 2.307 (3) Å observed in Fe(MeX)$_3$ shows that the Fe atom is in a low-spin state. The components along the Fe—S bonds of the anisotropic displacement parameters of the six S atoms are systematically larger than that of the Fe atom by an average ΔU of 0.0026 (4) Å^2, which also shows that the Fe atom is in spin equilibrium among the low-spin states (Chandrasekhar & Bürgi, 1984). The average S$_2$C—O distance of 1.317 (3) Å is significantly shorter than the average O—CH$_3$ distance of 1.445 (4) Å, showing that the S$_2$C—O bond has partial double-bond character.

The molecular structure of Fe(MeX)$_3$ is very similar to that of iron ethylxanthate, Fe(EtX)$_3$, except for the different terminal alkyl groups (Hoskins & Kelly, 1970). The Fe(EtX)$_3$ molecule has a crystallographic threefold rotation symmetry, and the Fe—S distances are 2.308 (3) and 2.326 (3) Å.

Experimental

1.0 g of potassium methylxanthate and 0.7 g of iron(III) nitrate were each dissolved in 10 ml of pure water, and Fe(MeX)$_3$ powder was precipitated by combining the two solutions. Recrystallization from an ether solution at room temperature gave black polyhedral crystals.

Crystal data

[Fe(C$_2$H$_3$OS$_2$)$_3$]	$D_x = 1.773$ Mg m^{-3}
$M_r = 377.40$	Mo Kα radiation
Monoclinic, $P2_1/n$	Cell parameters from 25
$a = 11.329$ (1) Å	reflections
$b = 13.595$ (2) Å	$\theta = 16.2–16.5°$
$c = 9.565$ (1) Å	$\mu = 1.94$ mm^{-1}
$\beta = 106.32$ (1)°	$T = 295$ K
$V = 1413.8$ (3) Å^3	Polyhedron, black
$Z = 4$	$0.47 \times 0.42 \times 0.42$ mm

Data collection

Rigaku AFC-5S diffractometer	$R_{int} = 0.031$
$\omega/2\theta$ scans	$\theta_{max} = 27.5°$
Absorption correction: ψ scan	$h = -14 \rightarrow 14$
(Molecular Structure Corpora-	$k = 0 \rightarrow 17$
tion, 1985)	$l = 0 \rightarrow 12$
$T_{min} = 0.418$, $T_{max} = 0.443$	3 standard reflections
3585 measured reflections	every 150 reflections
3249 independent reflections	intensity decay: 0.4%
2467 reflections with $I > 3\sigma(I)$	

Refinement

Refinement on F	H-atom parameters constrained
$R = 0.026$	$w = 1/\sigma^2(F)$
$wR = 0.034$	$(\Delta/\sigma)_{max} = 0.002$
$S = 1.42$	$\Delta\rho_{max} = 0.23$ e Å^{-3}
2467 reflections	$\Delta\rho_{min} = -0.29$ e Å^{-3}
145 parameters	

Table 1
Selected geometric parameters (Å, °).

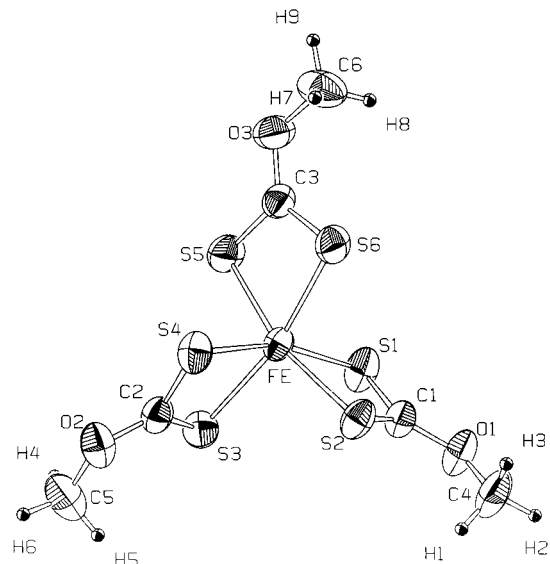| Fe—S1	2.306 (1)	Fe—S4	2.308 (1)
Fe—S2	2.319 (1)	Fe—S5	2.301 (1)
Fe—S3	2.307 (1)	Fe—S6	2.299 (1)
S1—Fe—S2	75.56 (3)	S2—Fe—S6	92.98 (3)
S1—Fe—S3	93.46 (3)	S3—Fe—S4	75.84 (3)
S1—Fe—S4	163.94 (3)	S3—Fe—S5	94.87 (3)
S1—Fe—S5	95.32 (3)	S3—Fe—S6	166.95 (3)
S1—Fe—S6	96.73 (3)	S4—Fe—S5	97.48 (3)
S2—Fe—S3	97.46 (3)	S4—Fe—S6	95.74 (3)
S2—Fe—S4	93.73 (3)	S5—Fe—S6	76.11 (3)
S2—Fe—S5	165.04 (3)		

Figure 1
*ORTEP*II (Johnson, 1976) drawing of the iron methylxanthate complex. Displacement ellipsoids are drawn at the 50% probability level.

H atoms were placed in geometrically calculated positions and made to ride on their parent atoms with U_{iso} parameters equal to 1.2 times the U_{eq} parameters of their parent atoms.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1985); program(s) used to solve structure: *MITHRIL* (Gilmore, 1984); program(s) used to refine structure: *TEXSAN*; molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *TEXSAN*.

References

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