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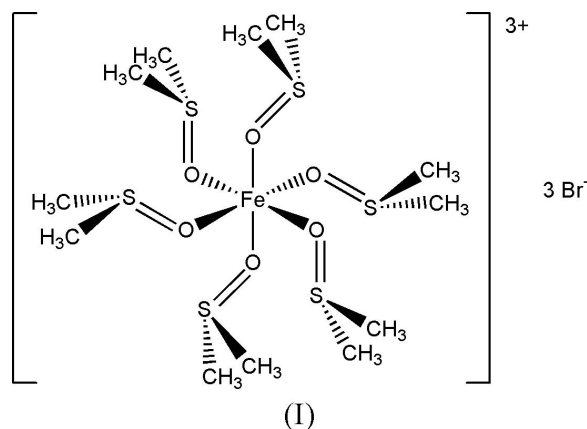
Key indicators

Single-crystal X-ray study
 $T = 294$ K
Mean $\sigma(S-C) = 0.003$ Å
 R factor = 0.026
 wR factor = 0.067
Data-to-parameter ratio = 19.1For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.Hexakis(dimethyl sulfoxide- κ O)iron(III)
tribromide

The title compound, $[\text{Fe}\{\text{OS}(\text{CH}_3)_2\}_6]\text{Br}_3$, is isostructural with $[\text{Fe}\{\text{OS}(\text{CH}_3)_2\}_6](\text{NO}_3)_3$ [Tzou, Mullaney, Normand & Chang (1995), *Acta Cryst.* C51, 2249–2252]. The Fe^{III} centre in the cation occupies a crystallographic $\bar{3}$ site and has a distorted octahedral coordination, with an $\text{Fe}-\text{O}$ distance of $2.000(2)$ Å and $\text{O}-\text{Fe}-\text{O}$ angles of $92.01(7)$ and $87.99(7)^\circ$.

Comment

The structure of the title compound, (I), comprises discrete $[\text{Fe}(\text{DMSO})_6]^{3+}$ [DMSO = $(\text{CH}_3)_2\text{SO}$, dimethyl sulfoxide] cations and bromide anions. The closest $\text{Fe}\cdots\text{Br1}$ contact is $5.525(3)$ Å, indicating that there are no significant interactions between the Fe and Br atoms (Fig. 1). The $\text{Fe}-\text{O}$ distance of $2.000(2)$ Å differs significantly from the value reported for the nitrate analogue at 2.020 Å (Tzou *et al.*, 1995), but compares well with those of *trans*- $[\text{FeCl}_2(\text{DMSO})_4][\text{FeCl}_4]$ at 2.006 Å (Bennett *et al.*, 1967) and $[\text{FeCl}(\text{DMSO})_5][\text{Fe}_2\text{Cl}_6\text{O}]$ at 1.998 Å (Ponomarev *et al.*, 1984). As expected, the observed $\text{Fe}-\text{O}$ distance is shorter than the distances found in the $[\text{Fe}(\text{DMSO})_6]^{2+}$ cation, which have an average of $2.128(3)$ Å (Müller *et al.*, 1989), owing to the higher oxidation state in the former compound.



The coordination polyhedron around the Fe atom is a distorted octahedron flattened in the direction of the threefold axis with the two axial O_3 faces $[\text{O1}, \text{O1}B(-y, x - y, z), \text{O1}D(-x + y, -x, z)]$ and $[\text{O1A}(-x, -y, -z), \text{O1}C(y, -x + y, -z)]$ and $[\text{O1E}(x - y, x, -z)]$ having longer [$2.878(3)$ Å] $\text{O}\cdots\text{O}$ than the remaining edges in the equatorial region [$2.778(3)$ Å]. The $\text{S1}-\text{O1}$ distance of $1.543(2)$ Å clearly shows the loss of $\text{S}=\text{O}$ double-bond character upon coordination *via* the O atom. The $\text{S}-\text{O}$ vector lies nearly perpendicular to the O_3 faces (angle between the $\text{S}-\text{O}$ vector and the

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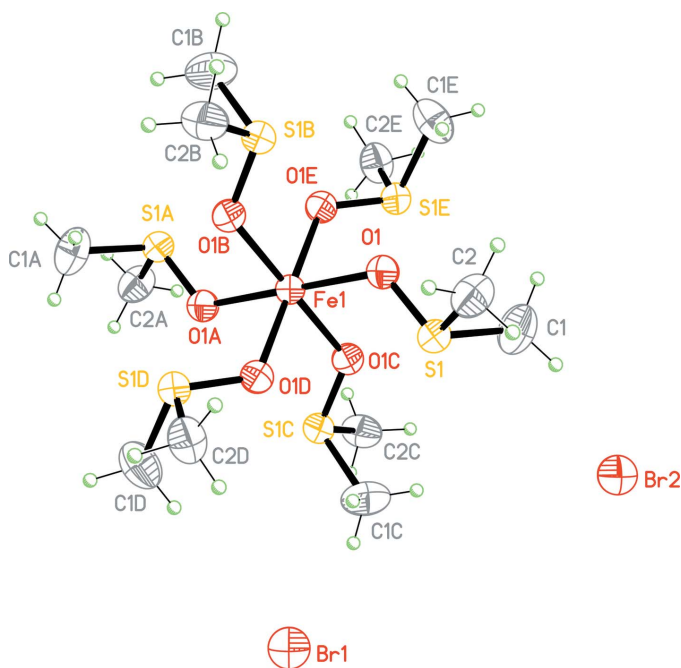


Figure 1
The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are shown at the 40% probability level.

vector normal to the O_3 plane: 2.8°). As found in the nitrate analogues of Fe (Tzou *et al.*, 1995) and Cr (Öhrström & Svensson, 2000), the bromide anion Br1 resides on a site of 3 symmetry, and Br2 resides on a site of $\bar{3}$ symmetry. This structure, however, does not have the disorder problems associated with one of the nitrate anions in the aforementioned analogues. There are two Br1 and one Br2 anions for each cation.

Experimental

Anhydrous iron(II) bromide (0.35 g, 1.62 mmol) was dissolved in DMSO (10 ml) while stirring with a magnetic bar. Air oxidation to iron(III) resulted in a yellow solution, which was stirred overnight. The reaction mixture was then filtered and left standing for the DMSO to evaporate, when yellow crystals of (I) were obtained [yield: 0.53 g, 43%; m.p. 436–437 K (decomposition)]. IR (CHCl_3): 2986, 2918, 2466, 1624, 1493, 1434, 1414, 1403, 1309, 1289, 1237, 1053, 1014, 984, 948, 925, 891 cm^{-1} ; UV–Vis 415, 291, 245 nm.

Crystal data

$[\text{Fe}(\text{C}_2\text{H}_6\text{OS})_6] \cdot 3\text{Br}^-$
 $M_r = 764.35$
 Hexagonal, $R\bar{3}$
 $a = 10.7528(7) \text{ \AA}$
 $c = 22.281(3) \text{ \AA}$
 $V = 2231.0(4) \text{ \AA}^3$
 $Z = 3$
 $D_x = 1.707 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation
 Cell parameters from 2896 reflections
 $\theta = 2.4\text{--}24.9^\circ$
 $\mu = 4.98 \text{ mm}^{-1}$
 $T = 294(2) \text{ K}$
 Prism, yellow
 $0.25 \times 0.25 \times 0.22 \text{ mm}$

Data collection

Bruker SMART APEX CCD diffractometer
 ω scans

Absorption correction: analytical (Bruker, 1999)
 $T_{\text{min}} = 0.339$, $T_{\text{max}} = 0.414$
 6099 measured reflections

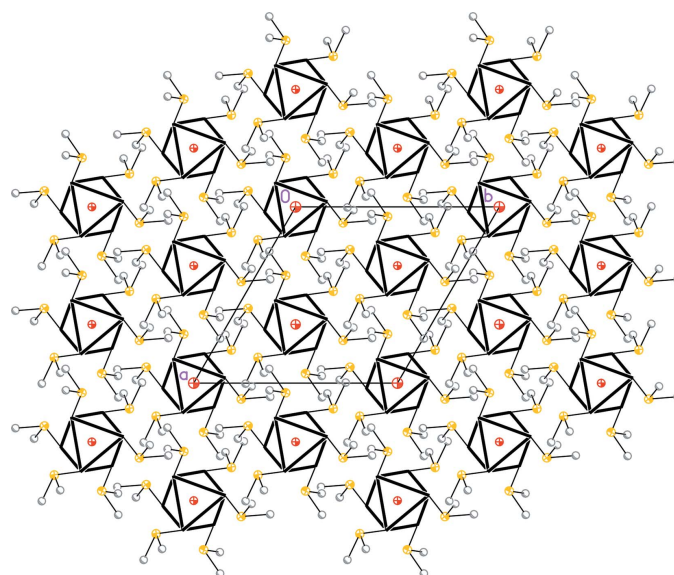


Figure 2
Crystal packing diagram of (I), viewed along the c axis. Fe, S and C atoms are depicted as ellipsoids, and the O atoms define the polyhedra around Fe.

879 independent reflections
 702 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.044$
 $\theta_{\text{max}} = 25.0^\circ$

$h = -12 \rightarrow 12$
 $k = -12 \rightarrow 12$
 $l = -26 \rightarrow 26$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.026$
 $wR(F^2) = 0.067$
 $S = 0.99$
 879 reflections
 46 parameters

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.037P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.27 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.17 \text{ e \AA}^{-3}$

The positional parameters of the H atoms were calculated geometrically, and they were refined as riding, with a fixed $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ and $\text{C}—\text{H} = 0.96 \text{ \AA}$.

Data collection: *SMART* (Bruker, 1999); cell refinement: *SAINT-Plus* (Bruker, 1999); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXTL* (Bruker, 1999); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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