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Hexakis(dimethyl sulfoxide-*O*)iron(III) Trinitrate

Ji-REN TZOU, MATTHEW MULLANEY AND
RICHARD E. NORMAN

*Department of Chemistry and Biochemistry,
Duquesne University, Pittsburgh, PA 15282, USA*

SHIH-CHI CHANG

*Department of Physics, Duquesne University,
Pittsburgh, PA 15282, USA*

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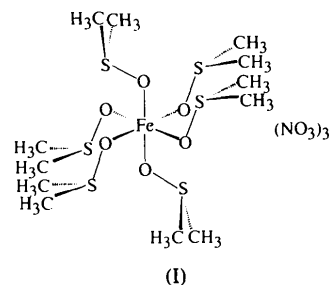
Abstract

The title compound, $[\text{Fe}(\text{C}_2\text{H}_5\text{OS})_6](\text{NO}_3)_3$, was prepared by dissolving an iron(III) complex of *N,N,N',N'*-tetrakis(2-benzimidazolylmethyl)-2-hydroxy-1,3-diaminopropane in a 20% *v/v* solution of dimethyl sulfoxide in acetonitrile for NMR studies. Crystals of hexakis(dimethyl sulfoxide-*O*)iron(III) trinitrate formed upon standing. The iron(III) atom sits on a site of $\bar{3}$ symmetry and has approximately octahedral coordination [the O—Fe—O angles are 87.40 (9) and 92.60 (9)°, and the Fe—O distance is 2.020 (2) Å]. One nitrate anion is centered on a site of 3 symmetry and the other is disordered about a site of $\bar{3}$ symmetry. The first nitrate anion appears twice per iron center, while the second appears only once.

Comment

Dimethyl sulfoxide (DMSO) is used widely as a solvent for metal complexes and is a known ligand for virtually all metal ions (Davies, 1981; Reynolds, 1970). During our studies of the reactions of iron(III) nitrate nonahydrate with *N,N,N',N'*-tetrakis(2-benzimidazolylmethyl)-2-hydroxy-1,3-diaminopropane (HPTB) (Tzou & Norman, unpublished results; Tzou, Chang & Norman, 1993), we isolated four crystals of hexakis(di-

methyl sulfoxide-*O*)iron(III) trinitrate, (I), the structure of which is reported herein. The preparation of this complex has been reported previously (Langford & Chung, 1968).



Only a few crystallographic determinations of the $[M(\text{DMSO})_6]^{n+}$ unit have been carried out, namely, $[\text{Hg}(\text{DMSO})_6](\text{ClO}_4)_2$ (Sandström & Persson, 1978), $[\text{Cd}(\text{DMSO})_6](\text{ClO}_4)_2$ (Sandström, 1978; Lyubeznova & Ponomarev, 1989), $[\text{Ru}(\text{DMSO})_6](\text{BF}_4)_2$ (Davies, Einstein, Farrell, James & McMillan, 1978), $[\text{Zn}(\text{DMSO})_6](\text{ClO}_4)_2$ (Persson, 1982), $[\text{Fe}(\text{DMSO})_6]^{2+}$ in a non-stoichiometric complex (Huang, Jian, Wang & Lu, 1985), $[\text{Fe}(\text{DMSO})_6][\text{Cl}_2\text{Fe}(\text{MoS}_4)]$ and $[\text{Fe}(\text{DMSO})_6][\text{Cl}_2\text{Fe}(\text{MoOS}_3)]$ (Müller *et al.*, 1989), $[\text{In}(\text{DMSO})_6](\text{ClO}_4)_3$ (Harrowfield, Skelton & White, 1990), $[\text{Mn}(\text{DMSO})_6][\text{W}_6\text{O}_{19}]$ and $[\text{Cu}(\text{DMSO})_6][\text{W}_6\text{O}_{19}]$ (Chen, Zhu & Gu, 1990), and $[\text{Cd}(\text{DMSO})_6][\text{Cd}(\text{DMSO})_6]_2 \cdot \text{C}_2\text{H}_5\text{OH}$ and $[\text{Cd}(\text{DMSO})_6][\text{CdI}_4]$ (Nieuwenhuyzen, Wen & Wilkins, 1992). The title complex contains an approximately octahedral iron(III) center located at a site of $\bar{3}$ symmetry (Fig. 1) and two distinct nitrate ion environments, one ordered at a site of 3 symmetry and the other disordered at a site of $\bar{3}$ symmetry. Similarly, in $[\text{In}(\text{DMSO})_6](\text{ClO}_4)_3$, the metal center is located at a site of $\bar{3}$ symmetry and the anions are disordered about sites of 3 and $\bar{3}$ symmetry (Harrowfield *et al.*, 1990). The Fe—O distance of 2.020 (2) Å compares well with the value of 2.006 (6) Å reported for *trans*- $[\text{FeCl}_2(\text{DMSO})_4][\text{FeCl}_4]$ (Bennett, Cotton & Weaver, 1967) and the distances reported for Fe—O not *trans* to Cl [2.003 (4)–2.032 (4) Å] in $[\text{FeCl}(\text{DMSO})_5][\text{Fe}_2\text{Cl}_6\text{O}]$ (Ponomarev, Arutyunyan & Atovmyan, 1984), and is, as expected, shorter than the distances of 2.132 (3), 2.102 (3) and 2.149 (3) Å found in $[\text{Fe}(\text{DMSO})_6]^{2+}$ (Müller *et al.*, 1989). The metrical parameters of DMSO are typical for O-bonded metal complexes (Davies, 1981; Sandström & Persson, 1978; Sandström, 1978; Davies *et al.*, 1978; Persson, 1982; Lyubeznova & Ponomarev, 1989; Harrowfield *et al.*, 1990; Müller *et al.*, 1989; Ponomarev *et al.*, 1984; Bennett *et al.*, 1967; Chen *et al.*, 1990; Nieuwenhuyzen *et al.*, 1992).

The ordered nitrate (located at a site of 3 symmetry) is unremarkable. However, the nitrate disordered at the site of $\bar{3}$ symmetry deserves comment. One possible interpretation of this disordered anion would be as a

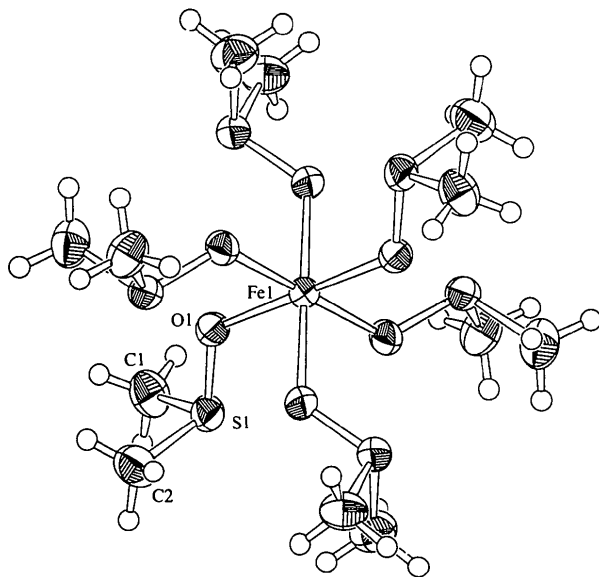


Fig. 1. Perspective view of [Fe(DMSO)₆]³⁺ showing 50% probability ellipsoids.

linear ion with sixfold disorder, such as cyanate or thiocyanate. To clarify the identity of the disordered anion, we measured several IR spectra. Ionic cyanates exhibit features near 2150 cm⁻¹ (2160, 2155 and 2135 cm⁻¹; Nakamoto, 1986) and ionic thiocyanates exhibit features near 2050 cm⁻¹ (Nakamoto, 1986). The title complex gives a weak IR feature at 2046 cm⁻¹ and no features near 2150 cm⁻¹. Thus, cyanate was ruled out. NaSCN gives a strong feature at 2074 cm⁻¹. A physical 'mixture' of the title compound and NaSCN (one milled between salt plates, the other on the exterior surface of one of the salt plates) gives a broader and more intense feature at 2057 cm⁻¹, while direct addition of NaSC to the title compound results in a color change (to brownish red) and gives an IR feature at 2048 cm⁻¹. This latter feature has a different band shape and intensity pattern than the original feature at 2046 cm⁻¹. We suggest that the weak feature at 2046 cm⁻¹ is a combination band of the ν_3 and ν_4 features of the nitrate ion. KNO₃ gives a similar weak feature at 2062 cm⁻¹. NaNO₃ is calculated to give this feature at 2097 cm⁻¹, while [Fe(NO₃)₃].9H₂O gives a feature at 2102 cm⁻¹. Thus, this nitrate combination band is cation sensitive.

There are additional reasons to exclude thiocyanate as a possible anion in this structure. The reaction of SCN⁻ with [Fe(DMSO)₆](NO₃)₃ has been studied (Langford & Chung, 1968) and an equilibrium constant of 1180 at 298 K was reported, suggesting that if SCN⁻ were present in our crystals, it would bind to Fe^{III}. To see if we could put SCN⁻ into the crystals on purpose, we mixed [Fe(NO₃)₃].9H₂O and NaSCN in DMSO (and DMSO/acetonitrile mixtures) in various ratios. We obtained red solutions, indicative of SCN⁻ binding to Fe^{III}, which is the classic test for the presence of SCN⁻.

It is interesting to note that we did obtain a small amount of yellow crystalline material from this reaction that gave an IR similar to the title compound. This material also gives a paramagnetically shifted ¹H NMR signal at 34 p.p.m. (referenced to the CD₃CN residual signal) for DMSO bound to iron(III). The original elemental analysis reported by Langford & Chung (1968) on [Fe(DMSO)₆](NO₃)₃ rules out the presence of SCN⁻; the calculated C content is 20.28% and the calculated C content for [Fe(DMSO)₆](NO₃)₂(SCN) is 22.09%, compared with the observed content of 19.89%. Finally, the chemistry to make SCN⁻ from DMSO, acetonitrile and nitrate is unprecedented. Thus, SCN⁻ is ruled out.

We maintain that the anion is a disordered nitrate 'rattling around' this site of $\bar{3}$ symmetry. The anion was modelled with an N atom located on the $\bar{3}$ site and an O atom (0.5 occupancy) at a distance of 1.261 (9) Å. The $\bar{3}$ operation generates a total of six O atoms about this N atom with a total ratio of 3:1 (O:N), appropriate for nitrate. However, the geometry is not appropriate, giving a nearly octahedral arrangement. We offer the following interpretation of this disorder. If this nitrate were six superimposed nitrates, from the position of atom O3 one would expect there to be two additional O atoms at a comparable distance from the N atom, but with a different angle dependence (being 120° to either side). Symmetry considerations of the site would then 'generate' five other positions for O3 and up to ten additional O atoms. This would give a total of 18 O atoms to account for three O atoms per N atom, so each would have 1/6 occupancy. However, attempts to model this explicitly failed. This model of the disorder assumes that the ordering of the second two O atoms must be relatively rigid. Instead, it is quite likely that the two additional O atoms trace out a toroid (which would arise from rotation about the N2—O3 bond), similar to the pattern of disorder typically observed for perchlorate ions. Thus, we suggest that an appropriate view for the disorder would be six well ordered O atoms of 1/6 occupancy and six corresponding toroids of 1/3 occupancy. These toroids, assuming that the initial six O-atom positions lie at the apices of a perfect octahedron, intersect at 24 points on the surface of the sphere in which the octahedron is inscribed. These intersections come in groups of three which are clustered within 0.3–0.4 Å of one another, which would give local maxima of electron density. We crudely modeled this by six O atoms at half occupancy, where each O-atom position models three different atom positions. In none of the 'six' orientations which give rise to this model is the nitrate anything other than planar.

Experimental

0.0396 g of [Fe(NO₃)₃].9H₂O was added to a solution of 0.0300 g of *N,N,N',N'*-tetrakis(2-benzimidazolylmethyl)-2-hydroxy-1,3-diaminopropane (HPTB) in 10 ml of 2-propanol.

From the resulting yellow–orange solution, a pale yellow–orange precipitate formed in about 1 min. The precipitate was filtered, washed with 2-propanol and dried *in vacuo* for several hours. Some of the precipitate was dissolved for ^1H NMR studies in 0.5 ml of 20% *v/v* d_6 -DMSO in d_3 -acetonitrile. After a period of 28 d, four irregular yellow crystals were noted and removed for structural studies. Alternatively, the compound can be prepared following the method of Langford & Chung (1968). However, crystals initially formed by this method, *i.e.* heating $[\text{Fe}(\text{NO}_3)_3]\cdot 9\text{H}_2\text{O}$ in DMSO, gave inconsistent results. Upon standing for extended periods of time (several weeks), crystals of the title complex are obtained.

Crystal data

$[\text{Fe}(\text{C}_2\text{H}_6\text{OS})_6](\text{NO}_3)_3$	Mo $K\alpha$ radiation
$M_r = 710.64$	$\lambda = 0.7107 \text{ \AA}$
Trigonal	Cell parameters from 24
$R\bar{3}$	reflections
$a = 11.518 (1) \text{ \AA}$	$\theta = 26.43\text{--}29.50^\circ$
$c = 19.966 (4) \text{ \AA}$	$\mu = 0.947 \text{ mm}^{-1}$
$V = 2293.8 (5) \text{ \AA}^3$	$T = 294 \text{ K}$
$Z = 3$	Irregular
$D_x = 1.543 \text{ Mg m}^{-3}$	$0.55 \times 0.40 \times 0.30 \text{ mm}$
	Pale yellow

Data collection

Rigaku AFC-7R diffractometer	1412 observed reflections
$\omega/2\theta$ scans	$[I > 3\sigma(I)]$
Absorption correction:	$R_{\text{int}} = 0.0282$
ψ scan (Molecular Structure Corporation, 1988)	$\theta_{\text{max}} = 32.48^\circ$
$T_{\text{min}} = 0.909$, $T_{\text{max}} = 1.000$	$h = 0 \rightarrow 15$
2017 measured reflections	$k = -15 \rightarrow 15$
1854 independent reflections	$l = -15 \rightarrow 15$
	3 standard reflections
	monitored every 150
	reflections
	intensity decay: 0.03%

Refinement

Refinement on F	$\Delta\rho_{\text{max}} = 0.593 \text{ e \AA}^{-3}$
$R = 0.0435$	$\Delta\rho_{\text{min}} = -0.547 \text{ e \AA}^{-3}$
$wR = 0.0540$	Extinction correction:
$S = 5.165$	Zachariasen (1968) type
1408 reflections	2, Gaussian isotropic
62 parameters	Extinction coefficient:
H-atom parameters not refined	2.8×10^{-7}
Weighting scheme based on measured e.s.d.'s	Atomic scattering factors
$(\Delta/\sigma)_{\text{max}} = 0.0781$	from <i>International Tables for X-ray Crystallography</i> (1974, Vol. IV)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)

$$U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	U_{eq}
Fe1	0	0	0	0.0313 (1)
S1	0.18212 (9)	-0.08524 (9)	0.07947 (5)	0.0395 (3)
O1	0.1585 (2)	0.0281 (2)	0.0557 (1)	0.0376 (6)
O2	0.1054 (3)	0.1066 (3)	0.2518 (2)	0.0775 (11)
O3	0.089 (1)	0.093 (1)	0.4652 (6)	0.1732 (6)
N1	0	0	0.2517 (3)	0.0490 (1)

N2	0	0	1/2	0.1010 (4)
C1	0.2724 (4)	-0.0204 (4)	0.1543 (2)	0.0537 (1)
C2	0.3128 (4)	-0.0705 (5)	0.0276 (2)	0.0594 (1)

Table 2. Selected geometric parameters (\AA , $^\circ$)

Fe1—O1	2.020 (2)	S1—C2	1.763 (4)
S1—O1	1.536 (2)	O2—N1	1.221 (3)
S1—C1	1.759 (4)	O3—N2	1.261 (9)
O1—Fe1—O1 ⁱ	92.60 (9)	Fe1—O1—S1	124.3 (1)
O1—Fe1—O1 ⁱⁱ	87.40 (9)	O2—N1—O2 ⁱ	120.00 (2)
O1—S1—C1	102.7 (2)	O3—N2—O3 ⁱⁱⁱ	92.6 (8)
O1—S1—C2	104.0 (2)	O3—N2—O3 ^{iv}	87.4 (8)
C1—S1—C2	99.4 (2)		

Symmetry codes: (i) $\frac{2}{3} + x, \frac{1}{3} + y, \frac{1}{3} + z$; (ii) $\frac{2}{3} - y, \frac{1}{3} + x - y, \frac{1}{3} + z$; (iii) $\frac{2}{3} - y, \frac{1}{3} + x - y, \frac{2}{3} + z$; (iv) $\frac{1}{3} - y, \frac{2}{3} + x - y, \frac{2}{3} + z$.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN PROCESS* (Molecular Structure Corporation, 1985). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *TEXSAN LS*. Software used to prepare material for publication: *TEXSAN FINISH*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BK1054). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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A μ -Oxo-bis[iron(III) porphyrin] Complex

WILLIAM P. SCHAEFER

*Division of Chemistry & Chemical Engineering,
The Beckman Institute, Mail Code 139-74,
California Institute of Technology, Pasadena,
California 91125, USA*

PAUL E. ELLIS, JAMES E. LYONS AND S. N. SHAIKH

*Research and Development Department, Sun Company
Inc., Marcus Hook, Pennsylvania 19061, USA*

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Abstract

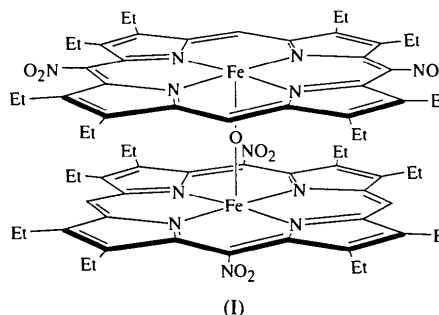
Partial nitration of iron(III) 2,3,7,8,12,13,17,18-octaethylporphyrin chloride [Fe^{III}(OEP)Cl] gives the μ -oxo-bis(5,15-dinitro) compound μ -oxo-bis[2,3,7,8,12,13,17,18-octaethyl-5,15-dinitroporphyrinato]iron(III)], [Fe₂(C₃₆H₄₂N₆O₄)₂O], which is similar to other μ -oxo-iron(III) porphyrin complexes but with less ruffling of the porphyrin structure. The porphyrin planes are not parallel [the angle between plane normals is 169 (2)°] and the Fe—O—Fe angle is 167.9 (3)°. As expected, the Fe atoms are significantly displaced from the porphyrin planes towards the bridging O atom: 0.46 Å for Fe1 and 0.49 Å for Fe2. The two porphyrin residues are eclipsed with respect to their C atoms, but the nitro groups are staggered by 90° from one residue to the other.

Comment

The unsubstituted μ -oxo-bis[iron(III) octaethylporphyrin] complex is inactive as a catalyst for the oxidation of alkanes, but incorporation of highly electron-withdrawing groups in the *meso* position leads

to a soluble active catalyst for these reactions. Both dinitro and tetranitro porphyrins give active μ -oxo-dimer catalysts, with the tetranitro compound being roughly twice as active. Both species show similar selectivities in the production of alcohols from alkanes.

The dinitro compound described here, (I), is prepared by nitration of Fe(OEP)Cl by NO₂ under N₂ in CH₂Cl₂ (Ellis, Lyons & Shaikh, 1994).



An ORTEPII (Johnson, 1976) drawing of the title molecule, (I), is shown in Fig. 1, tilted about 12° from its least-squares plane and showing the numbering system. The two porphyrin skeletons are nearly superimposed. This is the same conformation as observed in μ -oxo-bis(iron 5,15-dimethyloctaethylporphyrin) (Lay, Buchler, Kenny & Scheidt, 1986) and in μ -oxo-bis[octaethylporphyrinatoiron(III)] (Cheng, Hobbs, Debrunner, Erlebacher, Shelmutt & Scheidt, 1995), but it is different from the staggered geometry found in the tetraphenyl derivative (Hoffman, Collins, Day, Fleischer, Srivastava & Hoard, 1972; Strauss, Pawlik, Skowrya, Kennedy, Anderson, Spartalian & Dye, 1987) and the tetrakis(pentafluorophenyl) compound (Gold, Jayaraj, Doppelt, Fischer & Weiss, 1988). In all these compounds, the Fe^{III} atom is significantly out of porphyrin mean plane [by 0.49 and 0.50 Å (Strauss *et al.*, 1987), and 0.67 Å (Gold *et al.*, 1988)]. The present dinitro compound shows the least displacement [0.46 and 0.49 Å]. Additionally, the porphyrin skeleton is less ruffled in the dinitro compound than in others with bulkier substituents in the β positions (see Henling, Schaefer, Hodge, Hughes, Gray, Lyons & Ellis, 1993, for two examples). The maximum displacements from the porphyrin plane are 0.24 Å in one porphyrin (by atom C15), and 0.18 Å in the other (C41). Again, these distances are comparable to those observed in the dimethyloctaethyl compound (Lay *et al.*, 1986) and the tetrakis(pentafluorophenyl) compound (Gold *et al.*, 1988), but slightly smaller than the maximum of 0.30 Å found in the tetraphenyl compound (Strauss *et al.*, 1987). The octaethyl compound (Cheng *et al.*, 1995) is the least ruffled of all, with maximum displacements of only 0.12 and 0.15 Å from the mean porphyrin plane. Highly ruffled porphyrins show pyrrole C atoms as much as 1.2 Å out of plane.