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μ-Acetato-*O*:*O*′-μ-oxo-bis{[tris(2-pyridylmethyl)amine-*N*,*N*′,*N*″,*N*‴]iron(III)} Tris(trifluoromethanesulfonate) Dihydrate

RICHARD E. NORMAN,[a] NORMAN L. PETERSON[a] AND SHIH-CHI CHANG[b]

[a]*Department of Chemistry and Biochemistry, Duquesne University, Pittsburgh, PA 15282, USA, and* [b]*Department of Physics, Duquesne University, Pittsburgh, PA 15282, USA. E-mail: chnorman@alpha.nlu.edu*

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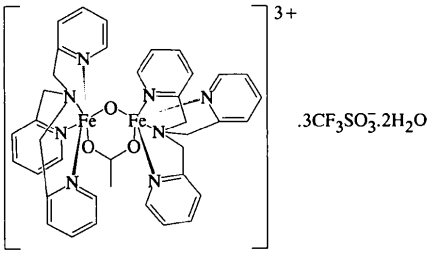
Abstract

The title compound, $[Fe_2O(C_2H_3O_2)(C_{18}H_{18}N_4)_2](CF_3O_3S)_3.2H_2O$, was isolated from a reaction designed to produce the sulfido-bridged analog. The metrical parameters for this complex are typical of μ-oxo-μ-carboxylato-diiron(III) complexes.

Comment

As the result of an attempt to synthesize a new class of diiron(III) complexes with a μ-sulfido-μ-carboxylato-diiron(III) core, the title complex, (I), was prepared and structurally characterized. Since the replacement of a μ-oxo ligand by a μ-sulfido ligand has been little studied (Mukherjee, Stack & Holm, 1988), we were not entirely sure what spectroscopic changes would accompany this replacement. To determine whether we had synthesized the desired sulfido-bridged species or the oxo-bridged species, we determined the structure.



(I)

The structures and spectral properties of several μ-oxo-μ-carboxylato-diiron(III) complexes with the TPA ligand [TPA is tris(2-pyridylmethyl)amine] have been previously reported (Norman, Yan, Que, Backes, Ling, Sanders-Loehr, Zhang & O'Connor, 1990; Norman, Holz, Ménage, O'Connor, Zhang & Que, 1990), including an acetate form, $[Fe_2(TPA)_2O(OAc)](ClO_4)_3.CH_3COCH_3.H_2O$. With μ-1,3-carboxylates, these diiron(III) complexes always have inequivalent iron sites and distinctly asymmetric oxo bridges, as does the title compound. The metrical parameters of the current complex are similar to those previously reported (typically falling within 3σ) and show the same patterns, *i.e.* lengthening of bonds *trans* to the oxo bridge, asymmetry of the coordination of the carboxylate, *etc.* The separation of the two Fe^{III} atoms is 3.271 (1) Å.

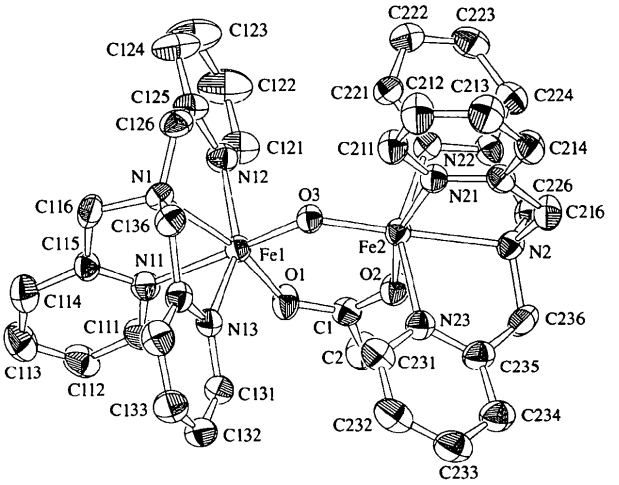


Fig. 1. Perspective drawing of the $[Fe_2(TPA)_2O(OAc)]^{3+}$ cation with displacement ellipsoids drawn at the 50% probability level. H atoms have been omitted.

Experimental

For the preparation of the title complex, tris[(2-pyridinium)-methyl]amine perchlorate (0.5917 g, 1.00 mmol) and triethylamine (0.630 ml, 4.50 mmol) were dissolved in 40 ml MeOH. $Fe(ClO_4)_3.10H_2O$ (0.5366 g, 1.00 mmol) was dissolved in 1–2 ml MeOH and this solution was added to the ligand solution. Anhydrous sodium acetate (0.0410 g, 0.500 mmol) was added, giving a brown–green solution. $Na_2S.9H_2O$ (0.1318 g, 0.549 mmol) was subsequently added giving a dark green solution. After several days, a green precipitate was noted. This precipitate was metathesized with excess $K(CF_3SO_3)$ yielding green crystals, one of which was selected for structure determination.

Crystal data

$[Fe_2O(C_2H_3O_2)(C_{18}H_{18}N_4)_2](CF_3O_3S)_3.2H_2O$	Mo $K\alpha$ radiation
M_r = 1250.71	λ = 0.71069 Å
Triclinic	Cell parameters from 25 reflections
$P\bar{1}$	θ = 12.28–14.82°
a = 13.576 (4) Å	μ = 0.772 mm^{-1}
b = 17.947 (3) Å	T = 293 (2) K
c = 12.262 (3) Å	Prism
α = 105.11 (2)°	0.75 × 0.20 × 0.15 mm
β = 114.19 (2)°	Green
γ = 83.55 (2)°	
V = 2630.9 (11) $Å^3$	
Z = 2	
D_x = 1.579 Mg m^{-3}	
D_m not measured	

Data collection

Rigaku AFC-7*R* diffractometer
$\omega/2\theta$ scans
Absorption correction:
ψ scan (Molecular Structure Corporation, 1985, 1992)
T_{min} = 0.83, T_{max} = 0.89
9508 measured reflections
9300 independent reflections
5467 reflections with $I > 2\sigma(I)$
R_{int} = 0.0245
θ_{max} = 25.02°
$h = 0 \rightarrow 16$
$k = -21 \rightarrow 21$
$l = -14 \rightarrow 12$
3 standard reflections
every 150 reflections
intensity decay: 4.09%

Refinement

Refinement on F^2
$R(F)$ = 0.0545
$wR(F^2)$ = 0.1653
S = 1.048
9300 reflections
604 parameters
H atoms riding
$w = 1/[\sigma^2(F_o^2) + (0.0431P)^2 + 0.3079P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.519 e Å^{-3}
$\Delta\rho_{min}$ = −0.391 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Fe1—O3	1.814 (3)	Fe2—N21	2.124 (3)
Fe1—O1	1.974 (3)	Fe2—N22	2.135 (4)
Fe1—N13	2.133 (4)	Fe2—N23	2.156 (4)
Fe1—N12	2.134 (4)	Fe2—N2	2.241 (3)
Fe1—N1	2.192 (3)	O1—C1	1.251 (5)
Fe1—N11	2.192 (4)	O2—C1	1.254 (5)
Fe2—O3	1.778 (3)	C1—C2	1.490 (6)
Fe2—O2	2.054 (3)		
O3—Fe1—O1	99.84 (12)	O3—Fe2—N23	105.13 (14)
O3—Fe1—N13	94.09 (13)	O3—Fe2—N2	177.96 (13)
O3—Fe1—N12	96.73 (14)	Fe2—O3—Fe1	131.26 (15)
O3—Fe1—N1	96.97 (13)	C1—O1—Fe1	133.5 (3)
O3—Fe2—O2	98.53 (13)	C1—O2—Fe2	132.2 (3)
O3—Fe2—N21	99.30 (13)	O1—C1—O2	124.5 (4)
O3—Fe2—N22	102.59 (14)		

During the course of refinement, it became obvious that one of the trifluoromethanesulfonate counterions was highly disordered. The contribution of the density of this trifluoromethanesulfonate ion and two water molecules was therefore subtracted from the measured structure factors using the *SQUEEZE* option (Spek, 1994) in *PLATON*95 (Spek, 1995). Subsequent refinement then converged with slightly lower R factors than when the trifluoromethanesulfonate ion was modeled with either a rigid model or when the atoms were allowed to move from chemically reasonable positions. There were no signifcant changes in the geometry of the diiron cation.

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, 1992). Program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993).

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Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: FG1185). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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