Aquabis(4-morpholinyldithiocarbamato)-iron(III) trifluoromethanesulfonate

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In the title compound, $[Fe(C_5H_8NOS_2)_2(H_2O)]CF_3SO_3$, the Fe atom has five-coordinate square-pyramidal stereochemistry, with the Fe atom 0.472 (1) Å above the plane of four S atoms and a water molecule O atom at the apex. The cation has m (C_s) symmetry, with the crystallographic mirror plane passing through the Fe, O and N atoms. One O atom of the anion forms a strong hydrogen bond with the coordinated water molecule $[O \cdots O = 2.642 (5)$ Å]. This is the first report of a cationic $[Fe(dithiocarbamate)_2L]^{n+}$ species.

Comment

Iron dithiocarbamate (dtc) complexes are of special interest as they have been shown to undergo thermal spin equilibria (Martin & White, 1968). There are applications for these compounds in new technologies, such as nanotechnology, where they can be used as nanomagnets for information storage or thermal switches for sensors. Five-coordinate iron–dtc complexes are few in comparison with the much larger number of tris-dtc complexes, $[Fe(dtc)_3]$. There are only a few examples of X-ray structure determinations for five-coordinate iron(III) bisdithiocarbamate complexes. All these are neutral complexes containing two dithiocarbamate (R_2dtc) moieties and one coordinated anion. They all have the formula $[Fe(R_2dtc)_2X]$, where R is an alkyl/aryl substituent and X = Cl (Hoskins et al., 1966; Mitra et al., 1979; Kettman et al., 1981), Br (Decurtins et al., 1983; Christidis et al., 1984), I (Healy et al., 1972; Etemadi et al., 1988), nitrosyl (Butcher & Sinn, 1980; Colapietro et al., 1967) or isothiocyanate (Raston et al., 1980). They are characterized by square-pyramidal geometry, formed by the two dithiocarbamates in an approximately square-planar arrangement and the X group occupying an apical position above the plane. In all but one example, the R group on dtc is a simple alkyl chain, usually ethyl or isopropyl, although in one case R_2dtc is a piperidine derivative (Kettman et al., 1981). Therefore, we were extremely surprised to identify the title complex, (I), as the first example of a stable salt with a similar five-coordinate geometry. This species is a 1:1 electrolyte in solution (acetonitrile or acetone).
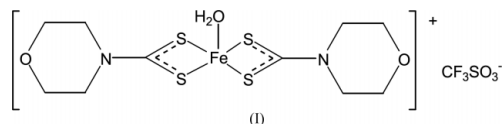
In the title compound, $[Fe(Mordtc)_2(H_2O)]CF_3SO_3$ (Mordtc = $C_5H_8NOS_2$), (I), the Fe atom has five-coordinate square-pyramidal stereochemistry, with the Fe atom 0.472 (1) Å above the plane of four S atoms and with a water molecule O atom at the apex. The cation has m (C_s) symmetry,

with the crystallographic mirror plane passing through the Fe, O and N atoms (Fig. 1). The water molecule forms hydrogen bonds to O3*b* (in its two alternative positions with 0.5 occupancy) of the trifluoromethanesulfonate anion and O1 of an adjacent cation (Table 2).

Compound (I) is formed by the removal of one dtc ligand from the tris-Mordtc complex, [Fe(Mordtc)$_3$], by treatment with silver trifluoromethanesulfonate. Formation of an intermediate four-coordinate complex, possibly [Fe(Mordtc)$_2$]$^+$, is believed to occur and it is this species which extracts moisture from the air during recrystallization from toluene, resulting in (I). The water molecule coordinated at the apex of the square pyramid can be exchanged for other ligands (Wu *et al.*, 2003).

Experimental

Fe(Mordtc)$_3$ (0.54 g, 1 mmol) was reacted with Ag(CF$_3$SO$_3$) (0.257 g, 1 mmol) in hot toluene (30 ml). A yellow precipitate of Ag(Mordtc) was produced and was filtered off immediately from the hot solution. The black filtrate was cooled very slowly to room temperature and left to stand overnight. Red–black single crystals were collected from the filtrate and dried in the air (yield 53%, 0.29 g). IR (KBr, cm^{-1}): $\nu_{(CH)}$ 2929 (*mw*), 2861 (*w*); $\nu_{(CN)}$ 1530 (*vs*); $\nu_{(CF)}$1267 (*vs*); $\nu_{(SO)}$ 1030 (*s*); $\nu_{(C=S)}$ 996 (*w*). UV/Vis; $\lambda_{(max)}$, nm ($\varepsilon = L$ mol^{-1} cm^{-1}): 441 nm (1.1 $\times$ 10^3), 616 nm (4.0 $\times$ 10^2) Microanalysis as C$_{11}$H$_{16}$F$_3$FeN$_2$O$_5$S$_5$, experimental: C 24.84, H 3.19, N 4.91%; theoretical: C 24,94, H 3.02, N 5.29%.

Crystal data

[Fe(C$_5$H$_8$NOS$_2$)$_2$(H$_2$O)]CF$_3$SO$_3$	Mo $K\alpha$ radiation
$M_r = 547.44$	Cell parameters from 7138
Orthorhombic, $Pnma$	reflections
$a = 18.929$ (6) Å	$\theta = 2.1$–26.1°
$b = 10.197$ (3) Å	$\mu = 1.23$ mm^{-1}
$c = 11.214$ (4) Å	$T = 168$ K
$V = 2164.5$ (12) Å^3	Needle, dark red
$Z = 4$	$0.50 \times 0.08 \times 0.08$ mm
$D_x = 1.68$ Mg m^{-3}	

Data collection

Bruker SMART CCD area-detector	1677 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{int} = 0.059$
Absorption correction: multi-scan	$\theta_{max} = 26.4°$
(*SADABS*; Bruker, 1997)	$h = -23 \rightarrow 23$
$T_{min} = 0.829$, $T_{max} = 0.906$	$k = -12 \rightarrow 8$
26 787 measured reflections	$l = -13 \rightarrow 13$
2316 independent reflections	

Refinement

Refinement on F^2	H-atom parameters not refined
$R[F^2 > 2\sigma(F^2)] = 0.042$	$w = 1/[\sigma^2(F_o^2) + (0.03F_o^2)^2]^{1/2}$
$wR(F^2) = 0.094$	$(\Delta/\sigma)_{max} = 0.018$
$S = 1.01$	$\Delta\rho_{max} = 0.94$ e Å^{-3}
2157 reflections	$\Delta\rho_{min} = -0.61$ e Å^{-3}
169 parameters	

Table 1
Selected geometric parameters (Å, °).

Fe—O3	2.013 (4)	Fe—S2	2.2870 (11)
Fe—S1	2.2849 (11)		
O3—Fe—S1	99.38 (9)	S1^i—Fe—S2	156.19 (5)
O3—Fe—S2	104.42 (9)	S1—Fe—S2	98.46 (4)
S1^i—Fe—S1	76.69 (4)	S2^i—Fe—S2	76.45 (4)

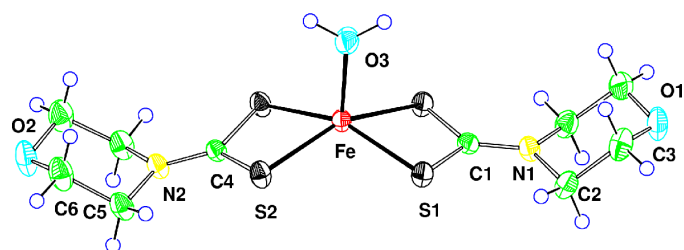Symmetry code: (i) $x, \frac{1}{2} - y, z$.

Figure 1
The cation of (I), with displacement ellipsoids at the 50% probability level. Atoms O1, N1, C1, Fe, O3, C4, N2 and O2 lie on a mirror plane.

Table 2
Hydrogen-bonding geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O3—H3$\cdots$O3*b*	0.93	1.76	2.642 (5)	158
O3—H3$\cdots$O3*b*^{i}	0.93	1.76	2.642 (5)	158
O3—H3'$\cdots$O1^{ii}	0.93	1.73	2.654 (5)	174

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

The trifluoromethanesulfonate anion C and S atoms lie on a mirror plane with O and F atoms disordered. This has been modelled in a staggered conformation using restraints to keep the geometry within acceptable limits. Water molecule H atoms were located in a difference map. H atoms bonded to C atoms were positioned geometrically and repositioned periodically during the refinement. C—H bond lengths were set at 0.95 Å, with U_{iso}(H) = 1.3U_{eq}(C). O—H bonds were set at 0.925 Å, with U_{iso}(H) = 1.5U_{eq}(O). The discrepancy between the numbers of independent and refined reflections is a result of all reflections with $F^2 > 0$ being included in the refinement.

Data collection: *SMART* (Bruker, 1999); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 2000) and *Xtal*3.7 *ADDREF* and *SORTRF* (Hall *et al.*, 2000); program(s) used to solve structure: *SIR*97 (Altomare *et al.*, 1994); program(s) used to refine structure: *Xtal*3.7 *CRYLSQ*; molecular graphics: *Xtal*3.7; software used to prepare material for publication: *Xtal*3.7 *BONDLA* and *CIFIO*.

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