

Ammonium heptanitrosyltrithiotetraferrate monohydrate

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Key indicators

Single-crystal X-ray study

T = 123 K

Mean $\sigma(\text{O}-\text{N}) = 0.003 \text{ \AA}$

R factor = 0.033

wR factor = 0.088

Data-to-parameter ratio = 11.8

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

The title compound, $(\text{NH}_4)[\text{Fe}_4\text{S}_3(\text{NO})_7]\cdot\text{H}_2\text{O}$, contains an Fe_4S_3 partial cubane core in which the apical iron is coordinated by one nitrosyl group and three S atoms above the plane of three Fe atoms. These three Fe atoms are in turn each coordinated by two S atoms and two nitrosyl groups. The axial O atoms hydrogen bond with the ammonium cation, creating a 'tight' ion-pair, consistent with the solubility of the salt in diethyl ether.

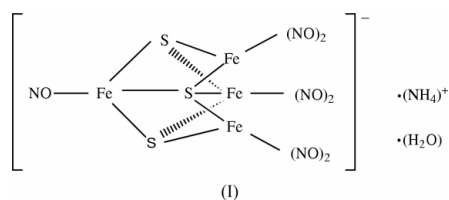
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Comment

Iron–sulfur-containing clusters are ubiquitous in nature, especially in electron-transfer proteins called ferredoxins (Frazzon & Dean, 2003). One important role for ferredoxins is to provide electrons to the enzyme nitrogenase, which is responsible for the reduction of dinitrogen to ammonia. This essential contribution to the global nitrogen cycle is achieved at a structurally unique iron–sulfur cluster called the FeMo cofactor (Christiansen *et al.*, 2001). This unique structure of the FeS-containing cluster of FeMo cofactor is able to achieve this kinetically challenging reaction under ambient conditions and thus has attracted significant interest (Howard & Rees, 1996). The classical Roussin's black salt anion contains an iron–sulfur cluster with geometrical similarities to the FeMo cofactor from nitrogenase. In particular, the $[\text{Fe}_4\text{S}_3(\text{NO})_7]^-$ contains the same structural unit as one half of the FeMo cofactor (Martin *et al.*, 2001).



Although the structure of $[\text{Fe}_4\text{S}_3(\text{NO})_7]^-$ has been reported previously (D'Addario *et al.*, 1993; Chu & Dahl, 1977; Johansson & Lipscomb, 1958; Glidewell *et al.*, 1990; Scott & Holm, 1993; Goh & Holm, 1998), the title compound is the first example of the ammonium salt of Roussin's black anion, (1). This salt is an interesting addition to the family of crystal structures because of the strong ion-pair formed by the cation and anion, resulting in good solubility in diethyl ether. The molecular structure of the title compound (Fig. 1) can be described as an Fe_4S_3 partial cubane in which the apical iron (Fe2) is coordinated by one nitrosyl group and three S atoms and has the formal oxidation state $\text{Fe}^+(d^7)$. The other three Fe atoms (Fe1, Fe3 and Fe4) are each coordinated by two S atoms and two nitrosyl groups and have a formal oxidation state

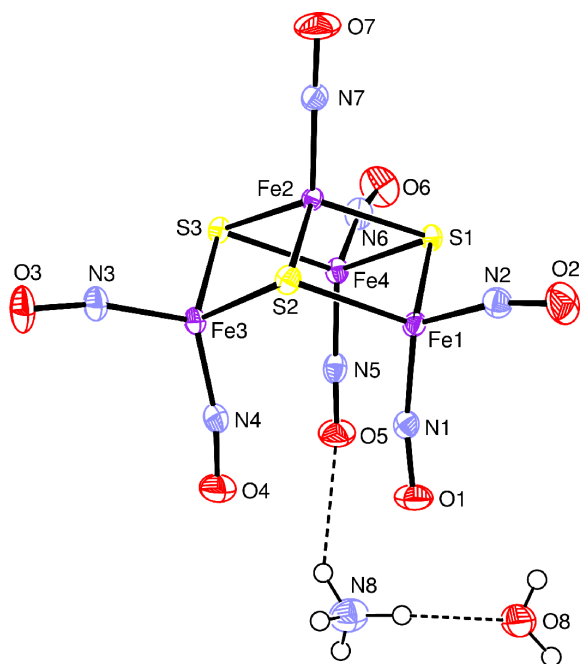


Figure 1
View of (I) (50% probability displacement ellipsoids). Hydrogen bonds are indicated by dashed lines.

$\text{Fe}^- (d^9)$ (Chu & Dahl, 1977). The complex crystallizes with one water molecule of hydration.

Experimental

$(\text{NH}_4)[\text{Fe}_4\text{S}_3(\text{NO})_7]\cdot\text{H}_2\text{O}$ was synthesized by a reported procedure (Martin *et al.*, 2001). A mixture of 25% ammonia solution (50 ml), 10% by weight ammonium sulfide solution (20 ml) and water (50 ml) was added to a stirred solution of sodium nitrite (0.232 mol, 18.01 g) in water (80 ml). The solution was heated to boiling and produced a bright red solution. $\text{Fe}(\text{SO}_4)\cdot 7\text{H}_2\text{O}$ (0.187 mol, 40.010 g) in water (320 ml) was added to this boiling mixture, resulting in an instantaneous color change to black. The solution was rapidly reheated to vigorous boiling and upon reaching boiling a distinct change in color from black to brown and formation of an orange precipitate was observed. Boiling was continued for 20 min, and during this time 25% ammonia solution (50 ml) was added in small portions. The hot solution was filtered. The filtrate was allowed to cool slowly to room temperature and was then cooled in an ice bath, resulting in deposition of a black solid. A second crop of material was obtained by dissolving the filter cake with diethyl ether (2 l). Filtration of the ether solution and then concentration *in vacuo* gave a black solid. Combination of both black solids together and recrystallization from hot water (about 343 K) gave black crystals (2.871 g, 24%) of the product.

Crystal data

$(\text{NH}_4)[\text{Fe}_4\text{S}_3(\text{NO})_7]\cdot\text{H}_2\text{O}$
 $M_r = 565.71$
 Triclinic, $P\bar{1}$
 $a = 9.4373$ (1) Å
 $b = 9.9388$ (1) Å
 $c = 10.1736$ (2) Å
 $\alpha = 117.1273$ (6)°
 $\beta = 101.3320$ (7)°
 $\gamma = 101.0689$ (10)°
 $V = 788.169$ (19) Å³

$Z = 2$
 $D_x = 2.384$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 11004 reflections
 $\theta = 3.8\text{--}25^\circ$
 $\mu = 4.05$ mm⁻¹
 $T = 123$ (2) K
 Prism, black
 0.12 × 0.10 × 0.08 mm

Data collection

Nonius KappaCCD diffractometer
 Thick-slice φ and ω scans
 Absorption correction: multi-scan (SORTAV; Blessing, 1997)
 $T_{\min} = 0.638$, $T_{\max} = 0.715$
 11004 measured reflections
 2741 independent reflections
 2682 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.034$
 $\theta_{\max} = 25.1^\circ$
 $h = -11 \rightarrow 11$
 $k = -11 \rightarrow 11$
 $l = -12 \rightarrow 12$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.033$
 $wR(F^2) = 0.088$
 $S = 1.13$
 2741 reflections
 232 parameters
 All H-atom parameters refined
 $w = 1/[\sigma^2(F_o^2) + (0.0614P)^2 + 0.3376P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.65$ e Å⁻³
 $\Delta\rho_{\min} = -1.12$ e Å⁻³

Table 1

Hydrogen-bonding geometry (Å, °).

$D\text{--}H\cdots A$	$D\text{--}H$	$H\cdots A$	$D\cdots A$	$D\text{--}H\cdots A$
$\text{N8--H3}\cdots\text{O8}$	0.89 (5)	2.00 (5)	2.879 (4)	168 (4)
$\text{N8--H4}\cdots\text{O5}$	0.85 (8)	2.51 (7)	3.237 (4)	144 (6)
$\text{N8--H4}\cdots\text{O4}$	0.85 (8)	2.72 (7)	3.290 (4)	126 (6)
$\text{N8--H3}\cdots\text{O1}$	0.89 (5)	2.80 (4)	3.059 (4)	99 (3)
$\text{N8--H4}\cdots\text{S3}^i$	0.85 (8)	3.01 (7)	3.470 (3)	116 (6)
$\text{N8--H5}\cdots\text{O8}^{ii}$	0.89 (5)	2.13 (5)	2.961 (4)	154 (4)
$\text{O8--H2}\cdots\text{O3}^{iii}$	0.83 (6)	2.41 (6)	3.026 (3)	131 (5)
$\text{O8--H1}\cdots\text{S1}^{iv}$	0.76 (7)	2.67 (7)	3.390 (3)	158 (6)
$\text{N8--H6}\cdots\text{O6}^v$	0.74 (7)	2.62 (7)	3.120 (4)	126 (6)
$\text{N8--H6}\cdots\text{S2}^{vi}$	0.74 (7)	3.01 (7)	3.610 (3)	139 (6)

Symmetry codes: (i) $-x, 1-y, 1-z$; (ii) $1-x, 2-y, 2-z$; (iii) $1+x, y, 1+z$; (iv) $1-x, 1-y, 1-z$; (v) $x, 1+y, 1+z$; (vi) $x, y, 1+z$.

H atoms were located in difference Fourier maps; their positions and U_{iso} values were refined. The deepest hole is located 0.98 Å from atom Fe2.

Data collection: COLLECT (Nonius, 1997–2002); cell refinement: HKL SCALEPACK (Otwinowski & Minor, 1997); data reduction: HKL DENZO (Otwinowski & Minor, 1997) and SCALEPACK; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: ORTEP-3 for Windows (Farrugia, 1997); software used to prepare material for publication: WinGX publication routines (Farrugia, 1999).

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