

Tetrakis(diethylenetriammonium) tris[hexacyanoferrate(II)] octahydrate

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Key indicators

Single-crystal X-ray study
 T = 293 K
 Mean $\sigma(\text{C}-\text{C}) = 0.002 \text{ \AA}$
 R factor = 0.026
 wR factor = 0.073
 Data-to-parameter ratio = 14.2

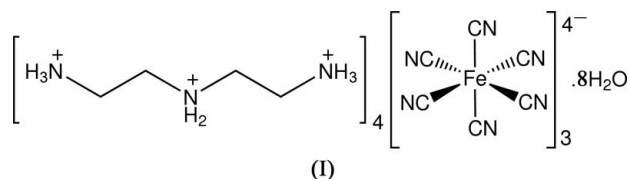
For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The asymmetric unit of the title complex, $(\text{C}_4\text{H}_{16}\text{N}_3)_4\text{[Fe}(\text{CN})_6\text{]}_3 \cdot 8\text{H}_2\text{O}$, comprises two $[\text{H}_3\text{N}(\text{CH}_2)_2\text{NH}_2(\text{CH}_2)_2\text{NH}_3]^{3+}$ cations, 1.5 octahedral $[\text{Fe}(\text{CN})_6]^{4-}$ anions and four solvent water molecules; one anion is located on a center of inversion. Extensive hydrogen bonding of the types $\text{O}-\text{H} \cdots \text{O}$, N and $\text{N}-\text{H} \cdots \text{N}$, involving all components of the structure, leads to a three-dimensional array.

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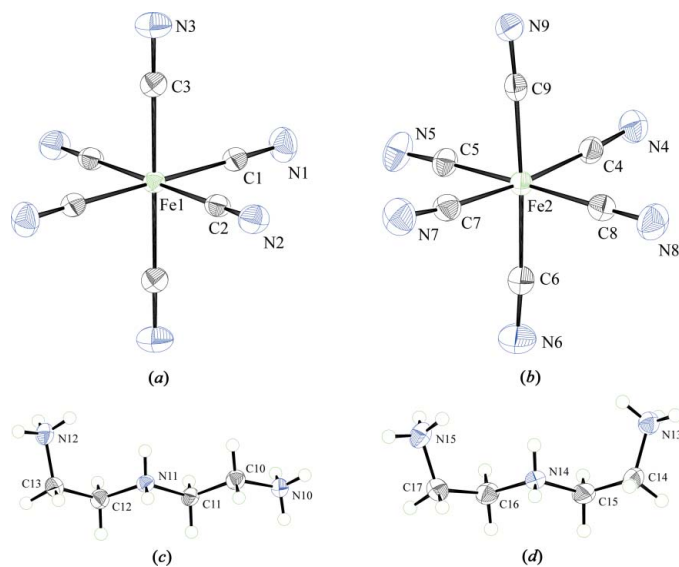
Comment

Transition metal complexes containing ferromagnetic centers have been studied extensively for many years (*e.g.* Batten & Robson, 1998; Evans *et al.*, 1999; Hagrman *et al.*, 1999; Yu *et al.*, 2000) as these complexes may play an important role in various applications such as electrochromic devices, biological sensors, photoelectrochemical devices and electrocatalysts. Polynuclear cyanide complexes and double metal cyanide complexes (DMC) are considered to be good electrocatalysts in fuel cells and are active species in propylene oxide polymerization (Abe *et al.*, 2004). Our interest in this area led to the preparation and crystallographic characterization of the title complex, (I).

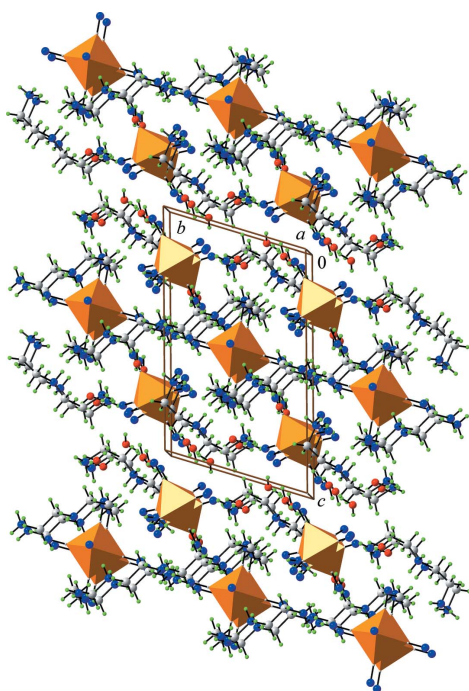


The structure of (I) (Fig. 1) comprises $[\text{H}_3\text{N}(\text{CH}_2)_2\text{NH}_2(\text{CH}_2)_2\text{NH}_3]^{3+}$ cations, $[\text{Fe}(\text{CN})_6]^{4-}$ anions and water molecules in the ratio 4:3:8; one anion, containing Fe1, is located on a center of inversion. The anions show the expected N_6 octahedral coordination with only minor deviations from the ideal geometry (Table 1). By contrast, the conformations of the cations differ slightly. In the cation containing atom N10, one terminal ammonium group is coplanar with the central NC_2 plane but the other occupies a position approximately normal to this plane. In the second cation, containing N13, both terminal ammonium groups are perpendicular to the central NC_2 plane. This difference between the cations is quantified in the torsion angle data, in particular in the corresponding $\text{N10}-\text{C10}-\text{C11}-\text{N11}$ and $\text{N13}-\text{C14}-\text{C15}-\text{N14}$ torsion angles of -173.48 (12) and -81.99 (19) $^\circ$, respectively.

Extensive hydrogen bonding is found in the crystal structure involving all constituents. Geometric data associated with these interactions are summarized in Table 2. Each solvent water molecule is involved in two donor interactions so that


Figure 1

The molecular structures of components of (I) [(a) and (b) $[\text{Fe}(\text{CN})_6]^{4-}$, (c) and (d) $[\text{H}_3\text{N}(\text{CH}_2)_2\text{NH}_2(\text{CH}_2)_2\text{NH}_3]^{3+}$], showing 50% probability displacement ellipsoids and the atom-numbering scheme. In (a), atom Fe1 lies on a center of inversion and unlabeled atoms are related by $(-x, 1 - y, 1 - z)$.


Figure 2

Packing diagram for (I) (Crystal Impact, 2002). Colour code: Fe (orange), O (red), N (blue), C (grey) and H (green).

the O1 water molecule bridges a pair of Fe1- and Fe2-containing anions. In the same way, the O2 and O4 water molecules link three Fe2-containing anions *via* a common terminal cyano N6 atom that accepts two hydrogen bonds from water molecules. A fourth water molecule, containing atom O3, links an Fe2-containing anion to an O4 water molecule. Each acidic N-bound H atom forms at least one hydrogen bond, with N12–H12C being bifurcated. Three of

these interactions involve water molecules, indicating that each water molecule is involved in three hydrogen bonds. There are a large number of N–H···N interactions, of varying strength, so that each cyanide atom functions as a hydrogen-bond acceptor. The most prominent C–H···N interaction in the structure, Table 2, also involves a terminal cyano N6 atom. The majority of cyanide N atoms accept two H atoms, but atoms N6 and N7 accept three H atoms and atom N9 accepts four. It is noted that the additional hydrogen bonds for the latter atoms are significantly weaker than those formed by atoms involved in only two hydrogen-bonding interactions (Table 2). The net result of the myriad of hydrogen-bonding interactions is the formation of a stable three-dimensional array with hydrogen-bonding contacts, mediated by cations and water molecules linking the FeN_6 octahedra. This leads to a discernible pattern of Fe1- and Fe2-containing octahedra, so that successive planes of Fe1N_6 octahedra, stacked along the *c* axis, are separated by two planes of Fe2N_6 octahedra as illustrated in Fig. 2.

Experimental

Reagents were available commercially and were used without further purification. Williamson's violet $[\text{KFe}[\text{Fe}(\text{CN})_6]]$, 0.5 mmol, 158.2 mg) and diethylenetriamine (0.5 mmol, 51.5 mg) were dissolved in a water/methanol (2:1 *v/v*) solution (10.0 ml). Hydrochloric acid (1.5 mmol) was added to this solution until the pH was in the range 6.8–7. The mixture was stirred for approximately 10 min to obtain a clear yellow solution. After keeping the resulting solution in air for a week, brown crystals were formed. These were isolated, washed with anhydrous methanol three times and dried under vacuum (yield 55%). Found: C 33.18, H 6.70, N 34.80%; $\text{C}_{34}\text{H}_{80}\text{Fe}_3\text{N}_{30}\text{O}_8$ requires: C, 33.89; H, 6.70; N, 34.89%.

Crystal data

$(\text{C}_4\text{H}_{16}\text{N}_3)_4[\text{Fe}(\text{CN})_6]_3 \cdot 8\text{H}_2\text{O}$
 $M_r = 1204.76$
 Triclinic, $P\bar{1}$
 $a = 9.4971$ (16) Å
 $b = 9.6841$ (16) Å
 $c = 16.098$ (3) Å
 $\alpha = 106.158$ (2)°
 $\beta = 102.418$ (2)°
 $\gamma = 90.951$ (2)°
 $V = 1384.2$ (4) Å³

$Z = 1$
 $D_x = 1.445$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 3961 reflections
 $\theta = 2.2$ – 28.3 °
 $\mu = 0.85$ mm⁻¹
 $T = 293$ (2) K
 Block, brown
 $0.48 \times 0.33 \times 0.15$ mm

Data collection

Siemens SMART CCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Shelldrick, 1996)
 $T_{\text{min}} = 0.686$, $T_{\text{max}} = 0.883$
 12848 measured reflections

4817 independent reflections
 4504 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.019$
 $\theta_{\text{max}} = 25.0$ °
 $h = -12 \rightarrow 12$
 $k = -12 \rightarrow 12$
 $l = -20 \rightarrow 21$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.026$
 $wR(F^2) = 0.073$
 $S = 1.05$
 4817 reflections
 340 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0428P)^2 + 0.3465P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.44$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.18$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

Fe1—C1	1.9085 (15)	Fe2—C6	1.9186 (17)
Fe1—C2	1.9172 (15)	Fe2—C7	1.9144 (17)
Fe1—C3	1.9081 (16)	Fe2—C8	1.9372 (17)
Fe2—C4	1.9146 (16)	Fe2—C9	1.8895 (16)
Fe2—C5	1.9009 (16)		
C1—Fe1—C2	91.56 (6)	C5—Fe2—C6	87.16 (7)
C1—Fe1—C3	89.79 (6)	C5—Fe2—C7	87.12 (7)
C1—Fe1—C2 ⁱ	88.44 (6)	C5—Fe2—C8	176.56 (6)
C1—Fe1—C3 ⁱ	90.21 (6)	C5—Fe2—C9	89.88 (6)
C2—Fe1—C3	87.60 (6)	C6—Fe2—C7	91.13 (7)
C2—Fe1—C3 ⁱ	92.40 (6)	C6—Fe2—C8	90.28 (7)
C4—Fe2—C5	89.72 (7)	C6—Fe2—C9	176.68 (6)
C4—Fe2—C6	93.05 (7)	C7—Fe2—C8	95.24 (7)
C4—Fe2—C7	174.63 (6)	C7—Fe2—C9	87.22 (7)
C4—Fe2—C8	88.12 (7)	C8—Fe2—C9	92.74 (6)
C4—Fe2—C9	88.43 (6)		

Symmetry code: (i) $-x, -y + 1, -z + 1$.

Table 2

Hydrogen-bond geometry (Å, °).

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
O1—H1A···N2 ⁱⁱ	0.85	2.17	3.0160 (17)	175
O1—H1B···N9 ⁱⁱ	0.85	2.43	3.0781 (16)	134
O2—H2A···N6 ⁱⁱⁱ	0.85	2.41	3.128 (2)	142
O2—H2B···N7 ^{iv}	0.85	2.20	3.022 (2)	161
O3—H3A···N7	0.85	2.29	3.071 (2)	154
O3—H3B···O4	0.85	1.97	2.809 (2)	169
O4—H4A···N8 ^v	0.85	2.16	2.991 (2)	168
O4—H4B···N6 ⁱⁱⁱ	0.85	1.93	2.764 (2)	165
N10—H10A···N2 ⁱⁱ	0.89	2.03	2.867 (2)	155
N10—H10B···N9 ^{vi}	0.89	2.11	2.984 (2)	169
N10—H10C···N4	0.89	2.03	2.905 (2)	168
N11—H11A···N9	0.90	2.01	2.823 (2)	149
N11—H11B···N3 ^{vii}	0.90	1.93	2.780 (2)	157
N12—H12A···N5 ⁱⁱⁱ	0.89	1.95	2.793 (2)	158
N12—H12B···O3	0.89	1.84	2.7202 (19)	170
N12—H12C···N3	0.89	2.29	2.949 (2)	131
N12—H12C···N9	0.89	2.60	3.219 (2)	128
N13—H13A···N1 ^{vii}	0.89	2.16	3.024 (2)	163
N13—H13B···N8	0.89	2.04	2.931 (2)	175
N13—H13C···N7 ⁱⁱ	0.89	2.08	2.953 (2)	167
N14—H14A···N1 ^{vii}	0.90	1.89	2.777 (2)	169

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
N14—H14B···O2 ⁱⁱ	0.90	1.85	2.7357 (18)	168
N15—H15A···N4 ⁱⁱⁱ	0.89	2.05	2.849 (2)	149
N15—H15B···N5 ^{viii}	0.89	2.09	2.789 (2)	134
N15—H15C···O1 ⁱⁱⁱ	0.89	1.99	2.848 (2)	162
C16—H16A···N6 ^v	0.97	2.55	3.393 (3)	146

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

All H atoms were allowed to ride on their parent atoms in the riding model approximation at distances of 0.97 (C—H), 0.89–0.90 (N—H) and 0.85 Å (O—H), and with $U_{iso}(H)$ values of 1.2 $U_{eq}(C)$ and 1.5 $U_{eq}(N,O)$.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINTE* (Siemens, 1996); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL97*.

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