

The three-dimensional coordination polymer tetraethylammonium (ethylenediamine)cadmium(II) hexacyanoferrate(III), $(\text{Et}_4\text{N})\{[\text{Cd}(\text{en})_4[\text{Fe}(\text{CN})_6]_3\}$

Miroslava Mařárová,^a Juraj Kuchár,^a Juraj Černák^{a*} and Werner Massa^b

^aInstitute of Chemistry, P. J. Šafárik University, Moyzesova 11, 041 54 Košice, Slovakia, and ^bFachbereich Chemie, Philipps-Universität, 35032 Marburg, Germany
Correspondence e-mail: cernakju@kosice.upjs.sk

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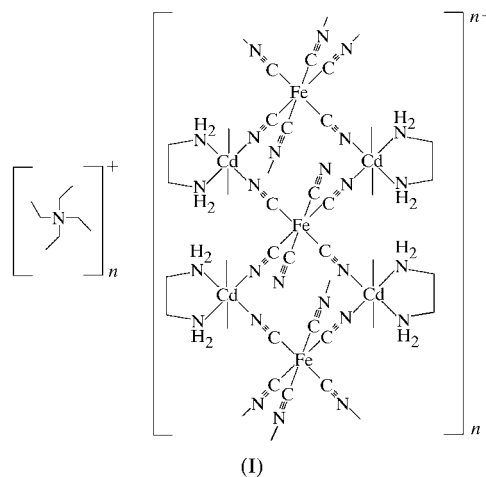
The title compound, tetraethylammonium dodeca- μ -cyano-hexacyanotetrakis(ethylenediamine)tetracadmium(II)triferrate(III), $(\text{C}_8\text{H}_{20}\text{N})[\text{Cd}_4\text{Fe}_3(\text{CN})_{18}(\text{C}_2\text{H}_8\text{N}_2)_4]$, was prepared from a reaction mixture containing CdCl_2 , $\text{K}_3[\text{Fe}(\text{CN})_6]$, ethylenediamine (en) and $[\text{Et}_4\text{N}]\text{Br}$ in a 1:1:3:1 molar ratio. The crystal structure consists of a negatively charged three-dimensional framework of $\{[\text{Cd}(\text{en})_4[\text{Fe}(\text{CN})_6]_3\}_n^{n-}$ anions, with $[\text{Et}_4\text{N}]^+$ cations located in the cavities of the framework. The Cd atom is octahedrally coordinated by one disordered chelating en molecule [mean Cd–N = 2.35 (3) Å] and four N-bonded bridging cyano groups [Cd–N distances are in the range 2.283 (2)–2.441 (2) Å]. There are two crystallographically independent $[\text{Fe}(\text{CN})_6]^{3-}$ anions in the structure and in each the Fe atom lies on a twofold axis. In the first [mean Fe–C = 1.941 (5) Å], all the cyano groups are bridging ligands, while in the second [mean Fe–C = 1.945 (2) Å], there are two terminal cyano ligands in *trans* positions. The Cd–N–C angles range from 128.6 (2) to 172.8 (2)°.

Comment

Because of their structural diversity, cyano complexes are suitable for use in the study of various physical phenomena associated with magnetism, such as spin crossover, photomagnetism, spin dynamics in low-dimensional systems and high-temperature magnetic ordering (Dunbar & Heintz, 1997; Verdaguer *et al.*, 1999; Ohba & Okawa, 2000). The synthetic design of cyano complexes can be based on the so-called 'brick-and-mortar' method (Willet *et al.*, 1993, and references therein), in which complex cations form 'bricks' and complex cyano anions behave as 'mortar', linking the cations *via* bridging cyano ligands. The desired dimensionality of the

coordination polymer can be achieved by a suitable choice of the number and types of 'blocking' ligands coordinated to the central cation, leaving only some coordination sites free for N-bonded cyano ligands from the anion.

We are interested in the synthesis, characterization, crystal chemistry and magnetostructural correlations of low-dimensional magnetic systems (Černák *et al.*, 2002). In continuation of this study and taking into account the known structure of the diamagnetic one-dimensional coordination polymer $\text{Cd}(\text{en})_2\text{Ni}(\text{CN})_4$ (en is ethylenediamine), which displays two polymorphs, one monoclinic and one orthorhombic (Yuge *et al.*, 1995), we have tried to replace the square tetracyanonickelate anion by the octahedral hexacyanoferrate(III) anion. From the aqueous $[\text{NET}_4]^+ - \text{Cd}^{2+} - \text{en} - [\text{Fe}(\text{CN})_6]^{3-}$ system, we have isolated the title compound, (I), which contains only one en ligand coordinated to the central Cd atom. Our attempts to prepare compounds with a higher en/Cd ratio (such as 2:1) by raising the initial en/Cd ratio (to 6:1) failed. The structures of two similar Cd–Fe compounds are described in the literature, *viz.* $[\text{Cd}(\text{tet})]_2[\text{Fe}(\text{CN})_6] \cdot 3\text{H}_2\text{O}$ (tet is triethylenetetramine), with a one-dimensional structure (Zhang *et al.*, 2000), and $[\text{Cd}(\text{tren})]_3[\text{Fe}(\text{CN})_5\text{NO}]$ [tren is tris(2-aminoethyl)amine], with a three-dimensional structure (Zhang *et al.*, 2002).



X-ray structural analysis revealed that the structure of (I) consists of a negatively charged three-dimensional framework of composition $\{[\text{Cd}(\text{en})_4[\text{Fe}(\text{CN})_6]_3\}_n^{n-}$, which encapsulates the $[\text{Et}_4\text{N}]^+$ cations. A similar negatively charged three-dimensional framework based on a cyanometallate system, with tetraalkylammonium ions placed in the voids, has been described for $[\text{N}(\text{CH}_3)_4]_2[\text{Mn}(\text{H}_2\text{O})_3][\text{Mo}(\text{CN})_7]_2 \cdot 2\text{H}_2\text{O}$ (Larionovova *et al.*, 2002).

A perspective view of the asymmetric unit of (I) is shown in Fig. 1, and selected bond lengths and angles are listed in Table 1. There are two crystallographically independent Fe^{III} atoms in the structure (Fig. 1), both of which are hexacoordinated by C-bonded cyano groups. In the coordination polyhedron of atom Fe1, all six cyano groups exhibit bridging character. Atom Fe2 is coordinated by two terminal (in axial positions) and four bridging cyano groups. The Fe–C bond

lengths in both anions range between 1.9349 (19) and 1.9467 (18) Å. Similar distances, ranging between 1.942 (8) and 1.949 (5) Å, were found in $[\text{Ni}(\text{pn})_2][\text{Fe}(\text{CN})_6]\text{ClO}_4 \cdot 2\text{H}_2\text{O}$ (pn is 1,2-diaminopropane; Ohba *et al.*, 1995). The Fe—C—N angles deviate only slightly from linearity (maximum deviation = 6.3°), which accounts for the presence of π back donation.

The Cd^{II} atom exhibits a distorted octahedral coordination, involving one disordered chelate-like en ligand and four N-bonded bridging cyano groups. Three of the latter link the Cd atom to three neighbouring $\text{Fe1}(\text{CN})_6$ groups, thus forming double layers (Fig. 2) with composition $[\{\text{Cd}(\text{en})\}_2(\mu\text{-NC})_6\text{-Fe}]$ parallel to the *ab* plane at heights of $z = 0, \frac{1}{4}, \frac{1}{2}$ and $\frac{3}{4}$ (Fig. 3). The fourth cyano group connects Cd and Fe2 atoms and thus participates in linking of the layers *via* the $\text{Fe2}(\text{CN})_6$ groups. The Cd—N bond distances are in the range 2.2833 (16)–2.4412 (17) Å; the octahedron around the Cd atom is axially elongated and involves two longer Cd— N_{CN} bonds in the layer [mean 2.439 (3) Å]. The remaining two pairs of Cd—N bonds (Cd— N_{en} and Cd— N_{CN}) in the equatorial plane exhibit a mean value of 2.32 (4) Å (Table 1). The N—Cd—N angles are variable; the lowest value, $74.88 (6)^\circ$, is found for the N—Cd—N angle within the chelate ring. A similar value, $75.9 (1)^\circ$, was found in the monoclinic form of $\text{Cd}(\text{en})_2\text{Ni}(\text{CN})_4$ (Yuge *et al.*, 1995). The en ligand is in a δ conformation (more populated position = 72%) and has geometric parameters exhibiting typical values (Yuge *et al.*, 1995).

The $\text{Fe}(\text{CN})_6$ groups connecting the Fe1/Cd double layers at $z = \frac{1}{8}, \frac{3}{8}, \frac{5}{8}$ and $\frac{7}{8}$ (Fig. 3) have Fe2...Fe2 separations of 9.65 Å. In the large cavities of these layers, the $[\text{Et}_4\text{N}]^+$ cations alternate with the Fe2-atom octahedra. By operation of the 4_1 screw axis, the building units are stacked along the *c* axis (combined with 90° rotations), giving rise to the large translation period along *c* (> 5 nm).

As a consequence of the formation of the three-dimensional framework, some of the Cd—N—C units are strongly bent, the

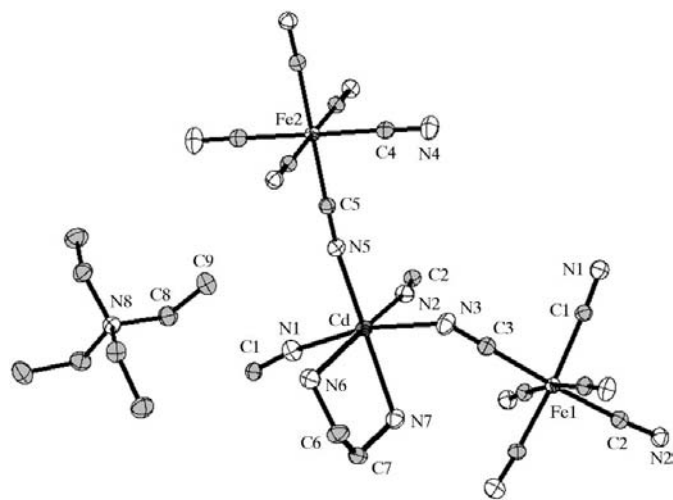


Figure 1

A view of the asymmetric part of the structure of (I), with the atom-numbering scheme. H atoms and the low-occupancy C-atom positions of the ethylenediamine ligand have been omitted for clarity.

smallest Cd—N—C angle being $128.64 (15)^\circ$. Such values are not uncommon in polymeric cyano complexes (Zhang *et al.*, 2000). The cyano groups exhibit typical distances (Sharpe, 1976). The $[\text{Et}_4\text{N}]^+$ cations are located in the holes of the three-dimensional framework (Fig. 3). The N—C and C—C bonds show normal values (Li *et al.*, 2001).

Note that, in the IR spectrum, two absorption bands are present in the $2000\text{--}2200\text{ cm}^{-1}$ region, which can be assigned to the presence of terminal (2115 cm^{-1} , weak) and bridging (2137 cm^{-1} , strong) cyano groups (Nakamoto, 1997).

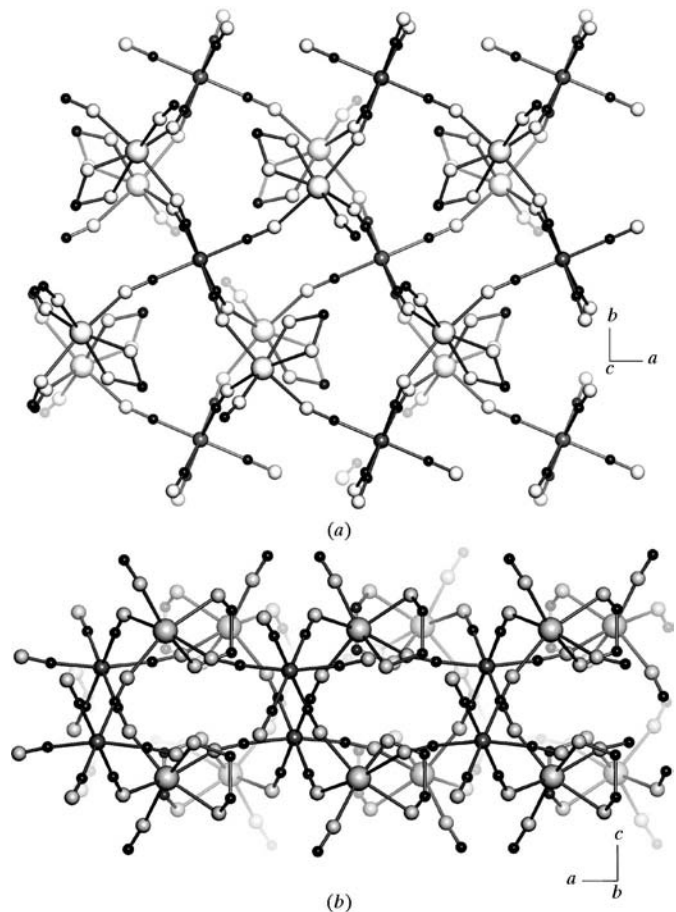


Figure 2

A view of the double layers of $\text{Fe1}(\text{CN})_6$ and $\text{Cd}(\text{en})$ units (a) approximately along $[001]$ and (b) approximately along $[010]$. Large pale spheres denote Cd atoms, small pale spheres denote Fe1 atoms, black spheres denote C atoms and dark-grey spheres denote N atoms.

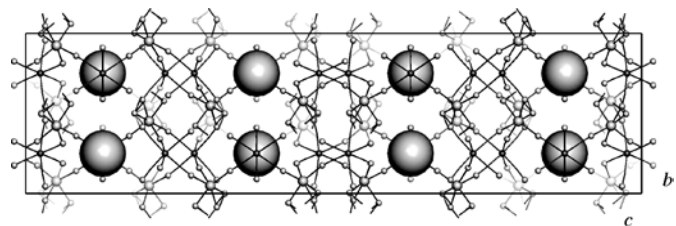


Figure 3

The unit cell projected along $[100]$, with $[\text{Et}_4\text{N}]^+$ cations shown as large spheres.

Experimental

Clear single crystals of (I) were prepared by slow addition of a 0.1 M aqueous solution of $K_3[Fe(CN)_6]$ (7.5 ml, 1 mmol) to a solution of $CdCl_2 \cdot 2.5H_2O$ (1 mmol), en and $[Et_4N]Br$ in a 1:3:1 molar ratio. After 1 d, the solution was filtered to remove the formed turbidity. From the yellow filtrate, red cube-like crystals appeared after several days. The crystals were filtered off, washed with a small amount of water and ethanol, and dried in air (yield 30%). IR (Nicolet Magna 750 spectrometer, cm^{-1} , KBr disc): $\nu(NH_2)$: 3372 (s), 3331 (s), 3273 (s), 3210 (w); $\nu(CH_3)$: 2965 (m); $\nu(CH_2)$: 2988 (w); $\nu(CN)$: 2137 (vs), 2115 (vs); $\delta(NH_2)$: 1601 (s); $\delta(CH_2)$: 1487 (m), 1458 (m), 1441 (m); $\nu(Fe-C)$: 588 (m).

Crystal data

$(C_8H_{20}N)[Cd_4Fe_3(CN)_{18}(C_2H_8N_2)_4]$
 $M_r = 1456.18$
 Tetragonal, $I4_1/acd$
 $a = 13.6532(3) \text{ \AA}$
 $c = 52.696(2) \text{ \AA}$
 $V = 9823.1(5) \text{ \AA}^3$
 $Z = 8$
 $D_x = 1.969 \text{ Mg m}^{-3}$
 $D_m = 1.945 \text{ Mg m}^{-3}$
 D_m measured by flotation in a mixture of bromoform and acetone

Mo $K\alpha$ radiation
 Cell parameters from 56 335 reflections
 $\theta = 1.8\text{--}29.5^\circ$
 $\mu = 2.62 \text{ mm}^{-1}$
 $T = 120(1) \text{ K}$
 Cube, red
 $0.14 \times 0.13 \times 0.13 \text{ mm}$

Data collection

Stoe IPDS-II diffractometer
 ω scans
 Absorption correction: multi-scan (*XPREP* in *SHELXTL*; Sheldrick, 1996)
 $T_{\min} = 0.630$, $T_{\max} = 0.712$
 40 110 measured reflections

3360 independent reflections
 3012 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.029$
 $\theta_{\text{max}} = 29.4^\circ$
 $h = -18 \rightarrow 18$
 $k = -18 \rightarrow 18$
 $l = -63 \rightarrow 71$

Table 1

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

Cd—N5	2.2833 (16)	C1—N1	1.150 (2)
Cd—N2 ⁱ	2.2893 (17)	C2—N2	1.151 (3)
Cd—N6	2.3314 (17)	C3—N3	1.149 (3)
Cd—N7	2.3731 (17)	C4—N4	1.150 (4)
Cd—N3	2.4366 (17)	C5—N5	1.149 (3)
Cd—N1 ⁱⁱ	2.4412 (17)	N6—C6	1.525 (4)
Fe1—C3	1.9349 (19)	C6—C7	1.498 (5)
Fe1—C2	1.9432 (19)	C7—N7	1.409 (3)
Fe1—C1	1.9457 (17)	C8—C9	1.512 (3)
Fe2—C4	1.943 (3)	C8—N8	1.515 (2)
Fe2—C5	1.9467 (18)		
N5—Cd—N2 ⁱ	95.78 (6)	C4—Fe2—C5	89.95 (5)
N6—Cd—N7	74.88 (6)	C5 ⁱⁱⁱ —Fe2—C5 ^{iv}	179.91 (12)
N5—Cd—N3	90.67 (6)	C1—N1—Cd ^v	159.14 (16)
N5—Cd—N1 ⁱⁱ	101.74 (6)	C2—N2—Cd ^{vi}	162.76 (15)
N3—Cd—N1 ⁱⁱ	167.57 (6)	C3—N3—Cd	128.64 (15)
C3—Fe1—C2	173.48 (8)	C5—N5—Cd	172.76 (15)
C3—Fe1—C1	84.46 (8)	C6—N6—Cd	107.46 (15)
C2—Fe1—C1	91.86 (8)		

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

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.023$
 $wR(F^2) = 0.064$
 $S = 1.03$
 3360 reflections
 166 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.05P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.91 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.75 \text{ e \AA}^{-3}$
 Extinction correction: *SHELXL97*
 Extinction coefficient: 0.00043 (3)

H atoms were treated as riding, with C—H distances of 0.98 or 0.99 \AA and N—H distances of 0.92 \AA .

Data collection: *WinExpose* in *X-AREA* (Stoe & Cie, 2002); cell refinement: *WinCell* in *X-AREA*; data reduction: *WinIntegrate* in *X-AREA*; program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Crystal Impact, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD1248). Services for accessing these data are described at the back of the journal.

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