

One-dimensional structure of catena-poly[tetraethylammonium [tetra-cyanoiron(III)- μ -cyano-[bis(ethylenediamine)cadmium(II)]- μ -cyano] tetra-hydrate]

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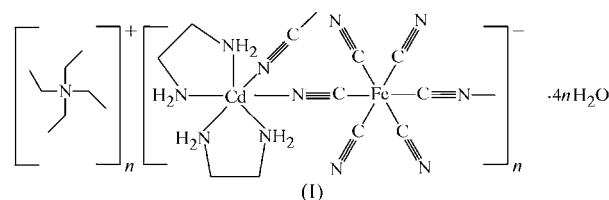
The title compound, $\{(C_8H_{20}N)[CdFe(CN)_6(C_2H_8N_2)_2] \cdot 4H_2O\}_n$, was isolated from the aqueous system Cd^{2+} /ethylenediamine (en)/ $[Fe(CN)_6]^{3-}$ in the presence of $[Et_4N]Br$. The crystal structure is dominated by a one-dimensional motif, *viz.* a negatively charged 2,2-CT (*cis-trans*) $[-Cd(en)_2-NC-Fe(CN)_4-CN-]_n^{3-}$ chain. The Cd and Fe atoms of the anion and the N atom of the cation all lie on twofold axes. The ethyl groups of the cation are equally disordered over two orientations. The cationic building block of the chain consists of a Cd^{II} atom coordinated by two chelating en ligands, and the distorted octahedral coordination is completed by two bridging cyano ligands in *cis* positions. The anionic building block is an $[Fe(CN)_6]^{3-}$ anion in which the Fe^{III} atom is octahedrally coordinated by six cyano ligands; two of the cyano ligands, in *trans* positions, are bridging. The uncoordinated water molecules link neighbouring chains through $O-H \cdots N$ and $N-H \cdots O$ hydrogen bonds.

Comment

Cyano complexes have been considered attractive subjects for study because of their ability to form host-guest and mineralomimetic systems (Iwamoto, 1996; Iwamoto *et al.*, 1997; Hoskins & Robson, 1990; Dunbar & Heintz, 1997), and also because of their uses in such diverse areas as heterogeneous catalysis and sorption processes (Boellaard *et al.*, 2002; Ayrault *et al.*, 1998; Loos-Neskovic & Fedoroff, 1989). At present, oligomeric and polymeric cyano complexes attract the interest of both chemists and physicists from the point of view of magnetic properties (Larionova *et al.*, 2000; Verdaguer *et al.*, 1999; Bernhardt *et al.*, 2005; Sato *et al.*, 1996).

Polymeric cyano complexes can be built up of cationic and anionic building blocks linked *via* bridging cyano ligands; the cationic block is a complex cation coordinated by suitable,

mainly N-donor, ligands (blocking ligands) and the anionic block is a complex cyano anion. The dimensionality of the cyano complex formed can be tuned to some extent by the number and type of the blocking ligands coordinated to the cationic central atom (Willett *et al.*, 1993). Following this approach, we have investigated the system Cd^{2+} /ethylenediamine (en)/ $[Fe(CN)_6]^{3-}$ in the presence of $[Et_4N]Br$ for compensation of charge differences between the respective building blocks and have occasionally isolated the title compound, $(Et_4N)[CdFe(CN)_6(en)_2] \cdot 4H_2O$, (I), along with the main crystalline product $(Et_4N)[Cd(en)]_4[Fe(CN)_6]_3$, (II). Compound (II) formed at all Cd/en ratios up to 1:6. It exhibits a three-dimensional crystal structure with $[Et_4N]^+$ cations located in octahedral cavities of the cyano complex skeleton (Mal'arová *et al.*, 2003). Further attempts to prepare (I) were unsuccessful, but we were able to determine its structure; the results are reported here.



The structure of (I) consists of anionic $[-Cd(en)_2-NC-Fe(CN)_4-CN-]_n^{3-}$ chains, $[Et_4N]^+$ cations (the Cd atom, the Fe atom and the N atom of the cation occupy special posi-

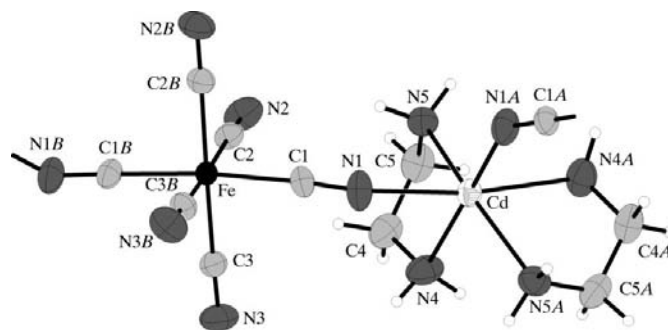


Figure 1

The structure of the anion of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry codes: (A) $y, x, -z$; (B) $1 - y, 1 - x, \frac{1}{2} - z$.]

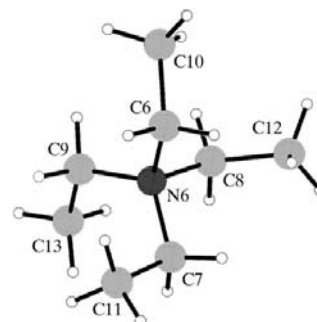


Figure 2

A view of the $[Et_4N]^+$ cation (only one disordered congener is shown).

tions), and two crystallographically independent uncoordinated water molecules, which are located between the chains (Figs. 1, 2 and 3). Heretofore, besides (II), only one crystal structure based on a Cd^{II} central atom and an [Fe(CN)₆]³⁻ anion has been reported. (Me₄N)[CdFe(CN)₆].3H₂O exhibits a three-dimensional crystal structure, and is built up of [CdN₄(OH₂)₂]²⁺ octahedra and [CdN₅]²⁺ square pyramids linked *via* [Fe(CN)₆]³⁻ octahedra; tetramethylammonium

cations and water molecules are located in the cavities formed (Witzel *et al.*, 2000).

The Cd^{II} atoms in (I) are six-coordinated by two chelating en molecules and two N-bound μ_2 -bridging cyano groups in *cis* (C) positions. As the bridging cyano ligands are in *trans* (T) positions in the anion, and the connectivities of both building blocks are 2, the chain is of the 2,2-CT type [for details of notation, see Černák *et al.* (2002)]. The Cd–N bond distances are in the range 2.339 (2)–2.376 (2) Å (Table 1). Similar bond distances and N–Cd–N angles were found in the one-dimensional compound [Cd(tet)]₂[Fe(CN)₆].3H₂O (tet is triethylenetetramine; Zhang, Tong *et al.*, 2000). The Cd–N1–C1 angle in (I) is 145.0 (2)°; such a deviation from linearity is usual in this type of structure (Zhang, Cai *et al.*, 2000; Zhang, Tong *et al.*, 2000). Both en ligands are in the δ conformation and exhibit typical values for their geometric parameters (Yuge *et al.*, 1995).

The Fe^{III} atom is six-coordinated by six cyano ligands, of which two, located in *trans* positions, are bridging (Fig. 1). The [FeC₆] octahedron is regular and the observed geometric parameters are in line with those reported for other hexacyanoferrates(III) (Witzel *et al.*, 2000).

The tetraethylammonium cations are located between the chains; the cation is disordered about the twofold axis upon which atom N6 lies. Two crystallographically independent water molecules are interconnected *via* hydrogen bonds of the O–H...O type; moreover, the water molecules link neighbouring chains *via* O–H...N and N–H...O hydrogen bonds (Fig. 4 and Table 2). N–H...N hydrogen bonds between the chains contribute to the stability of the structure (Fig. 4 and Table 2).

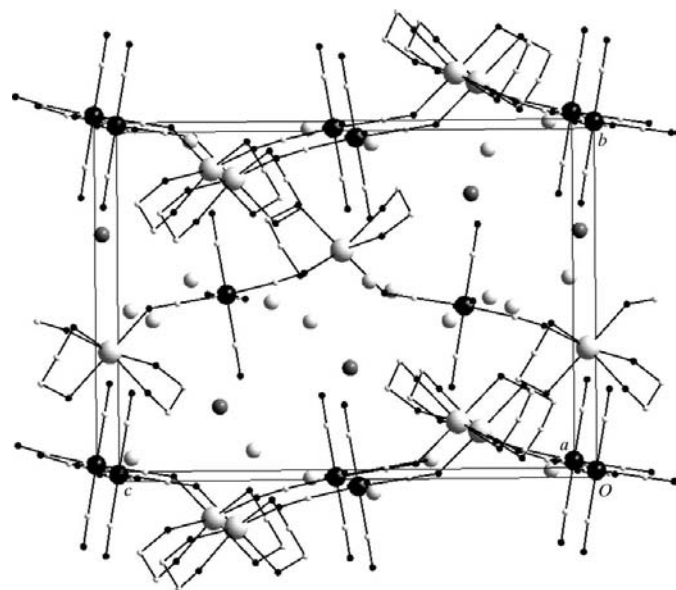


Figure 3
A packing diagram for (I), displaying its one-dimensional character. Key: large black balls: Fe; large white balls: Cd; medium white balls: O; small black balls: N; small white balls: C. For the sake of clarity, the [Et₄N]⁺ cations are represented only by N atoms (medium grey balls) and H atoms have been omitted.

Experimental

Compound (I) crystallized from the same reaction mixture as (II). To an aqueous solution of CdCl₂.2.5H₂O (0.23 g, 1 mmol), aqueous solutions of en (0.136 ml, 2 mmol) and [Et₄N]Br (0.15 g, 1 mmol) were added, and the mixture was stirred at room temperature for 10 min. To this colourless solution was added an aqueous solution of K₃[Fe(CN)₆] (0.33 g, 1 mmol). The resulting yellow solution was left to crystallize at two temperatures. From the solution kept at room temperature, red prismatic crystals of (II) were obtained after two days, and from the second solution, kept within the temperature range 281–286 K, yellow prismatic crystals of (I) separated after two weeks (yield 30%). Analysis calculated for C₁₈H₄₄CdFeN₁₁O₄: C 23.70, H 6.89, N 33.05%; found: C 23.82, H 6.86, N 33.42%. IR (cm⁻¹; Nicolet Magna 750 spectrometer, KBr disc): 3430, 3358, 3295, 2934, 2122, 1604, 1463, 1186, 1001, 961, 415, 398.

Crystal data

(C₈H₂₀N)[CdFe(CN)₆(C₂H₈N₂)₂].4H₂O
M_r = 646.89
Tetragonal, P4₃2₁2
a = 13.0444 (5) Å
c = 17.8599 (9) Å
V = 3039.0 (2) Å³
Z = 4
D_x = 1.414 Mg m⁻³
D_m = 1.390 Mg m⁻³

D_m measured by flotation in a mixture of bromoform and acetone
Mo K α radiation
Cell parameters from 29777 reflections
 θ = 1.9–29.4°
 μ = 1.22 mm⁻¹
T = 173 (2) K
Prism, yellow
0.2 × 0.18 × 0.1 mm

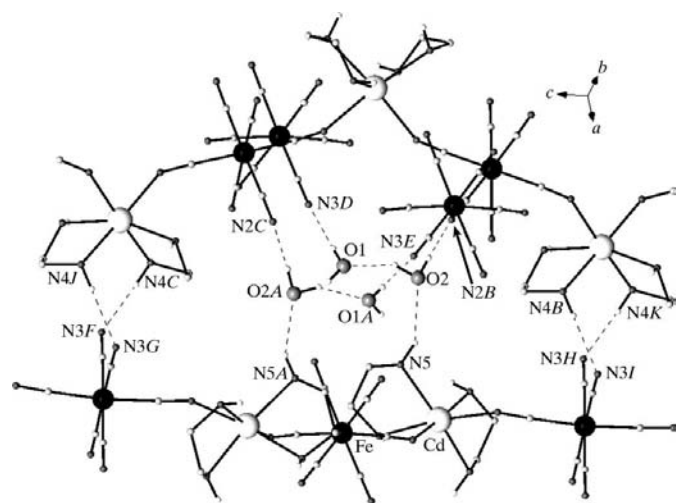


Figure 4
The hydrogen bonds in (I). [Et₄N]⁺ cations and H atoms not involved in hydrogen-bond formation have been omitted for clarity. [Symmetry codes: (A) 1 – y, 1 – x, $\frac{1}{2}$ – z; (B) $\frac{1}{2}$ – y, $\frac{1}{2}$ + x, $-\frac{1}{4}$ + z; (C) $\frac{1}{2}$ – x, $\frac{1}{2}$ + y, $\frac{3}{4}$ – z; (D) –y, 1 – x, $\frac{1}{2}$ – z; (E) x, 1 + y, z; (F) y, x, 1 – z; (G) 1 – x, 1 – y, $\frac{1}{2}$ + z; (H) y, x, –z; (I) 1 – x, 1 – y, z – $\frac{1}{2}$; (J) $\frac{1}{2}$ – y, $\frac{1}{2}$ + x, $\frac{3}{4}$ + z; (K) $\frac{1}{2}$ – x, $\frac{1}{2}$ + y, $-\frac{1}{4}$ – z.]

Data collection

Stoe IPDS-II diffractometer 4164 independent reflections
 ω scans 4043 reflections with $I > 2\sigma(I)$
 Absorption correction: numerical
 (*XPREP* in *SHELXTL*;
 Sheldrick, 1996)
 $T_{\min} = 0.610$, $T_{\max} = 0.701$
 29777 measured reflections

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.023$
 $wR(F^2) = 0.063$
 $S = 1.03$
 4164 reflections
 191 parameters
 H atoms treated by a mixture of
 independent and constrained
 refinement

$w = 1/[\sigma^2(F_o^2) + (0.0383P)^2 + 1.3052P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.46 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.42 \text{ e } \text{Å}^{-3}$
 Extinction correction: *SHELXL97*
 Extinction coefficient: 0.0026 (6)
 Absolute structure: (Flack, 1983),
 1728 Friedel pairs
 Flack parameter: 0.02 (2)

Table 1

Selected geometric parameters (Å, °).

Cd—N1	2.339 (2)	Fe—C3	1.931 (2)
Cd—N5	2.360 (2)	Fe—C1	1.932 (2)
Cd—N4	2.376 (2)	Fe—C2	1.937 (2)
N1—Cd—N1 ⁱ	87.74 (11)	C3—Fe—C1	86.64 (9)
N1—Cd—N5 ⁱ	110.21 (8)	C1—Fe—C1 ⁱⁱ	174.34 (14)
N1—Cd—N5	84.86 (8)	C3 ⁱⁱ —Fe—C2	177.54 (9)
N5 ⁱ —Cd—N5	159.56 (11)	C3—Fe—C2	88.79 (9)
N1—Cd—N4 ⁱ	171.56 (9)	C1—Fe—C2	90.95 (9)
N1—Cd—N4	86.50 (9)	C1—Fe—C2 ⁱⁱ	93.10 (9)
N5 ⁱ —Cd—N4	91.36 (8)	C2—Fe—C2 ⁱⁱ	88.77 (12)
N5—Cd—N4	75.40 (8)	C1—N1—Cd	145.0 (2)
N4 ⁱ —Cd—N4	99.86 (14)	N1—C1—Fe	175.9 (2)
C3 ⁱⁱ —Fe—C3	93.66 (14)	N2—C2—Fe	179.1 (2)
C3 ⁱⁱ —Fe—C1	89.49 (9)	N3—C3—Fe	178.2 (2)

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

Table 2

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1—H11 \cdots N3 ⁱⁱⁱ	0.77 (6)	2.06 (6)	2.817 (3)	171 (6)
O1—H12 \cdots O2 ^{iv}	0.91 (6)	1.87 (6)	2.748 (3)	162 (5)
O2—H21 \cdots N2 ^v	0.95 (4)	1.90 (4)	2.849 (3)	178 (4)
O2—H22 \cdots O1	0.94 (4)	1.86 (4)	2.715 (3)	152 (4)
N4—H4A \cdots N3 ^{vi}	0.92	2.31	3.190 (4)	160
N5—H5B \cdots O2	0.92	2.28	3.103 (3)	150

Symmetry codes: (iii) $-y, -x + 1, -z + \frac{1}{2}$; (iv) $y - \frac{1}{2}, -x + \frac{1}{2}, z + \frac{3}{4}$; (v) $-y + \frac{1}{2}, x + \frac{1}{2}, z - \frac{3}{4}$; (vi) $-y + \frac{1}{2}, x - \frac{1}{2}, z - \frac{1}{4}$.

In the tetraethylammonium cation, the ethyl groups are disordered over two positions related by a twofold axis parallel to [110]. Accordingly, the site-occupation factors of all atoms of the relevant ethyl groups were set at 0.5. Owing to the observed disorder, the N—C bonds in the cation were restrained to be the same and the anisotropic displacement parameters of the C atoms of methyl groups were assumed to have the same values. The H atoms of the water molecules were located in a difference Fourier map; their positional

parameters were refined, while their $U_{\text{iso}}(\text{H})$ values were set at $1.5U_{\text{eq}}(\text{O})$. For the remaining H atoms, a riding model was used with constrained displacement parameters [$C-H = 0.98$ and 0.99 Å , and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C}, \text{N})$ and $1.5U_{\text{eq}}(\text{C}_{\text{methyl}})$].

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, 2000); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FA3001). Services for accessing these data are described at the back of the journal.

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