

Ammonium bis(tetraethylammonium)  
hexacyanidoferrate(III) trihydrateMiroslava Matiková Mařarová,<sup>a,†</sup> Juraj Černák<sup>a,\*</sup> and  
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In the structure of the title salt,  $(\text{NH}_4)(\text{C}_8\text{H}_{20}\text{N})_2[\text{Fe}(\text{CN})_6] \cdot 3\text{H}_2\text{O}$ , the O atom of one of the water molecules shares its crystallographic site with the N atom of the ammonium cation in a 1:1 ratio. The second O atom from the two crystallographically independent water molecules is disordered over two positions separated by 0.551 (1) Å. The water molecules and ammonium cations form tetrameric hydrogen-bonded units that, along with the complex anion, form the hydrophilic part of the structure. The hydrophobic part of the structure, represented by the tetraethylammonium cation, is located in cube-like cavities of the hydrophilic framework.

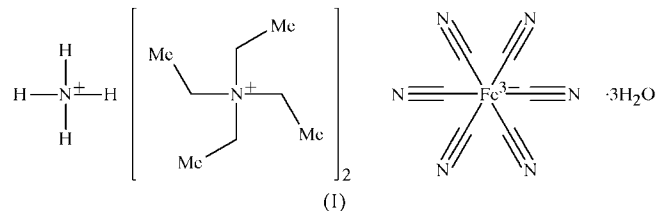
## Comment

The structural and compositional diversity of cyanide complexes make this class of compounds attractive from several aspects, but during the past two decades cyanide complexes have been studied mainly because of their interesting magnetic properties (Dunbar & Heintz, 1997; Ohba & Okawa, 2000; Verdager *et al.*, 1999; Bernhardt *et al.*, 2005).

Within our broader programme on cyanide complexes as model compounds for studies of physical phenomena associated with magnetism (Černák *et al.*, 2002), we dealt, among others, with  $\text{Cd}^{\text{II}}$  complexes based on hexacyanoferrates(III) (Mařarová, Černák & Massa, 2006; Mařarová, Černák, Kuchár *et al.*, 2006). Apart from their magnetic character (having a low-spin  $\text{Fe}^{\text{III}}$  atom with  $S = \frac{1}{2}$ ), these  $\text{Cd}^{\text{II}}\text{-Fe}^{\text{III}}$  compounds may serve for the sake of structural comparison with hexacyanoferrates(III) containing paramagnetic cationic central atoms. Moreover, such complexes are suitable models for Mössbauer studies, for example, studies of line broadening on lowering the temperature (Iijima *et al.*, 2003).

As a continuation of our studies, we aimed to prepare a  $\text{Cd}^{\text{II}}\text{-Fe}^{\text{III}}$  compound built up of  $[\text{Cd}(\text{NH}_3)_6]^{2+}$  and  $[\text{Fe}(\text{CN})_6]^{3-}$  building blocks. There are a few examples of

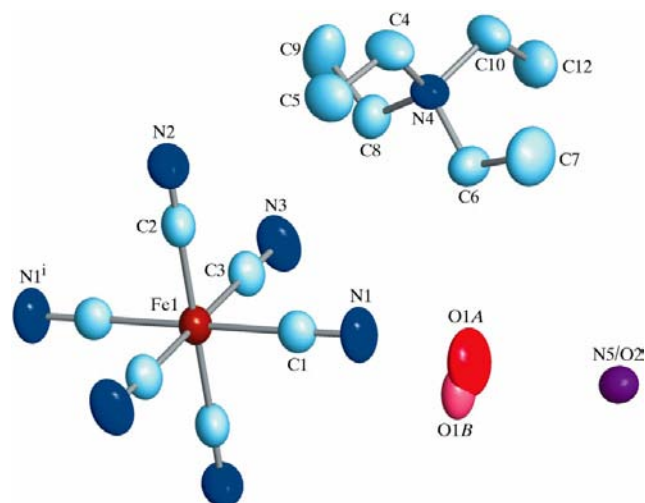
structures containing a  $[\text{Cd}(\text{NH}_3)_6]^{2+}$  building block {e.g.  $[\text{Cd}(\text{NH}_3)_6](\text{C}_{20}\text{H}_{12}\text{O}_2) \cdot 2\text{C}_{20}\text{H}_{14}\text{O}_2$ ; Paul *et al.*, 2004}, but, to our knowledge, no structure with a complex cyanide anion. On the other hand, other cyanide complexes with ammine-type complex cations have already been described (Escorihuela *et al.*, 2001; Petříček *et al.*, 2005).



In order to balance the different charges of the outgoing complex ions during synthesis,  $(\text{NEt}_4)\text{Br}$  (Et is ethyl) was added to the aqueous reaction mixture, which thus comprised  $(\text{NEt}_4)\text{Br}$ ,  $\text{CdCl}_2$ ,  $\text{NH}_3$  and  $\text{K}_3[\text{Fe}(\text{CN})_6]$ . Instead of the desired compound, we unexpectedly obtained the title compound,  $(\text{NH}_4)(\text{Et}_4\text{N})_2[\text{Fe}(\text{CN})_6] \cdot 3\text{H}_2\text{O}$ , (I), in low yield. Its composition was first checked chemically (see *Experimental*). A search of the Cambridge Structural Database (Allen, 2002) indicates that only one similar compound, exhibiting composition  $(\text{Et}_4\text{N})_3[\text{Fe}(\text{CN})_6] \cdot 5\text{H}_2\text{O}$ , has been structurally characterized up to now (Mascharak, 1986).

The X-ray structure analysis reveals that the structure of (I) is ionic and built up of  $\text{NH}_4^+$  and  $\text{Et}_4\text{N}^+$  cations,  $[\text{Fe}(\text{CN})_6]^{3-}$  anions, and two crystallographically independent uncoordinated water molecules. A view of the asymmetric unit with the atomic numbering scheme is shown in Fig. 1 and selected bond lengths and angles are listed in Table 1.

The  $\text{Fe}^{\text{III}}$  atom in (I) is six-coordinated by C-bound terminal cyanide groups in the form of a regular octahedron, with  $\text{Fe}-\text{C}$  bond lengths in the range 1.937 (2)–1.945 (2) Å. Similar



**Figure 1**  
A view of the asymmetric unit of (I), along with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. The site occupied simultaneously by atoms O2 and N5 is labelled as N5/O2. H atoms have been omitted for clarity. [Symmetry code: (i)  $-x, -y + 1, -z + 2$ .]

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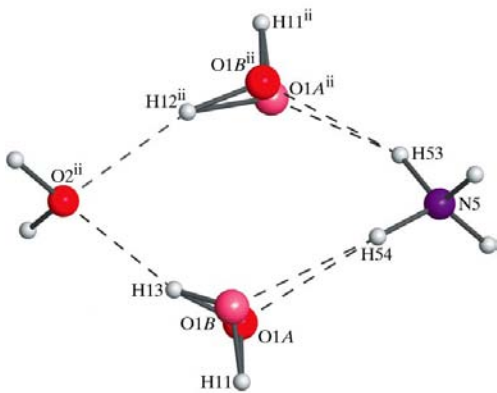
distances ranging between 1.921 (4) and 1.952 (3) Å were found in  $(\text{Hbet})_3[\text{Fe}(\text{CN})_6]\cdot 4\text{H}_2\text{O}$  and  $(\text{C}_{30}\text{H}_{51}\text{N}_6)[\text{Fe}(\text{CN})_6]\cdot 8\text{H}_2\text{O}$  [Hbet is  $(\text{CH}_3)_3\text{N}^+\text{CH}_2\text{CO}_2^-$ ; Yan *et al.*, 2001; Christofi *et al.*, 2002]. The Fe—C—N angles are almost linear, with a maximum deviation of 1.1° from linearity (Table 1), accounting for the presence of  $\pi$  back donation. All remaining geometric parameters in the anion are normal.

In line with the terminal character of all cyanide ligands in the complex anion, the measured IR spectrum displays only one strong absorption band, at 2119  $\text{cm}^{-1}$ , due to the stretching vibration of the cyanide group.

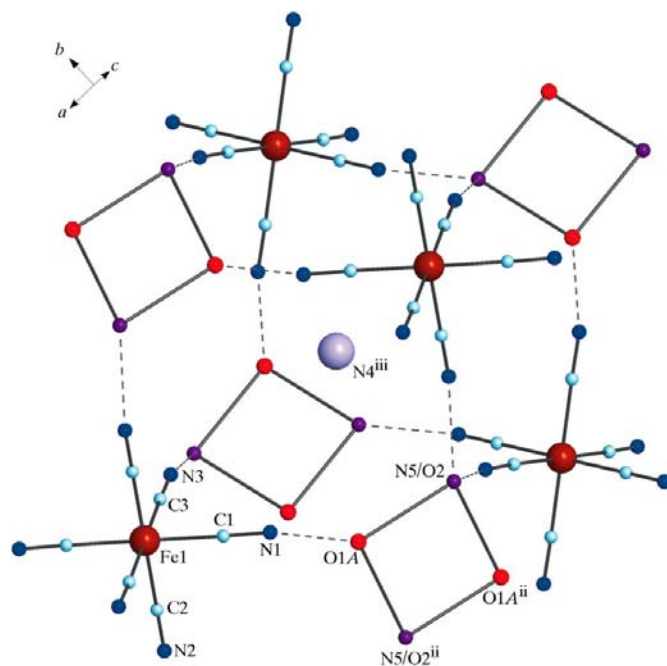
The negative charge of the complex anion is counterbalanced by one ammonium and two tetraethylammonium cations. The geometric parameters of the organic cation exhibit usual values and are similar to those found in other compounds (Iijima *et al.*, 2003; Mařarová *et al.*, 2003).

Atom O2 of one of the uncoordinated water molecules shares its crystallographic site with atom N5 of the ammonium cation in a 1:1 ratio as required by stoichiometry. Moreover, the O1 water molecule is disordered over two positions (O1A and O1B), separated by 0.551 (1) Å, with site-occupation factors of 0.5 (Fig. 2).

Owing to the presence of a symmetry centre, the uncoordinated water molecules and ammonium cations (O1 and N5/O2 atomic sites) form a cyclic  $\{(\text{NH}_4)(\text{H}_2\text{O})_3\}$  tetrameric unit in which the component species are held together by N—H...O and O—H...N,O hydrogen bonds (Table 2 and Fig. 2). These tetrameric units are linked to the N atoms of the terminal cyanide ligands by further hydrogen bonds. As a consequence, deformed cubes can be distinguished in the structure; four of the corners are formed by  $\text{Fe}^{\text{III}}$  atoms and four others by the tetrameric units. The edges of the cubes are formed by an Fe—C—N...O,N arrangement of atoms (Fig. 3). The tetraethylammonium cations are placed in the holes of the cubes. Such a view of the structure leads to an alternative



**Figure 2**  
The centrosymmetric  $\{(\text{NH}_4)(\text{H}_2\text{O})_3\}$  tetrameric unit. For the sake of clarity, only one of the two possible orientations linked by a centre of symmetry placed in the middle of the tetrameric unit is displayed. Position O1B of the disordered water molecule is shown in a paler colour than the other O atoms. Hydrogen bonds are shown as dashed lines. [Symmetry code: (ii)  $-x + 1, -y + 2, -z + 2$ .]



**Figure 3**  
The deformed cube of the hydrophilic part of the structure. The position of the tetraethylammonium cations within the cube (N atom) is shown by the large ball at the centre of the figure (light violet in the electronic version of the paper). [Symmetry codes: (ii)  $-x + 1, -y + 2, -z + 2$ ; (iii)  $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{3}{2}$ .]

description of (I) as composed of a hydrophilic part (complex anions, water molecules and ammonium cations) which encloses a hydrophobic part of the structure represented by the  $\text{Et}_4\text{N}^+$  cation, as in a host–guest system. Certainly, electrostatic forces play an important role in this structure. A similar situation was found in the structure of  $[\text{Ni}(\text{bpy})_3]_2[\text{Ag}(\text{CN})_2]_3\text{Cl}\cdot 9\text{H}_2\text{O}$  (bpy is 2,2'-bipyridine), in which the chloride anions and O atoms of uncoordinated water molecules share crystallographic positions (Černák *et al.*, 1994).

### Experimental

Yellow single crystals of  $(\text{NH}_4)(\text{Et}_4\text{N})_2[\text{Fe}(\text{CN})_6]\cdot 3\text{H}_2\text{O}$ , (I), were prepared by slow addition of a 0.1 M aqueous solution (10 ml) of  $\text{K}_3[\text{Fe}(\text{CN})_6]$  (1 mmol) to an aqueous solution of  $\text{CdCl}_2\cdot 2.5\text{H}_2\text{O}$  (1 mmol),  $(\text{Et}_4\text{N})\text{Br}$  (1 mmol) and  $\text{NH}_3$  (25%, 60 mmol) at 313 K. A yellow precipitate formed immediately and was dissolved by addition of 0.5 ml of concentrated aqueous ammonia. The resulting clear solution was filtered and the filtrate left aside for crystallization at room temperature. Within one week, a few large yellow prismatic single crystals were formed with a green microcrystalline powder as an admixture. The mixture was filtered off, washed with a small portion of cold water and dried in air. The yellow crystals were separated mechanically (yield 10%). The green precipitate has not been further analysed as it was inhomogeneous under the microscope. Analysis calculated for  $\text{C}_{22}\text{H}_{50}\text{FeN}_9\text{O}_3$ : C 48.6, H 9.1, N 23.1, Fe 10.3%; found: C 48.2, H 9.1, N 22.6, Fe 10.8%. IR (KBr disc,  $\text{cm}^{-1}$ ),  $\nu(\text{NH}_2)$ : 3404 (s), 3275 (s), 3003 (m);  $\nu(\text{CH}_3)$ : 2955 (m);  $\nu(\text{CH}_2)$ : 2901 (w);  $\nu(\text{CN})$ : 2119 (s);  $\delta(\text{NH}_2)$ : 1635 (s);  $\delta(\text{CH}_2)$ : 1481 (m), 1437 (m), 1367 (m);  $\nu(\text{Fe—C})$ : 398 (m).

Crystal data

(NH<sub>4</sub>)(C<sub>8</sub>H<sub>20</sub>N)<sub>2</sub>[Fe(CN)<sub>6</sub>]·3H<sub>2</sub>O  
*M<sub>r</sub>* = 544.56  
 Monoclinic, *P*2<sub>1</sub>/*n*  
*a* = 10.4720 (10) Å  
*b* = 10.2339 (7) Å  
*c* = 14.518 (2) Å  
 β = 99.051 (9)°

Data collection

Stoe IPDS diffractometer  
 Absorption correction: numerical  
 (XPREP in SHELXTL;  
 Sheldrick, 1996)  
*T*<sub>min</sub> = 0.055, *T*<sub>max</sub> = 0.146

*V* = 1536.5 (3) Å<sup>3</sup>  
*Z* = 2  
 Mo *K*α radiation  
 μ = 0.53 mm<sup>-1</sup>  
*T* = 193 (2) K  
 0.35 × 0.3 × 0.2 mm

Refinement

*R*[*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.039  
*wR*(*F*<sup>2</sup>) = 0.100  
*S* = 1.01  
 3710 reflections  
 187 parameters

H atoms treated by a mixture of  
 independent and constrained  
 refinement  
 Δρ<sub>max</sub> = 0.29 e Å<sup>-3</sup>  
 Δρ<sub>min</sub> = -0.47 e Å<sup>-3</sup>

Table 1

Selected geometric parameters (Å, °).

Fe1—C1	1.937 (2)	N1—C1	1.156 (3)
Fe1—C2	1.941 (2)	C3—N3	1.151 (3)
Fe1—C3	1.945 (2)	C2—N2	1.153 (3)
C1—Fe1—C2	89.76 (9)	C9—C8—N4	116.5 (2)
C1—Fe1—C3	87.03 (8)	C7—C6—N4	115.5 (2)
C2—Fe1—C3	90.27 (9)	N3—C3—Fe1	178.10 (19)
C12—C10—N4	115.17 (19)	N1—C1—Fe1	178.09 (18)
N4—C4—C5	115.26 (19)	N2—C2—Fe1	179.7 (3)

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 <i>B</i> —H11 <i>B</i> ...N1	0.83 (3)	1.97 (3)	2.722 (10)	152 (3)
N5—H53...O1 <i>B</i> <sup>ii</sup>	0.89 (2)	1.94 (3)	2.785 (9)	158 (5)
N5—H53...O1 <i>A</i> <sup>ii</sup>	0.89 (2)	1.87 (3)	2.687 (11)	152 (5)
N5—H54...O1 <i>B</i>	0.88 (2)	1.94 (2)	2.809 (8)	173 (5)
N5—H54...O1 <i>A</i>	0.88 (2)	1.84 (3)	2.669 (11)	157 (5)
N5—H51...N2 <sup>iii</sup>	0.827 (17)	1.996 (17)	2.822 (3)	177 (3)
N5—H52...N3 <sup>iv</sup>	0.859 (16)	1.961 (17)	2.820 (2)	179 (3)

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

The alkyl H atoms were treated as riding on their parent atoms and the *U*<sub>iso</sub>(H) parameters were set at 1.2 (methylene) or 1.5 (methyl) times *U*<sub>eq</sub> of the parent C atoms. The H atoms of the water molecules and ammonium cation were found in a difference map. Around the O1*A* and O1*B* atoms, three H-atom positions were found. Several models were tried; the best results were obtained assuming that the position of the H11 atom is fully occupied and the remaining two H atoms exhibit half-occupation. The positional parameters of water and ammonium H atoms were refined with N—H distances restrained

to 0.90 (2) Å and the O1—H13 distance restrained to 0.93 (2) Å. For the water and ammonium H atoms, isotropic displacement parameters common by groups were refined, one group was formed by O1 H atoms and the second by H atoms attached to the N5/O2 atoms. Possible hydrogen bonds were calculated using the program PARST (Nardelli, 1995) and are displayed in Table 2.

Data collection: EXPOSE in IPDS Software (Stoe & Cie, 1999); cell refinement: CELL in IPDS Software; data reduction: INTEGRATE in IPDS Software; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: DIAMOND (Brandenburg & Putz, 2006); 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: DN3040). Services for accessing these data are described at the back of the journal.

References

Allen, F. H. (2002). *Acta Cryst.* **B58**, 380–388.  
 Bernhardt, P. V., Bozoglian, F., Macpherson, B. P. & Martínez, M. (2005). *Coord. Chem. Rev.* **249**, 1902–1916.  
 Brandenburg, K. & Putz, H. (2006). *DIAMOND*. Version 3.1c. Crystal Impact GbR, Bonn, Germany.  
 Černák, J., Kaňuchová, M., Chomič, J., Potočňák, I., Kameníček, J. & Žák, Z. (1994). *Acta Cryst.* **C50**, 1563–1566.  
 Černák, J., Orendáč, M., Potočňák, I., Chomič, J., Orendáčová, A., Skoršepa, J. & Feher, A. (2002). *Coord. Chem. Rev.* **224**, 51–66.  
 Christofi, A. M., Garratt, P. J., Hogarth, G., Ibbett, A. J., Ng, Y.-F. & Steed, J. W. (2002). *Tetrahedron*, **58**, 4543–4547.  
 Dunbar, K. R. & Heintz, R. A. (1997). *Prog. Inorg. Chem.* **45**, 283–391.  
 Escorihuela, I., Falvello, L. R. & Tomás, M. (2001). *Inorg. Chem.* **40**, 636–640.  
 Iijima, S., Mizutani, F., Watanabe, M. & Sato, M. (2003). *J. Radioanal. Nucl. Chem.* **255**, 503–508.  
 Maľarová, M., Černák, J., Kuchár, J., Varret, F. & Massa, W. (2006). *Z. Anorg. Allg. Chem.* **632**, 495–500.  
 Maľarová, M., Černák, J. & Massa, W. (2006). *Acta Cryst.* **C62**, m119–m121.  
 Maľarová, M., Kuchár, J., Černák, J. & Massa, W. (2003). *Acta Cryst.* **C59**, m280–m282.  
 Mascharak, P. K. (1986). *Inorg. Chem.* **25**, 245–247.  
 Nardelli, M. (1995). *J. Appl. Cryst.* **28**, 659.  
 Ohba, M. & Okawa, H. (2000). *Coord. Chem. Rev.* **198**, 313–328.  
 Paul, B., Nather, C., Walfort, B., Fromm, K. M., Zimmermann, B., Lang, H. & Janiak, C. (2004). *CrystEngComm*, **6**, 293–297.  
 Petříček, V., Dušek, M. & Černák, J. (2005). *Acta Cryst.* **B61**, 280–286.  
 Sheldrick, G. M. (1996). *SHELXTL*. Version 5.03. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.  
 Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.  
 Stoe & Cie (1999). *IPDS Software*. Version 2.92. Stoe & Cie, Darmstadt, Germany.  
 Verdaguer, M., Bleuzen, A., Marvaud, V., Vaissermann, J., Seuleiman, M., Desplanches, C., Sculler, A., Train, C., Garde, R., Gelly, G., Lomenech, C., Rosenman, I., Veillet, P., Cartier, C. & Villain, F. (1999). *Coord. Chem. Rev.* **190–192**, 1023–1047.  
 Yan, B., Wang, H. D. & Chen, Z. D. (2001). *J. Mol. Struct.* **569**, 65–70.