

Poly[[hexa- μ -cyanido-manganese(II)-iron(III)] pentahydrate]

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Key indicators: single-crystal X-ray study; $T = 90$ K; mean $\sigma(\text{Mn}-\text{O}) = 0.012$ Å; H-atom completeness 1%; disorder in main residue; R factor = 0.047; wR factor = 0.136; data-to-parameter ratio = 13.2.

The structure of the title compound, $\text{Mn}^{\text{II}}[\text{Fe}^{\text{III}}(\text{CN})_6]_{2/3} \cdot 5\text{H}_2\text{O}$, features a face-centered cubic $-\text{Mn}-\text{NC}-\text{Fe}-$ framework with both Mn and Fe having site symmetry $m\bar{3}m$. Since one-third of the $[\text{Fe}(\text{CN})_6]^{3-}$ units are missing for a given formula in order to maintain charge neutrality, each Mn atom around such a vacancy is coordinated not only by the N atoms of the CN groups but also by the O atoms of the ligand water molecules. In addition to ligand water molecules, two types of non-coordinated water molecules, so-called zeolitic water molecules, exist in the interstitial sites of the $-\text{Mn}-\text{NC}-\text{Fe}-$ framework. The positions of the O atoms of the zeolitic water molecules are fixed by the linkage *via* hydrogen bonds between ligand water and zeolitic water molecules. The structure is related to a recently reported rubidium manganese hexacyanoferrate. Site occupancy factors for Fe, C, N are 0.67; for two O atoms the value is 0.83 and for one O atom is 0.17.

Related literature

For structure and properties of the related rubidium manganese hexacyanoferrate, see: Kato *et al.* (2003); Tokoro *et al.* (2007). For general background on Prussian blue compounds, see: Ludi & Güdel (1973). For related literature, see: Egan *et al.* (2006); Ferlay *et al.* (1995); Güdel *et al.* (1973); Gadet *et al.* (1992); Hatlevik *et al.* (1999); Holmes & Girolami (1999); Ludi *et al.* (1970); Margadonna *et al.* (2004); Ohkoshi & Hashimoto (2001); Ohkoshi *et al.* (1997, 2000, 2004, 2005); Sato *et al.* (1996); Tokoro *et al.* (2003, 2004); Zeigler *et al.* (1999).

Experimental

Crystal data

$\text{Mn}[\text{Fe}(\text{CN})_6]_{2/3} \cdot 5\text{H}_2\text{O}$
 $M_r = 286.50$
Cubic, $Fm\bar{3}m$
 $a = 10.3859$ (13) Å
 $V = 1120.3$ (2) Å³

$Z = 4$
Mo $K\alpha$ radiation
 $\mu = 2.02$ mm⁻¹
 $T = 90$ (1) K
 $0.25 \times 0.20 \times 0.15$ mm

Data collection

Rigaku R-Axis RAPID
diffractometer
Absorption correction: multi-scan
(*ABSCOR*; Higashi, 1995)
 $T_{\text{min}} = 0.655$, $T_{\text{max}} = 0.739$

15777 measured reflections
278 independent reflections
268 reflections with $F^2 > 2\sigma(F^2)$
 $R_{\text{int}} = 0.032$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.047$
 $wR(F^2) = 0.136$
 $S = 1.37$
278 reflections

21 parameters
H-atom parameters not defined
 $\Delta\rho_{\text{max}} = 0.59$ e Å⁻³
 $\Delta\rho_{\text{min}} = -1.41$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

Fe1—C1	1.918 (8)	N1—C1	1.169 (15)
Mn1—N1	2.105 (13)	Mn1—O1	2.247 (12)
O1—Mn1—O1 ⁱ	87.8 (4)	O1—Mn1—N1 ^{iv}	78.69 (14)
O1—Mn1—O1 ⁱⁱ	157.4 (3)	O1—Mn1—N1 ^v	163.90 (14)
O1—Mn1—O1 ⁱⁱⁱ	180		

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

Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *CrystalStructure* (Rigaku, 2007); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *VESTA* (Momma & Izumi, 2006); software used to prepare material for publication: *CrystalStructure*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SQ2003).

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Poly[[hexa- μ -cyanido-manganese(II)iron(III)] pentahydrate]

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Comment

In the last decade, various interesting magnetic functionalities have been reported with Prussian blue analogs, *e.g.*, high Curie temperatures (T_C) (Ferlay *et al.*, 1995; Holmes & Girolami, 1999; Hatlevik *et al.*, 1999; Ohkoshi *et al.*, 2000), humidity-response (Ohkoshi *et al.*, 2004), photomagnetism (Ohkoshi & Hashimoto, 2001; Sato *et al.*, 1996; Ohkoshi *et al.*, 1997), and zero thermal expansion (Margadonna *et al.*, 2004). Prussian blue analogs have two types of crystal structures, $M_A[M_B(\text{CN})_6]_{2/3} \cdot z\text{H}_2\text{O}$ (Ludi *et al.*, 1970; Ludi & Güdel, 1973; Güdel *et al.*, 1973) and $AM_A[M_B(\text{CN})_6]$ (Gadet *et al.*, 1992; Zeigler *et al.*, 1999; Kato *et al.*, 2003), where M_A and M_B are transition metal ions and A is an alkali metal ion. Recently, rubidium manganese hexacyanoferrate, $\text{Rb}_x\text{Mn}[\text{Fe}(\text{CN})_6]_{(x+2)/3} \cdot z\text{H}_2\text{O}$, has received attention due to its various functionalities such as a charge-transfer phase transition (Tokoro *et al.*, 2004; Ohkoshi *et al.*, 2005), a pressure-induced magnetic pole inversion (Egan *et al.*, 2006), and a photomagnetic effect (Tokoro *et al.*, 2003). Although the crystal structure of rubidium manganese hexacyanoferrate was determined (Kato *et al.*, 2003; Tokoro *et al.*, 2007), the structure of manganese hexacyanoferrate of $M_A[M_B(\text{CN})_6]_{2/3} \cdot z\text{H}_2\text{O}$ has not been determined yet. In this work, we successfully synthesized a single-crystal of $\text{Mn}[\text{Fe}(\text{CN})_6]_{2/3} \cdot 5\text{H}_2\text{O}$ and analyzed the crystal structure.

The crystal structure of the title compound consists of Mn^{II} and Fe^{III} with cyanide bridges to form a three-dimensional face-centered cubic structure (space group; $Fm\bar{3}m$), containing ligand water and zeolitic water molecules (Fig. 1). Fe, Mn, C, and N atoms occupy the positions 4a (0, 0, 0), 4 b (1/2, 1/2, 1/2), 24 e (0.1847 (8), 0,0), and 24 e (0.2973 (12), 0, 0), respectively. The Fe atoms are coordinated to six C atoms with octahedral geometries. On the other hand, the Mn atoms are coordinated to four N atoms and two O1 atoms of ligand water, since there are vacancies of $1/3 \times [\text{Fe}(\text{CN})_6]^{3-}$ to maintain charge neutrality. The O1 atoms occupy the 96k (0.4576 (10), 0.4576 (10), 0.2922 (11)) positions with occupancy of 1/12. The coordination geometry in the $\text{MnN}_x\text{O}_{6-x}$ ($x = 0-5$) moiety is octahedral with some potentially large distortions [O1-Mn-N bond angles of 78.19 (14)°, and 163.9 (2)°] due to the location of the disordered O1 water molecule. The oxygen atoms (O2 and O3) of zeolitic waters occupy 8c (1/4, 1/4, 1/4) positions with occupancy of 5/6 and 32f (0.1550 (16), 0.1550 (16), 0.1550 (16)) positions with occupancy of 1/6. The contact distances of 3.081 (11), 2.76 (2), 2.79 (2) Å between O1-O2^{i} , O1-O3 , and O3-O3^{ii} [Symmetry codes: (i) 1 - x , y , z ; (ii) 1 - z , 1 - x , y], respectively, suggest the existence of hydrogen bonds.

The structure of the title compound differs from that of the rubidium phase in the position of the O1 atom of the ligand water. This atom occupies the 96k position in $\text{Mn}[\text{Fe}(\text{CN})_6]_{2/3} \cdot 5\text{H}_2\text{O}$ and the 24 e position in $\text{Rb}_{0.61}\text{Mn}[\text{Fe}(\text{CN})_6]_{0.87} \cdot 1.7\text{H}_2\text{O}$ (Tokoro *et al.*, 2007). This difference may be explained by the hydrogen bonding between ligand water and zeolitic water in the title compound. The O2 atom of the zeolitic water exists on the 8c (1/4, 1/4, 1/4) position in $\text{Mn}[\text{Fe}(\text{CN})_6]_{2/3} \cdot 5\text{H}_2\text{O}$. The shortest length between the 8c and 24 e positions is 3.67 Å which is rather far to construct a hydrogen bond. In our refinement with the O1 atom in the 96k position, the distance of 3.081 (11) Å between O1 and O2^{i} [Symmetry code: (i) 1 - x , y , z] is acceptable as a hydrogen bond. By contrast, in $\text{Rb}_{0.61}\text{Mn}[\text{Fe}(\text{CN})_6]_{0.87} \cdot 1.7\text{H}_2\text{O}$, since the Rb cation is contained in the

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channels between the –Mn–NC–Fe– framework and the amount of vacant space is thus less than in $\text{Mn}[\text{Fe}(\text{CN})_6]_{2/3} \cdot 5\text{H}_2\text{O}$, the O2 atom of zeolitic water does not exist on the 8c position in the Rb compound, so no similar O1...O2 interaction occurs.

Experimental

Single crystals of $\text{Mn}[\text{Fe}(\text{CN})_6]_{2/3} \cdot 5\text{H}_2\text{O}$ were prepared by slow diffusion of aqueous solutions of $\text{MnCl}_2 \cdot 5\text{H}_2\text{O}$ (0.1 mmol) and $\text{K}_3[\text{Fe}(\text{CN})_6]$ (0.07 mmol) at 40 °C. After one month, dark brown block-shaped crystals were obtained. Elemental analysis of Mn and Fe was performed using inductively coupled plasma mass spectrometry (ICP-MS). The observed ratio of metal ions was Mn:Fe = 0.67:1.00. The density measured by the flotation method in toluene and tetrabromoethane was 1.64 (1) g cm^{-3} , which is consistent with the expected value of 1.63 g cm^{-3} calculated considering the lattice constant of 10.480 Å at 293 K. The CN stretching vibrations are observed at 2151 cm^{-1} in the IR spectrum.

Refinement

The H atoms of the water molecules could not be located. The site occupancy factors for Fe, C, and N were constrained to 2/3. The O1 atoms of the coordinated water molecules were located in a difference Fourier map and the site occupancy factor for O1 was constrained to 1/12, according to the formula of the crystal. The obtained anisotropic displacement factor of the N atom is rather large, but this is understood by the rotational vibration of CN around Fe—Mn.

Figures

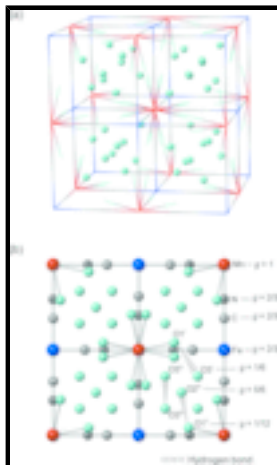


Fig. 1. (a) Three dimensional crystal structure of $\text{Mn}[\text{Fe}(\text{CN})_6]_{2/3} \cdot 5\text{H}_2\text{O}$, showing the distribution of zeolitic water molecules (teal spheres). The –Mn–NC–Fe– framework is described in stick form for clarity. Blue, red, dark gray, light gray and teal represent Fe, Mn, C, N and O atoms, respectively. (b) Projection of the structure in the ab plane. The value g is the occupancy for each atom. [Symmetry codes: (i) $1/2 - z, 1/2 - x, 1 - y$; (ii) $z, -x, 1 - y$; (iii) $z, -y, x$; (iv) $z, 1/2 - x, 1/2 + y$.]

Poly[[hexa- μ -cyanido-manganese(II)iron(III)] pentahydrate]

Crystal data

$\text{Mn}[\text{Fe}(\text{CN})_6]_{0.6667} \cdot 5\text{H}_2\text{O}$

$M_r = 286.50$

Cubic, $Fm\bar{3}m$

$Z = 4$

$F_{000} = 577.68$

$D_x = 1.699 \text{ Mg m}^{-3}$

$D_m = 1.64 (1) \text{ Mg m}^{-3}$

D_m measured by flotation in toluene and tetrabromo-methane

Hall symbol: -F 4 2 3

$a = 10.3859 (13) \text{ \AA}$

$b = 10.3859 (13) \text{ \AA}$

$c = 10.3859 (13) \text{ \AA}$

$\alpha = 90^\circ$

$\beta = 90^\circ$

$\gamma = 90^\circ$

$V = 1120.3 (2) \text{ \AA}^3$

Mo $K\alpha$ radiation

$\lambda = 0.71075 \text{ \AA}$

Cell parameters from 3216 reflections

$\theta = 5.6\text{--}45.1^\circ$

$\mu = 2.02 \text{ mm}^{-1}$

$T = 90 (1) \text{ K}$

Block, brown

$0.25 \times 0.20 \times 0.15 \text{ mm}$

Data collection

Rigaku R-Axis RAPID
diffractometer

Detector resolution: $10.00 \text{ pixels mm}^{-1}$

ω scans

Absorption correction: multi-scan
(ABSCOR; Higashi, 1995)

$T_{\min} = 0.655$, $T_{\max} = 0.739$

15777 measured reflections

278 independent reflections

268 reflections with $F^2 > 2\sigma(F^2)$

$R_{\text{int}} = 0.032$

$\theta_{\max} = 45.1^\circ$

$h = -20 \rightarrow 20$

$k = -20 \rightarrow 20$

$l = -20 \rightarrow 20$

Refinement

Refinement on F^2

$R[F^2 > 2\sigma(F^2)] = 0.047$

$wR(F^2) = 0.136$

$S = 1.37$

278 reflections

21 parameters

H-atom parameters not defined

$$w = 1/[\sigma^2(F_o^2) + (0.0526P)^2 + 2.6431P]$$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.59 \text{ e \AA}^{-3}$

$\Delta\rho_{\min} = -1.41 \text{ e \AA}^{-3}$

Extinction correction: SHELXL97 (Sheldrick, 1997)

Extinction coefficient: $0.002 (2)$

Special details

Refinement. Refinement was performed using all reflections. The weighted R -factor (wR) and goodness of fit (S) are based on F^2 . R -factor (gt) are based on F . The threshold expression of $F^2 > 2.0 \sigma(F^2)$ is used only for calculating R -factor (gt).

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
Fe1	0.5000	0.5000	0.0000	0.0176 (2)	0.6667
Mn1	0.5000	0.5000	0.5000	0.0183 (2)	
O1	0.4576 (10)	0.4576 (10)	0.2922 (11)	0.036 (3)	0.0833
O2	0.7500	0.2500	0.2500	0.096 (6)	0.8333
O3	0.6550 (16)	0.3450 (16)	0.1550 (16)	0.054 (6)	0.1667
N1	0.5000	0.5000	0.2973 (12)	0.086 (3)	0.6667

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C1 0.5000 0.5000 0.1847 (8) 0.064 (2) 0.6667

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Fe1	0.0176 (2)	0.0176 (2)	0.0176 (2)	0.0000	0.0000	0.0000
Mn1	0.0183 (2)	0.0183 (2)	0.0183 (2)	0.0000	0.0000	0.0000
O1	0.052 (5)	0.052 (5)	0.006 (3)	-0.026 (5)	-0.002 (2)	-0.002 (2)
O2	0.096 (6)	0.096 (6)	0.096 (6)	0.0000	0.0000	0.0000
O3	0.054 (6)	0.054 (6)	0.054 (6)	-0.018 (6)	0.018 (6)	-0.018 (6)
N1	0.114 (5)	0.114 (5)	0.030 (3)	0.0000	0.0000	0.0000
C1	0.085 (4)	0.085 (4)	0.023 (2)	0.0000	0.0000	0.0000

Geometric parameters (\AA , $^\circ$)

Fe1—C1	1.918 (8)	Mn1—O1 ^{ix}	2.247 (12)
Fe1—C1 ⁱ	1.918 (8)	Mn1—O1 ^{xiii}	2.247 (12)
Fe1—C1 ⁱⁱ	1.918 (8)	Mn1—O1 ^x	2.247 (12)
Fe1—C1 ⁱⁱⁱ	1.918 (8)	Mn1—O1 ^{xiv}	2.247 (12)
Fe1—C1 ^{iv}	1.918 (8)	Mn1—O1 ^{xv}	2.247 (12)
Fe1—C1 ^v	1.918 (8)	Mn1—O1 ^{xvi}	2.247 (12)
Mn1—N1	2.105 (13)	Mn1—O1 ^{xvii}	2.247 (12)
Mn1—N1 ^{vi}	2.105 (13)	Mn1—O1 ^{xviii}	2.247 (12)
Mn1—N1 ^{vii}	2.105 (13)	Mn1—O1 ^{xix}	2.247 (12)
Mn1—N1 ^{viii}	2.105 (13)	Mn1—O1 ^{xx}	2.247 (12)
Mn1—N1 ^{ix}	2.105 (13)	Mn1—O1 ^{xxi}	2.247 (12)
Mn1—N1 ^x	2.105 (13)	Mn1—O1 ^{xxii}	2.247 (12)
N1—C1	1.169 (15)	Mn1—O1 ^{xxiii}	2.247 (12)
Mn1—O1	2.247 (12)	Mn1—O1 ^{xxiv}	2.247 (12)
Mn1—O1 ^{vi}	2.247 (12)	Mn1—O1 ^{xxv}	2.247 (12)
Mn1—O1 ^{vii}	2.247 (12)	Mn1—O1 ^{xxvi}	2.247 (12)
Mn1—O1 ^{viii}	2.247 (12)	Mn1—O1 ^{xxvii}	2.247 (12)
Mn1—O1 ^{xi}	2.247 (12)	Mn1—O1 ^{xxviii}	2.247 (12)
Mn1—O1 ^{xii}	2.247 (12)		
C1—Fe1—C1 ⁱ	180.0000	N1 ^{ix} —Mn1—N1 ^x	90.0000
C1—Fe1—C1 ⁱⁱ	90.0000	Mn1—N1—C1	180.0000
C1—Fe1—C1 ⁱⁱⁱ	90.0000	Fe1—C1—N1	180.0000
C1—Fe1—C1 ^{iv}	90.0000	O1—Mn1—O1 ^{vi}	65.5 (4)
C1—Fe1—C1 ^v	90.0000	O1—Mn1—O1 ^{vii}	65.5 (4)
C1 ⁱ —Fe1—C1 ⁱⁱ	90.0000	O1—Mn1—O1 ^{viii}	147.8 (3)
C1 ⁱ —Fe1—C1 ⁱⁱⁱ	90.0000	O1—Mn1—O1 ^{xi}	87.8 (4)
C1 ⁱ —Fe1—C1 ^{iv}	90.0000	O1—Mn1—O1 ^{xii}	87.8 (4)
C1 ⁱ —Fe1—C1 ^v	90.0000	O1—Mn1—O1 ^{ix}	109.8 (4)

C1 ⁱⁱ —Fe1—C1 ⁱⁱⁱ	180.0000	O1—Mn1—O1 ^{xiii}	92.2 (4)
C1 ⁱⁱ —Fe1—C1 ^{iv}	90.0000	O1—Mn1—O1 ^x	109.8 (4)
C1 ⁱⁱ —Fe1—C1 ^v	90.0000	O1—Mn1—O1 ^{xiv}	157.4 (3)
C1 ⁱⁱⁱ —Fe1—C1 ^{iv}	90.0000	O1—Mn1—O1 ^{xv}	92.2 (4)
C1 ⁱⁱⁱ —Fe1—C1 ^v	90.0000	O1—Mn1—O1 ^{xvi}	157.4 (3)
C1 ^{iv} —Fe1—C1 ^v	180.0000	O1—Mn1—O1 ^{xvii}	180.0 (5)
N1—Mn1—N1 ^{vi}	90.0000	O1—Mn1—O1 ^{xviii}	114.5 (4)
N1—Mn1—N1 ^{vii}	90.0000	O1—Mn1—O1 ^{xix}	114.5 (4)
N1—Mn1—N1 ^{viii}	180.0000	O1—Mn1—O1 ^{xxi}	92.2 (4)
N1—Mn1—N1 ^{ix}	90.0000	O1—Mn1—O1 ^{xxii}	92.2 (4)
N1—Mn1—N1 ^x	90.0000	O1—Mn1—O1 ^{xxiii}	70.2 (4)
N1 ^{vi} —Mn1—N1 ^{vii}	90.0000	O1—Mn1—O1 ^{xxiv}	87.8 (4)
N1 ^{vi} —Mn1—N1 ^{viii}	90.0000	O1—Mn1—O1 ^{xxv}	70.2 (4)
N1 ^{vi} —Mn1—N1 ^{ix}	180.0000	O1—Mn1—O1 ^{xxvii}	87.8 (4)
N1 ^{vi} —Mn1—N1 ^x	90.0000	O1—Mn1—N1 ^{vi}	78.69 (14)
N1 ^{vii} —Mn1—N1 ^{viii}	90.0000	O1—Mn1—N1 ^{vii}	78.19 (14)
N1 ^{vii} —Mn1—N1 ^{ix}	90.0000	O1—Mn1—N1 ^{viii}	163.90 (14)
N1 ^{vii} —Mn1—N1 ^x	180.0000	O1—Mn1—N1 ^{ix}	101.31 (14)
N1 ^{viii} —Mn1—N1 ^{ix}	90.0000	O1—Mn1—N1 ^x	101.31 (14)
N1 ^{viii} —Mn1—N1 ^x	90.0000		

Symmetry codes: (i) $x, y, -z$; (ii) $y, z+1/2, x-1/2$; (iii) $y, -z+1/2, -x+1/2$; (iv) $z+1/2, x, y-1/2$; (v) $-z+1/2, x, -y+1/2$; (vi) y, z, x ; (vii) z, x, y ; (viii) $x, y, -z+1$; (ix) $y, -z+1, -x+1$; (x) $-z+1, x, -y+1$; (xi) $y, z, -x+1$; (xii) $z, x, -y+1$; (xiii) $z, -x+1, -y+1$; (xiv) $-x+1, y, -z+1$; (xv) $-y+1, z, -x+1$; (xvi) $x, -y+1, -z+1$; (xvii) $-x+1, -y+1, -z+1$; (xviii) $-y+1, -z+1, -x+1$; (xix) $-z+1, -x+1, -y+1$; (xx) $-x+1, -y+1, z$; (xxi) $-y+1, -z+1, x$; (xxii) $-z+1, -x+1, y$; (xxiii) $-y+1, z, x$; (xxiv) $-z+1, x, y$; (xxv) $z, -x+1, y$; (xxvi) $x, -y+1, z$; (xxvii) $y, -z+1, x$; (xxviii) $-x+1, y, z$.

Fig. 1

