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Key indicators

Single-crystal X-ray study  
 T = 293 K  
 Mean  $\sigma(C-C)$  = 0.004 Å  
 R factor = 0.034  
 wR factor = 0.112  
 Data-to-parameter ratio = 12.8

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

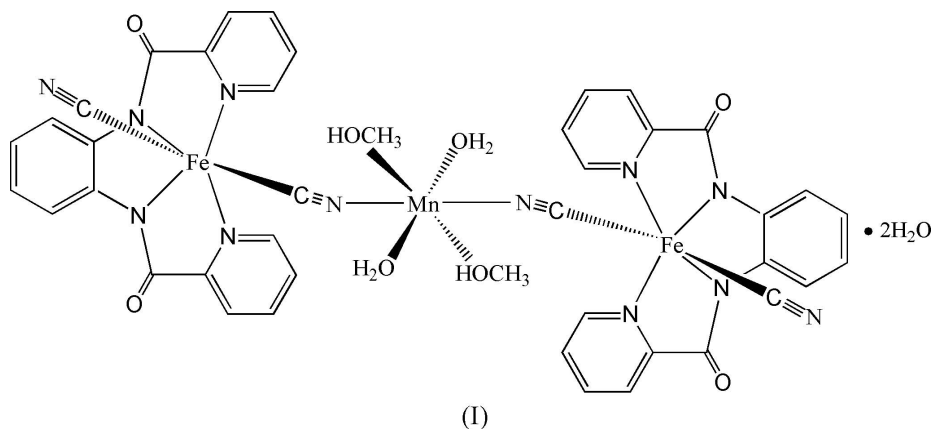
A cyano-bridged trimeric complex  
 $[Mn(CH_3OH)_2(H_2O)_2][Fe(bpb)(CN)_2]_2 \cdot 2H_2O$   
 [bpb<sup>2-</sup> is 1,2-bis(pyridine-2-carboxamido)-  
 benzenate]

The structure of the title complex, diaquadi- $\mu$ -cyano-dicyano-dimethanolbis[*N,N'*-*o*-phenylenebis(pyridine-2-carboxamido)]diiron(III)manganese(II),  $[MnFe_2(C_{18}H_{12}N_4O_2)_2(CN)_4 \cdot (CH_4O)_2(H_2O)_2] \cdot 2H_2O$ , consists of neutral centrosymmetric  $[Mn(CH_3OH)_2(H_2O)_2][Fe(bpb)(CN)_2]_2$  heterotrimeric units [bpb<sup>2-</sup> = 1,2-bis(pyridine-2-carboxamido)benzene(2-)] and water molecules of crystallization. Each  $[Fe(bpb)(CN)_2]^-$  unit acts as a monodentate ligand through one of its two cyanide groups toward the central Mn<sup>II</sup> ion (site symmetry  $\bar{1}$ ) in a bent fashion [C–N–Mn = 159.7 (2)°].

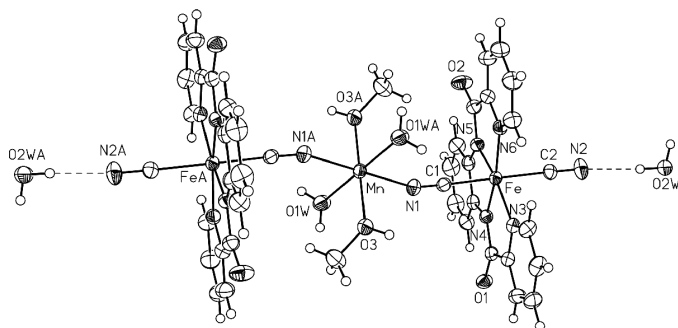
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Comment

In the past two decades, much attention has been paid to assembling cyano-bridged hybrid Prussian blue complexes as possible new molecular magnetic materials using hexacyano-metalate units  $[M(CN)_6]^{q-}$  ( $M = Fe, Cr, Mn$  or  $V$ ) as paramagnetic building blocks. More recently, a new synthetic strategy for assembling cyano-bridged complexes has been developed, based on the introduction of more versatile building blocks  $[M(L)_x(CN)_y]^{q-}$  ( $M = Fe, Cr$  or  $Ru$ ;  $L$  represents a blocking ligand), for example,  $[M(bipy)CN_4]^-$  ( $M = Fe$  and  $Cr$ ) (Lescouezec *et al.*, 2003) and  $[M(L)(CN)_3]$  [ $M = Fe$  and  $Cr$ ;  $L = 1,3,5$ -triaminocyclohexane (tach) (Yang *et al.*, 2003),  $L = 1,4,7$ -triazacyclononane (tacn) (Berseth *et al.*, 2002)]. This strategy results in a wide variety of molecular structures over a range of dimensionalities, including binuclear and polynuclear complexes, one-dimensional chain-like complexes, as well as two-dimensional networks with fascinating magnetic properties.

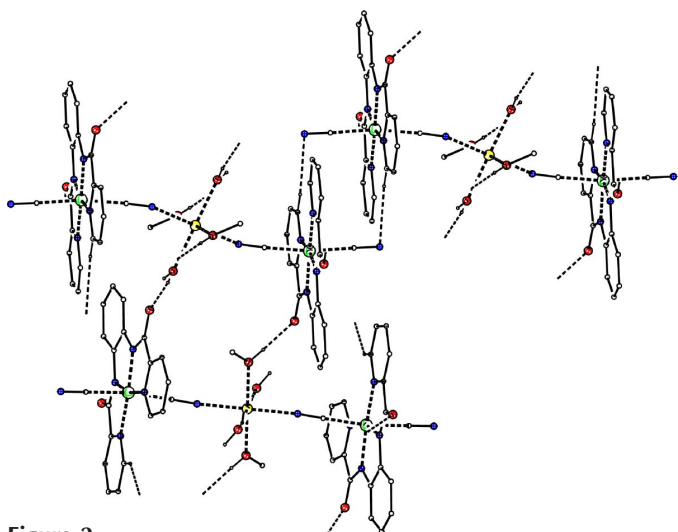


Manganese(III) Schiff base units have been shown to be very good building blocks in assembling cyano-bridged complexes with interesting properties because the high-spin



**Figure 1**

A view of (I) with the unique atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level. Atoms labelled with the suffix A are generated by the symmetry code  $(-x, -y, -z)$ .



**Figure 2**

The hydrogen-bonded network in (I). Hydrogen bonds are indicated by dashed lines. H atoms not involved in hydrogen bonding have been omitted.

$\text{Mn}^{3+}$  ( $3d^4$ ) ion has both relatively large anisotropy and more unpaired electrons than low-spin  $\text{Mn}^{3+}$  ions. In this paper, we report the title bimetallic trinuclear complex, (I) (Fig. 1 and Table 1), that arose as an unexpected product from our attempts to construct a cyano-bridged  $[\text{Mn}^{\text{III}}(\text{salphen})\text{Fe}(\text{bpb})(\text{CN})_2]_n$  [ $\text{H}_2\text{salphen}$  = bis(salicylaldehyde)phenylenediimine and  $\text{bpb}^{2-}$  = 1,2-bis(pyridine-2-carboxamido)benzene(2-)] neutral chain-like complex.

The centrosymmetric complex has a sandwich-like structure made up of a neutral trinuclear entity of formula  $[\text{Mn}(\text{CH}_3\text{OH})_2(\text{H}_2\text{O})_2][\text{Fe}(\text{bpb})(\text{CN})_2]_2 \cdot 2\text{H}_2\text{O}$ , in which each  $[\text{Fe}(\text{bpb})(\text{CN})_2]^-$  unit uses one of its two cyanide groups to coordinate to the central  $\text{Mn}^{\text{II}}$  ion. The bridging  $\text{Mn}-\text{N}1-\text{C}1$  bond angle deviates significantly from linearity [ $159.75$  ( $19$ ) $^\circ$ ], which is common in cyano-bridged complexes, although a perfectly linear cyano bridge has occasionally been observed (Zhou *et al.*, 2002). The intramolecular  $\text{Fe} \cdots \text{Mn}$  separation through the bridging cyanide ion is  $5.203$  ( $1$ )  $\text{\AA}$ .

The iron(III) ion in (I) is coordinated by four  $\text{bpb}^{2-}$  N atoms and two cyanide C atoms, in a slightly distorted octahedral geometry. The  $\text{Fe}-\text{C}1$  (unbridging cyano) and  $\text{Fe}-\text{C}2$

(bridging cyano) bond distances are almost identical at  $1.965$  ( $2$ ) and  $1.969$  ( $2$ )  $\text{\AA}$ , respectively. The  $\text{Fe}-\text{C}-\text{N}$  bond angles are almost linear (Table 1). The  $\text{Fe}-\text{N}$  bond distances range from  $1.8842$  ( $19$ ) to  $1.969$  ( $2$ )  $\text{\AA}$ , close to that for related  $\text{Fe}-\text{bpb}$  complexes (Ray *et al.*, 1993; Ni *et al.*, 2005). The short  $\text{Fe}-\text{N}$  (imide) bond distances suggest the presence of strong donor-acceptor interactions between the iron(III) species and the imide N atoms. This might be due to the steric strain of the rigid  $\text{bpb}$  ligand.

The  $\text{Mn}^{\text{II}}$  ion in (I) is hexacoordinated by two cyanide N atoms from two  $[\text{Fe}(\text{bpb})(\text{CN})_2]^-$  units in *trans* positions and four O atoms from two water molecules and two methanol molecules, yielding a  $\text{MnO}_4\text{N}_2$  grouping. The  $\text{Mn}-\text{N}$  (cyano) bond distance of  $2.195$  ( $2$ )  $\text{\AA}$  is slightly longer than those in  $[(\text{Tp})\text{Fe}(\text{CN})_3]_2[\text{Mn}(\text{CH}_3\text{OH})_4] \cdot 2\text{CH}_3\text{OH}$  [ $2.174$  ( $2$ )  $\text{\AA}$ ; Wang *et al.*, 2004] and  $[\text{Fe}(\text{bipy})(\text{CN})_4]_2[\text{Mn}(\text{H}_2\text{O})_4] \cdot 4\text{H}_2\text{O}$  [ $2.183$  ( $6$ )  $\text{\AA}$ ; Lescouezec *et al.*, 2002].

Between the cyano-bridged trinuclear complexes, uncoordinated water molecules are present, and these form  $\text{O}-\text{H} \cdots \text{N}$  hydrogen bonds to cyano N atoms and  $\text{O}-\text{H} \cdots \text{O}$  bonds to the coordinated water molecules (Table 2). Also, a methanol molecule interacts with an imide O atom of a neighbouring complex, as shown in Fig. 2.

The formation of (I) involves the redox reaction of  $\text{Mn}^{\text{III}}$  ions with the Schiff base ligand. A similar phenomenon has been observed during the reaction between  $(\text{Me}_4\text{N})_2\text{K}_2[\text{Nb}_6\text{Cl}_{12}(\text{CN})_6]$  and  $[\text{Mn}(\text{salen})]\text{ClO}_4$  to yield  $(\text{Me}_4\text{N})_2[\text{MnNb}_6\text{Cl}_{12}(\text{CN})_6]$  (Yan *et al.*, 2003).

## Experimental

$[\text{Mn}(\text{salphen})]\text{ClO}_4$  (Przychodzen *et al.*, 2004) and  $\text{K}[\text{Fe}(\text{bpb})(\text{CN})_2]$  (Ray *et al.*, 1993) were synthesized using literature procedures. Black block-like single crystals of (I) suitable for X-ray diffraction analysis were obtained at room temperature by the slow diffusion of a methanol solution (5 ml) of  $[\text{Mn}(\text{salphen})]\text{ClO}_4$  (46.8 mg, 0.1 mmol) into a mixed methanol-water solution (5 ml) of  $\text{K}[\text{Fe}(\text{bpb})(\text{CN})_2]$  (46.1 mg, 0.1 mmol) for about one week.

### Crystal data

$[\text{MnFe}_2(\text{C}_{18}\text{H}_{12}\text{N}_4\text{O}_2)_2(\text{CN})_4 \cdot (\text{CH}_4\text{O})_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$   
 $M_r = 1039.50$   
 Monoclinic,  $P2_1/c$   
 $a = 14.011$  ( $3$ )  $\text{\AA}$   
 $b = 13.247$  ( $2$ )  $\text{\AA}$   
 $c = 12.701$  ( $2$ )  $\text{\AA}$   
 $\beta = 106.834$  ( $15$ ) $^\circ$   
 $V = 2256.5$  ( $7$ )  $\text{\AA}^3$   
 $Z = 2$

$D_x = 1.530$   $\text{Mg m}^{-3}$   
 Mo  $K\alpha$  radiation  
 Cell parameters from 1748 reflections  
 $\theta = 2.4-22.5$  $^\circ$   
 $\mu = 0.98$   $\text{mm}^{-1}$   
 $T = 293$  ( $2$ )  $\text{K}$   
 Block, black  
 $0.25 \times 0.18 \times 0.14$   $\text{mm}$

### Data collection

Bruker  $P4$  diffractometer  
 $\omega$  scans  
 Absorption correction:  $\psi$  scan (North *et al.*, 1968)  
 $T_{\text{min}} = 0.820$ ,  $T_{\text{max}} = 0.873$   
 4141 measured reflections  
 3946 independent reflections  
 3403 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.025$   
 $\theta_{\text{max}} = 25.0$  $^\circ$   
 $h = -16 \rightarrow 15$   
 $k = 0 \rightarrow 15$   
 $l = 0 \rightarrow 15$   
 3 standard reflections every 97 reflections  
 intensity decay: none

Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.034$   
 $wR(F^2) = 0.112$   
 $S = 1.08$   
 3946 reflections  
 309 parameters  
 H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0744P)^2 + 0.0733P]$$

where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.001$   
 $\Delta\rho_{\max} = 0.30 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\min} = -0.21 \text{ e } \text{\AA}^{-3}$

**Table 1**  
 Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ).

Fe—N5	1.8842 (19)	Mn—O1W	2.1876 (17)
Fe—N4	1.8958 (18)	Mn—N1	2.195 (2)
Fe—C1	1.966 (2)	Mn—O3	2.2007 (17)
Fe—C2	1.969 (2)	C2—N2	1.139 (3)
Fe—N6	2.0014 (19)	C1—N1	1.138 (3)
Fe—N3	2.0067 (19)		
N5—Fe—N4	83.87 (8)	C1—Fe—N3	86.12 (8)
N5—Fe—C1	94.35 (9)	C2—Fe—N3	88.21 (9)
N4—Fe—C1	93.79 (8)	N6—Fe—N3	112.04 (8)
N5—Fe—C2	92.93 (9)	O1W—Mn—N1	92.13 (8)
N4—Fe—C2	92.52 (8)	O1W <sup>o</sup> —Mn—N1	87.87 (8)
C1—Fe—C2	170.84 (9)	O1W—Mn—O3	90.61 (7)
N5—Fe—N6	82.22 (8)	O1W <sup>o</sup> —Mn—O3	89.39 (7)
N4—Fe—N6	166.05 (8)	N1—Mn—O3	90.93 (7)
C1—Fe—N6	86.15 (8)	N1 <sup>i</sup> —Mn—O3	89.07 (7)
C2—Fe—N6	89.33 (8)	N2—C2—Fe	178.3 (2)
N5—Fe—N3	165.72 (8)	N1—C1—Fe	177.0 (2)
N4—Fe—N3	81.85 (8)	C1—N1—Mn	159.75 (19)

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

**Table 2**  
 Hydrogen-bonding geometry ( $\text{\AA}$ ,  $^\circ$ ).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O1W—H100 $\cdots$ O2 <sup>ii</sup>	0.85	1.91	2.747 (4)	169
O1W—H101 $\cdots$ O2W <sup>iii</sup>	0.87	1.86	2.723 (4)	175
O3—H50 $\cdots$ O1 <sup>iv</sup>	0.85	1.89	2.738 (4)	178
O2W—H200 $\cdots$ O1 <sup>v</sup>	0.85	1.91	2.738 (4)	164
O2W—H201 $\cdots$ N2	0.85	2.04	2.881 (4)	173

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

The H atoms of the water molecules were found in difference Fourier maps and normalized to have O—H = 0.85  $\text{\AA}$ . H atoms bound to C atoms were visible in difference maps and were placed in idealized positions (C—H = 0.93–0.96  $\text{\AA}$ ). All H atoms were refined as riding, with  $U_{\text{iso}}(\text{H}) = 1.2$  or 1.5 times  $U_{\text{eq}}(\text{parent atom})$ .

Data collection: *XSCANS* (Bruker, 1997); cell refinement: *XSCANS*; data reduction: *SHELXTL* (Bruker, 1997); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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References

Berseth, P. A., Sokol, J. J., Shores, M. P., Heinrich, J. L. & Long, J. R. (2002). *J. Am. Chem. Soc.* **122**, 9655–9622.  
 Bruker (1997). *XSCANS* and *SHELXTL*. Bruker AXS Inc., Madison, Wisconsin, USA.  
 Lescouezec, R., Lloret, F., Julve, M., Vaissermann, J. & Verdager, M. (2002). *Inorg. Chem.* **41**, 818–826.  
 Lescouezec, R., Vaissermann, J., Ruiz Perez, C., Lloret, F., Carrasco, R., Julve, M., Verdager, M., Dromzee, Y., Gatteschi, D. & Wernsdorfer, W. (2003). *Angew. Chem. Int. Ed.* **42**, 1483–1486.  
 Ni, Z. H., Kou, H.-Z., Zhao, Y.-H., Zheng, L., Wang, R.-J., Cui, A.-L. & Sato, O. (2005). *Inorg. Chem.* **44**, 2050–2059.  
 North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–359.  
 Przychodzen, P., Lewinski, K., Balanda, M., Pelka, P., Rams, M., Wasiutynski, T., Guyard-Duhayon, C. & Sieklucka, B. (2004). *Inorg. Chem.* **43**, 2967–2974.  
 Ray, M., Mukherjee, R., Richardson, J. F. & Buchanan, R. M. (1993). *J. Chem. Soc. Dalton Trans.* pp. 2451–2457.  
 Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.  
 Wang, S., Zuo, J. L., Zhou, H. C., Song, Y., Gao, S. & You, X. Z. (2004). *Eur. J. Inorg. Chem.* pp. 3681–3687.  
 Yan, B., Zhou, H. & Lachgar, A. (2003). *Inorg. Chem.* **42**, 8818–8822.  
 Yang, J. Y., Shores, M. P., Sokol, J. J. & Long, J. R. (2003). *Inorg. Chem.* **42**, 1403–1419.  
 Zhou, B. C., Kou, H.-Z., He, Y., Xiong, M., Wang, R.-J. & Li, Y. (2002). *Acta Cryst.* **C58**, m478–m480.