

Cyanide- and phenoxo-bridged heterobimetallic Fe(III)-Mn(III) complexes: Synthesis, crystal structures and magnetic properties

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Abstract. By employing two *mer*-tricyanidoiron(III) precursors $[\text{Ph}_4\text{P}][\text{Fe}^{\text{III}}(\text{pcq})(\text{CN})_3]$ and $[\text{Ph}_4\text{P}][\text{Fe}^{\text{III}}(\text{pzq})(\text{CN})_3]$ as building blocks and a salen-type Schiff-base manganese (III) compound as assembling segment, two tetranuclear cyanide- and phenoxo-bridged heterobimetallic Fe(III)-Mn(III) complexes $\{[\text{Mn}(\text{saltmen})][\text{Fe}(\text{pcq})(\text{CN})_3]\}_2 \cdot 2\text{CH}_3\text{OH}$ (**1**) and $\{[\text{Mn}(\text{saltmen})][\text{Fe}(\text{pzq})(\text{CN})_3]\}_2 \cdot 2\text{CH}_3\text{OH}$ (**2**) (pcq = 8-(pyridine-2-carboxamido, pzq = 8-(pyrazine-2-carboxamido, saltmen²⁻ = *N, N'*-(1,1,2,2-tetramethylethylene)bis(salicylideneamino)dianion) have been synthesized and characterized by elemental analysis, IR spectroscopy and X-ray structure determination. Single x-ray analysis reveals their isostructural cyanide-bridged Fe(III)-Mn(III) binuclear structure. The binuclear entity is self-complementary through phenoxo oxygen from the neighbouring complex, giving cyanide- and phenoxo-bridged tetranuclear structure. Furthermore, under the help of the intermolecular π - π interaction, these two complexes can be constructed into 1D infinite chain supramolecular structure. Investigation over magnetic susceptibilities reveals the overall ferromagnetic coupling between the adjacent Fe(III) and Mn(III) ions bridged by cyanide group with $J = 5.34 \text{ cm}^{-1}$ and 5.55 cm^{-1} for complexes **1** and **2**, respectively.

Keywords. Cyanide-bridged; heterobimetallic; crystal structure; magnetic property.

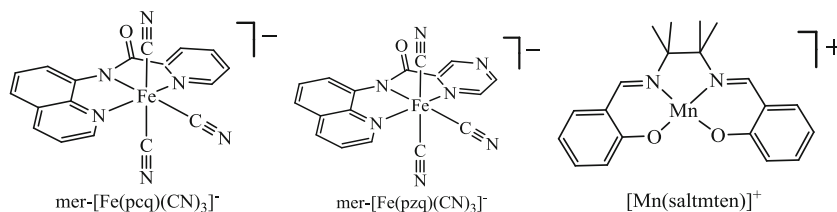
1. Introduction

Over the past three decades, due to the well-known ability of the cyanide group to mediate exchange interactions between the paramagnetic centres, cyanide-bridged complexes have been given continuous attention in molecule magnetism field. Till now, a large number of cyanide-bridged molecule-based magnetic materials with high- T_c , single-molecule magnets (SMMs), single-chain magnets (SCMs), spin crossover (SCO) and photomagnetic materials with different types of structures ranging from discrete polynuclear compounds to one-dimensional chains and two- and three-dimensional networks have been synthesized on the basis of rational selection of magnetic centres and cyanide-containing building blocks.^{1–15}

Investigation results have revealed that the design and preparation of novel cyanide-containing building blocks of polycyanideiron(III) $[\text{Fe}(\text{L})(\text{CN})_m]^{n-}$ (L represents blocking ligand) play an important role in the synthesis of cyanide-bridged molecular magnetic materials. So far a number of polycyanideiron(III) building

blocks including $[\text{Fe}(\text{L})(\text{CN})_5]^{2-}$ (L = 1-methylimidazole),¹⁶ $[\text{Fe}(\text{L})(\text{CN})_4]^-$ (L = bipy, phen, bpym),¹⁷ *fac*- $[\text{Fe}(\text{L})(\text{CN})_3]^-$ (L = Tp, Tp*, pzTp, tach),^{18–20} and *mer*- $[\text{Fe}(\text{L})(\text{CN})_3]^-$ (L = bpca, pzcq, mpzcq, qcq, pcq, icq)^{21–23} and $[\text{Fe}(\text{L})(\text{CN})_2]^-$ (L = bpb derivatives or salen)²⁴ have been designed, synthesized and employed in assembling into cyanide-bridged molecular magnetic materials. Among which, the tricyanoiron(III) precursor *mer*- $[\text{Fe}^{\text{III}}(\text{pcq})(\text{CN})_3]^-$ and its analogues have been proved to be suitable building blocks for the assembling of low-dimensional heterometallic cyanide-bridged magnetic complexes.^{21–23} Being also interested in this type of cyanide-building blocks, we investigated the reactions of *mer*-tricyanoiron(III) building blocks $[\text{Ph}_4\text{P}][\text{Fe}^{\text{III}}(\text{pcq})(\text{CN})_3]$ ^{22d,23} (pcq = 8-(pyridine-2-carboxamido) and $[\text{Ph}_4\text{P}][\text{Fe}^{\text{III}}(\text{pzq})(\text{CN})_3]$ ^{22b,e} (pzq = 8-(pyrazine-2-carboxamido) with Schiff base manganese compound $[\text{Mn}(\text{saltmen})(\text{H}_2\text{O})_2]\text{ClO}_4$ (saltmen²⁻ = *N, N'*-(1,1,2,2-tetramethylethylene)bis(salicylideneimino)dianion) (scheme 1), resulting in two cyano and phenoxo oxygen atom mix-bridged tetranuclear heterobimetallic complexes. The synthesis, crystal structure and magnetic properties of $\{[\text{Mn}(\text{saltmen})][\text{Fe}(\text{pcq})(\text{CN})_3]\}_2 \cdot 2\text{CH}_3\text{OH}$ (**1**) and $\{[\text{Mn}(\text{saltmen})][\text{Fe}(\text{pzq})(\text{CN})_3]\}_2 \cdot 2\text{CH}_3\text{OH}$ will be described in this paper.

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Scheme 1. The starting materials used to prepare complexes **1** and **2**.

2. Experimental

2.1 General procedures and materials

All the reactions were carried out under an air atmosphere and all chemicals and solvents used in the synthesis were reagent grade without further purification. $[\text{Ph}_4\text{P}][\text{Fe}(\text{pcq})(\text{CN})_3]$, $[\text{Ph}_4\text{P}][\text{Fe}(\text{pzq})(\text{CN})_3]$ and $[\text{Mn}(\text{saltmen})(\text{H}_2\text{O})_2]\text{ClO}_4$ were prepared according to the previous works.^{22b,23a,25}

Caution! Perchlorate salts of metal complexes with organic ligands are potentially explosive. They should be handled in small quantities with care.

2.2 The preparation of complexes **1** and **2**

A solution containing $\text{PPh}_4[\text{Fe}(\text{pcq})(\text{CN})_3]$ (0.1 mmol, 72.4 mg) or $\text{PPh}_4[\text{Fe}(\text{pzq})(\text{CN})_3]$ (0.1 mmol, 72.5 mg) in methanol (10 mL) was added to a stirred methanol and acetonitrile solution (10 mL, 1:1, v:v) of $[\text{Mn}(\text{saltmen})(\text{H}_2\text{O})_2]\text{ClO}_4$ (0.1 mmol, 51.3 mg). The mixture was stirred for a few minutes at room temperature and filtered. Then the filtrate was allowed to

evaporate slowly without disturbance. The dark brown crystals so obtained several days later, which were suitable for X-ray diffraction, were collected by filtration, washed with cool methanol, and dried in air. Yield 51.1 mg, 64.4%. Anal. Calcd. For $\text{C}_{78}\text{H}_{72}\text{Fe}_2\text{Mn}_2\text{N}_{16}\text{O}_8$: C, 59.18; H, 4.58; N, 14.16. Found: C, 59.36; H, 4.77; N, 13.95. Main IR bands (cm^{-1}): 2158, 2120 (s, $\nu\text{C}\equiv\text{N}$), 1616, 1623 (vs, $\nu\text{C}=\text{N}$).

Complex **2**: 49.5 mg, 62.5%. Anal. Calcd. for $\text{C}_{76}\text{H}_{70}\text{Fe}_2\text{Mn}_2\text{N}_{18}\text{O}_8$: C, 57.59; H, 4.45; N, 15.91. Found: C, 57.36; H, 4.27; N, 15.68. Main IR bands (cm^{-1}): 2160, 2121 (s, $\nu\text{C}\equiv\text{N}$), 1618, 1625 (vs, $\nu\text{C}=\text{N}$).

2.3 X-ray data collection and structure refinement

Single crystals of all the complexes for X-ray diffraction analyses with suitable dimensions were mounted on the glass rod and the crystal data were collected on a Bruker SMART CCD diffractometer with a $\text{MoK}\alpha$ sealed tube ($\lambda = 0.71073 \text{ \AA}$) at 293 K, using a ω scan mode. The structures were solved by direct method and expanded using Fourier difference techniques

Table 1. Crystallographic data for complexes **1** and **2**.

	1	2
chemical formula	$\text{C}_{78}\text{H}_{72}\text{Fe}_2\text{Mn}_2\text{N}_{16}\text{O}_8$	$\text{C}_{76}\text{H}_{70}\text{Fe}_2\text{Mn}_2\text{N}_{18}\text{O}_8$
Fw	1583.10	1585.08
crystal system	monoclinic	monoclinic
Space group	C2/c	C2/c
$a/\text{\AA}$	24.925(6)	24.939(8)
$b/\text{\AA}$	12.898(3)	12.805(3)
$c/\text{\AA}$	22.151(5)	22.346(6)
α/deg	90	90
β/deg	92.724(4)	92.615(8)
γ/deg	90	90
$V/\text{\AA}^3$	7113(3)	7129(3)
Z	4	4
completeness	97.6%	99.7%
$F(000)$	3272	3272
θ/deg	1.78 to 24.83	1.79 to 25.01
GOF	1.023	1.021
$R_1[I > 2\sigma(I)]$	0.0522	0.0532
$wR_2(\text{all data})$	0.1564	0.1604

with the SHELXTL-97 program package. The non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were introduced as fixed contributors and assigned isotropic displacement coefficients $U(H)=1.2U(C)$ or $1.5U(C)$, and their coordinates were allowed to ride on their respective carbons using SHELXL97. For the disordered contents, the partially occupied atoms were refined isotropically. Details of the crystal parameters, data collection and refinement are summarized in table 1.

3. Results and Discussion

3.1 Synthesis and general characterization

Due to the facile preparation and the large spin state ($S = 2$) as well as the usually negative magnetic anisotropy of the central Mn(III) ions, manganese(III)-salen types of compounds with N_2O_2 equatorial salen-type ligands (salen = N,N-ethylene-bis(salicylideneimine)) have been widely used to prepare cyanide-bridged magnetic complexes by assembling with many cyanide-containing building blocks.²⁶ In this paper, we investigated the reactions of $[Mn(salmten)(H_2O)_2]ClO_4$ with $[Ph_4P][Fe(pcq)(CN)_3]$ or $[Ph_4P][Fe(pzq)(CN)_3]$, and obtained two binuclear cyanide-bridged Fe(III)-Mn(III) complexes. Furthermore, due to the coordination of the phenoxo oxygen atoms from the neighbouring complex to the Mn(III) atom, the neutral binuclear unit can be self-assembled into cyano and phenoxo oxygen mix-bridged tetranuclear entity. The crystal structure of these two complexes is different from the reported compound $[Fe(pcq)(CN)_3Mn(salmten)(CH_3OH)] \cdot CH_3OH$,^{22d} which belongs to cyanide-bridged binuclear type with the two axial positions of the Mn(III) ion occupied by the N atom of the bridging cyanide group and the O atom of the coordinated solvent methanol molecule. The two cyanide-bridged heterometallic complexes have been characterized by IR spectroscopy. In the IR spectra of complexes **1** and **2**, two sharp peaks due to the cyanide-stretching vibration were observed at about 2125 and 2155 cm^{-1} respectively, indicating the presence of bridging and nonbridging cyanide ligands in these complexes.

3.2 Crystal structures of complexes **1** and **2**

Some important structural parameters for complexes **1** and **2** are collected in table 2. The neutral tetranuclear structure for these two complexes, their representative 1D supramolecular structure formed by the intermolecular $\pi-\pi$ interactions and cell packing

Table 2. Selected bond lengths (Å) and angles (°) for complexes **1** and **2**.

	1	2
Fe(1)-C(1)	1.952(6)	1.962(6)
Fe(1)-C(2)	1.945(6)	1.958(6)
Fe(1)-C(3)	1.958(7)	1.968(7)
Fe(1)-N(4)	1.984(4)	1.970(4)
Fe(1)-N(5)	1.872(4)	1.881(4)
Fe(1)-N(6)	1.968(4)	1.956(4)
Mn1-N1	2.211(5)	2.229(5)
Mn(1)-N(8)	1.971(4)	1.981(4)
Mn(1)-N(9)	1.995(4)	1.974(4)
Mn1-O1	1.895(3)	1.863(4)
Mn1-O2	1.861(4)	1.881(3)
Mn1-O2#1	2.620(3)	2.638(1)
C(1)-N(1)-Mn(1)	163.3(5)	163.5(5)
N(1)-C(1)-Fe(1)	174.6(5)	174.5(5)
N(2)-C(2)-Fe(1)	177.3(5)	177.4(5)
N(3)-C(3)-Fe(1)	177.7(6)	177.6(6)

Symmetry transformations used to generate equivalent atoms: #1: $-x+1/2, y+3/2, -z+3/2$.

diagram along *a* axis are shown in figures 1–3, respectively.

As can be found in table 2, complexes **1** and **2** are isostructural and crystallize in monoclinic space group $C2/c$. In these two complexes, the tricyanide-containing building block acts as a monodentate ligand through one of its two axial cyanide groups towards the Mn(III) ion, affording a cyanide-bridged binuclear Fe-Mn structure. The Fe(III) ion is coordinated by three N atoms of tridentate organic ligand and three C atoms of cyanide groups in *mer*-position, so that involved in a distorted octahedral geometry, which can be proved by the bond parameters around for the Fe(III) ion (table 2). The parameters around the Fe(III) ion is almost same to those found in the free $[Fe(pcq)(CN)_3]^-$ or $[Fe(pzq)(CN)_3]^-$,^{22b,e,23a} indicating that the coordination of the cyanide group to the Mn(III) ion has no obvious influence on the geometry of the Fe(III) ion. The bond angles of Fe-C \equiv N in a very narrow range of 174.5(5)–177.7(6)° clearly indicate that the three atoms are in a good linear configuration.

The coordination sphere for the Mn atom in these two complexes is also described as a distorted octahedral, in which four equatorial positions are occupied by two N atoms and two O atoms from the Schiff base ligand, and the other two axial ones come from the N atoms of the bridging cyanide group and the phenoxo oxygen atom of the neighbouring binuclear molecule. As shown in table 2, the average distances between the Mn atom and the N, O atoms of the Schiff-base ligand in complexes **1** and **2** are 1.983 and 1.978 Å respectively,

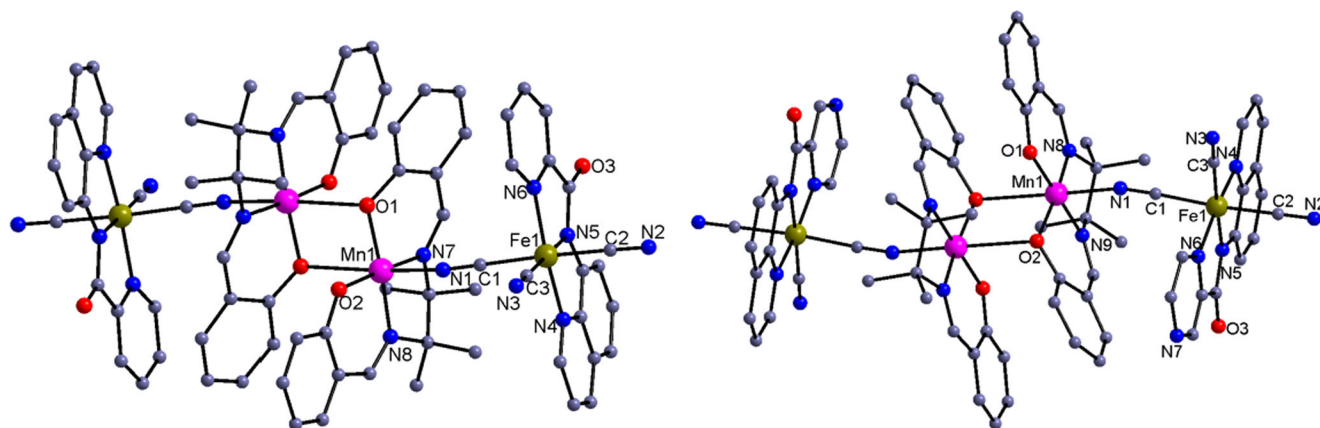


Figure 1. The tetranuclear structure of complexes **1**(left) and **2**(right). The solvent molecules and all the H atoms are omitted for clarity.

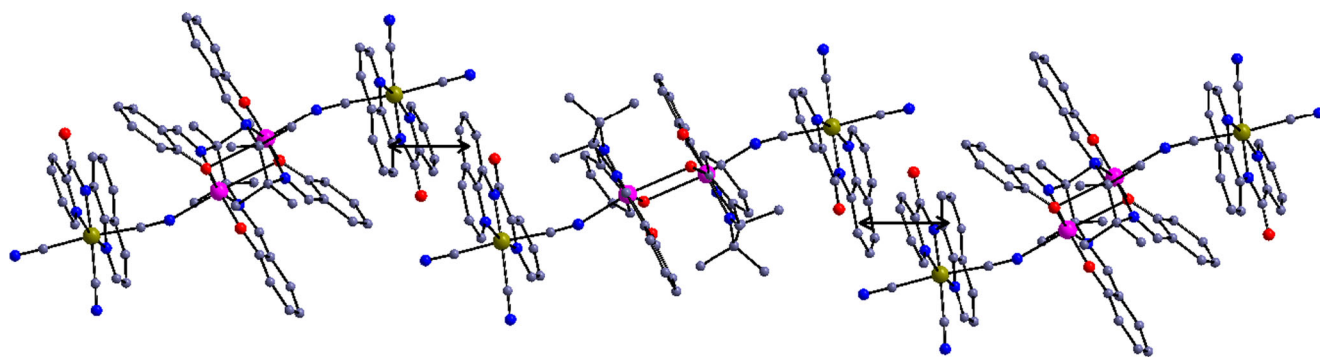


Figure 2. The 1D single chain structure constructed by intermolecular π - π interaction for complexes **1** and **2**. The solvent molecules and all the H atoms are omitted for clarity.

while the Mn-N_{cyanide} and Mn-O_{phenoxo} bond lengths are 2.211(5), 2.620(3) Å and 2.229(5), 2.638(1) Å, which gives further information about the elongation octahedron surrounding the Mn(III) ion, typically accounting for the well-known JahnTeller effect. The angles of C(1)≡N(1)-Mn(1) in these two complexes are with the values to about 163°, indicative of the fact that these three atoms deviate slightly from a linear configuration. The bond parameters around the Mn(III) ion in complexes **1** and **2** are basically comparable to those found in [Fe(pcq)(CN)₃Mn(saltmen)(CH₃OH)]·CH₃OH,^{22d} while the C≡N-Mn bond angle here is obviously larger than that in the above complex (163° vs. 153.2(2)°). The intramolecular Fe^{III}-Mn^{III} separation through bridging cyanide(s) in complexes **1** and **2** are 5.221 and 5.255 Å, respectively, which are obviously shorter than the shortest intermolecular metal-metal distance with the value of about 7.61 Å. It is worth noting that, with the help of the intermolecular π - π interaction, these two complexes can be linked into one-dimensional supramolecular chain structure (figure 2).

3.3 Magnetic properties of complexes **1** and **2**

The temperature dependence of $\chi_m T$ for complexes **1** and **2** measured in the range of 2–300 K is shown in figure 4. The $\chi_m T$ value at 300 K is 3.59 emu K mol⁻¹ for **1** and 3.58 emu K mol⁻¹ for **2**, respectively, which are slightly higher than the spin only value 3.38 emu K mol⁻¹ for one high spin Mn(III) ($S = 2$) and one low spin Fe(III) ($S = 1/2$). The $\chi_m T$ value increases slowly to about 4.00 emu K mol⁻¹ with the temperature decreasing about 50 K. After that, the $\chi_m T$ value starts to increase rapidly to the maximum of 4.87 and 4.97 emu K mol⁻¹ at about 6 K for complexes **1** and **2**, respectively, and then the $\chi_m T$ value decreases sharply to 4.24 emu K mol⁻¹ for **1** and 3.90 emu K mol⁻¹ for **2** with the temperature down to 2 K. The changing tendency of the $\chi_m T$ curve gives primary information that there exists overall ferromagnetic coupling between the cyanide-bridged Mn(III) and Fe(III) ions in the above two complexes.

The inset of figure 4 shows the field-dependent magnetization measured up to 50 kOe at 2 K for these two

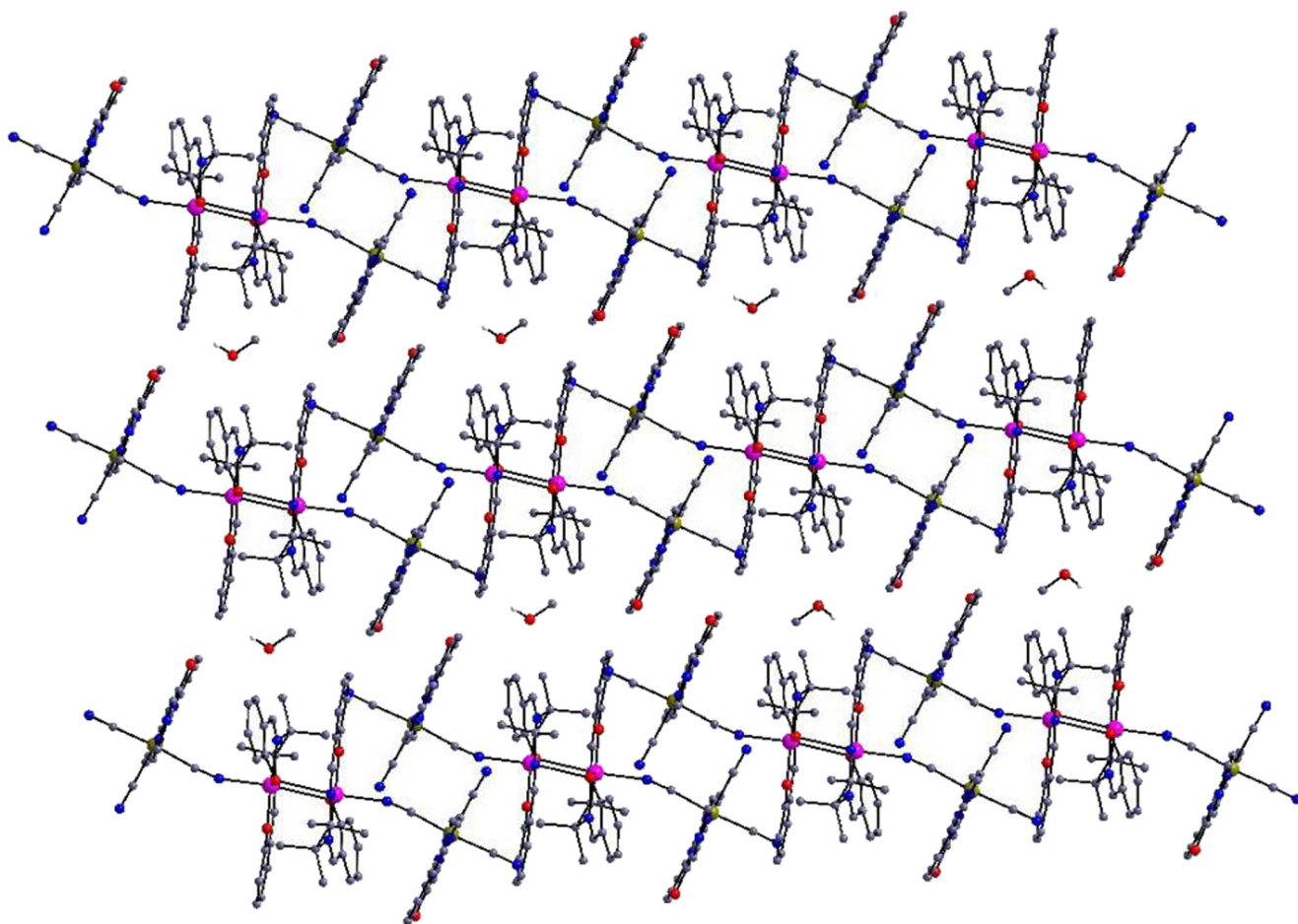


Figure 3. The representative cell packing diagram for complexes **1** and **2** along *b* axis. All the non-solvent hydrogen atoms are omitted for clarity.

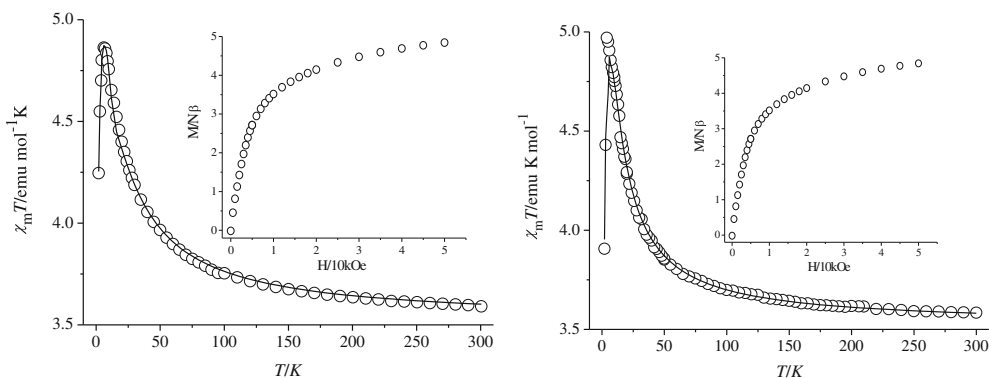


Figure 4. Temperature dependence of $\chi_m T$ of complexes **1** (left) and **2** (right). Inset: Field dependence of magnetization of **2** at 2 K.

complexes. The magnetization increases rapidly up to 10 kOe, and then the curve becomes relatively even and attains the maximum value at about $4.90 N\beta$. These data can also confirm that there exist ferromagnetic coupling interactions between the Fe(III) and Mn(III) ions in the three complexes.

As can be found from the structural data of complexes **1** and **2**, there are two different magnetic coupling pathways, cyano bridges (J) and phenoxo bridges (J'). It has been reported by Miyasaka *et al.* that $|J| \gg |J'|$,^{25,27,28} therefore the magnetic coupling through phenoxo bridges can be safely neglected during

the fitting process. On the basis of the binuclear Fe^{III}-Mn^{III} ($S = 1/2$ and 2) model, the magnetic susceptibilities for these two complexes can be fitted by the expression below derived from the isotropic exchange spin Hamiltonian $\hat{H} = -2J\hat{S}_{\text{Fe}}\hat{S}_{\text{Mn}}$:

$$\chi_d = \frac{Ng^2\beta^2}{2kT} \frac{35 \exp(2J/kT) + 10 \exp(-3J/kT)}{6 \exp(2J/kT) + 4 \exp(-3J/kT)}$$

$$\chi_m = \frac{\chi_d}{1 - \chi_d(2zJ'/Ng^2\beta^2)}$$

The best-fit parameters obtained are $J = 5.34(3) \text{ cm}^{-1}$, $g = 2.01(2)$, $zJ' = -0.11(5) \text{ cm}^{-1}$, $R = 2.91 \times 10^{-5}$ for complex **1** and $J = 5.55(3) \text{ cm}^{-1}$, $g = 2.01(4)$, $zJ' = -0.13(6) \text{ cm}^{-1}$, $R = 3.14 \times 10^{-5}$ for complex **2**, respectively. These results further testified the ferromagnetic coupling between the neighbouring Fe-Mn ion pair bridged by cyanide group, which is also consistent with the fact that almost all the cyanide-bridged Fe(III)-Mn(III) complexes show the ferromagnetic coupling nature.

4. Conclusion

We obtained two heterobimetallic cyanide- and phenoxo- co-bridged tetranuclear clusters with two *mer*-tricyanidoiron(III) precursors as cyanide building blocks and schiff-base manganese(III) compound as assembling segment, which can be linked into a one-dimensional infinite chain supramolecular structure depending on the intermolecular π - π interaction. Investigation over the magnetic properties of these two complexes reveals ferromagnetic coupling between the adjacent Mn(III) and Fe(III) ions through the linear cyanide bridge.

Supplementary Information

The CIF tables of **1** and **2** have been deposited at the Cambridge Crystallographic Data Centre with the deposition numbers CCDC 985441 and 985442, respectively.

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