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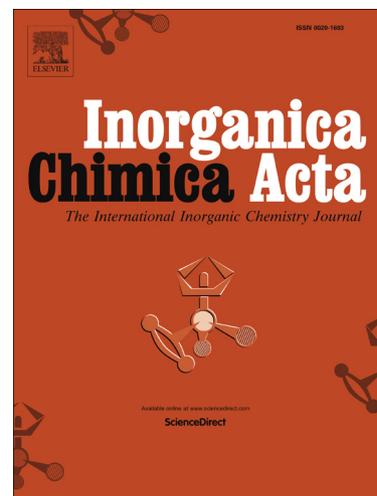
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Tuning the Structures of Manganese (III) (Schiff base) Complexes: Syntheses, Crystal Structures and Magnetic Properties

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ABSTRACT

Four new coordination complexes, $[\text{Mn}^{\text{III}}(3\text{-EtO-salpn})(\text{H}_2\text{O})(\text{CH}_3\text{OH})]\text{ClO}_4$ (**1**), $[\text{Mn}^{\text{III}}(3\text{-EtO-salpn})(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O} \cdot \text{ClO}_4$ (**2**), $\{[\text{Mn}^{\text{III}}(3\text{-EtO-salpn})(\text{H}_2\text{O})][\text{Fe}^{\text{III}}(\text{qcq})(\text{CN})_3]\} \cdot 3\text{H}_2\text{O} \cdot \text{CH}_3\text{OH} \cdot \text{CH}_3\text{CN}$ (**3**) and $\{[\text{Mn}^{\text{III}}(3\text{-EtO-salpn})(\text{H}_2\text{O})][\text{Fe}^{\text{III}}(\text{qcq})(\text{CN})_3]\} \cdot 3\text{H}_2\text{O} \cdot \text{CH}_3\text{CN}$ (**4**) (salpn = *N,N'*-1,2-propylenebis(salicylideneiminato)dianion; qcq = 8-(2-quinoline-2-carboxamido)quinoline anion) were synthesized and characterized both structurally and magnetically. The results reveal that complexes **1** and **2** are mononuclear Mn^{III} structures crystallizing in different space groups, while **3** and **4** are dinuclear $\text{Mn}^{\text{III}}\text{-NC-Fe}^{\text{III}}$ entities with different local arrangement of the subunits. Interestingly, the structures of these complexes are highly dependent on the reaction conditions though the reaction precursors are the same. Magnetic investigation indicates that intra- and/or intermolecular antiferromagnetic interactions are presented in complexes **1-4**. Notably, these weak antiferromagnetic interactions could be overcome by high direct-current magnetic field, showing the field induced metamagnetic behaviors.

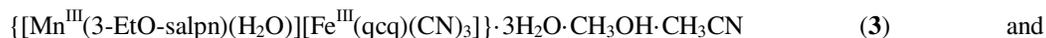
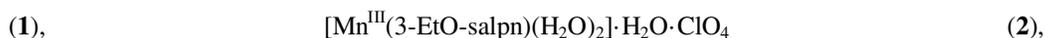
Keyword: Mn^{III} (Schiff base), cyanometalate, tricyanidoferrate, supramolecular, magnetism

1. Introduction

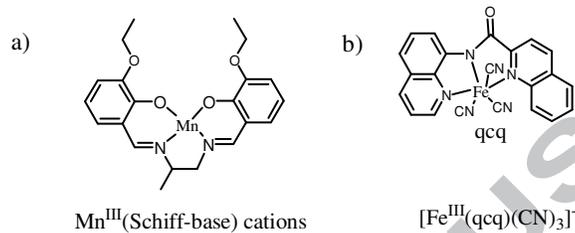
Low-dimensional magnets such as the single molecule magnets (SMM), single chain magnets (SCMs) have been attracting much attention because of their interesting structures and magnetism as well as their potential applications in molecular devices, high-density information storages and quantum computers, *etc.*[1-10] To date, it is still one of the most important tasks for chemists to design new low dimensional systems and tune their structures and magnetism.

In this research field, the building blocks of Mn^{III}(Schiff base) cations (Scheme 1a) are especially remarkable because they have contributed to a series of low-dimensional magnets with novel structures and interesting magnetic properties.[11-28] The results indicated that the low-dimensional magnetic properties of these complexes were originated from the large ground state spin (S_T) and strong easy-axis anisotropy of Mn^{III} ions. On the other hand, various electron donors especially the cyanometalate anions such as [M1(CN)₆]³⁻, [M2(CN)₈]³⁻ and [(L)M(CN)_p]^{q-} (M1 = Mn, Fe, Cr, Co; M2 = W, Mo; L = blocking group) have been assembled with Mn^{III}(Schiff base) cations and afforded a large number of bimetallic complexes ranging from 0-D, 1-D to 2-D structures.[11-68] In these complexes, the functional groups on the Schiff base ligands often play a very important role in determining the final structures. For example, for the reaction of Mn^{III}(Schiff base) cation and [Cr^I(CN)₅NO]³⁻ anion, H.-Z. Kou, *et al* have successfully synthesized a series of bimetallic complexes ranging from polynuclear to 1-D and 2-D by changing the substituting groups on the Schiff base ligands.[38] Similarly, in our previous works, when [Mn(3-CH₃)salen(H₂O)]ClO₄·H₂O and [Mn(5-CH₃)salen(H₂O)]ClO₄·H₂O were used to assemble with [Cr^I(CN)₅NO]³⁻, 1-D zigzag neutral chain and 2-D grid network were obtained respectively.[46] Interestingly, even if the same Schiff base ligands are used, different structural fashions could be obtained when the reaction conditions are fine tuned. Our latest work demonstrated that the reaction of [Mn^{III}(salen)(H₂O)]ClO₄ and [Fe^{III}(qcq)(CN)₃] (Scheme 1b) was able to produce two types of typical 1-D chain arrangement: 1-D regular zigzag chain and 1-D branch chain.[45]

In this work, two new examples of subtle reaction conditions dependent self-assembly process were observed, and four new coordination complexes, [Mn^{III}(3-EtO-salpn)(H₂O)(CH₃OH)]ClO₄



$\{[\text{Mn}^{\text{III}}(3\text{-EtO-salpn})(\text{H}_2\text{O})][\text{Fe}^{\text{III}}(\text{qcq})(\text{CN})_3]\} \cdot 3\text{H}_2\text{O} \cdot \text{CH}_3\text{CN}$ (4) (salpn = N,N' -1,2-propylenebis(salicylideneiminato)dianion; qcq = 8-(2-quinoline-2-carboxamido)quinoline anion) were synthesized and characterized both structurally and magnetically. Interestingly, the structures of these complexes are highly dependent on the reaction conditions though the reaction precursors are the same. Herein, we report the syntheses, crystal structures and magnetic properties of these four complexes.



Scheme 1 (a) The electron acceptor of Mn^{III}(Schiff base) cation; (b) The tricyanidoferate building block of [Fe^{III}(qcq)(CN)₃]⁻

2. Experimental Section

2.1. Physical Measurements

Elemental analyses for C, H and N were performed at a Perkin-Elmer 240C analyzer. IR spectra were recorded in the 4000-400 cm⁻¹ range on a Nicolet FT-170SX spectrometer using KBr pellets. Magnetic susceptibility measurements of the microcrystalline samples (22.27, 20.63, 11.43 and 12.47 mg for **1**, **2**, **3** and **4**, respectively) were conducted on a Quantum Design MPMP-XL7 superconducting quantum interference device (SQUID) magnetometer. Direct current (dc) measurements were carried out from 300 to 1.8 K and between 0-70 kOe applied dc fields. The alternating current (ac) susceptibility measurements were performed at various frequencies ranging from 1 to 1500 Hz with an ac field amplitude of 3 Oe in zero dc field. Corrections of the measured susceptibilities were carried out considering both the sample holder as the background and the diamagnetism of the constituent atoms according to Pascal's tables.[69]

2.2. Preparations

All chemicals and solvents in this study were reagent grade and were used as received without further purification. K[Fe^{III}(qcq)(CN)₃] and PPh₄[Fe^{III}(qcq)(CN)₃] were synthesized according to the methods reported previously.[70]

Caution! Cyanides are very toxic and perchlorate salts of metal complexes are potentially explosive. So they should be handled in small quantities and with great caution for safety.

2.3. Synthesis of complex $[Mn^{III}(3-EtO-salpn)(H_2O)(CH_3OH)]ClO_4(1)$

3-ethoxysalicylaldehyde (7.46 mmol) and 1,2-diaminopropane (3.73 mmol) were mixed in 200 mL of methanol and refluxed for an hour. The resulting yellow mixture was then added manganese(III) acetate dehydrate (3.73 mmol) and anhydrous sodium perchlorate (5.64 mmol) in water (80 mL). After evaporation to 50 mL and cooling, the resulting black precipitate was collected by suction filtration. Then the precipitate was recrystallized in a mixed solvent of methanol and water (v:v = 1:1), and gave the brown crystals suitable for X-ray structure determination. Anal. found: C, 46.32; H, 5.52; N, 4.52%. Calcd for $C_{22}H_{30}ClMnN_2O_{10}$: C, 46.12; H, 5.28; N, 4.89%. IR (ν_{max}/cm^{-1}): 3420s, 1611s, 1556m, 1446m, 1338w, 1292m, 1255m, 1085s, 732w, 622w.

2.4. Synthesis of complex $[Mn^{III}(3-EtO-salpn)(H_2O)_2] \cdot H_2O \cdot ClO_4(2)$

Complexes **2** was synthesized using the same procedure as **1** except that the precipitate was recrystallized in acetonitrile and water (v:v = 1:1). Anal. found: C, 43.52; H, 5.34; N, 4.72%. Calcd for $C_{21}H_{30}ClMnN_2O_{11}$: C, 43.72; H, 5.24; N, 4.86%. IR (ν_{max}/cm^{-1}): 3421s, 1611s, 1556m, 1444m, 1342w, 1292m, 1253m, 1089s, 732m 622w.

2.5. Synthesis of complex $\{[Mn^{III}(3-EtO-salpn)(H_2O)][Fe^{III}(qcq)(CN)_3]\} \cdot 3H_2O \cdot CH_3OH \cdot CH_3CN$

(3)

A methanol solution (10 mL) of $PPh_4[Fe^{III}(qcq)(CN)_3]$ (0.1 mmol) was slowly added to an acetonitrile solution (10 mL) of complexes **1** or **2** (0.1 mmol). The resulting solution was filtrated and the filtrate was left to allow slow evaporation in dark at room temperature. Black block crystals were formed in two weeks. The product was washed with methanol and acetonitrile, respectively, and dried in air. Anal. found: C, 55.34; H, 5.28; N, 12.49%. Calcd for $C_{46}H_{51}FeMnN_9O_{10}$: C, 55.21; H, 5.14; N, 12.60%. IR (ν_{max}/cm^{-1}): 3421(s), 2120(s), 1625(s), 1542(m), 1461(m), 1436(m), 1388(s), 1341(m), 1210(m), 850(m).

2.6. Synthesis of complex $\{[Mn^{III}(3-EtO-salpn)(H_2O)][Fe^{III}(qcq)(CN)_3]\} \cdot 3H_2O \cdot CH_3CN(4)$

A methanol solution (10 mL) of $K[Fe^{III}(qcq)(CN)_3]$ (0.1 mmol) was slowly added to an acetonitrile solution (10 mL) of complexes **1** or **2** (0.1 mmol). Then, one drop of triethylamine was added into the mixture. The resulting solution was filtrated and the filtrate was left to allow slow

evaporation in dark at room temperature. Black block crystals were formed in two weeks. The product was washed with acetonitrile and water, respectively, and dried in air. Anal. found: C, 55.62; H, 4.65; N, 12.85%. Calcd for $C_{45}H_{47}FeMnN_9O_9$: C, 55.80; H, 4.89; N, 13.01%. IR (ν_{max}/cm^{-1}): 3420(s), 2122(s), 1629(s), 1542(m), 1460(m), 1436(m), 1390(s), 1342(m), 1211(m), 852(m).

2.7. X-ray Crystallography

Single crystal X-ray crystallographic data were collected at 293 K on a Bruker *SMART APEX* CCD area detector diffractometer using graphite-monochromated Mo- $K\alpha$ radiation ($\lambda = 0.71073$ Å) with the φ and ω scan mode. Diffraction data analysis and reduction were performed with *SMART*, *SAINT* and *XPREF*.^[71] The structures were solved using direct methods and refined by a full-matrix least-squares method on F^2 using the *SHELXL* crystallographic software package.^[72] All the non-hydrogen atoms were refined anisotropically. The H atoms on C atoms were calculated at idealized positions, whereas water-H atoms were located from the residual peaks and included in the refinement in a riding mode with isotropic thermal parameters derived from the parent atoms. For complex **3**, the water and acetonitrile molecules (H-atoms are not found) are disordered and were treated using an anisotropic refinement with partial occupancy. For complex **4**, the water oxygen atoms of O7, O8 (H-atoms are not found) are also refined with partial occupancy. Furthermore, the 1,2-diaminopropane group on 3-EtO-salpn ligands (C10, C11, C12 in **2**; C13 in **3**; C34 in **4**) are disordered and split into two positions. It is worth noting that some H atoms in **1-4** (disordered groups, solvent molecules) could not be well located in the refinement of the structures and thus the missing ones were manually included in the formulas for chemical rationality. Crystallographic data for **1-4** are summarized in Table 1.

Table 1. Details of the crystallographic data collection, structural determination and refinement for **1-4**.

	1	2	3	4
Formula	$C_{22}H_{30}ClMnN_2O_{10}$	$C_{21}H_{30}ClMnN_2O_{11}$	$C_{46}H_{51}FeMnN_9O_{10}$	$C_{45}H_{47}FeMnN_9O_9$
F_w	572.87	576.86	1000.73	968.70
Crystal system	Orthorhombic	Triclinic	Triclinic	Monoclinic
Space group	Pbca	P-1	P-1	P 21/c
$a/\text{Å}$	13.6603(14)	9.766(2)	13.163(3)	16.1021(12)
$b/\text{Å}$	14.8191(15)	11.480(2)	14.420(3)	15.7153(12)
$c/\text{Å}$	24.5901(27)	12.756(3)	14.790(3)	17.6241(13)
$\alpha/^\circ$	90.00	69.25(3)	62.12(3)	90.00
$\beta/^\circ$	90.00	70.27(3)	89.34(3)	98.7020(10)
$\gamma/^\circ$	90.00	80.83(3)	71.20(3)	90.00
$V/\text{Å}^3$	4977.8564(1)	1257.6(6)	2316.3(13)	4408.4(6)
Z	8	2	2	4
$\rho_{calcd}/g\text{ cm}^{-3}$	1.526	1.523	1.422	1.407

$F(000)$	2376	600	1008	1918.2
$\theta / ^\circ$	3.54-26.02	3.25-24.99	3.23-25.00	1.28-25.00
Index ranges	$-15 \leq h \leq 16$ $-18 \leq k \leq 17$ $-20 \leq l \leq 30$	$-10 \leq h \leq 11$ $-13 \leq k \leq 12$ $-15 \leq l \leq 15$	$-15 \leq h \leq 13$ $-17 \leq k \leq 17$ $-17 \leq l \leq 17$	$-19 \leq h \leq 18$ $-17 \leq k \leq 18$ $-20 \leq l \leq 20$
Total/unique data	21846/4825	10226/4351	20341/8023	31803/7755
Observed data [$I > 2\sigma(I)$]	4495	3885	6978	5834
R_{int}	0.0345	0.0228	0.0339	0.0298
Data/restraints /parameters	4495/0/337	3885/0/355	6978/18/652	5834/23/600
GOF on F^2	0.999	1.020	1.080	1.092
$R_1^{\text{[a]}}$ [$I > 2\sigma(I)$]	0.0584	0.0439	0.0585	0.0628
$wR_2^{\text{[b]}}$ (all data)	0.1461	0.1201	0.1572	0.2015

$$[\text{a}] R_1 = \sum(|F_o| - |F_c|) / \sum |F_o|. [\text{b}] wR_2 = \{\sum[w(F_o^2 - F_c^2)^2] / \sum[w(F_o^2)^2]\}^{1/2}$$

3. Results and Discussion

3.1. Syntheses and characterization

The reported methods [30] for the synthesis of Mn^{III} (Schiff base) precursors have been slightly modified in this work. The reaction mixtures containing fresh formed Schiff base ligands were used to react directly with manganese(III) acetate dehydrate and sodium perchlorate without further purification. Interestingly, two types of mononuclear Mn^{III} (Schiff base) complexes derived from the same reaction precursor were isolated, as shown by complexes **1** and **2**. It is believed that there is a balance between the two crystallized forms that might be very sensitive to the solvent polarity. Such phenomenon is comparable to the fact that mononuclear $[\text{Mn}^{\text{III}}(\text{Schiff base})]^+$ and dinuclear $[\text{Mn}^{\text{III}}_2(\text{Schiff base})_2]^{2+}$ are often in equilibrium in the solution.[11,73-75] Similar to **1** and **2**, two types of discrete dinuclear Mn-NC-Fe complexes were also formed. Considering that the components of K^+ and triethylamine were introduced in the synthesis of **4** while these were nonexistent in **3**, thus the K^+ and triethylamine should be responsible for the formation of complex **4**. IR spectra of 1-4 also present differences, **1** and **2** display no absorption peaks in the range of $2100\text{-}2150\text{ cm}^{-1}$, which is in agreement with their mononuclear Mn^{III} (Schiff base) structures without cyanide groups. In contrast, characteristic $\nu(\text{CN})$ bands are observed in **3** and **4**, indicating the presence of cyanide groups in them.[76] Besides, these $\nu(\text{CN})$ bands ($2120\text{-}2122\text{ cm}^{-1}$) also shift slightly to higher energies compared to that (2108 cm^{-1}) of the $[\text{Fe}^{\text{III}}(\text{qcq})(\text{CN})_3]^-$ precursor, [70] which implies the CN groups are involved in bridging the transition metal ions in **3** and **4**. The absorption bands at $1620\text{-}1630\text{ cm}^{-1}$ and $1400\text{-}1600\text{ cm}^{-1}$ could be assigned to stretching vibrations of N=C and benzene ring in these complexes.

3.2. Description of the structures

Selected bond distances and angles are listed in Table 2. The crystal structures of complexes **1-4** are shown in Fig. 1 and Fig. 2. The intermolecular short contacts and π - π stacking for the four complexes are depicted in Figs. S1-S4 in the supplementary information.

Table 2. Selected bond lengths [\AA] and angles [$^{\circ}$] for **1-4**

1	2	3	4				
Mn1-N1	1.985(3)	Mn1-O1	1.8754(18)	C1-Fe1	1.949(4)	C1-Fe1	1.920(4)
Mn1-N2	1.977(3)	Mn1-O2	1.875(2)	C2-Fe1	1.966(4)	C2-Fe1	1.956(5)
Mn1-O1	2.301(2)	Mn1-N1	1.968(3)	C3-Fe1	1.940(4)	C3-Fe1	1.951(4)
Mn1-O2	2.225(2)	Mn1-N2	1.986(2)	Fe1-N5	1.888(3)	Fe1-N5	1.904(4)
Mn1-O3	1.880(2)	Mn1-O4	2.239(2)	Fe1-N6	1.984(3)	Fe1-N4	1.998(4)
Mn1-O4	1.879(2)	Mn1-O3	2.2597(19)	Fe1-N4	2.030(3)	Fe1-N6	2.035(4)
O4-Mn1-O3	94.02(10)	O1-Mn1-O2	92.97(8)	Mn1-O3	1.880(2)	Mn1-O2	1.882(3)
O4-Mn1-N2	91.77(10)	O1-Mn1-N1	92.55(10)	Mn1-O2	1.880(3)	Mn1-O3	1.887(3)
O3-Mn1-N1	91.96(11)	O2-Mn1-N2	91.68(10)	Mn1-N8	1.979(3)	Mn1-N8	1.970(4)
N2-Mn1-N1	82.16(12)	N1-Mn1-N2	82.80(11)	Mn1-N7	1.988(3)	Mn1-N7	1.983(4)
O4-Mn1-O2	94.46(10)	O1-Mn1-O4	91.71(8)	Mn1-N1	2.265(3)	Mn1-N1	2.261(4)
O3-Mn1-O2	90.33(10)	O2-Mn1-O4	87.23(9)	Mn1-O7	2.279(3)	Mn1-O6	2.292(3)
N2-Mn1-O2	91.10(11)	N1-Mn1-O4	92.08(11)	N1-C1-Fe1	175.2(3)	N1-C1-Fe1	174.9(4)
N1-Mn1-O2	88.52(12)	N2-Mn1-O4	89.13(9)	N2-C2-Fe1	178.7(3)	N2-C2-Fe1	177.3(4)
O4-Mn1-O1	91.55(9)	O1-Mn1-O3	90.54(8)	N3-C3-Fe1	174.9(4)	N3-C3-Fe1	177.0(4)
O3-Mn1-O1	88.73(10)	O2-Mn1-O3	92.95(8)	C1-N1-Mn1	151.8(3)	C1-N1-Mn1	161.2(4)
N2-Mn1-O1	89.23(11)	N1-Mn1-O3	87.52(11)				
N1-Mn1-O1	85.56(11)	N2-Mn1-O3	88.61(9)				

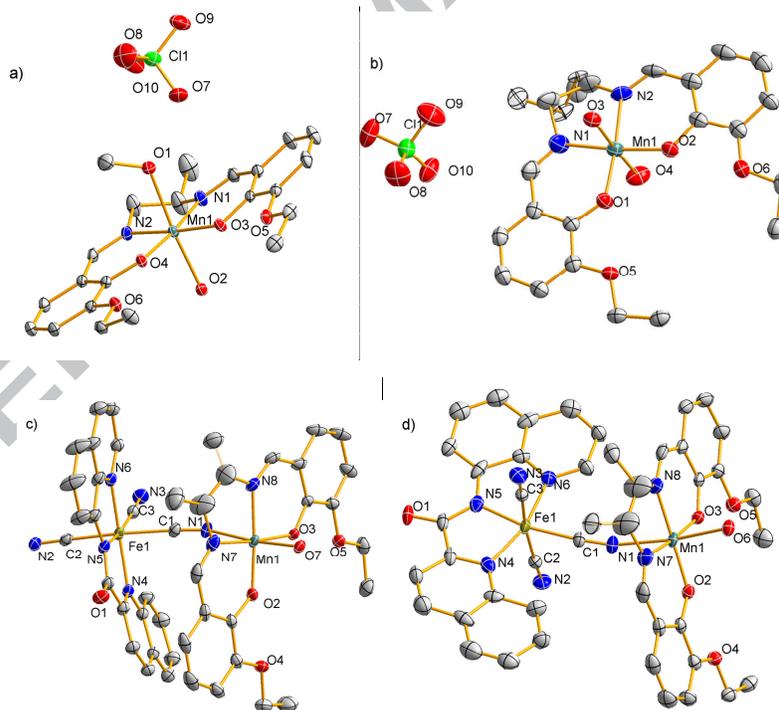


Fig. 1 ORTEP (30%) diagrams of asymmetric units with selected atom-labeling schemes for **1** (a), **2** (b), **3**(c) and **4**

(d) (Hydrogen atoms and crystallized solvent molecules are omitted for clarity)

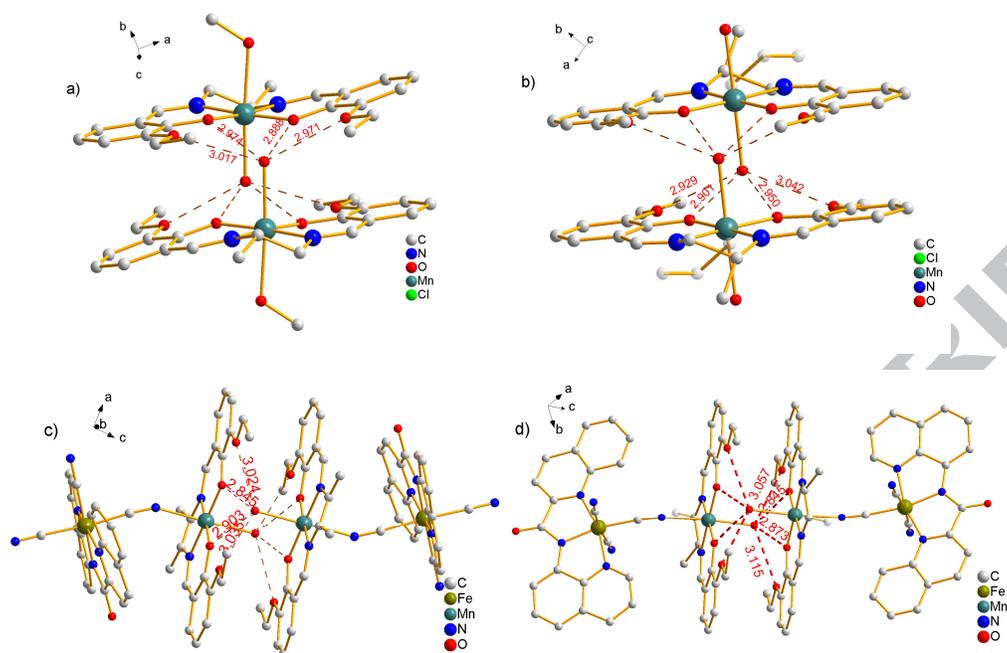


Fig. 2 The formed supramolecular structures for complexes **1**(a), **2**(b), **3**(c) and **4**(d) (The red dashed lines represent the hydrogen bonds interactions between coordinated water molecules and oxygen atoms from the neighboring Schiff base ligands).

Complexes **1** and **2** are both mononuclear Mn^{III} structures, and crystallize in the space groups of $Pbca$ and $P-1$, respectively. Their asymmetric units [Fig. 1(a, b)] consist of one $[\text{Mn}^{\text{III}}(3\text{-EtO-salpn})]^+$ cation, one ClO_4^- anion and several coordinated or lattice solvent molecules. The structure of $[\text{Mn}^{\text{III}}(\text{Schiff base})]^+$ unit is well known [11] and here we will focus on the description of the formed supramolecular Mn_2 dimers. The water molecules (For **1**: O2; For **2**: O3) in the axial positions of the Mn^{III} ion are involved in hydrogen bond interactions with the ethoxido- and phenolato- oxygen atoms of a neighboring $[\text{Mn}^{\text{III}}(3\text{-EtO-salpn})]^+$ unit, as shown in Fig. 2(a, b). The hydrogen bond interactions lead to the formation of supramolecular Mn_2 dimers, which are comparable to the complexes constructed by 3-MeO-salen ligand.[34,77-79] It deserves noting that the packing structures of **1** and **2** (Figs. S1-S2) are quite different. For **1**, the supramolecular Mn_2 dimers are formed with two different orientations, forming the layers parallel to ab plane where the ClO_4^- anions are located between them. In contrast to **1**, all the formed supramolecular Mn_2 dimers in **2** adopt the same orientation with the counter anions of ClO_4^- intercalated between them.

Complexes **3** and **4** crystallize in the space groups of P-1 and P 21/c, respectively. As shown in Fig. 1(c, d), the molecular structures of **3** and **4** are discrete neutral dinuclear Fe-CN-Mn entities in which one $[\text{Mn}^{\text{III}}(3\text{-EtO-salpn})]^+$ cation and one $[\text{Fe}^{\text{III}}(\text{qcq})(\text{CN})_3]^-$ anion are connected through a single cyanide (CN) bridge. Such neutral dinuclear structures are comparable to the previously reported complexes derived from other Mn^{III} (Schiff base) and tricyanideferrate building blocks.[22,37,47,70] For **3** and **4**, one of the axial sites on $[\text{Mn}^{\text{III}}(3\text{-EtO-salpn})]^+$ is occupied by the N atom from cyanide groups of $[\text{Fe}^{\text{III}}(\text{qcq})(\text{CN})_3]^-$ while the other site is capped by the water molecule which is responsible of the supramolecular association in dimers of dinuclear $\text{Mn}^{\text{III}}\text{-NC-Fe}^{\text{III}}$ species. The axial Mn-N/O bond lengths [2.261(4)-2.292(3) Å] are significantly longer than the equatorial Mn-N/O distances [1.880(2)-1.9887(3) Å], revealing the Jahn-Teller effect of Mn^{III} ions. The Mn-N-C angles of the cyanide bridge in **3** and **4** are 151.8(3)° and 161.2(4)°, respectively. From the point of magnetism, the critical Mn-N-C angles could govern magnetic orbital overlaps and thus influence the final magnetic properties.[45,79] For the moiety of $[\text{Fe}^{\text{III}}(\text{qcq})(\text{CN})_3]^-$, it has been also well described in previous report.[70] Interestingly, the local arrangement for the two building units of $[\text{Fe}^{\text{III}}(\text{qcq})(\text{CN})_3]^-$ and $[\text{Mn}^{\text{III}}(3\text{-EtO-salpn})]^+$ in **3** and **4** are quite different. For **3**, the molecular plane of $[\text{Fe}^{\text{III}}(\text{qcq})(\text{CN})_3]^-$ is approximately parallel to the equatorial plane of $[\text{Mn}^{\text{III}}(3\text{-EtO-salpn})]^+$ and the two uncoordinated cyanide groups are presented in *cis*-mode. In contrast to **3**, the two planes in **4** are found to be nearly perpendicular to each other and the two uncoordinated cyanide groups are arranged in *trans*-mode. To the best of our knowledge, the coordination fashion shown by **3** is often observed but that for **4** is quite rare.[22,37,47,70] As mentioned above, the supramolecular dimers of the dinuclear $\text{Mn}^{\text{III}}\text{-NC-Fe}^{\text{III}}$ species [Fig. 2(c, d)] are formed in **3** and **4** via hydrogen bond interactions. For the extended structures of **3** and **4**, the π - π stacking between adjacent aromatic ring on $[\text{Fe}^{\text{III}}(\text{qcq})(\text{CN})_3]^-$ and the hydrogen bond interactions induce the formation of quasi-2-D layers, as shown in Figs. S3-S4. The shortest intralayer metal...metal distances in **3** and **4** are 4.797 and 4.788 Å, respectively. Furthermore, the layers further stack into 3-D structures and the shortest interlayer metal...metal separations in **3** and **4** are 12.99 Å and 8.13 Å, respectively.

3.3. Magnetic properties

Temperature dependence of the direct-current (dc) magnetic susceptibility data of **1** and **2** are plotted in Fig. 3(a, b). At 300 K, the $\chi_{\text{M}}T$ values of **1** and **2** per Mn^{III} were both determined to be

3.0 cm³ K mol⁻¹, which correspond to the value expected for a single HS Mn^{III} ion (3d⁴, *S* = 2) assuming *g* = 2.0. Upon cooling, the $\chi_M T$ values of the complexes remain almost constant and then decrease rapidly down to 0.23 and 0.22 cm³ K mol⁻¹ at 1.8 K for **1** and **2**, respectively. The rapid decrease of $\chi_M T$ values in low temperature region could be ascribed to intermolecular antiferromagnetic interactions and/or zero-field splitting effect (ZFS) of the Mn^{III} ion.[11,24] The very small residual spin values of **1** and **2** at 1.8 K indicate that an diamagnetic ground state is formed through the intermolecular antiferromagnetic interactions between the spin carriers. This is actually confirmed by Curie–Weiss fit that the experimental data almost perfectly matches the calculated data down to 20 K, giving the negative Weiss constants of –3.7 and –3.6 K for **1** and **2**, respectively. The χ_M vs *T* curves of **1** and **2** both show a peak at about 3.5 K, further confirming the antiferromagnetic nature of the two complexes at very low temperature. From the crystal structures, the supramolecular dimers of Mn₂ are formed via hydrogen bonds interactions. Thus, a dinuclear Mn₂ model [48] could be used for fitting the susceptibility data of **1** and **2**. The spin Hamiltonian can be written as:

$$H = -2J (S_{Mn1} \cdot S_{Mn2}) + D_{Mn}(S_{z,Mn1}^2 + S_{z,Mn2}^2) \quad (J \text{ represents the intradimer Mn...Mn magnetic coupling constant and } D_{Mn} \text{ represents the ZFS effect of Mn}^{III} \text{ ions.})$$

The Magpack program[80-82] was used to perform the calculation, and the experimental data in the whole temperature region was used for simulation. The best fitting parameters obtained are: *J* = –0.5 cm⁻¹, *g* = 2.0, |*D*_{Mn}| = 1.8 cm⁻¹ for **1** and *J* = –0.4 cm⁻¹, *g* = 2.0, |*D*_{Mn}| = 2.8 cm⁻¹ for **2**, respectively. The fitting result further confirms the presence of intradimer antiferromagnetic coupling in **1** and **2**, and the antiferromagnetic nature of the *J* interaction leads to an overall diamagnetic ground state of the dinuclear supramolecular Mn₂ assemblies. The obtained *D* values are also comparable to those of the reported Mn^{III} complexes.[24-26,49]

The weak intradimer antiferromagnetic coupling of the supramolecular Mn₂ dimers was further evidenced by the measurements of field-dependent magnetization at 1.8 K, as shown in Fig. S5(a, b). The magnetization of **1** and **2** increases with the increasing applied dc field and reaches 3.58 and 3.40 *N*μ_B at 70 kOe, respectively. The high field values are lower than the theoretical saturated values of 4.0 *N*μ_B expected for single Mn^{III} ion, suggesting the magnetization values for **1** and **2** remain unsaturated even at 70 kOe.

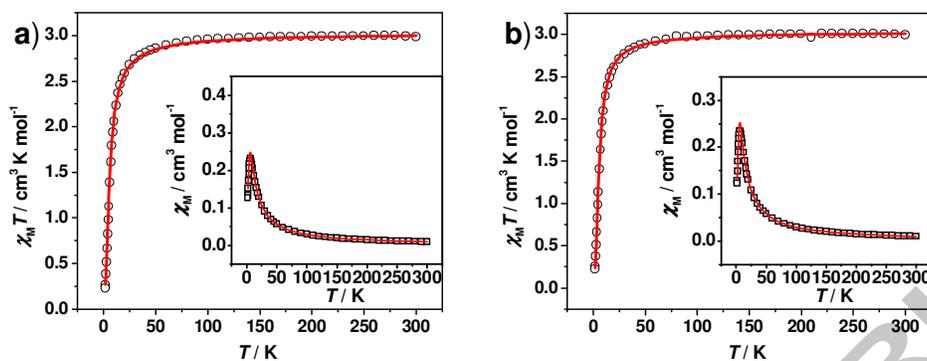


Fig. 3. Temperature dependence of $\chi_M T$ and χ_M (inset) for **1** (a) and **2** (b) measured at 2 kOe (The red solid lines represent the best fits to the models described in the text)

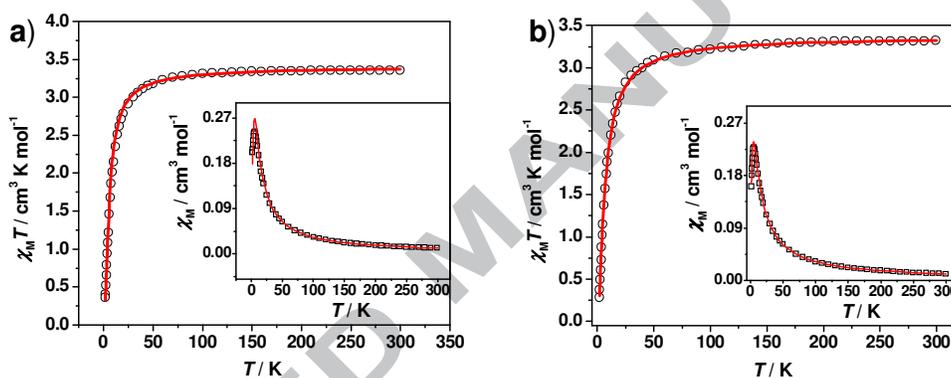


Fig. 4. Temperature dependence of $\chi_M T$ and χ_M (inset) for **3** (a) and **4**(b) measured at 2 kOe (The red solid lines represent the best fits to the models described in the text)

The M - H curves of **1** and **2** both show typical field dependence “S” shape that reveal the weak antiferromagnetic interactions between the Mn centers are compensated by the applied dc magnetic field. This magnetic phenomenon is typical of metamagnetic behaviors that are often observed when the intermolecular antiferromagnetic interactions are actually very weak.[22,50,83] Besides, the “S” shape field-dependent magnetization curves of **1** and **2** were satisfactorily simulated by the Magpack program [Fig. S5(a, b)] using the set of parameters extracted from the susceptibility data, further confirming the magnetic model developed is reasonable. Though the packing structures of **1** and **2** are different, the magnetic properties of them are overall identical, revealing their magnetic properties are mostly affected by the magnetic interactions within the Mn_2 dimers.

At 300 K, the $\chi_M T$ values of **3** and **4** per $\text{Mn}^{\text{III}}\text{Fe}^{\text{III}}$ are 3.4 and 3.3 $\text{cm}^3 \text{K mol}^{-1}$, respectively, which correspond to the spin-only value of 3.38 $\text{cm}^3 \text{K mol}^{-1}$ for non-magnetically interacting Mn^{III} and Fe^{III} spin centers (one $s_{\text{Fe}} = 1/2$, one $S_{\text{Mn}} = 2$) with $g = 2$. Upon cooling, the values decrease gradually and then drop rapidly until reach the value of 0.36 and 0.28 $\text{cm}^3 \text{K mol}^{-1}$ at 1.8 K for **3** and **4**, respectively. Comparable to **1** and **2**, the χ_M vs T curves of **3** and **4** also show a peak at about 6.0 K, which indicate the presence of typical antiferromagnetic interactions that might originate from the intra- and/or intermolecular antiferromagnetic couplings. It is worth noting that a series of antiferromagnetic $\text{Mn}^{\text{III}}\text{-Fe}^{\text{III}}$ dinuclear complexes were reported in the literatures. [22,37,47,70] For the dinuclear structures of **3** and **4**, the dinuclear $\text{Mn}^{\text{III}}\text{-Fe}^{\text{III}}$ model could be used to describe their magnetism. However, **3** and **4** should be better described as tetranuclear supramolecular assembly, $\text{Fe}^{\text{III}}\text{-Mn}^{\text{III}}\dots\text{Mn}^{\text{III}}\text{-Fe}^{\text{III}}$ [22] considering the presence of hydrogen bonds interactions between two $\text{Mn}^{\text{III}}\text{-Fe}^{\text{III}}$ unit. Thus, the magnetic susceptibility data of the tetranuclear entity was modeled based on following spin Hamiltonian:

$$H = -2J_1 (S_{\text{Mn1}} \cdot S_{\text{Fe1}} + S_{\text{Mn1}} \cdot S_{\text{Fe2}}) - 2J' S_{\text{Mn1}} \cdot S_{\text{Mn2}}$$

(J_1 and J' represent the magnetic coupling between Mn(III) and Fe(III) centers and the magnetic interaction between Mn(III) metal ions, respectively). The susceptibility data in the whole temperature range was simulated using Magpack,[80-82] affording $J_1 = -1.0 \text{ cm}^{-1}$, $J' = -0.4 \text{ cm}^{-1}$, $g = 2.0$ for **3** and $J_1 = -1.9 \text{ cm}^{-1}$, $J' = -0.4 \text{ cm}^{-1}$, $g = 2.0$ for **4**, respectively. The result confirms that weak intra- and intermolecular antiferromagnetic interactions are dominant in **3** and **4**. Consequently, the antiferromagnetic nature of the J' interaction produces a diamagnetic ground state of the tetranuclear supramolecular assembly at very low temperature. To further study the magnetism of **3** and **4**, field-dependent magnetizations were then measured, as shown in Figs S5 (c, d). As the dc field increase, the M - H curves of **3** and **4** increase but show typical "S" shape that is an indicative of metamagnetic behavior. Unexpectedly, the saturated magnetization at 70 kOe for **3** ($4.0 N\mu_B$) is much larger than that for **4** ($2.9 N\mu_B$) and also larger than the theoretical saturated values ($3.0 N\mu_B$) expected for antiferromagnetic coupled $\text{Mn}^{\text{III}}\text{-Fe}^{\text{III}}$ unit. Moreover, the M - H curves of **3** and **4** could be well simulated [Figs S5 (c, d)] using the set of parameters obtained from the susceptibility data. Therefore, such phenomenon might imply that the intramolecular antiferromagnetic $\text{Fe}^{\text{III}}\dots\text{Mn}^{\text{III}}$ coupling in **3** is weak enough to be decoupled by the dc field.

Comparable behaviors were also observed for the $\text{Mn}^{\text{III}}\text{-Cr}^{\text{III}}$ [51] and $\text{Cu}^{\text{II}}\text{-Fe}^{\text{III}}$ [83] systems. Because the antiferromagnetic $\text{Fe}^{\text{III}}\dots\text{Mn}^{\text{III}}$ interaction in **3** is weaker than that in **4**, so the magnetic coupling strength between spin carriers should be the main factor to determine whether or not such interactions are overcome by the strong dc field. Furthermore, the measurements of ac susceptibility of **3** and **4** (Fig. S6) both show broad frequency independent χ_{M}' peaks without the response of the χ_{M}'' part, indicating the presence of various short range antiferromagnetic ordering in these systems. Indeed, the formed tetranuclear supramolecular assemblies in **3** and **4** could further contact with each other via the $\pi\text{-}\pi$ interactions, as shown by the structural analysis.

From the structural and magnetic studies, **1** and **2** show dinuclear supramolecular Mn_2 assemblies whose magnetic properties are actually independent of packing structures. For **3** and **4**, the different local arrangements of $[\text{Fe}^{\text{III}}(\text{qcq})(\text{CN})_3]^-$ and $[\text{Mn}^{\text{III}}(3\text{-EtO-salpn})]^+$ lead to the comparable exchange interactions (weak antiferromagnetic nature) between Mn^{III} and Fe^{III} , where the $\text{Mn}^{\text{III}} \dots \text{Fe}^{\text{III}}$ antiferromagnetic coupling in **3** could be overcome by a strong dc field. The tetranuclear supramolecular entities, $\text{Fe}^{\text{III}}\text{-Mn}^{\text{III}}\dots\text{Mn}^{\text{III}}\text{-Fe}^{\text{III}}$ mediated via hydrogen bonds were observed in **3** and **4**, which strengthen the antiferromagnetic effect between the spin carriers and produce the nearly diamagnetic ground state of **3** and **4** in the low temperature region.

4. Conclusions

In summary, four new complexes **1-4** constructed from $[\text{Mn}^{\text{III}}(\text{Schiff base})]^+$ and/or *mer*- $[\text{Fe}^{\text{III}}(\text{qcq})(\text{CN})_3]^-$ have been synthesized and characterized. Using the same building blocks, different structural fashions could be obtained by slightly changing the reaction conditions. The subtle balance of these structural forms could be ascribed to the reaction conditions such as solvents polarity and acid-base property. Magnetic investigation reveals the dominant antiferromagnetic properties of **1-4**. Complexes **1-4** further demonstrate the strategy of fine tuning the structures of Mn^{III} (Schiff base) complexes is high effective to obtain suitable magnetic molecular units and thus enhance the magnetic properties.

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Appendix A. Supplementary material

CCDC: 991277-991280 for **1-4** contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.ica. XXXX.XX.XXX>.

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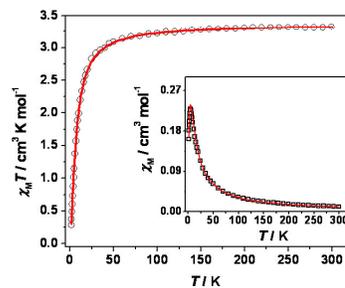
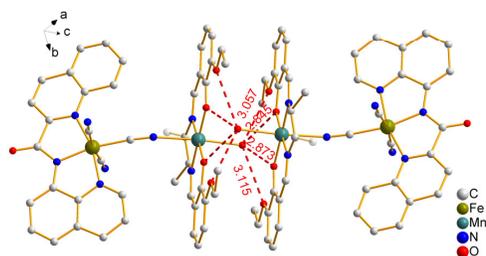
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ACCEPTED MANUSCRIPT

Four new 0-D **magnetic** complexes constructed by manganese(III)-(Schiff-base) and/or the building block of $[\text{Fe}^{\text{III}}(\text{qcq})(\text{CN})_3]^-$ have been synthesized and characterized both structurally and magnetically. The result reveals the structural styles of **1** and **2** or **3** and **4** are interesting because they differs with each other in very subtle ways though they share the same reaction precursors. Field induced metamagnetic like behaviors were observed for these complexes.



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- New coordination fashion of dinuclear entity derived from Mn(III)-(Schiff-base) and $[\text{Fe}^{\text{III}}(\text{qcq})(\text{CN})_3]^-$
- Using same reaction precursors, different structure fashions could be obtained.
- Field induced metamagnetic like behaviors were observed for these complexes.

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