Syntheses, structures, and magnetic properties of three new cyano-bridged complexes based on the [Mn(CN)₆]³⁻ building block†

Shao-Liang Zhang, Xin-Hua Zhao and Xin-Yi Wang*

With three pentadentate macrocyclic ligands, three new [Mn(CN)₆]³⁻ based complexes, [Mn(L₉SCD₂)₂(H₂O)]₃[Mn(CN)₆][ClO₄] · 3H₂O (1), [Mn(L₉SCD₂)L₃]³[Mn(CN)₆]₂Cl·10H₂O (2) and [Mn(L₉SCD₂)L₃][Mn(CN)₆]₂Cl·10H₂O (3) [L₉SCD₂ = 2,13-dimethyl-6,9-dioxa-3,12,18-triazabicyclo[12.3.1]octadeca-1(18),2,12,14,16-pentaene, L₉SCS = 2,13-dimethyl-3,6,9,12,18-pentaazabicyclo[12.3.1]octadeca-1(18),2,12,14,16-pentaene, L₉SCMS₆ = 2,6-bis[1-(2-(N-methylamino)ethylamino)ethyl]pyridine], have been synthesized and characterized structurally and magnetically. The structure of 1 was found to be a linear Mn₁²M₃ trinuclear cluster with two Mn³⁺ capping groups and one Mn³⁺ ion connected via two trans-cyano groups. In contrast, compounds 2 and 3 are cyano-bridged 2D networks. Magnetic investigation revealed antiferromagnetic coupling between the Mn³⁺ and Mn¹⁺ ions via the bridging cyanide groups. Complex 1 showed paramagnetic behavior down to 2.0 K with no sign of SMM behavior. The magnetic coupling constant of J = −1.63 cm⁻¹ from the Hamiltonian H = −2J[S₉₃S₉₃] + S₉₃S₉₃ was obtained from the fitting of the magnetic susceptibility. For 2 and 3, ferrimagnetic ordering was observed with magnetic phase transition temperatures (Tₘ) being 7.5 K and 7.0 K, respectively. These compounds are rare examples of a small number of [Mn(CN)₆]³⁻ based magnetic materials.

Introduction

Molecule-based magnetic materials have been explored intensively not only because of their fundamental interest but also due to their potential applications as functional materials. Among all the molecular magnetic materials, the cyano-bridged compounds are of great importance. Various cyano-bridged materials of interesting magnetic properties, including single-molecule magnets (SMMs), single-chain magnets (SCMs), high Tₘ magnets, photo-responsive magnets, chiral magnets, and spin-crossover (SCO) compounds, have been prepared and reported. For the synthesis of these materials, the building block approach utilizing the carefully designed precursors as the starting materials is most widely used. In this sense, cyanometallate precursors offer a number of distinct advantages. Except for some rare cases, they are generally stable in solution; the spin states of the cyanometallate precursors can be controlled by choosing the appropriate metal centers with suitable chemical valence; the nature of magnetic coupling (ferromagnetic vs. antiferromagnetic) is typically predictable using the simple and straightforward Goodenough-Kanamori rule; the structure and dimensionality can be largely controlled by introducing specific capping ligands on one or more of the starting materials. For all the studied cyanometallates, [M(CN)₆]³⁻ and [ML(CN)₆]³⁻ (L = ligands), the [M(CN)₆]³⁻ (M = Fe³⁺, Cr³⁺, Mn³⁺) motifs are with no doubt the most intensively investigated. Based on these starting materials, the resulting Prussian Blue (PB) analogues, M₄X₄[M'⁴(CN)₆]₄·nH₂O (A = alkali metal; M and M' = divalent and trivalent transition metal ions, respectively), are the reservoir of many intriguing physical properties mentioned above such as room temperature magnets, photomagnets, and SCO. In this sense, the PB type compounds are like a chameleon in the molecule magnetism, as the perovskite compounds are in the field of inorganic materials.

Due to the magnetic anisotropy of the low spin Mn³⁺ center (ground strong field configuration: t₂g⁴, ground strong field term in O₉ symmetry: T₂g), the effective magnetic coupling via CN⁻, and the possible anisotropic magnetic coupling, the building block [Mn³⁺(CN)₆]³⁻ has gained considerable attention for designing magnetic materials. However, compared...
to the widely studied [Cr(III)(CN)6]3− and [Fe(III)(CN)6]3− units, the limited stability of [Mn(III)(CN)6]3− in solution hinders the study of [Mn(III)(CN)6]3−-based materials. Generally, single crystals of [Mn(III)(CN)6]3−-containing materials are quite difficult to obtain as [Mn(CN)6]3− decomposes in solution. To date, there are only limited examples reported in the literature, including a trigonal bipyramidal SMM [{[Mn(III)(tmphen)]3}3−, {Mn(III)(CN)6}3−,16a a triplesalen-based SMM [{[(talen)(OEt2)](Mn(III), (MeOH))}3]3−,16b) a 1D SCM [Mn(III)(5-TMAMsalen)Mn(III)(CN)6]2−,16c the 2D chiral ferromagnets [Mn(II)(HL)(H2O)][Mn(III)(CN)6]2−,16d a 1D SCM [Mn(III)(5-TMAMsalen)Mn(III)(CN)6]2−,16e the 2D chiral ferromagnets [Mn(II)(HL)(H2O)][Mn(III)(CN)6]2−,16f a 1D SCM [Mn(III)(5-TMAMsalen)Mn(III)(CN)6]2−,16g an interpenetrated 3D ferromagnet [{(Mn(4dmap)4)[Mn(CN)6]2·4H2O,17a [{[(dmap)Mn(III)(CN)6]2·4H2O,17b [(TPP)−(NEt4)][(Tp*)Mn(III)(CN)3],17c [{[(TPP)−(NEt4)][(Tp*)Mn(III)(CN)3],17d}·3H2O]·(ClO4)2,17e CsIMnII[MnIII(CN)6]·H2O,17f [{[(TPP)−(NEt4)][(Tp*)Mn(III)(CN)3],17g·8H2O,17h [{[(TPP)−(NEt4)][(Tp*)Mn(III)(CN)3],17i·3H2O],17j [{[(TPP)−(NEt4)][(Tp*)Mn(III)(CN)3],17k·3H2O],17l CsINiII[MnIII(CN)6]·H2O,17m [{[(TPP)−(NEt4)][(Tp*)Mn(III)(CN)3],17n·8H2O,17o [{[(TPP)−(NEt4)][(Tp*)Mn(III)(CN)3],17p·3H2O],17q [{[(TPP)−(NEt4)][(Tp*)Mn(III)(CN)3],17r·3H2O],17s [{[(TPP)−(NEt4)][(Tp*)Mn(III)(CN)3],17t·3H2O],17u [{[(TPP)−(NEt4)][(Tp*)Mn(III)(CN)3],17v·3H2O],17w}·3H2O],17x}·3H2O],17y}·3H2O],17z}·3H2O].17−

Scheme 1 Building blocks and precursors used to prepare complexes 1–3.

Experimental section

Physical measurements

Elemental analyses of carbon, hydrogen, and nitrogen were carried out using a Vario EL II Elemental. Infrared spectra of the samples were obtained using a Bruker Tensor 27 FT-IR spectrometer with KBr pellets. Powder X-ray diffraction (PXRD) data were recorded at 298 K using a Bruker D8 Advance diffractometer with Cu Kα X-ray source (operated at 40 kV and 40 mA). Magnetic properties of 1 to 3 were measured using a Quantum Design SQUID VSM magnetometer on polycrystalline samples. All magnetic data were corrected for the diamagnetism of the sample holder and of the constituent atoms according to Pascal’s constants.

Materials

The starting materials, K2[Mn(CN)6]21− Mn(I−N3O2)Cl2,19a [Mn(I−N3O2)(H2O)Cl]ClO4−,19b Mn(II−N5Me)Cl2,19c were synthesized according to the methods mentioned in literature. The syntheses of 1–3 were carried out in deoxygenated solvents under cold conditions in the dark to avoid the possible oxidation of the Mn2+ starting materials and decomposition of K2[Mn(CN)6].
Dalton Transactions

Caution!
Cyanides are highly toxic and perchlorate salts of metal complexes are potentially explosive. They should be handled in small quantities with care.

Preparations

$$[{\text{Mn(L}_{18\text{crown-6}})\text{H}_2\text{O}}]{\text{[Mn(CN)\text{6}]}}\text{(ClO}_4\text{-3H}_2\text{O}}$$ (1). A mixture of $K_3\text{Mn(CN)}\text{6}$ (16.4 mg, 0.05 mmol) and $\text{LiClO}_4$ (53 mg, 0.5 mmol) was dissolved in 2 mL of water and then mixed with a solution of $\text{Mn(L}_{18\text{crown-6})\text{Cl}_2}$ (40 mg, 0.10 mmol in 2 mL of $\text{H}_2\text{O}$) in one side and a 3 mL solution of $\text{Mn(L}_{18\text{crown-6})\text{Cl}_2}$ (30 mg, 0.075 mmol in $\text{MeOH}$/$\text{H}_2\text{O}$ with $V/V = 1:1$) in the other side. Another 4 mL of solvent ($\text{MeOH}$/$\text{MeCN} = 1:1$) was carefully layered on the top of the solutions as a buffer. The tube was then sealed and stored in the dark at 4 °C. Red-brown single crystals suitable for X-ray diffraction were obtained after several days. Yield: 28.7 mg, 54%. Elemental analysis (%) calculated for $C_{36}\text{H}_{52}\text{N}_{12}\text{O}_{13}\text{ClMn}_3$: C, 40.75; H, 4.94; N, 15.84. Found: C, 40.76; H, 4.92; N, 15.95. IR (KBr): 2113(s) cm$^{-1}$.

$$[{\text{Mn(L}_{18\text{crown-6}})\text{K}}]{\text{[Mn(CN)\text{6}]}}$$ (2). A solution of $[(18\text{-crown-6})\text{K}]_3\text{[Mn(CN)}\text{6]}$ was prepared by stirring $K_3\text{[Mn(CN)}\text{6]}$ (16.4 mg, 0.05 mmol) and 18-crown-6 (39.6 mg, 0.15 mmol) in 3 mL methanol for 3 h. An H-shaped tube was charged with a 3 mL solution of $\text{Mn(L}_{18\text{crown-6})\text{Cl}_2}$ (40 mg, 0.10 mmol in 2 mL of $\text{DMF}$) with $V/V = 1:1$. The resulting solution was stirred for 5 minutes and then filtered and kept in the dark at 4 °C without any disturbance. Red-brown single crystals suitable for X-ray diffraction were obtained after several days. Yield: 28.7 mg, 54%. Elemental analysis (%) calculated for $C_{57}\text{H}_{69}\text{N}_{27}\text{Mn}_5$: C, 48.66; H, 4.94; N, 26.88. Found: C, 48.78; H, 5.80; N, 23.95. IR (KBr): 2111(s) cm$^{-1}$.

$$\text{[Mn(L}_{18\text{crown-6})\text{Me})\text{Cl}_2]\text{[Mn(CN)}\text{6}]\text{2}$$ (3). Compound 3 was prepared by a similar method as that for 2, except for the solvent. An H-tube was charged with a 3 mL methanol solution of $[(18\text{-crown-6})\text{K}]_3\text{[Mn(CN)}\text{6]}$ in one side and a 3 mL solution of $\text{Mn(L}_{18\text{crown-6})\text{Cl}_2}$ (30 mg, 0.075 mmol in $\text{MeOH}$/$\text{H}_2\text{O}$ with $V/V = 1:1$) in the other side. Another 4 mL of solvent ($\text{MeOH}$/$\text{MeCN} = 1:1$) was carefully layered on the top of the solutions as a buffer. The tube was then sealed and stored in the dark at 4 °C. Red-brown single crystals suitable for X-ray diffraction were obtained after several days. Yield: 11.9 mg, 30%. Elemental analysis (%) calculated for $C_{57}\text{H}_{95}\text{N}_{27}\text{O}_{10}\text{Mn}_5$: C, 42.97; H, 6.01; N, 26.88. Found: C, 42.89; H, 5.80; N, 23.95. IR (KBr): 2114(s) cm$^{-1}$ for $\nu$(C≡N).

X-ray data collection and structure determination

X-ray data for compounds 1–3 were collected using a Bruker APEX II diffractometer with a CCD area detector (Mo-K$_\alpha$ radiation, $\lambda = 0.71073$ Å) under nitrogen at 120 K. The APEX program was used to determine the unit cell parameters and for data collection. Data were integrated using SAINT25 and SADABS.26 The structures of all three compounds were solved by direct methods and refined by full matrix least-square methods based on $F^2$ using the SHELXTL program.26 Anisotropic thermal parameters were used for the non-hydrogen atoms and isotropic parameters for the hydrogen atoms. Hydrogen atoms of the organic ligands were refined as riding on the corresponding non-hydrogen atoms. Crystal data and experimental details of the structure determinations are listed in Table 1. Selected bond lengths and bond angles for complexes 1–3 are given in Tables S1–S3 (ESI†). The phase purity of all three compounds was confirmed by their PXRD spectra (Fig. S1–S3†).

Table 1 Crystallographic data and structure refinement parameters for complexes 1–3

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<tr>
<th>Complex</th>
<th>1</th>
<th>2</th>
<th>3</th>
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<tr>
<td>Formula</td>
<td>$C_{36}\text{H}<em>{52}\text{N}</em>{12}\text{O}_{13}\text{ClMn}_3$</td>
<td>$C_{57}\text{H}<em>{69}\text{N}</em>{27}\text{Mn}_5$</td>
<td>$C_{57}\text{H}<em>{95}\text{N}</em>{27}\text{O}_{10}\text{Mn}_5$</td>
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<tr>
<td>$M$</td>
<td>1061.17</td>
<td>1407.09</td>
<td>1593.23</td>
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<td>Triclinic</td>
<td>Triclinic</td>
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<tr>
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<td>P1</td>
<td>P1</td>
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<td>11.418(2)</td>
<td>11.467(6)</td>
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<td>$b$ [Å]</td>
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<td>17.402(10)</td>
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<td>100.383(8)</td>
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<tr>
<td>$\beta$ [°]</td>
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<td>90.651(8)</td>
<td>90.651(8)</td>
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<tr>
<td>$\gamma$ [°]</td>
<td>90.651(8)</td>
<td>90.651(8)</td>
<td>90.651(8)</td>
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<tr>
<td>$V$ [Å$^3$]</td>
<td>3769.6(12)</td>
<td>3804(4)</td>
<td>3804(4)</td>
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<td>$Z$</td>
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<td>2</td>
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<tr>
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<td>$f(000)$</td>
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<td>1450</td>
<td>1622</td>
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<td>Crystal size [mm]</td>
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<td>13 371</td>
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<td>0.0783</td>
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<td>$R_{1}$, w$R_{2}$ ($I &gt; 2\sigma(I)$)</td>
<td>0.0398, 0.1177</td>
<td>0.0885, 0.2330</td>
<td>0.0842, 0.1775</td>
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Results and discussion

Syntheses and crystal structure descriptions

The macrocyclic ligands reported in this work can be obtained easily by a metal templated Schiff-base condensation of 2,6-diacetylpyrididine and polyamine. Due to their planar character, the resulting metal complexes are usually seven coordinated with approximate pentagonal bipyramid geometry, where the axial positions are usually coordinated by the weakly bonded ligands such as the solvent molecules or the anions. These ligands can be easily substituted by the nitrogen atoms from the cyanide groups to form extended structures.\(^{2d,18-20}\) Due to the low stability of the \([\text{Mn}^{\text{III}}(\text{CN})_6]^{3-}\) starting material in the solution, the reactions of these macrocyclic building blocks with \([\text{Mn}^{\text{III}}(\text{CN})_6]^{3-}\) have to be performed at low temperatures.

Complex 1 crystallizes in the monoclinic space group \(C2/c\) and has a linear \(\text{Mn}^{\text{II}}\text{Mn}^{\text{III}}\) trinuclear structure where two \([\text{Mn-}(\text{LN}_3\text{O}_2)]^{2+}\) capping groups are connected to the \(\text{Mn}^{\text{III}}\) center via two \(\text{CN}^{-}\)groups in the \(trans\) position (Fig. 1). The positive charge of the cluster is balanced by a \(\text{ClO}_4^{-}\) anion. Interestingly, there are two unique trinuclear units (units A and B) in the crystal structure. In unit A, the central \(\text{Mn}^{\text{III}}\) ion lies on a special position \((0.00, 0.74, 0.25)\) with a \(C_2\) axis, whereas in unit B, the \(\text{Mn}^{\text{III}}\) center is sited in the inversion center \((0.25, 0.75, 0.50)\). All the \(\text{Mn}^{\text{II}}\) ions in 1 are in a slightly distorted pentagonal bipyramidal environment with seven coordinated atoms, five of which are from the macrocyclic ligand \(\text{LN}_3\text{O}_2\) with the remaining two being a nitrogen atom from a bridging cyanide and an oxygen atom from the coordinated water. The \(\text{Mn}-\text{N}\) and \(\text{Mn}-\text{O}\) distances lie in the range of 2.203–2.248 Å (av. 2.229 Å) and 2.257–2.288 Å (av. 2.277 Å). Using the program SHAPE \(^{21,27}\) the continuous shape measures (CShMs) of the \(\text{Mn}^{\text{II}}\) centers relative to the ideal pentagonal bipyramid are calculated to be 0.110 and 0.322 for \(\text{Mn}2\) and \(\text{Mn}4\), respectively. As for the \([\text{Mn}(\text{CN})_6]^{3-}\) unit, the \(\text{Mn}^{\text{III}}\) center is in a distorted octahedron environment with CShMs being 0.105 and 0.019 relative to the ideal octahedron for \(\text{Mn}1\) and \(\text{Mn}3\), respectively. While the octahedron of the \([\text{Mn}(\text{CN})_6]^{3-}\) is tetragonally compressed for unit A (the axial bond \(\text{Mn}1-C1 = 1.992(2)\) Å, the equatorial ones \(\text{Mn}1-C2 = 2.003(2)\) Å, \(\text{Mn}1-C3 = 2.008(2)\) Å), it is tetragonally elongated for unit B (the axial bond \(\text{Mn}3-C19 = 2.015(2)\) Å, the equatorial ones \(\text{Mn}3-C20 = 2.000(3)\) Å, \(\text{Mn}3-C21 = 2.004(2)\) Å). Bridged by the \(\text{CN}^{-}\) groups, the \(\text{Mn}^{\text{II}}-\text{Mn}^{\text{III}}\) distances for units A and B are 5.253 and 5.361 Å, respectively.

Connected by the \(\text{C}-\text{H}⋯\text{N}\) hydrogen bonds for units A between the \(\text{C}-\text{H}\) groups of the macrocyclic ligands and the \(\text{CN}^{-}\) groups \((\text{C}_{15}⋯\text{N}_3 = 3.484\) Å, \(\text{C}_{6}⋯\text{N}_2 = 3.403\) Å) and the \(\text{O}-\text{H}⋯\text{N}\) hydrogen bonds for units B between the coordinated water molecules and the \(\text{CN}^{-}\) groups \((\text{O}_6⋯\text{N}_9 = 2.829\) Å), both units form 2D supramolecular networks along the \(bc\) plane (Fig. 2). These layers are then stacked alternatively along the \(a\) axis and are linked together by a large number of \(\text{O}-\text{H}⋯\text{O}\) hydrogen bonds involving the \(\text{ClO}_4^{-}\) anions and the \(\text{H}_2\text{O}\) molecules with the \(\text{O}⋯\text{O}\) distances being in the range of 2.733–3.213 Å.

Although the macrocyclic ligands \(\text{L}_{\text{N}5}\) and \(\text{L}_{\text{N}5\text{Me}}\) are very similar to the \(\text{L}_{\text{N}3\text{O}2}\) ligand in 1, the crystal structures of complexes 2 and 3 are totally different from that of 1, indicating a significant influence of the macrocyclic ligands on the resulting products. Bridged by the \([\text{Mn}(\text{CN})_6]^{3-}\) units, both compounds 2 and 3 have a very similar 2D layered structure, despite the significantly different numbers of crystallized water molecules in the structure. We will only discuss the structure of 2. Synthesized from the anhydrous solvent, 2 crystallizes in a triclinic space group \(\text{Pl}\) and has no solvent molecules in the structure. As can be seen from Fig. 3, the asymmetric unit of 2 consists of three \([\text{Mn}^{\text{III}}(\text{LN}_5)]^{2+}\) units, one \([\text{Mn}^{\text{III}}(\text{CN})_6]^{3-}\) unit \((\text{Mn}1)\) in a general position and two half of the \([\text{Mn}^{\text{III}}(\text{CN})_6]^{3-}\) units \((\text{Mn}3\) and \(\text{Mn}5)\) in the \((1, 0, 0)\) and \((1, 0, 0.5)\) positions. All the \(\text{Mn}^{\text{II}}\) ions are in the slightly distorted pentagonal bipyramidal geometry (the CShMs are 0.541,

![Fig. 1](image1.png)

**Fig. 1** Perspective view of the linear trinuclear structure in complex 1. Units A and B are two unique trinuclear clusters. All the hydrogen atoms and the solvent molecules have been omitted for clarity.

![Fig. 2](image2.png)

**Fig. 2** The 2D layers of 1 constructed from the trinuclear units A (left) and B (right). Middle: the 3D structure of 1 formed by the alternatively stacked layers along the \(a\) axis. The dashed lines represent the hydrogen bonds.
The temperature dependent magnetic susceptibility data for 1 measured over the temperature range of 2–300 K under 1000 Oe are displayed in Fig. 4 as the $\chi_M(T)$ and $\chi_M^{-1}(T)$ curves per Mn$^{II}$Mn$^{II}$ unit. The room-temperature value of $\chi_M$ is 9.59 cm$^3$ mol$^{-1}$ K, which is slightly lower than the spin-only value of 9.75 cm$^3$ mol$^{-1}$ K for two high-spin Mn$^{II}$ ($S = 5/2$) and one low-spin Mn$^{III}$ ($S = 1$) centers. On decreasing the temperature, the $\chi_M$ value decreases to 8.01 cm$^3$ mol$^{-1}$ K at 14 K and increases again to a maximum of 9.71 cm$^3$ mol$^{-1}$ K at 2 K. The magnetic susceptibility above 100 K obeys the Curie–Weiss law with a Weiss constant $\theta = -6.31$ K and a Curie constant $C = 9.81$ cm$^3$ mol$^{-1}$ K. The negative Weiss constant and the decrease of the $\chi_M$ curve at high temperature indicate the antiferromagnetic coupling between the Mn$^{II}$ and Mn$^{III}$ centers via the CN$^-$ groups. The increase of the $\chi_M$ curve below 14 K indicates the high-spin ground state of compound 1. The $\chi_M$ value at 2 K is only slightly smaller than the value of 10 cm$^3$ mol$^{-1}$ K for a state of $S = 4$ ($g = 2.0$), resulting from the antiparallel alignment of two Mn$^{II}$ and one Mn$^{III}$ centers. As the two trinuclear units in the structure are similar, the magnetic coupling between the Mn$^{II}$ and Mn$^{III}$ centers can be described by one single coupling constant $J$ with the Hamiltonian $H = -2J(\mathbf{S}_{\text{Mn(III)}},\mathbf{S}_{\text{Mn(II)}},\mathbf{S}_{\text{Mn(II)}})$. Using the program PHI,$^{2}$ the $\chi_M$ data from 2 to 300 K can be fitted with the best-fit parameters $J = -1.63$ cm$^{-1}$, $g_{\text{Mn(II)}} = 2.003$, $g_{\text{Mn(III)}} = 1.967$ and $R = 0.010$. The negative $J$ value is consistent with those found in the reported cyanide-bridged Mn$^{II}$–Mn$^{II}$ complexes.$^{1,12}$

The field dependent magnetization of 1 was also measured at 2.0 K with field up to 70 kOe (Fig. S7†). Typical paramagnetic behaviour was observed. At the highest magnetic field, $M$ reaches the value of 8.98$\mu_B$, which is larger than the expected value of 8$\mu_B$ for the antiferromagnetically coupled trinuclear Mn$^{II}$Mn$^{II}$ Mn$^{III}$ cluster. The reduced magnetization of 1 was also measured at low temperature with dc field up to 70 kOe (Fig. S8†). As can be seen, magnetic anisotropy was suggested by the non-superposition of the reduced magnetization data to a single master curve. However, all attempts to fit the reduced magnetization data using both programs PHI and Anisofit2.0

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failed. This could be due to the fact that the ground state of 1 is not a well-isolated state of $S = 4$ because of the weak magnetic interaction. In addition, the situation could become more complicated because of the existence of two different tri-nuclear clusters in 1. To check whether 1 behaves as a SMM, ac susceptibility data under zero dc field were measured at low temperature. As can be seen from Fig. S9,† there is no observable out-of-phase signals down to 2.0 K, ruling out the SMM behaviour for 1.

As the magnetic properties of 2 and 3 are very similar due to their similar structures, the magnetic property of 2 will be discussed as representative, whereas the results of 3 can be found in the ESI (Fig. S10−S13†). The magnetic susceptibility data measured under 1000 Oe for 2 are displayed in Fig. 5 as the $\chi_M(T)$ and $\chi_M^{-1}(T)$ curves. At room temperature, the $\chi_M T$ value per Mn$^{III}_2$Mn$^{II}_3$ unit is 14.45 cm$^3$ mol$^{-1}$ K, which is consistent with the spin-only value of 15.13 cm$^3$ mol$^{-1}$ K expected for the magnetically isolated three Mn$^{III}$ ($S = 5/2$) and two Mn$^{II}$ ($S = 1$) ions. Upon cooling from 300 K, the $\chi_M T$ curve gradually decreases down to the minimum value of 11.68 cm$^3$ mol$^{-1}$ K at 37 K, and then rapidly increases up to the maximum peak of 124.6 cm$^3$ mol$^{-1}$ K at 6.3 K, followed by a drop down to 44.9 cm$^3$ mol$^{-1}$ K at 2 K. This behaviour is very typical for a long-range ordered ferrimagnet. The drop of the $\chi_M T$ curve below 6 K should be due to the field saturation effect of the magnetization. A Curie–Weiss fit above 100 K gave a negative Weiss constant of $\theta = -19.9$ K, which reflects the dominant antiferromagnetic interaction between the Mn$^{III}$ and Mn$^{II}$ ions, although it might partly come from spin–orbital coupling of the low-spin Mn$^{III}$ ions.

The occurrence of the long-range magnetic ordering at low temperature was further confirmed by the measurements at low temperatures, including the zero-field-cooled and field-cooled (ZFC/FC) magnetization measured in a dc field of 10 Oe and the ac susceptibilities measured under $H_{dc} = 0$ Oe and $H_{ac} = 2$ Oe. As can be seen from Fig. 6, the ZFC curve exhibits a peak and diverges from the FC curve at about 7.5 K, suggesting the magnetic phase transition from the paramagnetic phase to a long-range ordered phase and the hysteric effect at low temperature. As for the ac susceptibilities, the in-phase signals ($\chi_M'$) show a peak and the out-of-phase signals ($\chi_M''$) rapidly increase below 7.5 K (Fig. 7). These results are consistent with each other and confirm the magnetic ordering temperature $T_c = 7.5$ K. In addition, a very small frequency dependence for both the $\chi_M'$ and the $\chi_M''$ data was observed. The shift parameter $\varphi = (\Delta T_p/T_p)/\Delta(\log f)$ is only 0.007 (where $T_p$ represents the peak temperature of the in-phase $\chi_M'$ plots and $f$ is the frequency of the ac field), which is close to a value for a spin glass.²⁹ Because there are no disordered components and competitive interactions in the structure, the glassy behavior might
come from the movement of the domain walls and/or the natural defects in the structure.\textsuperscript{29}

To check the irreversibility of the magnetization suggested by the divergence of the ZFC/FC curves, the isothermal magnetization $M$ was also measured at 2 K. At low fields, $M$ increases very rapidly and then increases steadily with $H > 10$ kOe to reach a maximum value of $10.1\mu_B$ at 70 kOe (Fig. 8), which is slightly lower than the calculated saturation value of $11\mu_B$ for the antiferromagnetically coupled tripled Mn\textsuperscript{II} and two Mn\textsuperscript{III} ions. Furthermore, an evident hysteresis loop at 2 K can be observed with a remnant magnetization $M_R = 4.68\mu_B$ and a coercive field $H_c = 620$ Oe (Fig. 8). Compared with the corresponding Mn\textsuperscript{II}O\textsubscript{2}\textsuperscript{12c} the coercive field and the remnant magnetization of 2 are significantly larger. This could be associated with the magnetic anisotropy of Mn\textsuperscript{III} ion, compared with the isotropic Cr\textsuperscript{III} center.

As for complex 3, its magnetic properties are very similar to that of 2 with a slightly lower $T_c$ value of 7.0 K. Considering their similar structures and magnetic properties, the slightly lower $T_c$ of the hydrated 3 is consistent to the normal “magnetic sponges”, whose magnetic ordering temperature $T_c$ can change reversibly upon hydration/dehydration or upon sorption/desorption of guest molecules.\textsuperscript{20} The $T_c$ increases upon dehydration because of the closer distances between the spin centers and/or modified structures of the “dense” dehydrated form. For example, for a nanoporous magnet \{[Mn(HL)]$_3$Mn[Mo(CN)$_6$]$_2$\}$_n$H$_2$O (L = N,N\textsuperscript{-}dimethylalaninol), the $T_c$ value can be switched from 85 to 106 K by dehydration.\textsuperscript{20b} In our case, compound 2 can be treated as a “dehydrated” form of 3 as it contains no lattice solvent molecules and is isostuctural to 2. Due to the large number of water molecules in the structure, the shortest interlayer Mn...Mn distance of 3 (8.40 Å) is actually larger than that of 2 (7.98 Å), which leads to the weaker interlayer magnetic coupling and justifies the slightly lower $T_c$ of 3.

As discussed for the Mn\textsuperscript{II}-Cr\textsuperscript{III} compounds,\textsuperscript{12c} the $T_c$ value of compounds 2 and 3 can be approximately given in the following equation according to the molecular field theory:

$$T_c = \frac{2(n_{\text{Mn(III)}}/n_{\text{Mn(II)}})^{1/2}/f\left(S_{\text{Mn(III)}}(S_{\text{Mn(III)}} + 1)S_{\text{Mn(II)}}(S_{\text{Mn(II)}} + 1)\right)^{1/2}}{3k_B},$$

where $n_{\text{Mn(III)}}$ and $n_{\text{Mn(II)}}$ are the numbers of the nearest magnetic ions around Mn\textsuperscript{II} and Mn\textsuperscript{III} centers, respectively, and $f$ is the exchange interaction constant. According to this equation, we can see that the $T_c$ value is proportional to the $n_{\text{Mn(III)}}/n_{\text{Mn(II)}}$ and $f$ values. Of course, we have to emphasize that the parameter $f$ should be considered as the averaged value along three directions. For those with lower dimensionality, the $T_c$ is usually very low as the averaged $f$ is usually quite small due to the weak magnetic interactions between the clusters, chains or layers. In fact, for a perfect magnetic chain without any interchain magnetic interaction, the long-range ordering should only occur at 0 K. As we can see in Table 2, the PB analogues have the highest $T_c$ as they are 3D structures with large ($n_{\text{Mn(III)}}$, $n_{\text{Mn(II)}}$) values. Moreover, because of the lower ($n_{\text{Mn(III)}}$, $n_{\text{Mn(II)}}$) values, 2 and 3 have lower $T_c$ values than compound \{[Mn(HL)]$_3$Mn[Mo(CN)$_6$]$_2$\}$_n$H$_2$O (L = \{\} H$_2$O, although it has a 3D structure, its $T_c$ is quite low due to the very low ($n_{\text{Mn(III)}}$, $n_{\text{Mn(II)}}$) value and its highly porous structure.

### Conclusions

In conclusion, by carefully tuning the reaction conditions and using the auxiliary macrocyclic ligands, we have synthesized and characterized three rare examples of [Mn\textsuperscript{III}(CN)$_6$]$^{2-}$ based molecular magnetic complexes, including a linear trinuclear cluster and two 2D layered compounds. Antiferromagnetic exchange interactions between the Mn\textsuperscript{II} and Mn\textsuperscript{III} ions were verified. Paramagnetic behavior was observed for the trinuclear compound, whereas the 2D layered compounds show ferrimagnetic-long range ordering with $T_c$ around 7 K. Due to the

#### Table 2 $T_c$ values of the Mn\textsuperscript{II}-Mn\textsuperscript{III} compounds based on the [Mn(CN)$_6$]$^{2-}$ unit

<table>
<thead>
<tr>
<th>Compound</th>
<th>($n_{\text{Mn(III)}}$)/($n_{\text{Mn(II)}}$)</th>
<th>$T_c$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn\textsuperscript{II}[Mn\textsuperscript{III}(CN)$_6$]$_2$·12H$_2$O</td>
<td>(6, 4)$^a$</td>
<td>37</td>
<td>14b</td>
</tr>
<tr>
<td>Mn\textsuperscript{II}[Mn\textsuperscript{III}(CN)$_6$]$_2$·2H$_2$O (z = 12–16)</td>
<td>(6, 4)$^a$</td>
<td>35.5</td>
<td>14a</td>
</tr>
<tr>
<td>Mn\textsuperscript{II}[Mn\textsuperscript{III}(CN)$_6$]$_2$·12H$_2$O·1.7CH$_3$OH</td>
<td>(6, 4)$^a$</td>
<td>29</td>
<td>14c</td>
</tr>
<tr>
<td>CsMn\textsuperscript{II}[Mn\textsuperscript{III}(CN)$_6$]$_2$·0.5H$_2$O</td>
<td>(6, 6)</td>
<td>31</td>
<td>14b</td>
</tr>
<tr>
<td>[Me$_2$N]$_2$Mn\textsuperscript{II}[Mn\textsuperscript{III}(CN)$_6$]$_2$·8H$_2$O</td>
<td>(6, 6)</td>
<td>29</td>
<td>14c</td>
</tr>
<tr>
<td>[Mn(HL)]$_3$Mn[Mo(CN)$_6$]$_2$·H$_2$O</td>
<td>(4, 4)</td>
<td>21</td>
<td>12b</td>
</tr>
<tr>
<td>{[Mn(4dmap)$_3$]$_3$Mn[Mo(CN)$_6$]$_2$·10nH$_2$O</td>
<td>(3, 2)</td>
<td>6.4</td>
<td>12c</td>
</tr>
<tr>
<td>{[Mn(L$_{10}$)$_3$]$_3$Mn[Mo(CN)$_6$]$_2$·10nH$_2$O</td>
<td>(3, 2)</td>
<td>7.5</td>
<td>This work</td>
</tr>
<tr>
<td>{[Mn(L$_{10}$)$_3$]$_3$Mn[Mo(CN)$_6$]$_2$·10nH$_2$O</td>
<td>(3, 2)</td>
<td>7.0</td>
<td>This work</td>
</tr>
</tbody>
</table>

$^a$ $n_{\text{Mn(III)}}/n_{\text{Mn(II)}}$ is an average value.
very limited reports on the [MnIII(CN)6]3− based magnetic compounds, further efforts aiming at the preparation of more compounds with different macrocyclic ligands and different metal centers are of great value and are currently being undertaken in the lab.

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Notes and references


