Syntheses, structures, and magnetic properties of three new Mn\textsuperscript{II}–[Mo\textsuperscript{III}(CN)\textsubscript{7}]\textsuperscript{4–} molecular magnets\textsuperscript{†}

Xiao-Qin Wei,\textsuperscript{a} Qian Pi,\textsuperscript{a} Fu-Xing Shen,\textsuperscript{a} Dong Shao,\textsuperscript{a} Hai-Yan Wei\textsuperscript{b} and Xin-Yi Wang\textsuperscript{a}

By reaction of K\textsubscript{4}[Mo\textsuperscript{III}(CN)\textsubscript{7}]·2H\textsubscript{2}O, Mn(ClO\textsubscript{4})\textsubscript{2}·6H\textsubscript{2}O and bidentate chelating ligands, three new cyano-bridged compounds, namely Mn\textsubscript{2}(3-pypz)·(H\textsubscript{2}O)(CH\textsubscript{3}CN)[Mo(CN)\textsubscript{7}]. (1). Mn\textsubscript{2}(1-pypz)·(H\textsubscript{2}O)(CH\textsubscript{3}CN)[Mo(CN)\textsubscript{7}]. (2) and Mn\textsubscript{2}(pyim)·(H\textsubscript{2}O)(CH\textsubscript{3}CN)[Mo(CN)\textsubscript{7}]. (3) (3-pypz = 2-(1H-pyrazol-3-yl)pyridine, 1-pypz = 2-(1H-pyrazol-1-yl)pyridine, pyim = 2-(1H-imidazol-2-yl)pyridine), have been synthesized and characterized structurally and magnetically. Single crystal X-ray analyses revealed that although the chelating ligands are different, compounds 1 to 3 are isomorphous and crystallize in the same monoclinic space group C2\textsubscript{h}m. Connected by the bridging cyano groups, one crystallographically unique [Mo(CN)\textsubscript{7}]\textsuperscript{4–} unit and three crystallographically unique Mn\textsuperscript{II} ions of different coordination environments form similar three-dimensional frameworks, which have a four-nodal 3,4,4,7-connecting topological net with a vertex symbol of (4\textsuperscript{3})(4\textsuperscript{4}·6\textsuperscript{2})(4\textsuperscript{10}·6\textsuperscript{11}). Magnetic measurements revealed that compounds 1–3 display long-range magnetic ordering with critical temperatures of 64, 66 and 62 K, respectively. These compounds are rare examples of a small number of chelating co-ligand coordinated [Mo(CN)\textsubscript{7}]\textsuperscript{4–} based magnetic materials. Specifically, the bidentate chelating ligands were successfully introduced into the heptacyanomolybdate system for the first time.

Introduction

In the vein of molecule-based magnetic materials, the heptacyanomolybdate [Mo\textsuperscript{III}(CN)\textsubscript{7}]\textsuperscript{4–} unit has attracted much attention due to its great potential.\textsuperscript{1} As have been established by both experimental and theoretical studies,\textsuperscript{2} the Mo\textsuperscript{III} center in the [Mo\textsuperscript{III}(CN)\textsubscript{7}]\textsuperscript{4–} unit can have strong magnetic coupling between other metal centers through the multiple CN\textsuperscript{–} groups. The large amount of CN\textsuperscript{–} groups (7) and the high negative charge (−4) of the [Mo\textsuperscript{III}(CN)\textsubscript{7}]\textsuperscript{4–} unit make it easier to act as a high connection node, which usually favors high-dimensional extended coordination polymers with high magnetic ordering temperatures.\textsuperscript{3} In addition, deriving from either single-ion anisotropy or anisotropic magnetic exchange, the [Mo\textsuperscript{III}(CN)\textsubscript{7}]\textsuperscript{4–} unit makes it possible for the magnetic properties of the resulting materials. On the one hand, for magnets of long range ordering, the low symmetry of the [Mo\textsuperscript{III}(CN)\textsubscript{7}]\textsuperscript{4–} unit results in the low symmetric lattice and very interesting magnetic anisotropy properties, such as the spin reorientation phenomenon in the three-dimensional (3D) Mn\textsuperscript{II}–Mo\textsuperscript{III} compounds reported by Kahn et al.\textsuperscript{5} On the other hand, magnetic anisotropy, especially the anisotropic magnetic exchange, is very promising for the construction of high-temperature SMMs and SCMs.\textsuperscript{6}

Despite the abovementioned advantages, molecular magnetic materials based on the [Mo\textsuperscript{III}(CN)\textsubscript{7}]\textsuperscript{4–} unit are still quite limited compared to the widely investigated [M\textsuperscript{III}(CN)\textsubscript{6}]\textsuperscript{3–} (M = Fe and Cr) and [M\textsuperscript{IV/V}(CN)\textsubscript{8}]\textsuperscript{4–/3–} (M = Nb, Mo, and W) compounds,\textsuperscript{7} although the synthesis of the starting material K\textsubscript{4}[Mo\textsuperscript{III}(CN)\textsubscript{7}]·2H\textsubscript{2}O was reported early in 1932.\textsuperscript{8} The main reason for this lies in the synthetic challenges in the handling of this oxygen and light sensitive anion containing the low valence Mo\textsuperscript{III} center. On top of this, it is also very difficult to obtain good single crystals containing the [Mo\textsuperscript{III}(CN)\textsubscript{7}]\textsuperscript{4–} unit. As mentioned above, the large amount of CN\textsuperscript{–} groups and the high negative charge of this unit is very likely to cause fast precipitation of extended frameworks with poor crystallinity.

To overcome these difficulties, certain strategies have been adopted besides introducing the proper anaerobic atmosphere during the synthesis. One strategy is to introduce different cations to balance the negative charge of the [Mo\textsuperscript{III}(CN)\textsubscript{7}]\textsuperscript{4–} unit.

\textsuperscript{a} State Key Laboratory of Coordination Chemistry, Collaborative Innovation Center of Advanced Microstructures, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing, 210023, China. E-mail: wangy66@nju.edu.cn

\textsuperscript{b} Jiangsu Key Laboratory of Biofunctional Materials, School of Chemistry and Materials Science, Nanjing Normal University, Nanjing, 210023, China. E-mail: weihaiyan@nju.edu.cn

\textsuperscript{†} Electronic supplementary information (ESI) available: Structure information in detail, powder XRD spectra, and additional magnetic figures. CCDC 1835917–1835919. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c8dt01433g
chosen, as these bidentate ligands have been widely investi-
gated. As for the chelating ligands, three SMM based on the [MoIII(CN)7]4-
ion. This successfully leads to the formation of various 2D (two-dimensional) or 3D frameworks of diverse topologies.
For example, in the MnII–MoIII materials, the simple K+ cation led to the formation of a 2D Mn–Mo ferrimagnet with \( T_c = 39 \text{ K} \), while the NH\(_4\) cation led to a 3D MnII–MoIII framework of \( T_c = 53 \text{ K} \). Incorporation of the larger organic cation [Ni(CH\(_3\))\(_4\)]\(^+\) results in another 3D structure with \( T_c = 86 \text{ K} \). Very recently, we have also reported a 3D FeII–MoIII compound using the organic cation [NH\(_3\)(CH\(_3\))\(_2\)]\(^+\) in the synthesis. This compound is also a ferrimagnet with \( T_c = 65 \text{ K} \), and has a very different structure from the one formed without the organic cation.

Another successful strategy is to prevent the quick precipitation using secondary coordination ligands to block the available coordination sites of the other metal centers. For example, using two blocking ligands triethanolamine and dimethylalaninol (K- and S), Sutter et al. reported two new 3D MnII–MoIII compounds showing interesting magnetic sponge behaviour with \( T_c \) up to 106 K. By capping the MnII ion with the triazacyclononane ligand, another amorphous MnII–MoIII compound exhibiting ferromagnetic ordering below 90 K was reported. In addition, the highest \( T_c \) of 110 K in [MoIII(CN)\(_n\)]\(^+\)-based materials was obtained by introducing pyrimidine into the V\(_n\)-MoIII system, although its crystal structure was confirmed by its isomorphous MnII–MoIII compound.

Following this strategy, we have also been very successful in preparing the low-dimensional materials based on the [MoIII(CN)\(_2\)]\(^+\) unit, such as isolated clusters and one-dimensional (1D) chains. For example, using a series of macrocyclic pentadentate organic ligands, Wang and Dunbar et al. reported a series of molecule clusters, such as a docosa-nuclear Mo\(_8\)Mn\(_{14}\) cluster with a very high spin ground state, and several trinuclear Mn\(_2\)Mo molecules including the first SMM based on the [MoIII(CN)\(_2\)]\(^+\) unit. Very recently, we have reported a new Mn\(_2\)Mo cluster with a tetradentate ligand, which can undergo reversible ON/OFF switching of the SMM behaviour through a single-crystal-to-single-crystal transformation to a Mn\(_2\)MnO\(_2\) cluster. Furthermore, several 1D chain compounds have also been prepared very recently using the same synthetic strategy under slightly different experimental conditions.

To extend the research in the [MoIII(CN)\(_2\)]\(^+\) based materials, we continue synthesizing more magnetic materials using the same strategy. As for the chelating ligands, three bidentate ligands with structures similar to 2,2′-bpy were chosen, as these bidentate ligands have been widely investigated in the molecular magnetism. Herein, we report the syntheses, structures and magnetic properties of three new 3D MnII–MoIII complexes, namely Mn\(_2\)(3-pyzN)[H\(_2\)O](CH\(_3\)CN)[Mo(CN)\(_n\)] (1), Mn\(_3\)(1-pypz)[H\(_2\)O](CH\(_3\)CN)[Mo(CN)\(_n\)] (2) and Mn\(_2\)(pyim)[H\(_2\)O](CH\(_3\)CN)[Mo(CN)\(_n\)] (3) (3-pyz = 2-(1H-pyrazol-3-yl)pyridine, 1-pyz = 2-(1H-pyrazol-3-yl)pyridine, pyim = 2-(1H-imidazol-2-yl)pyridine, Fig. 1). Magnetic studies revealed that 1–3 exhibit ferrimagnetic ordering with \( T_c = 64, 66, \) and 62 K, respectively. These compounds are the first

**Experimental section**

**Physical measurements**

Elemental analyses for C, H, and N were carried out using a Vario MICRO Elementar instrument. Infrared spectra were obtained on a Bruker Tensor 27 FT-IR spectrometer in the range of 400–4000 cm\(^{-1}\) with KBr pellets. Powder X-ray diffraction (PXRD) was recorded at 298 K on a Bruker D8 Advance diffractometer with a Cu Kα X-ray source operated at 40 kV and 100 mA. Magnetic data were measured on ground single crystal samples embedded in eicosane to avoid oxidation with a Quantum Design SQUID VSM magnetometer. All data were corrected for diamagnetism of the eicosane and the sample holder and of the constituent atoms using Pascal’s constants.

**X-ray data collection and refinement**

The X-ray single-crystal data for complexes 1–3 were collected on a Bruker APEX DUO diffractometer equipped with a CCD area detector (Mo-K\(_\alpha\) radiation, \( \lambda = 0.71073 \text{ Å} \)) under a nitrogen flow at 173 K. The APEX II program was used to determine the unit cell parameters and for data collection. The data were integrated using SAINT and SADABS. All structures were solved by direct methods and refined by full matrix least-squares with anisotropic thermal parameters for non-hydrogen atoms based on \( F^2 \) using the SHELXTL program. Hydrogen atoms of the organic ligands were generated theoretically onto the specific atoms and refined isotropically with fixed thermal factors. For better refinements, the geometric restraints of DFIX and DANG were used to fix the positions of the hydrogen atoms in the coordinated waters. And the rigid bond restraint DELU and similarity restraint SIMU were used to constrain the displacement parameters for several bonding atoms. Additional details of the data collections and structural refinement parameters are provided in Table 1. Selected bond lengths and bond angles are listed in Table S1 in the ESI.†

**Materials and synthesis**

Because of the instability of MoIII compounds in solvent and their oxygen sensitivity, all manipulations were performed...
under an anaerobic atmosphere using standard Schlenk techniques or in a nitrogen-filled glove box. In addition, the reaction solutions were kept under dark conditions to avoid the possible light induced decomposition of the [Mo(CN)₇]⁴⁻ anion in solution. The starting material K₄[Mo(CN)₇]·2H₂O was synthesized as described in the literature. All solvents used were deoxygenated in advance. The three bidentate ligands were commercially available and used as received.

Synthesis of Mn₂(3-pypz)(H₂O)(CH₃CN)[Mo(CN)₇] (1). A solution of K₄[Mo(CN)₇]·2H₂O (0.05 mmol, 23.5 mg) in 2.0 mL mixed solvent of acetonitrile and water (v/v = 1:1) was placed at the bottom in one arm of a H-shaped tube, and 2.0 mL of the same solvent containing Mn(ClO₄)₂·6H₂O (0.05 mmol, 18.8 mg) and 3-pypz (0.1 mmol, 14.5 mg) was placed into the other arm. Then, about 12.0 mL identical solvent was layered on top of the solutions on both sides to provide a diffusion pathway. Dark brown X-ray quality single crystals were obtained after several weeks in the sealed single tube. The crystals were removed from the tube and washed with water. Yield: 5.4 mg, ∼29% based on Mn²⁺ salt. Elemental analysis: calcd for C₁₇H₁₂N₁₁OMn₂Mo (%): C 34.48, N 26.02, H 2.04. Found: C 34.55, N 26.82, H 2.35. IR (KBr, cm⁻¹): C 34.25, N 26.54, H 2.23. IR (KBr, cm⁻¹, C≡N): 2150 (s), 2089 (s), 1406 (s), 1356 (s), 1214 (s), 1030 (s), 720 (s). Found: C 34.25, N 26.54, H 2.23. IR (KBr, cm⁻¹, C≡N): 2150 (s), 2089 (s), 1406 (s), 1356 (s), 1214 (s), 1030 (s), 720 (s).

Synthesis of Mn₂(pyim)(H₂O)(CH₃CN)[Mo(CN)₇] (3). By replacing 1-pypz with pyim, dark brown single crystals of 3 were also obtained following the same procedure as that for 2. Yield: 4.9 mg, ∼33% based on Mn²⁺ salt. Elemental analysis: calcd for C₁₇H₁₂N₁₁OMn₂Mo (%): C 34.48, N 26.02, H 2.04. Found: C 34.48, N 26.02, H 2.04. Found: C 34.48, N 26.02, H 2.04. IR (KBr, cm⁻¹, C≡N): 2150 (s), 2089 (s), 1406 (s), 1356 (s), 1214 (s), 1030 (s), 720 (s). Found: C 34.48, N 26.02, H 2.04. Found: C 34.48, N 26.02, H 2.04. IR (KBr, cm⁻¹, C≡N): 2150 (s), 2089 (s), 1406 (s), 1356 (s), 1214 (s), 1030 (s), 720 (s).

Results and discussion

Syntheses of the materials

As we have stated in the Introduction part, the syntheses of the [Mo(CN)₇]⁴⁻-based magnetic materials are usually quite challenging. By introducing a secondary co-ligand and controlling the synthetic conditions, new complexes can be obtained including several interesting low dimensional magnetic materials. We noticed that in the literature, the organic ligands used in the [Mo(CN)₇]⁴⁻ system are usually multidentate with more than three coordination atoms such as the tetra- and penta-dentate ligands used by Sutter, Dunbar and us. However, complexes with the bidentate chelating co-ligands have not been reported to date, even though there are huge amounts of bidentate chelating ligands and they have been extensively used in the construction of molecular magnetic materials. However, attempts to prepare the
[MoIII(CN)7]4− based complexes using the usual bidentate ligands such as 2,2′-bipy, 1,10-phen and their derivatives have failed. Fortunately, after a lot of attempts, we were able to obtain three new compounds 1–3 with three bidentate ligands. Frankly speaking, we don’t know why these three bidentate ligands can lead to the successful isolation of single crystals of 1 to 3, although we suspect that the water solubility of these three ligands might benefit the synthesis of the title complexes.

Crystal structure descriptions

X-ray single crystal diffraction measurements revealed that all compounds 1–3 are isomorphic and crystallize in the monoclinic crystal system, space group C2/m. They are all of similar 3D structures where the main difference is the bidentate ligands. This means that the bidentate ligands have no considerable impact on their structures. The asymmetric unit and the ORTEP drawing with thermal ellipsoids at 50% probability of compounds 1–3 are displayed in Fig. 2, S3 and S4 (ESI†). As we can see, the asymmetric unit contains one-half of the [MoIII(CN)7]4− unit (with four unique CN− groups), one MnII ion (1/2Mn1 + 1/4Mn2 + 1/4Mn3), one-half bidentate ligand co-ordinated to Mn1, one-half acetonitrile coordinated to Mn2, and one-half water molecule coordinated to Mn3.

To have a better view of the structure, we show the local structures of the molybdenum and manganese sites in Fig. 3, using compound 1 as an example. The details of the bond lengths and bond angles of compounds 2 and 3 can be found in the ESI (Table S1†). As depicted, the coordination geometry of the MoIII center can be described as a distorted capped trigonal prism, rather than the pentagonal bipyramid. The C2, C3, and C4 atoms form the opposite base planes of the trigonal prism with Mo–C bond lengths 2.148(5), 2.114(5), and 2.149(5) Å, while the C1 atom acts as the cap of the prism with Mo1–C1 = 2.175(7) Å. The continuous shape measure (CShM) value calculated using the program SHAPE 2.119 is 0.536 relative to the ideal capped trigonal prism, and 1.742 relative to the ideal capped octahedron (Table S2, ESI†). With all of its seven CN− groups, the MoIII center connects to seven MnII centers, namely three Mn1 (through C1N1 and two C4N4 groups), two Mn2 (though two C2N2 groups), and two Mn3 centers (through two C3N3 groups). Bridged by the CN− groups, the Mo–Mn bond lengths are in the range of 5.323(12) to 5.4774(1) Å.

As for the MnII centers, there are three crystallographically unique sites, Mn1, Mn2, and Mn3, in the structure. The Mn1 ion is in a slightly distorted trigonal bipyramid geometry with five coordination nitrogen atoms, two of which (N6 and N7) are from the ligand 3-pypz and the remaining three (N1 and two N4) are from the CN− groups of three [MoIII(CN)7]4− units. The Mn–N bond lengths are in the range of 2.080(4)–2.242(7) Å. The CShM value relative to the ideal D3h trigonal bipyramid is calculated to be 2.115. As for the Mn2 and Mn3 centers, they are both in the slightly distorted octahedron environment, with the CShM values relative to the ideal O3h octahedron of 0.378 and 0.462 for Mn2 and Mn3, respectively. Besides the two coordinated solvent molecules in the trans-positions (two acetonitrile for Mn2 and two water molecules for Mn3), both Mn2 and Mn3 are coordinated by four crystallographically equivalent nitrogen atoms (N2 for Mn2, and N3 for Mn3) from four neighbouring [MoIII(CN)7]4− units. The bond lengths are 2.195(4) and 2.355(8) for Mn2–N2 and Mn2–N5, while they are...
2.177(4) and 2.289(7) for Mn3–N3 and Mn3–O1, respectively. These values are in the normal range for the MnII ion. As for the bond angles involving the CN− groups, the Mo–C–N bond angles are generally close to 180° (from 175.0(4)° to 177.6(6)°), while the Mn–N–C bond angles vary significantly from 116.7(3)° to 177.1(3)°.

Connected by the CN− groups, a complicated 3D structure was formed and can be described as follows. Firstly, using C1N1 and C4N4 groups, the Mo1 and Mn1 centers form a 1D folded belt structure along the b direction (Fig. 4a). These 1D belts are further connected by the Mn2 centers through the C2N2 groups, forming a 2D corrugated layer in the ab plane (Fig. 4b). These 2D layers were further connected to Mn3 through the remaining two CN− groups (C3N3) of the [MoIII(CN)7]4− unit along the c direction and construct the final complicated 3D framework (Fig. 4c). Since the [MoIII(CN)7]4− unit can be viewed as a 7-connected node, while the Mn1, Mn2, and Mn3 centers can be viewed as 3-, 4- and 4-connected nodes, the whole framework can be presented as a new four-nodal 3,4,4,7-connecting net with the vertex symbol of {41}{44·62}2{410·611}, as analysed by the TOPOS 4.0 program package (Fig. S5, ESI†).

Magnetic properties

As the magnetic properties of compounds 1–3 are very similar due to their isomorphic structures, only the magnetic properties of 1 will be discussed in detail as a representative, while the results of 2 and 3 can be found in the ESI (Fig. S6–S9†). The temperature dependence of the magnetic susceptibility data for 1 measured under a 1000 Oe dc field in the range of 2–300 K is shown in Fig. 5. At 300 K, the χMT value is 9.122 cm3 K mol−1, which is very close to the spin-only value of 9.125 cm3 K mol−1 calculated for two high-spin MnII (S = 5/2) units and one low-spin MoIII (S = 1/2) unit (g = 2.0). On decreasing the temperature, the χMT value increases slowly until about 90 K. Then it increases abruptly to a maximal value of 634.20 cm3 K mol−1 at about 50 K, below which it decreases abruptly to 43.75 at 2 K. This very sharp peak in the χMT versus T plot indicates the long-range magnetic ordering, and the decrease of the χMT curve below 50 K should be due to the field saturation effect of the magnetization.

As for the magnetic interaction between the MnII and MoIII centers, although the χMT curve increases upon cooling at the high temperature region and fitting of the data above 100 K using the Curie–Weiss law gives a rather large positive Weiss constant of 65.90 K, the magnetic interaction between the MnII and MoIII spin centers doesn’t necessarily correspond to the ferromagnetic interaction.21 Originally, for the two MnII–MoIII 3D compounds (α and β phases), the magnetic interactions were interpreted as ferromagnetic coupling based on the positive Weiss constants. However, further experiments, including the powder neutron diffraction measurements and polarized neutron diffraction on single crystals, and theoretical investigations, have all confirmed the antiferromagnetic coupling between the MnII and MoIII centers.22 As a matter of fact, the antiferromagnetic coupling has been reported for most of the

Fig. 4  (a) The 1D folded belt structure for 1 along the b direction constructed by Mo1 and Mn1 ions; (b) the 2D layer in the ab plane for 1. The green parts represent the 1D belts in (a); and (c) the 3D structure for 1 viewed along the b axis. The blue parts represent the 2D layers in (b). The bidentate ligands and acetonitrile molecules are depicted transparently and all the H atoms have been omitted for clarity.
Mn$^{II}/[\text{Mo}^{III}(\text{CN})_7]^{4-}$ compounds, including both the framework structures and also the molecule clusters. Therefore, we believe the magnetic interactions in compound 1 should also be antiferromagnetic. However, due to the very complicated structure, a rigorous analysis to obtain the exact coupling constants is very difficult and not carried out for 1.

To further confirm the long-range magnetic ordering of compound 1, the zero-field-cooled (ZFC) and field-cooled (FC) magnetizations were measured at $H_{\text{dc}} = 10$ Oe below 100 K. As can be seen in Fig. 6, the ZFC and FC curves rise sharply at 66 K and diverge from each other at about 64 K upon cooling, indicating a magnetic phase transition from the paramagnetic phase to a long-range ordered phase. In addition, ac (alternating current) susceptibility data were measured under $H_{\text{dc}} = 0$ Oe and $H_{\text{ac}} = 2$ Oe at three different frequencies (125, 500 and 999 Hz) and are depicted in Fig. 7. As we can see, the in-phase signals ($\chi'_M$) exhibit a very sharp peak at 64 K, where the out-of-phase signals ($\chi''_M$) start to increase rapidly. Almost no frequency dependence was observed. These phenomena confirmed that compound 1 shows a spontaneous magnetization below the critical temperature $T_c = 64$ K.

Besides, the field dependent magnetization $M(H)$ of 1 was measured at 2 K (Fig. 8). The magnetization increases rapidly at low fields and then increases steadily after 20 kOe until it reaches a maximum value of 8.74$\mu_B$ at 70 kOe. This value is very close to the calculated value of 9.00$\mu_B$ for the antiferromagnetically coupled two high-spin Mn$^{II}$ and one low-spin Mo$^{III}$ centers ($M_s = 2 \times 2S_{\text{Mn}} - 2S_{\text{Mo}} = 9.2\mu_B$, $g = 2.0$), instead of 11$\mu_B$ for the ferromagnetic arrangement. This result further confirmed the ferrimagnetic behavior of compound 1. In addition, an obvious hysteresis loop can be observed for 1 at 2 K with a coercive field $H_c = 820$ Oe and a remnant magnetization $M_R = 3.72\mu_B$ (inset of Fig. 8).

As for compounds 2 and 3, the magnetic data are very similar, including the room temperature $\chi_M T$ values, the shape of the $\chi_M T$ versus $T$ curves, and the maximum $M$ values at 70 kOe, indicating the very similar ferrimagnetic ordering below the ordering temperatures (Fig. S6–S9, ESI†). However, we noticed that there are several subtle differences in their magnetic properties. Firstly, from the ZFC/FC curves and ac data, the long-range ordering temperatures for 2 and 3 are determined to be 66 and 62 K, slightly different from that (64 K) for 1. This very small difference is reasonable considering their similar, but still of little differences, structures. Secondly, there is another phase transition at around 47 K for both compounds 2 and 3, as judged by the second peaks in both the in-phase and out-of-phase signals in the ac data (although the peaks are more pronounced for compound 2 than those for 3). This could be due to the spin reorientation phenomenon as...
has been reported in the α and β phases of the MnII/ [Mo(III)(CN)7]4+ compounds.5 Finally, we noticed that although hysteresis loops can both be observed at 2 K for 2 and 3, they are much smaller than that for 1. The coercive fields and remnant magnetizations are $H_C = 72$ and 146 Oe and $M_R = 0.38$ and 0.81$\mu_B$ for 2 and 3, respectively (inset of Fig. S7, ESI†). The reasons for the differences are currently unclear, and could be related to the very subtle differences of their crystal structures.

To have a better view on the magneto-structural relationship, the reported MnII–MoIII compounds with 3D structures are listed in Table 2, together with their $T_C$ values and structure details. For these 3D MnII–MoIII compounds, the $T_C$ values for the long-range magnetic ordering can be approximately represented by the following equation on the basis of the molecular field theory:23

$$T_C = \frac{2(n_{Mo(III)}n_{Mn(II)})^{1/2}J_1(S_{Mo(III)}(S_{Mo(III)} + 1)S_{Mn(III)(S_{Mn(III)} + 1)})^{1/2}}{3k_B},$$

where $n_{Mo(III)}$ and $n_{Mn(II)}$ denote the average numbers of the nearest paramagnetic ions around Mo(III) and Mn(II) centers, respectively; $J$ is the averaged exchange interaction constant along three directions; $S$ is the spin quantum number; and $k_B$ is the Boltzmann’s constant. In this equation, the $T_C$ value is proportional to the $n_{Mo(III)}$ $n_{Mn(II)}$ and $J$ values. As we can see in Table 2, these high-dimensional MnII–[Mo(III)(CN)7]4+ compounds usually have rather high $T_C$ values. Generally speaking, the bigger ($n_{Mo(III)}$ $n_{Mn(II)}$) values lead to higher $T_C$ values, which is reasonable if the averaged $J$ values are considered similar. However, there are also some exceptions such as compounds [N(CH3)4]2[Mn(H2O)5Mo(CN)7·4H2O], [Mn(H2O)5Mo(CN)7·4.75H2O] and {K2(H2O)4Mn5(H2O)8(MeCN)[Mo(CN)7]3}·2H2O, which have higher $T_C$ values than the others. This can be possibly ascribed to the slightly higher $J$ values and also the relatively higher $\mu_B$ values. Another exception is the compound $\{K_2(H_2O)\_2Mn_2(H_2O)\_2[MeCN]_2Mo(CN)\_7\}_2$·2H2O. Although it has the highest $(n_{Mo(III)}$ $n_{Mn(II)}$) value, its $T_C$ is only in the middle of the list. In addition, we have to mention that the $T_C$ values of these 3D compounds can sometimes be increased up to about 20 K by the de-solvation process. This magnetic sponge effect could be due to the increase of the $|J|$ values.24 Of course, the de-solvation might also change the structures by changing the coordination environments of the MnII centers and also the 3D connections.36

From the above discussion, it is obvious that to increase the $T_C$ values, a big $(n_{Mo(III)}$ $n_{Mn(II)}$) value is preferred. From this point, it seems that the chelating ligands, such as those ligands in this work, are not preferred because they will usually block some of the coordination sites of the metal centers and decrease the $n_{Mn(II)}$ values. However, from Table 2, we noticed that the $T_C$ values of those compounds with chelating ligands (marked with asterisks) are actually relatively high. Among them, compounds [(MnHL)(H2O)]2Mo(Mo(CN)7)3·2H2O and [Mn2(tea)Mo(CN)7]·H2O have the biggest $T_C$ value of 106 K in the MnII/ [Mo(III)(CN)7]4+ systems after dehydration. In fact, we can see that the resulting compounds with the chelating ligands do not necessarily have smaller $(n_{Mo(III)}$ $n_{Mn(II)}$) values compared to the ones without chelating ligands. This is due to the fact that in the compounds with no chelating ligands, the MnII centers can usually be coordinated by solvent water molecules, which is actually very difficult to avoid. Anyway, this analysis suggests that using chelating coligands might be an effective strategy for the construction of high-$T_C$ magnets based on the [Mo(CN)7]4+ building block. Of course, chances to prepare low-dimensional magnetic materials, such as 1D chains and 0D clusters, increase with the chelating ligands, especially for those multidentate ligands.11–14 This, on the other hand, is beneficial for the construction of molecular nanomagnets.12–14

<table>
<thead>
<tr>
<th>Table 2</th>
<th>Reported 3D MnII/MoIII compounds based on the [Mo(CN)7]4+ unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compound</td>
<td>Space group</td>
</tr>
<tr>
<td>[N(CH3)4]2[Mn(H2O)5Mo(CN)7·2H2O</td>
<td>Monoclinic C2/c</td>
</tr>
<tr>
<td>[Mn(HL)(H2O)]2Mn(Mo(CN)7)2·2H2O</td>
<td>Monoclinic C2</td>
</tr>
<tr>
<td>[Mn2(tea)Mo(CN)7]·H2O</td>
<td>Orthorhombic Pbca</td>
</tr>
<tr>
<td>Mn3[1-pyraz(H2O)]2[Mo(CN)7]2·2H2O</td>
<td>Monoclinic C2/m</td>
</tr>
<tr>
<td>Mn3[pyraz(H2O)]2[Mo(CN)7]2·2H2O</td>
<td>Monoclinic C2/m</td>
</tr>
<tr>
<td>(K2H10)[Mn(H2O)5Mo(CN)7]·2H2O</td>
<td>Monoclinic P21/n</td>
</tr>
<tr>
<td>[NH4]2Mn(H2O)5Mo(CN)7·4H2O</td>
<td>Monoclinic C2/c</td>
</tr>
<tr>
<td>[NH4]2Mn(H2O)5Mo(CN)7·nH2O (n = 4, 5)</td>
<td>Monoclinic C2/c</td>
</tr>
<tr>
<td>Mn(H2O)2Mo(CN)7·4H2O (α phase)</td>
<td>Monoclinic P2/c</td>
</tr>
<tr>
<td>Mn(H2O)2Mo(CN)7·4H2O (α phase)</td>
<td>Monoclinic P2/c</td>
</tr>
<tr>
<td>[Mn(tacn)][Mo(CN)7]·3H2O</td>
<td>No single crystal data</td>
</tr>
<tr>
<td>[Mn2(tea)Mo(CN)7]·H2O</td>
<td>No single crystal data</td>
</tr>
<tr>
<td>[Mn(HL)(H2O)]2Mn(Mo(CN)7)2·2H2O</td>
<td>No single crystal data</td>
</tr>
</tbody>
</table>

L = N,N-Dimethylanilino; tea = triethanolamine; tacn = triazaecyclonane. CTP = capped trigonal prism; MCO = mono-capped octahedron; PBP = pentagonal bipyramid; TBP = trigonal bipyramid; SP = square pyramid; OH = octahedron and TH = tetrahedral. * The digit in the front represents the number of MnII ions for the corresponding configuration. * The compounds marked with asterisks represent those with chelating ligands.
Conclusions

In summary, by introducing three bidentate secondary ligands, we have synthesized three new Mn$^{II}$-[Mo$^{III}$(CN)$_7$]$^{4-}$ complexes. These ligands lead to similar 3D framework structures of the same topology and similar magnetic properties. Due to the strong antiferromagnetic coupling between the Mn$^{II}$ and Mo$^{III}$ spin centers and the 3D structure, these complexes are all ferrimagnets with relatively high magnetic temperatures at around 64 K. Interestingly, these compounds are the first [Mo$^{III}$(CN)$_7$]$^{4-}$ compounds containing the bidentate secondary ligands. Further efforts will be devoted to the preparation of new [Mo$^{III}$(CN)$_7$]$^{4-}$-based materials with other divalent metal centers and more bidentate ligands. Considering the available large amount of bidentate ligands, new materials of different structures and magnetic properties are highly anticipated.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

We thank the NSFC (21522103, 21471077, 91622110) and the NSF of Jiangsu province (BK20150017) for financial support.

Notes and references


