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**PAPER**

# Three three-dimensional anionic metal–organic frameworks with (4,8)-connected alb topology constructed from a semi-rigid ligand and polynuclear metal clusters†

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Three three-dimensional coordination polymers, namely, $[NH_2(CH_3)_2][Co_2(MDIP)(OH)(H_2O)]\cdot C_3H_7NO\cdot H_2O$ (**1**), $[NH_2(CH_3)_2]_2[Mn_3(MDIP)_2]\cdot 2C_3H_7NO$ (**2**), and $[NH_2(CH_3)_2][Mg_3(MDIP)(HMDIP)(C_3H_7NO)]\cdot 4H_2O$ (**3**) (DMF = N,N′-dimethylformamide), have been synthesized by the solvothermal reaction of Co(II), Mn(II), or Mg(II) salts with methylenediisophthalic acid ($H_4MDIP$). All compounds have been characterized by thermogravimetric analysis, IR spectroscopy, elemental and single-crystal X-ray diffraction analyses. Complexes **1–3** are anionic frameworks with $[NH_2(CH_3)_2]^+$ ions occupying the voids, built upon tetra-, tri- and asymmetrical trimetallic cores, respectively. In particular, the asymmetrical trinuclear Mg(II) unit in complex **3** was scarcely observed. Topological analyses show that the three compounds possess binodal (4,8)-connected alb topology with a Schläfli symbol of $(4^{10}.6^{14}.8^4)(4^5.6)_2$. Magnetic investigations indicate that antiferromagnetic couplings are dominant in compounds **1** and **2**.

## Introduction

Current interest in metal–organic frameworks (MOFs) on the basis of the assembly of metal ions and multifunctional organic ligands is rapidly expanding owing to their intriguing aesthetic structures and topological features as well as their potential applications as functional materials.[1,2] An important subject within this area is the study and analysis of network topology, which is not only a powerful tool for simplifying the structure of complicated compounds but also plays an instructive role in the rational design of certain functional materials with desirable properties.

To date, uninodal network topologies based on three-, four-, and six-connected nodes are commonly encountered.[3] In contrast, higher-connectivity nets are relatively scarce due to the limited coordination numbers of single metal centers and the steric hindrance of ligands,[4] particularly those with binodal high-connected frameworks, such as (3,8)-, (4,8)-, (3,9)-, (3,10)-, (4,12)-, and (3,24)-connected nets.[5] Recently, using large polynuclear clusters instead of simple metal centers as the nodes to construct high-connected frameworks has proved to be a feasible route because the polynuclear cluster-based nodes generally possess larger sizes, more coordination sites, and smaller steric hindrance for ligands with respect to the simple metal center nodes.[6] However, there is still a long way to go with the design and synthesis of high-connected MOFs.

It is well-known that carboxylic acids are excellent building blocks for the construction of MOFs because the carboxylate group may induce core aggregation and link these discrete clusters into an extended framework by virtue of its bridging ability.[7] Taking these into account, we chose a semi-rigid tetracarboxylate ligand $H_4MDIP$ as the four-connected node and attempt to construct binodal high-connected frameworks using polynuclear metal clusters. As it is difficult to predict the final structures and conformations of the products exactly, we have tried a series of synthetic conditions, such as reaction temperature, counter-ions, solvent, and molar ratio of the raw materials. Fortunately, we have successfully obtained three target complexes with (4,8)-connected nets, namely, $[NH_2(CH_3)_2][Co_2(MDIP)(OH)(H_2O)]\cdot C_3H_7NO\cdot H_2O$ (**1**), $[NH_2(CH_3)_2]_2[Mn_3(MDIP)_2]\cdot 2C_3H_7NO$ (**2**), and $[NH_2(CH_3)_2][Mg_3(MDIP)(HMDIP)(C_3H_7NO)]\cdot 4H_2O$ (**3**), in which polynuclear metal clusters act as 8-connected nodes. The crystal structures, topological analyses, thermal and magnetic properties of these complexes are discussed in detail.

## Experimental

### Materials and measurements

Methylenediisophthalic acid ($H_4MDIP$) was synthesized as reported in the literature.[8] All other starting materials were of

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analytical grade and used as received without further purification. IR spectra were obtained from KBr pellets on a Perkin-Elmer 580B IR spectrometer in the 400–4000 $cm^{-1}$ region (ESI†). Elemental analyses (C, H, N) were performed with a VarioEL analyzer. Thermogravimetric analysis (TGA) was performed on a Perkin-Elmer TG-7 analyzer heated from 40 to 700 °C under nitrogen. Powder X-Ray diffraction data were collected on a Bruker D8-ADVANCE diffractometer equipped with Cu-K$\alpha$ at a scan speed of 2° $min^{-1}$. Temperature-dependent magnetic measurements were carried out on a Quantum Design SQUID MPMS-7 magnetometer with an applied field of 1000 Oe. The diamagnetic corrections for the compounds were estimated using Pascal's constants, and magnetic data were corrected for diamagnetic contributions of the sample holder.[9]

### Synthesis

**$[NH_2(CH_3)_2][Co_2(MDIP)(OH)(H_2O)]\cdot C_3H_7NO\cdot H_2O$ (1).** A mixture of $Co(CH_3COO)_2\cdot 4H_2O$ (49.9 mg, 0.20 mmol), $H_4MDIP$ (17.2 mg, 0.05 mmol), DMF (1.5 mL), and $H_2O$ (0.9 mL) was placed in a Teflon reactor (20 mL) and heated at 120 °C for 2 days. After the sample was gradually cooled to room temperature at a rate of 10 °C $h^{-1}$, purple block crystals of **1** were obtained with 72% yield based on $H_4MDIP$. Anal. Calcd for $C_{22}H_{30}Co_2N_2O_{13}$ ($Mr$ = 630.32): C, 41.01; H, 4.78; N, 4.58. Found: C, 40.83; H, 4.64; N, 4.38%. IR (4000–400 $cm^{-1}$): 3513(m), 2856(w), 1589(m), 1540(s), 1448(w), 1387(m), 1347(m), 941(w), 750(w), 682(w), 613(w), 478(w).

**$[NH_2(CH_3)_2]_2[Mn_3(MDIP)_2]\cdot 2C_3H_7NO$ (2).** A mixture of $MnCl_2\cdot 4H_2O$ (39.6 mg, 0.20 mmol), $H_4MDIP$ (17.2 mg, 0.05 mmol), DMF (1.5 mL), and $H_2O$ (0.6 mL) was placed in a Teflon reactor (20 mL) and heated at 120 °C for 2 days. After the sample was gradually cooled to room temperature at a rate of 10 °C $h^{-1}$, colorless block crystals of **2** were obtained with 55% yield based on $H_4MDIP$. Anal. Calcd for $C_{44}H_{46}Mn_3N_4O_{18}$ ($M_r$ = 1083.67): C, 48.76; H, 4.28; N, 5.17. Found: C, 48.66; H, 4.36; N, 5.25%. IR (4000–400 $cm^{-1}$): 3420(w), 3060(w), 2807(w), 2508(w), 1623(m), 1585(m), 1548(m), 1445(m), 1377(s), 1104(w), 804(w), 778(w), 722(w), 668(w), 602(w), 517(w), 438(w).

**$[NH_2(CH_3)_2][Mg_3(MDIP)(HMDIP)(C_3H_7NO)]\cdot 4H_2O$ (3).** Complex **3** was synthesized following the same synthetic procedure as that for complex **1** except that $Co(CH_3COO)_2\cdot 4H_2O$ was used instead of $Mg(NO_3)_2\cdot 6H_2O$. Colorless crystals of **3** were obtained with 58% yield based on $H_4MDIP$. Anal. Calcd for $C_{39}H_{40}Mg_3N_2O_{21}$ ($M_r$ = 945.66): C, 49.53; H, 4.26; N, 2.98. Found: C, 49.69; H, 4.32; N, 3.13%. IR (4000–400 $cm^{-1}$): 3381(m), 2489(w), 1615(m), 1559(m), 1444(m), 1374(m), 1117(w), 1027(w), 790(m), 720(m), 688(m), 438(w).

### X-ray crystallography

The X-ray intensity data for the three compounds were collected on a Bruker SMART APEX CCD diffractometer with graphite monochromatized Mo-K$\alpha$ radiation ($\lambda$ = 0.71073 Å) at 185 K. The crystal structure was solved by means of Direct Methods and refined employing full-matrix least squares on $F^2$ (SHELXTL-97).[10] The non-hydrogen atoms were refined with anisotropic displacement parameters, except for some atoms (C18, C20, C20′ for **2** and C22 for **1**) and guest $H_2O$ molecules in **3**. The anisotropic displacement parameters for atoms of coordinated DMF in **3** were constrained to be equal (EADP). The disordered C atoms of compound **2** (C20, C20′, C21, C21′) were refined using C atoms split over two sites, with a total occupancy of 1 and restrained thermal displacement parameters. The hydrogen atoms attached to carbons and nitrogens were generated geometrically except for one atom (N2 for **3**). The hydrogen atoms of disordered uncoordinated DMF and all free $H_2O$ were not included in the model. Crystal data and details of the structure determination for complexes **1–3** are listed in Table 1.

## Results and discussion

### Descriptions of crystal structures

**Structural description of 1.** Single-crystal X-ray diffraction shows that complex **1** consists of a 3D anionic network constructed by $[Co_4(OH)_2(CO_2)_8]^{2-}$ tetranuclear cobalt(II) subunits. Charge neutrality is achieved by the protonated dimethylamine cations. The asymmetric unit contains two crystallographically independent Co(II), one $\mu_3$-OH anion, one coordinated water and one $MDIP^{4-}$ ligand. The Co1 atom adopts a distorted octahedral geometry coordinated by five O atoms from five different $MDIP^{4-}$ ligands and one O atom from one $\mu_3$-OH anion (Co–O 2.009(2)–2.315(2) Å). The Co2 center also adopts a slightly distorted octahedral coordination geometry and its coordination sphere is composed of one water molecule, two $\mu_3$-O(H) bridges and three carboxylate oxygen atoms from three different $MDIP^{4-}$ ligands (Co–O 2.0481(2)–2.197(2) Å). The two Co atoms and their own symmetry-related atoms are integrated together by sharing two $\mu_3$-OH anions and four carboxyl groups, thus leading to the $[Co_4(OH)_2(CO_2)_8]^{2-}$ core (Fig. 1a). The four cobalt atoms (Co1, Co2, Co1D, Co2D) in the $Co_4$ unit lie in a plane, with non-bonding Co···Co distances of 3.182–3.593 Å. The deviation of the $\mu_3$-O(H) atom from this plane is 0.628 Å. The $[Co_4(OH)_2(CO_2)_8]^{2-}$ core is obviously different from the earlier $[Co_4(\mu_3\text{-}OH)_2(ntp)_2]$, $[Co_4(\mu_3\text{-}OH)_2(CO_2)_6]$, $[Co_4(CO_2)_8]$, $[Co_2(\mu_3\text{-}OH)(\mu_2\text{-}OH_2)(CO_2)_3]_2$, $[Co_4(\mu_2\text{-}OH_2)_4(MTB)_2]$ and $[Co_4(\mu_4\text{-}O)(CO_2)_8]^{2-}$ building blocks in which there are no net negative charges in metal units and $\mu_3$-OH bridging, at the same time.[11] Each tetranuclear unit is further connected to neighboring ones through eight $[MDIP]^{4-}$ ions (Fig. 1b) to generate an anionic 3D open framework. The anionic framework is balanced by two dimethylammonium counterions, which are formed *in situ* upon heating of DMF through the well-established decarbonylation reaction.[12] The effective free volume calculated with PLATON for the inclusion is 1033 $Å^3$ per unit cell (after free molecules and cations have been hypothetically removed) corresponding to 41.22% of the cell volume.

A better insight into the nature of the intricate framework can be achieved by the application of a topological approach, which is necessary to simplify the building blocks from which the 3D net of **1** is built. As illustrated in Fig. 2, each $[MDIP]^{4-}$ ligand can be considered as a four-connecting node since it links four $Co_4$ planar units and each $Co_4$ unit in turn links eight $[MDIP]^{4-}$ ligands, which can be regarded as an eight-connecting node. The resulting (4,8)-connected topological net with the Schläfli symbol

 

**Table 1** Crystal data and structure refinements for complexes **1–3**

| | **1** | **2** | **3** |
|---|---|---|---|
| Formula | $C_{22}H_{28}Co_2N_2O_{12}$ | $C_{44}H_{46}Mn_3N_4O_{18}$ | $C_{39}H_{40}Mg_3N_2O_{21}$ |
| Formula weight | 630.32 | 1083.67 | 945.66 |
| Crystal system | Monoclinic | Orthorhombic | Orthorhombic |
| Space group | $P2_1/n$ | $Pbca$ | $Pca2_1$ |
| $T$/K | 185(2) | 185(2) | 185(2) |
| $a$/Å | 11.0660(5) | 16.2417(11) | 10.7810(5) |
| $b$/Å | 13.8214(6) | 10.7616(7) | 15.8837(7) |
| $c$/Å | 16.8387(7) | 25.6486(17) | 25.1737(11) |
| $\beta$ (°) | 103.3100(10) | 90.00 | 90.00 |
| $V$/Å$^3$ | 2506.26(19) | 4483.0(5) | 4310.8(3) |
| $Z$ | 4 | 4 | 4 |
| $D_c$/g cm$^{-3}$ | 1.718 | 1.606 | 1.457 |
| $F$(000) | 1336 | 2228 | 1968 |
| data collected | 13 636 | 23 535 | 22 780 |
| unique data | 4940 | 4445 | 8471 |
| $R$(int) | 0.0334 | 0.0540 | 0.0640 |
| GOF on $F^2$ | 1.048 | 1.031 | 1.061 |
| $R_1{}^a$ [$I > 2\sigma(I)$] | 0.0357 | 0.0657 | 0.0717 |
| $wR_2{}^b$(all data) | 0.0952 | 0.2036 | 0.2173 |
| Flack ($\chi$) | | | 0.1(4) |

$^a$ $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $^b$ $\omega R_2 = \{\Sigma[\omega(F_o^2 - F_c^2)^2]/\Sigma[\omega(F_o^2)^2]\}^{1/2}$.

of $(4^{10}.6^{14}.8^4)(4^5.6)_2$ which is different from the known flu and scu. Up to date, examples of (4,8)-connected frameworks are very rare, and only a few examples of flu and scu topology have been observed in coordination polymers.[13] Fluorite is built from tetrahedral and cubical nodes. The scu network is built from square-planar and cubical nodes, and each four-connected node connects four eight-connected nodes. Here compound **1**, which is constructed from a distorted tetrahedral node and an irregular eight-connected node, is clearly different from them. A topological analysis using TOPOS4.0 indicates that compound **1** is a novel example of a (4,8)-connected binodal net with alb topology.

**Structural description of 2.** X-ray analysis on **2** revealed an anionic three-dimensional framework in which $[Mn_3(COO)_8]^{2-}$ units are linked *via* MDIP$^{4-}$ ligands. The centrosymmetric linear $Mn_3$ units consist of a central Mn2(II) ion coordinated octahedrally by six carboxylate oxygen atoms (Mn–O 2.139(3)–2.234(3) Å), and two equivalent outer Mn(II) ions (Mn1 and Mn1F), each coordinated by six carboxylate oxygen atoms from different [MDIP]$^{4-}$ ligands in a distorted octahedral geometry (Mn–O 2.094(4)–2.277(3) Å). The Mn2 atom is bridged to two neighboring Mn1 atoms by four –O–C–O– bridges and a pair of $\mu_2$-$O_{carboxyl}$ atoms (O1 and O1F) to afford a $Mn_3$ core with a Mn···Mn distance of 3.648 Å (Fig. 3a). As reported in the literature, trinuclear manganese structures are mainly precursors to construct higher nuclearity clusters exhibiting intriguing magnetic properties of their own. These trinuclear cage complexes have manganese ions arrayed in either triangular or linear geometries. Most of these trinuclear manganese units are linear and symmetrical in coordination polymers.[14] For one of them, the $[Mn_3(CO_2)_6]$ unit is the main metal building block. In complex **2**, the $[Mn_3(CO_2)_8]^{2-}$ core with two carboxyl groups holding terminal sites is a anionic unit, which is never observed and different from earlier $[Mn_3(CO_2)_6]$ units although some of them have the same bridging modes between manganese ions of trinuclear structures. There are eight carboxylate groups associated with each $Mn_3$ linear unit, and each [MDIP]$^{4-}$ ligand links four $Mn_3$ units using its four carboxylate groups to allow the formation of a 3D anionic framework with $[NH_2(CH_3)_2]^+$ ions occupying the voids (Fig. 3b). Because the $Mn_3$ units and MDIP$^{4-}$ serve as eight- and four-connected nodes respectively, the resultant framework of complex **2** can be rationalized as having the same topology with complex **1**. Calculations with PLATON show that the effective volume for the inclusion is 1820 Å$^3$ per unit cell (after DMF and dimethylammonium ions have been hypothetically removed) corresponding to 40.60% of the cell volume.

**Structural description of 3.** The crystal structure of **3** exhibits an anionic 3D network composed of asymmetrical trinuclear $Mg_3$ units, two tetracarboxylate ligands with different coordination modes and DMF molecules. There are three crystallographically independent magnesium atoms in **3** (Fig. 4a). Both Mg1 and Mg2 are six-coordinate with a distorted octahedral geometry surrounded by six oxygen atoms from four and six different MDIP$^{4-}$/HMDIP$^{3-}$ ligands, respectively (Mg1–O 2.013(4)–2.233(5) Å, Mg2–O 2.001(4)–2.144(4) Å). Mg3 also exhibits a distorted octahedral geometry coordinated by six oxygen atoms from four different MDIP$^{4-}$/HMDIP$^{3-}$ ligands and one DMF molecule (Mg3–O 2.017(4)–2.211(4) Å). The Mg2 atom is bridged to two neighboring Mg1 and Mg3 atoms by four –O–C–O– bridges and a pair of $\mu_2$-$O_{carboxyl}$ atoms (O1 and O9) to afford a linear $Mg_3$ core, which is asymmetrical (Mg1···Mg2 3.480 Å, Mg2···Mg3 3.588 Å). It should be noted that the trinuclear magnesium unit is the most important Mg cluster, because the same structural motif was found in almost all Mg MOFs with a rigid 3D framework and permanent porosity reported so far. However, we have never observed any $Mg_3$ unit like that reported here, which is an asymmetrical anionic cluster.[15] As shown in Fig. 4b, each $Mg_3$ unit is surrounded by eight MDIP$^{4-}$/HMDIP$^{3-}$ ligands to form an eight-connected

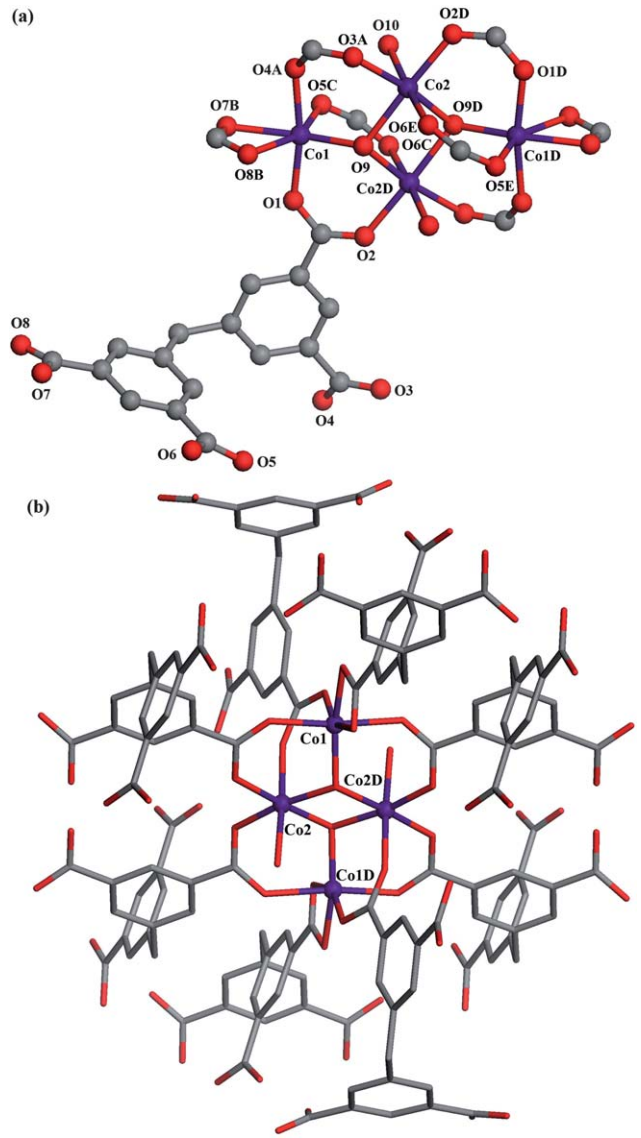


**Fig. 1** (a) Coordination environments of the Co(II) ions in **1**. Hydrogen atoms are omitted for clarity. Symmetry codes: A, $x + 1, y, z$; B, $-x, -y, -z + 1$; C, $-x - 1/2, y + 1/2, -z + 1/2$; D, $-x, -y, -z$; E, $x + 1/2, -y - 1/2, z - 1/2$. (b) View of the tetra-nuclear cobalt(II) unit surrounded by eight $MDIP^{4-}$ ligands in **1**.

node. Then each tetracarboxylate ligand connects four $Mg_3$ units and acts as a four-connected node to achieve a 3D anionic framework with $[NH_2(CH_3)_2]^+$ ions as counter-cations. Topological analysis suggests that the (4,8)-connected net of **3** also has the same Schläfli symbol as complex **1**. Without guest molecules and cations, the effective free volume is calculated by PLATON analysis to be 25.89% of the crystal volume.

Complexes **1–3** are synthesized under similar conditions except different metal ions were used. They have different structures consisting of tetranuclear, trinuclear and asymmetrical trinuclear metal units for complexes **1–3**, respectively, although they could be simplified to the same topological structure. It is found that the central metal ions have significant effects on the structures of the resulting complexes because different metal ions have different coordination configurations, metal radii and

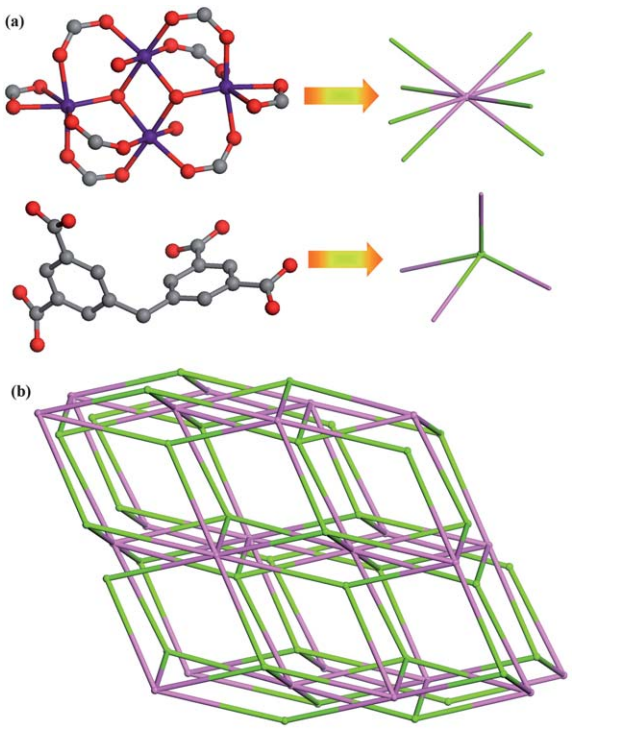


**Fig. 2** (a) Ball-and-stick and schematic representations of the 4- and 8-connected nodes. (b) Schematic illustration of the $(4^{10}\cdot6^{14}\cdot8^4)(4^5\cdot6)_2$ topology of the 3D network of **1** (green and pink balls represent four-connected $[MDIP]^{4-}$ anions and eight-connected $Co_4$ clusters, respectively).

coordination environments. In addition, it is worth noting that the coordination modes of the semi-rigid carboxylate ligand MDIP for complexes **1–3** are also different. The chelating-mono and bis-mono coordination modes exist in complex **1** (Fig. 5). In complex **2**, the carboxylate groups of MDIP adopt three kinds of coordination modes: bis-mono, bis-chelating, and chelating-mono coordination modes. In complex **3**, the carboxylate groups of one crystallographic MDIP ligand exhibit the same coordination modes as those of complex **2**, whereas the carboxylate groups of the other MDIP ligand adopt three kinds of coordination modes, that is, the mono, bis-chelating, and bis-mono coordination modes. It is also very interesting to note the dihedral angles between two aryl rings of MDIP: 94.63, 89.97 and 82.42/94° in **1–3**, respectively. From the diversities of the final products, it can be concluded that the coordination modes and flexibility of organic ligands also have some influence on the structures of the complexes.

## Magnetic properties

The magnetic susceptibilities of complexes **1–2** were measured at 0.1 T field in the temperature range 2–300 K. Phase purity of the powder sample of three complexes was confirmed by comparison of its powder diffraction (XRPD) pattern with that calculated from the single-crystal study (Fig. S1–S3, ESI†). As shown in Fig. 6, the $\chi_M T$ value is 12.12 $cm^3\ mol^{-1}$ K at 300 K, which is significantly larger than the spin-only value of 7.50 $cm^3\ mol^{-1}$ K calculated for four

 

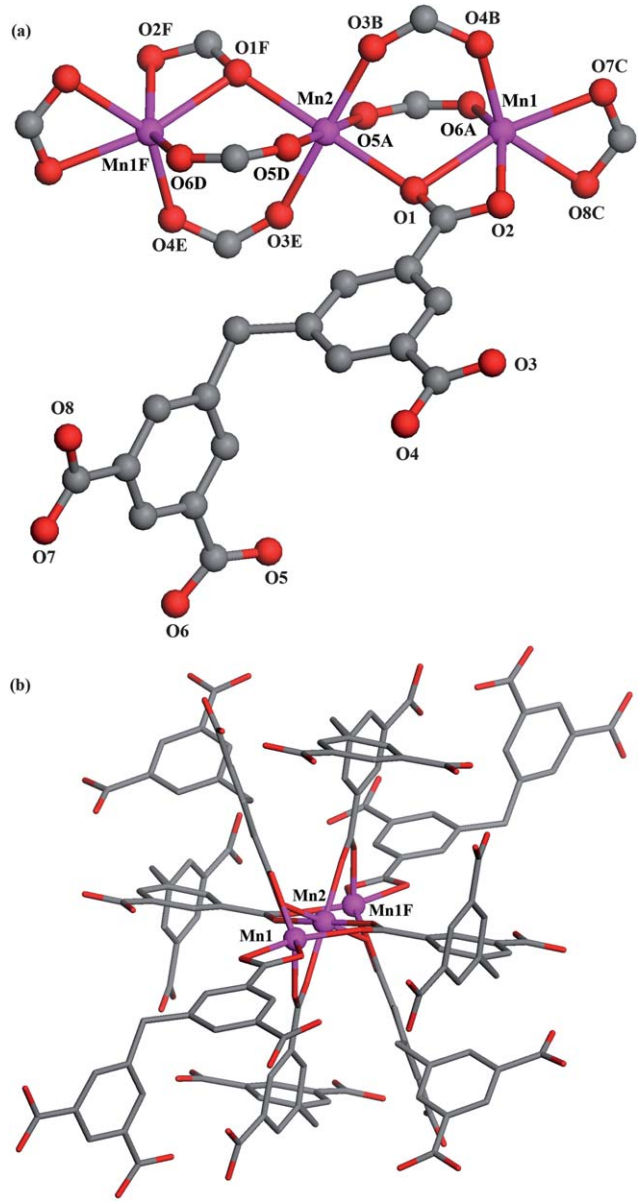


**Fig. 3** (a) Coordination environments of the Mn(II) ions in **2**. Hydrogen atoms are omitted for clarity. Symmetry codes: A, $x - 1/2, -y + 3/2, -z + 1$; B, $x - 1/2, -y + 1/2, -z + 1$; C, $-x + 1/2, -y + 1, z - 1/2$; D, $-x + 1/2, y - 1/2, z$; E, $-x + 1/2, y + 1/2, z$; F, $-x, -y + 1, -z + 1$. (b) View of the tri-nuclear manganese(II) unit surrounded by eight $MDIP^{4-}$ ligands in **2**.

high-spin Co(II) ions ($S = 3/2$, $g = 2$) due to the unquenched orbital-moment as a consequence of spin–orbit coupling from single octahedral Co(II) ions. Upon cooling, the $\chi_M T$ value decreases continuously, reaching a value of 0.57 $cm^3\ mol^{-1}\ K$ at 2 K, indicating the presence of an antiferromagnetic coupling. Values above 20 K obey the Curie–Weiss Law, with a Curie constant $C = 14.17\ cm^3\ mol^{-1}\ K$ and a Weiss constant $\theta = -48.94$ K. The negative Weiss constant indicates that the antiferromagnetic coupling dominates the major exchanges between Co(II) centers. As expected by consideration of the magnetostructural correlation of **1**, for the $\mu_3$-OH group in **1**, the interaction is predicted to be antiferromagnetic, with large Co–OH–Co (99.17–120.63°) angles.[16]

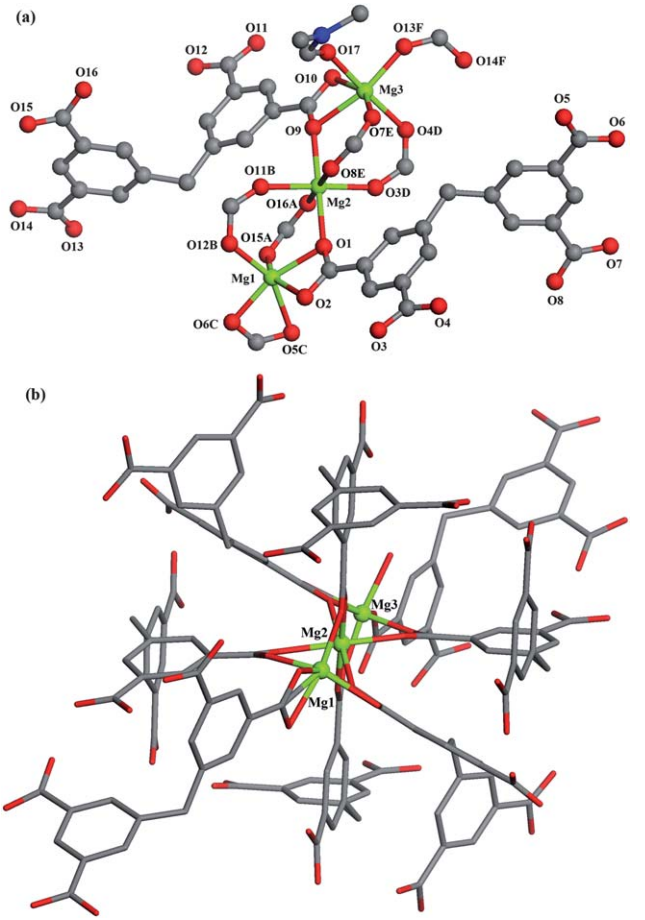


**Fig. 4** (a) Coordination environments of the Mg(II) ions in **3**. Hydrogen atoms are omitted for clarity. Symmetry codes: A, $x + 1/2, -y + 1, z$; B, $x - 1/2, -y + 1, z$; C, $-x, -y, z + 1/2$; D, $x - 1/2, -y, z$; E, $x + 1/2, -y, z$; F, $-x, -y + 1, z - 1/2$. (b) View of the tri-nuclear magnesium(II) unit surrounded by eight $MDIP^{4-}$ ligands in **3**.

In order to get an estimate of the strength of the antiferromagnetic exchange interaction, it has been shown in previous work that one may use the simple phenomenological eqn (1),[17]

$$\chi T = A\exp(-E_1/kT) + B\exp(-E_2/kT) \quad (1)$$

where $A + B$ equals the Curie constant, and $E_1$, $E_2$ represent the 'activation energies' corresponding to the spin–orbit coupling and the antiferromagnetic exchange interaction, respectively. This equation adequately describes the spin–orbit coupling, which results in a splitting between discrete levels. The experimental data of this work have been fitted and are very well described by this model. The obtained values of $A + B = 13.67\ cm^3\ mol^{-1}\ K$ agree with those obtained from the Curie–Weiss law in the high temperature range (see above), and the values for $E_1/k = +57.82$ K are consistent with those given in the literature for both the effects of spin–orbit coupling and site distortion ($E_1/k$ of the order of 100 K).[17b] The values for $-E_2/k = -7.34$ K reveal the presence of pronounced antiferromagnetic exchange interactions in complex **1**, which are consistent with that obtained from the above.

The magnetic susceptibility of **2** *versus* temperature is shown in Fig. 7, the $\chi_M T$ value at 300 K is 14.94 $cm^3\ mol^{-1}\ K$, slightly

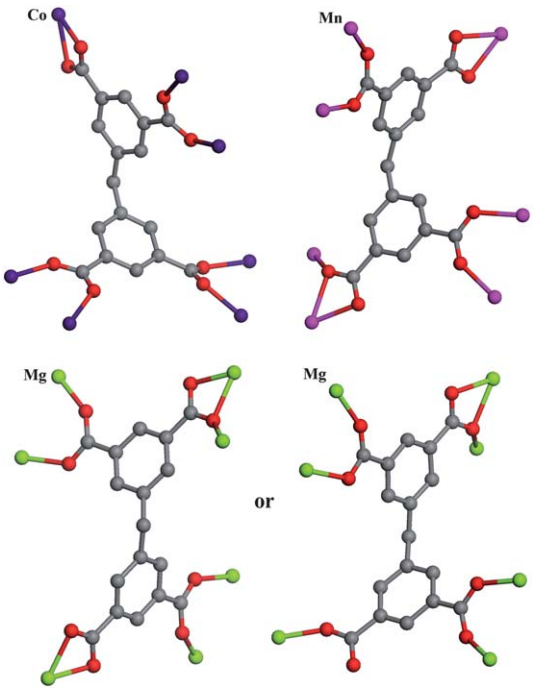


**Fig. 5** The coordination modes of MDIP ligands in complexes **1–3**.

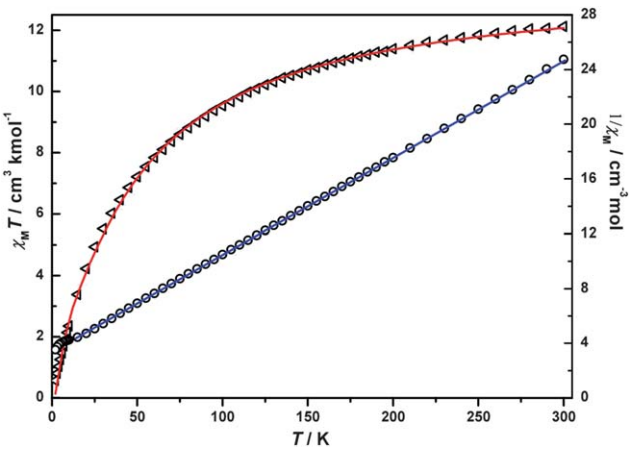


**Fig. 6** Temperature dependence of the $\chi_M T$ and $\chi_M^{-1}$ curve for **1**. The red line represents the best fit to the fitted to the equation in the text. The blue line show the Curie–Weiss fitting.

larger than the value expected for three Mn(II) ($S = 5/2$) noninteracting ions (13.125 cm$^3$ mol$^{-1}$ K, $g = 2$), which is indicates the sample is torquing in the magnetic field. This is corroborated by the continuous decrease of $\chi_M T$ upon cooling down to 12.25 cm$^3$ mol$^{-1}$ K at 70 K. Below that temperature, the decrease is more abrupt, with $\chi_M T$ reaching a value of 4.52 cm$^3$ mol$^{-1}$ K at 2 K, which is close to the spin-only ($g = 2$) value of 4.375 cm$^3$ mol$^{-1}$ K for a spin ground state $S = 5/2$. Additionally, a decrease in the low temperature $\chi_M T$ ($T$) data could also arise from zero-field splitting of the $^6A_{1g}$ ground state imposed by a distortion of the $Mn^{2+}$ octahedron.[18] The magnetic susceptibility above 14 K obeys the Curie–Weiss law with the Weiss constant, $\theta = -20.64$ K, and Curie constant, $C = 15.95$ cm$^3$ mol$^{-1}$ K per

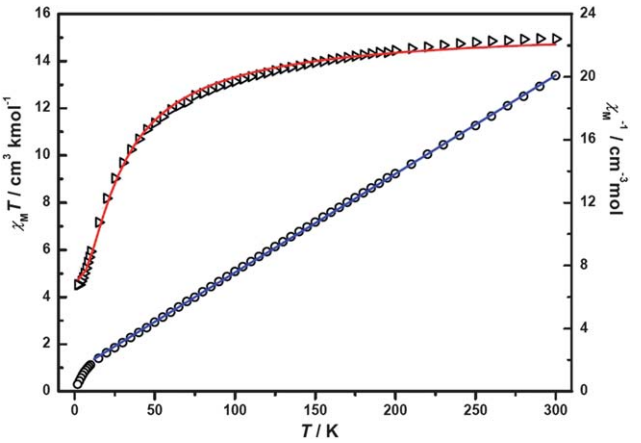


**Fig. 7** Temperature dependence of the $\chi_M T$ and $\chi_M^{-1}$ curve for **2**. The red line represents the best fit to the fitted to the equation in the text. The blue line shows the Curie–Weiss fitting.

$Mn_3$ unit. The negative weiss constants indicate weak antiferromagnetic interactions between the Mn(II) centers.

The magnetic analysis was carried out using the susceptibility equation based on the spin Hamiltonian, $\boldsymbol{H} = -2J(\boldsymbol{S_1S_2} + \boldsymbol{S_2S_3}) - 2j\boldsymbol{S_1S_3}$, assuming that the exchange integrals between the neighbouring manganese ions are identical ($J_{12} = J_{23} = J$) and $j$ describes the integral between the terminal manganese ions within the trinuclear unit. However, the magnetic interaction between the terminal manganese ions in a linear complex is negligible because of the large Mn···Mn separation (Mn···Mn 7.296 Å). The energy levels for this system are then inserted into the van Vleck equation eqn (2).[19]

$$\chi_{\text{trimer}} = \frac{Ng^2\beta^2}{3kT} \times \frac{\sum S_T(S_T+1)(2S_T+1)\exp(-E/k_BT)}{\sum(2S_T+1)\exp(-E/k_BT)} \quad (2)$$

$$\chi_m = \frac{\chi_{\text{trimer}}}{1 - \chi_{\text{trimer}} 2zJ'/Ng^2\beta^2} \quad (3)$$

To take into account the inter-trimer super-exchange coupling, the magnetic susceptibility can be corrected by the molecular field approximation eqn (3). The best fit gives $J = -1.16$ cm$^{-1}$, $zJ' = 0.0046$ cm$^{-1}$, $g = 2.04$ with $R^2 = 0.99755$. The negative sign of the $J$ factor verifies the antiferromagnetic nature of the exchange. The positive $zJ'$ value suggests weak ferromagnetic coupling between the trimers, which could be just caused by the sample torquing effect.

## Thermal analysis

To characterize the thermal stabilities of compounds **1–3**, their thermal behaviors were investigated by TGA under a nitrogen atmosphere with a heating rate of 10 °C min$^{-1}$ (Fig. S4, ESI†). In complex **1**, the first weight loss in the temperature range 40–110 °C corresponds to the loss of two guest water molecules (obsd 3.85%, calcd 2.86%). The second weight loss of 11.52% (calcd 11.59%) from 110–320 °C corresponds to the release of the DMF. The remaining weight may be attributed to the formation of CoO (obsd 20.48%, calcd 23.24%). For complex **2**, the weight loss corresponding to the release of two DMF molecules is observed from 40 to 290 °C (obsd 13.11%, calcd 13.48%). The

 

weight loss of 4.91% during the second step between 290–380 °C corresponds to the loss of one dimethylammonium cation (calcd 4.25%). Decomposition of **2** began above 430 °C. For complex **3**, the weight loss in the range 40–315 °C is attributed to the release of four guest water molecules and one coordinated DMF (obsd 14.86%, calcd 15.34%). The destruction of the framework occurs at *ca.* 400 °C with a residue of MgO (obsd 13.64%, calcd 12.79%). However, it is difficult to determine these weight losses accurately because these processes are overlapped in different degrees.

## Conclusions

We have successfully synthesized three novel coordination polymers under solvothermal conditions by reacting $H_4$MDIP with different metal ions. They all have the anionic 3D frameworks constructed by different metal subunits. The diverse structures of the complexes are caused by different coordination environments around central metal ions and the coordination modes of the organic ligands. Magnetic susceptibility measurements reveal dominant antiferromagnetic interactions for complexes **1** and **2**, respectively. We are currently pursuing further understanding the coordination chemistry of $H_4$MDIP and constructing various coordination polymers with intriguing structures and properties.

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