Tetracarboxylate-based Co(II), Ni(II) and Cu(II) three-dimensional coordination polymers: syntheses, structures and magnetic properties†

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Methylenediisophthalic acid (H₄MDIP), as semi-rigid 'V'-shaped carboxylate ligands, react with CoO, NiO and Cu(NO₃)₂·3H₂O to give three novel coordination polymers [H₃O]₂[Co₃(MDIP)₂]·2DMF (1), [Ni₂(HMDIP)(μ_2 -OH)(H₂O)₃(DMF)]·4H₂O·DMF (2) and [Cu₃(MDIP)(μ_2 -OH)₂(H₂O)₄]·6.5H₂O (3) (DMF = N,N'-dimethylformamide). All compounds have been characterized by thermogravimetric analysis, IR spectroscopy, elemental and single-crystal X-ray diffraction analyses. Complex 1 is an unusual open anionic framework that is defined as the metal–organic replica of fluorite. Both 2 and 3 features a 3D open framework with one-dimensional elliptical channels and R- and L-helical chains, and their resulting frameworks can be rationalized as **crb** and **pts** topology respectively. An interesting feature of complex 3 is the presence of the linear Cu₃ units that is formed by carboxylate and μ_2 -hydroxyl groups linking three Cu(II) metal centers. Magnetic investigations indicate that ferromagnetic couplings are dominant in the three compounds.

Introduction

In recent years, research on coordination polymers (CPs) has been rapidly expanding, not only for their potential applications in gas storage, ion exchange, catalysis, magnetism and luminescence¹⁻⁵ but also for their unique characteristics, such as structural regularity, flexibility, and functionalized high surface area.⁶ Among the reported studies about the construction of complexes, carboxylate ligands have been extensively used due to their versatile coordination conformations and strong coordination ability.⁷ Until now, much research has been devoted to the use of rigid carboxylate ligands, such as 1,4-benzenedicarboxylic acid (p-H₂BDC), 1,3-benzenedicarboxylic acid (m-H₂BDC), 1,3,5-benzenetricarboxylic acids (H₃BTC) and so on.⁸⁻¹⁰ Meanwhile, many interesting metal-organic frameworks based on flexible carboxylate ligands have also been reported widely.¹¹ But, in contrast, the investigation into the semi-rigid 'V'-shaped carboxylate ligands is still in its infancy.¹²

Methylenediisophthalic acid (H_4MDIP) is a 'V'-shaped tetracarboxylate ligand which can afford metal centers a variety of connection modes, thereby generating abundant structural motifs. At the same time, this ligand is relatively flexible, since the phenyl rings can freely rotate around the methylene ($-CH_2-$) groups according to the small change in the coordination environment with the result that various coordination conformations are

formed. As far as we know, coordination polymers constructed from the H_4MDIP ligand have rarely been reported.¹

On the other hand, the first row transition metals (Co, Ni and Cu) complexes have attracted extensive interest in recent years because their different oxidation states allow two important parameters to be varied, *i.e.* spin quantum number and magnetic anisotropy.¹⁴ These potential variable parameters would bring about a great challenge in the field of magnetic coordination polymers. So far the majority of magnetic frameworks are those containing the above paramagnetic metal centers.

With the above idea in mind, herein we report three unprecedented compounds, namely $[H_3O]_2[Co_3(MDIP)_2]\cdot 2DMF$ (1), $[Ni_2(HMDIP)(\mu_2-OH)(H_2O)_3(DMF)]\cdot 8H_2O$ (2) and $[Cu_3(MDIP)(\mu_2-OH)_2(H_2O)_4]\cdot 6.5H_2O$ (3) based on the assembly of H_4MDIP with cobalt(II), nickel(II) or copper(II) metal ions. The thermal and magnetic properties of these compounds are discussed.

Experimental

Materials and measurements

Methylenediisophthalic acid (H₄MDIP) was synthesized as reported in the literature,¹⁵ and the other reagents were purchased from commercial sources and used as received. IR spectra were obtained from KBr pellets on a Perkin–Elmer 580B IR spectrometer in the 400–4000 cm⁻¹ region (SI). 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 α 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

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the compounds were estimated using Pascal's constants,¹⁶ and magnetic data were corrected for diamagnetic contributions of the sample holder.

Synthesis

Synthesis of [H_3O]_2[Co_3(MDIP)_2]-2DMF (1). A mixture of CoO (0.0150 g, 0.2 mmol), H₄MDIP (0.0344 g, 0.1 mmol), DMF (1.5 mL), and H₂O (1.5 mL) was placed in a Teflon reactor (20 mL) and heated at 105 °C for 3 days. After the mixture 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 H₄MDIP. Anal. Calcd for C₄₀H₃₆Co₃N₂O₂₀ (M_r = 1041.50): C, 46.12; H, 3.48; N, 2.69. Found: C, 46.23; H, 3.46; N, 2.78%. IR (cm⁻¹): 3419(m), 3012(m), 2806(m), 2508(w), 1407(m), 1623(s), 1588(s), 1540(s), 1464(s), 1429(s), 1377(s), 1252(m), 1141(w), 1103(m), 1018(w), 925(w), 881(w), 811(m), 775(m), 725(s), 710(m), 676(w), 610(w), 587(w), 522(w), 501(w), 450(m).

Synthesis of $[Ni_2(HMDIP)(\mu_2-OH)(H_2O)_3(DMF)]\cdot 8H_2O$ (2). A mixture of NiO (0.0150 g, 0.2 mmol), H₄MDIP (0.0344 g, 0.1 mmol), DMF (1.5 mL), and H₂O (1.5 mL) was placed in a Teflon reactor (20 mL) and heated at 105 °C for 3 days. After the mixture was gradually cooled to room temperature at a rate of 10 °C h⁻¹, green block crystals of **2** were obtained with 69% yield based on H₄MDIP. Anal. Calcd for C₂₀H₃₉Ni₂NO₂₁ ($M_r = 746.94$): C, 32.16; H, 5.26; N, 1.88. Found: C, 31.87; H, 5.16; N, 1.93%. IR (cm⁻¹): 3391(s), 2083(w),1631(s), 1592(m), 1547(m), 1446(s), 1376(s), 1242(w), 1108(w), 1064(w), 917(w), 873(w), 784(m), 776(m), 717(s), 668(m), 620(m), 549(m), 464(m).

Synthesis of [Cu₃(MDIP)(μ_2 -OH)₂(H₂O)₄]-6.5H₂O (3). A mixture of Cu(NO₃)₂·3H₂O (0.0482 g, 0.2 mmol), H₄MDIP (0.0344 g, 0.1 mmol), and H₂O (15 ml) was placed in a beaker, and several drops of aqueous ammonia was added under stirring until the mixture became clear. The blue solution was filtered and allowed to slowly evaporate at room temperature to isolate a blue rod-like crystalline solid **3** with 52% yield based on H₄MDIP. Anal. Calcd for C₁₇H₃₁Cu₃O_{20.50} (M_r = 754.04): C, 27.08; H, 4.41. Found: C, 27.13; H, 4.56%. IR (cm⁻¹): 3401(m), 1610(m), 1568(s), 1449(m), 1411(m), 1359(m), 1239(m), 1119(w), 970(w), 907(w), 883(w), 800(m), 783(m), 733(m), 653(m), 564(m), 480(m).

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 α radiation ($\lambda = 0.71073$ Å). The crystal structure was solved by means of Direct Methods and refined employing full-matrix least squares on F^2 (SHELXTL-97).¹⁷ All the hydrogen atoms except for those of guest water molecules were generated geometrically and refined isotropically using the riding model. All non-hydrogen atoms were refined with anisotropic displacement parameters except for some disordered guest molecules. It should be noted that the guest molecules in the channels of 1 and 2 are highly disordered and could not be modeled properly so the diffused electron densities resulting from them were removed by the SQUEEZE routine in PLATON.¹⁸ Crystal data and details of the structure determination for complexes 1-3 are listed in Table 1. Selected bond lengths and angles are given in Table S1.[†]

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

	1	2	3
Formula	C40H36C03N2O20	C ₂₀ H ₃₉ Ni ₂ NO ₂₁	C ₁₇ H ₃₁ Cu ₃ O _{20 50}
Formula weight	1041.50	746.94	754.04
Crystal system	Orthorhombic	Monoclinic	Orthorhombic
Space group	Pbca	$P2_{1}/c$	Pccn
$\tilde{T/K}$	200(2)	200(2)	200(2)
a/Å	16.223(3)	10.247(2)	18.4609(10)
b/Å	10.633(2)	15.250(3)	18.6553(10)
c/Å	25.188(5)	20.946(4)	8.1387(4)
β (°)	90.00	99.91(3)	90.00
$V/Å^3$	4345.0(15)	3224.4(11)	2802.9(3)
Ζ	4	4	4
$D_{\rm c}/{\rm g~cm^{-3}}$	1.592	1.539	1.787
F(000)	2124	1560	1536
Data collected	22619	17162	14433
Unique data	4263	6279	2754
R(int)	0.0314	0.0337	0.0326
GOF on F^2	1.084	1.110	1.058
$R_1^a [I > 2\sigma(I)]$	0.0232	0.0818	0.0446
WR_2^b (all data)	0.0600	0.2023	0.1354
${}^{a}R_{1} = \sum F_{o} - F_{c} / \sum F_{o} \cdot {}^{b}WR_{2} = \{\sum [W(F_{o}^{2} - F_{c}^{2})^{2}] / \sum [W(F_{o}^{2})^{2}] \}^{\frac{1}{2}}$			

Descriptions of crystal structures

Structure of [H₃O]₂[Co₃(MDIP)₂]·2DMF (1). Single-crystal X-ray diffraction reveals that compound 1 consists of carboxylatebridged tri-nuclear cobalt clusters. The Co1 atom, located on the end of the Co₃ unit, adopts a distorted octahedral geometry coordinated by six oxygen atoms from four different MDIP⁴⁻ ligands (Co-O 2.0276(11)-2.2432(12) Å). The Co2 atom, situated at an inversion center in the space group, also exhibits a distorted octahedral geometry coordinated by six oxygen atoms from four different [MDIP]⁴⁻ ligands (Co-O 2.0515(11)-2.1650(11) Å). The Co2 atom is linked to two neighboring Co1 by four -O-C-Obridges and a pair of μ_2 -O_{carboxyl} atoms (O1 and O1A) to afford a Co_3 core with a $Co \cdots Co$ distance of 3.569 Å. (Fig. 1a). Each trinuclear unit is further connected to neighboring others through eight [MDIP]⁴⁻ ions to generate an anionic 3D open framework (Fig. 1b). The bond-valence calculations suggest all Co atoms are in the +2 oxidation state.¹⁹ This result is also supported by an XPS measurement of the compound in the energy region of Co2p^{1/2} and Co2p^{3/2}. The XPS spectrum (shown in Fig. S1[†]) gives one peak at 780.9 eV, attributable to Co²⁺.²⁰ A negatively charged framework, $Co_3(C_8H_4O_4)_4^{2-}$ and hydroxonium ion H_3O^+ occupy the voids based on the consideration of the charge balance. The effective free volume calculated with PLATON for the inclusion is 1724.2 $Å^3$ per unit cell (after free molecules have been hypothetically removed) corresponding to 39.68% 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 Co₃ linear units and each Co₃ unit in turn links eight [MDIP]⁴⁻ ligands, which can be regarded as an eight-connecting node. The resulting (4,8)-connected net resembles the fluorite structure with the Schläfli symbol of $(4^{10} \cdot 6^{14} \cdot 8^4)(4^5 \cdot 6)_2$.²¹ It is well-known that fluorite is one of the most important and frequently encountered structure types in minerals. Although it has been successfully replicated in several neutral metal–organic nets, what we describe



Fig. 1 (a) Coordination environment of the Co(II) ion in **1**. Hydrogen atoms are omitted for clarity. Symmetry codes: A, -x,-y+1,-z+1; B, x-1/2,-y+1/2,-z+1; C, x-1/2,-y+3/2,-z+1; D, -x+1/2,-y+1,z-1/2. (b) View of the tri-nuclear cobalt(II) unit surrounded by eight MDIP⁴⁻ ligands in **1**.

here represents the first example where the structure of fluorite is perfectly imitated in a magnetic anionic framework.

Structure of $[Ni_2(HMDIP)(\mu_2-OH)(H_2O)_3(DMF)]\cdot 8H_2O$ (2). When CoO was replaced by NiO, a fascinating 3D structure of **2** was obtained. As illustrated in Fig. 3a, compound **2** contains two distinctive nickel atoms, one μ_2 hydroxyl group, one coordinated DMF molecule, three coordinated aqua molecules, and one monoprotonated [HMDIP]³⁻ ligand (Fig. 3a). The Ni1 atom with a slightly distorted octahedral geometry is coordinated by six oxygen atoms from three [HMDIP]³⁻ anions (O2, O5C, and O8A), one coordinated aqua molecule (O11), one μ_2 -hydroxyl group (O9), and one DMF molecule (O10). Ni2 also adopts a distorted octahedral coordination geometry, surrounded by six oxygen atoms from three different [HMDIP]³⁻ (O1, O4B, and



Fig. 2 (a) Ball-and-stick and schematic representations of 4-connected and 8-connected nodes, respectively. (b) Structure showing the complete connectivity between the 8-connected Co_3 clusters and the 4-connected [MDIP]⁴⁻ anions (gray and blue balls represent four- and eight-connected nodes, respectively; the purple lines represent a unit cell).

O7A), two coordinated aqua molecules (O12 and O13) and one μ_2 -hydroxyl group (O9). The Ni1 and Ni2 centers are bridged through two carboxylate groups and one μ_2 -hydroxyl group to form a binuclear unit with a Ni…Ni distance of 3.507 Å. Interestingly, the Ni₂ units are linked into R- and L- helical chains along the *b*-axis through the isophthalate and [HMDIP]³⁻ respectively (Fig. 3b). There are four carboxylate groups associated with each Ni₂ unit, and each [HMDIP]³⁻ ligand links four Ni₂ units using its four carboxylate groups to allow the formation of a 3D open framework with elliptical channels viewed along the *a*-axis directions. Because the Ni₂ units and [HMDIP]³⁻ serve as four-connected nodes, the resultant framework can be rationalized as having **crb** topology with the Schläfli symbol of (4·6⁵) (Fig. 3c).²² PLATON analysis showed that the effective free volume of **2** is 30.98% of the crystal volume.

Structure of $[Cu_3(MDIP)(\mu_2-OH)_2(H_2O)_4]$ -6.5H₂O (3). Compound 3 was obtained under different reaction conditions to that of 1 and 2. As shown in Fig. 4a, the basic unit contains three Cu(II) metal centres arranged in linear that are bridged by one carboxylate group and one μ_2 -hydroxyl group. In the unit, the Cu1 is five-coordinated with a distorted square-pyramidal geometry ($\tau \approx 0.14$),²³ where one μ_2 -hydroxyl oxygen atom (O5), two carboxyl oxygen atoms (O2 and O4c) and one coordinated water molecule (O6) lie in the basic plane, while the other aqua ligand (O7) occupies the apical position. The Cu2 is ligated by



Fig. 3 (a) Coordination environment of the Ni(II) ion in complex **2.** Hydrogen atoms are omitted for clarity. Symmetry codes: A, -x+1,y+1/2,-z+1/2; B, x-1,-y+1/2,z-1/2; C, x-1,y,z. (b) Schematic representation of the L- and R- helical chains along *y*-axis. (c) Topological view showing the equivalent 3D framework for **2** along *x*-axis (green balls, Ni₂ dimers; pink balls, 4-connected H₄MDIP ligands).

four oxygen atoms (O3B, O3C, O5, and O5A), exhibiting a planar square geometry. Each tri-nuclear unit is connected to twelve others through four $[MDIP]^{4-}$ ions to generate a 3D framework with one-dimensional elliptical channels along the *c*-axis (Fig. 4b and Fig. 4c). Without guest molecules, the effective free volume

is calculated by PLATON analysis to be 26.14% of the crystal volume. R- and L-helical chains along the *x*-axis are formed by the isophathalic carboxylates between tri-nuclear copper units (Fig. S2†). If the tri-nuclear units and [MDIP]⁴⁻ are considered as four-connected nodes, the resulting network is of the **pts** topology with the Schläfli symbol of $(4^2 \cdot 8^4)$ (Fig. S3†).²⁴

For **3**, one of the most prominent structural characteristics is the one dimensional channels constituted by Cu_3 units and $[MDIP]^+$ ions (Fig. 4d). Along the *c*-axis, the Cu_3 units with the same orientation are merely arranged linearly rather than connect with each other, whereas those with different orientations are joined together by $[MDIP]^{4-}$ ions to form an open framework. To the best of our knowledge, such 3D open frameworks constructed by linear Cu_3 units and carboxylate ligands with the above structure have never been observed prior to this work.²⁵

In a comparison of the structures of 1–3, it is found that the coordination geometry of the central metal ions has significant effects on the structures of the resulting complexes. In addition, different coordination modes of the carboxylate ligand also have a significant effect on the structures, as evidenced by the fact that the structure of 1 is significantly different from that of 2 and 3. In complex 1, H₄MDIP carboxylate groups adopt three kinds of coordination modes, that is, the bis-mono, bis-chelating, and chelating-mono coordination modes. The mono and bis-mono coordination modes exist in complexes 2 and 3 (Fig. 5). In 1–3, the dihedral angles between two aryl rings of H₄MDIP are 89.03, 86.95 and 115.01° respectively, which are also related to their coordination mode. In complex 3, the [MDIP]⁴⁻ with a higher symmetrical configuration leads to a higher symmetrical 3D framework.

Magnetic properties

The magnetic susceptibilities of complexes 1-3 were measured at 0.1 T field in the temperature rang 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. S4–S6[†]). The magnetic susceptibility of 1 versus temperature is shown in Fig. 6, the $\chi_{\rm M}T$ value is 9.17 cm³ mol⁻¹ K at 300 K, which is significantly larger than the spin-only value of 5.63 cm³ mol⁻¹ K calculated for three 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 lowering the temperature, $\chi_M T$ decreases slowly to a minimum value of 6.42 cm³ mol⁻¹ K at 9 K resulting from the depopulation of the higher energy Kramers doublets associated with the high-spin Co(II) single ions.26 When the temperature continues to decrease from 9 K, the $\chi_{\rm M}T$ value abruptly increases abruptly to 7.11 cm³ mol⁻¹ K at 2 K, indicating the presence of intramolecular ferromagnetic interactions between the Co(II) ions mediated by the carboxylate bridges. The magnetic susceptibility above 30 K obeys the Curie–Weiss law with the Weiss constant, $\theta =$ -12.53 K, and Curie constant, C = 9.59 cm³ mol⁻¹ K per Co₃ unit.

To quantitatively evaluate the magnetic interactions in 1, the data above 50 K were fitted to the expression of susceptibility for linear tri-nuclear systems based on the Hamiltonian $H = -2J(S_1S_2+S_2S_3)$. We have assumed that the exchange constant between the terminal Co(II) ions was zero. And the inter-trimer interaction (zJ') was dealt with by the molecular-field



Fig. 4 (a) Coordination environment of the Cu(II) ion in **3**. Hydrogen atoms are omitted for clarity. Symmetry codes: A, -x, -y+1, -z+1; B, -x+1/2, y, z+1/2; C, x-1/2, -y+1, -z+1/2. (b) View of the tri-nuclear copper(II) unit and the tri-nuclear unit surrounded by four MDIP⁴⁻ ligands in **3**. (c) The network of **1** with 1D elliptical channels viewed along the *z*-axis. (d) Connectivity of tri-nuclear units in the *z*-axis in **3**.



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

approximation.²⁷ The best fit was obtained with values of $J = 2.71 \text{ cm}^{-1}$, $zJ' = 0.35 \text{ cm}^{-1}$, g = 2.59 and $R^2 = 0.97744$. This result indicates that ferromagnetic coupling interactions exist both between the adjacent Co(II) sites and between the adjacent trimers, although the latter is much weaker.

As shown in Fig. 7, for complex **2**, at room temperature the value of $\chi_M T$ is 2.55 cm³ mol⁻¹ K, which is larger than the expected value of 2.00 cm³ mol⁻¹ K for two magnetically uncoupled Ni^{II} (S = 1) centers. The $\chi_M T$ values gradually increase with decreasing temperature attesting to the presence of a ferromagnetic exchange interaction. The $\chi_M T$ versus T plot presents a maximum (2.71 cm³ mol⁻¹ K) at 9 K and then decreases until a value of 2.21 cm³ mol⁻¹ K at 2 K. The decrease of the $\chi_M T$ values at low temperature can be due to a zero-field splitting of the S = 2



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



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

ground spin state. The data above 30 K follows the Curie–Weiss law with the Weiss constant, $\theta = 2.72$ K, and Curie constant, C = 2.54 cm³ mol⁻¹ K per Ni₂ dimer.

It is possible to represent the intradimer magnetic exchange interaction (J) by two equivalent S = 1 ions using eqn (1) by means of the Hamiltonian $H = -2JS_1S_2$.²⁸

$$\chi_{dimer} = \frac{2Ng^2\beta^2}{kT} \times \frac{\exp(J/kT) + 5\exp(3J/kT)}{1 + 3\exp(J/kT) + 5\exp(3J/kT)}$$
(1)

$$\chi_{\rm m} = \frac{\chi_{\rm dimer}}{1 - \chi_{\rm dimer} 2zJ'/Ng^2\beta^2}$$
(2)

Considering the molecular field approach with zJ' as the exchange coupling between Ni₂ dimers, we can fit our experimental data with eqn (2). The best fit gives $J = 1.98 \text{ cm}^{-1}$, $zJ' = -0.26 \text{ cm}^{-1}$, g = 2.27 with $R^2 = 0.95699$. The positive sign of the J factor verifies the ferromagnetic nature of the exchange.

The variable-temperature magnetic susceptibility of **3** is shown in Fig. 8, the $\chi_M T$ value at 300 K is 1.65 cm³ mol⁻¹ K, which lies in the usual range expected for trimeric Cu(II) ions with $g > 2.^{29}$ Upon cooling of the sample, $\chi_M T$ increases and reaches



Fig. 8 Temperature dependence of the $\chi_M T$ and χ_M^{-1} curve for **3**. The red line represents the best fit to the equation in the text. The blue line shows the Curie–Weiss fitting.

a value of 2.04 cm³ mol⁻¹ K at 20 K. This behavior is indicative of strong ferromagnetic coupling between the adjacent Cu(II) in the tri-nuclear units. Below 20 K, $\chi_M T$ decreases rapidly down to 1.26 cm³ mol⁻¹ K, which is most likely due to zero-field splitting within the quartet ground state. The occurrence of inter-trimer antiferromagnetic interactions may also be operative at very low temperatures. A fitting of the data above 30 K using the Curie– Weiss law gives the Weiss constant, $\theta = 33.36$ K, and Curie constant, C = 6.64 cm³ mol⁻¹ K per Cu₃ unit.

The magnetic analysis was carried out using the susceptibility equation based on the spin Hamiltonian, $H = -2J(S_1S_2+S_2S_3) - 2jS_1S_3$, assuming that the exchange integrals between the neighbouring copper ions are identical $(J_{12} = J_{23} = J)$ and *j* describes the integral between the terminal copper ions within the tri-nuclear unit. The magnetic susceptibility for the linear tri-nuclear copper(II) system may be expressed by eqn (3).³⁰ To take into account the inter-trimer super-exchange coupling, the magnetic susceptibility can be corrected by the molecular field approximation eqn (4).

$$\chi_{trimer} = \frac{Ng^2\beta^2}{4kT} \times \frac{\exp(-2J/kT) + 10\exp(J/kT) + \exp(-2j/kT)}{\exp(-2J/kT) + 2\exp(J/kT) + \exp(-2j/kT)}$$
(3)

$$\chi_{\rm m} = \frac{\chi_{\rm trimer}}{1 - \chi_{\rm trimer} 2z J' / Ng^2 \beta^2} \tag{4}$$

A good fit with the experimental data was obtained for J = 20.94 cm⁻¹, j = -7.22 cm⁻¹, zJ' = -0.41 cm⁻¹, g = 2.38 and $R^2 = 0.96181$. The results show that the predominant ferromagnetic coupling is due to the interaction between neighbouring copper ions. A smaller antiferromagnetic contribution results from interaction between the terminal copper ions. The negative zJ' value suggests weak antiferromagnetic coupling between the trimers.

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. S7†). For compound 1, the weight loss corresponding to the release of two

water molecules and one DMF molecule is observed from 105 to 390 °C (obsd 10.32%, calcd 10.37%). The destruction of the frameworks occurs from 420 to 480 °C, leading to the formation of CoO as the residue (obsd 22.22%, calcd 21.58%). For **2**, the weight loss in the range of 40–105 °C is attributed to the release of eight guest water molecules (obsd 21.03%, calcd 19.28%). The destruction of the frameworks occurs at *ca.* 385 °C with a residue of NiO (obsd 20.12%, calcd 20.00%). Compound **3** lost its guest water molecules from 40 to 150 °C (obsd 15.34%, calcd 15.52%). The compound was stable up to 260 °C, and the removal of organic components occurs from 260 to 430 °C. The remaining weight corresponds to the formation of CuO (obsd 33.78%, calcd 31.67%).

Conclusions

We have successfully synthesized three new Co(II), Ni(II) and Cu(II) coordination polymers using the semi-rigid 'V'-shaped H_4 MDIP ligand. The results reveal that the distinct structures of the final products are caused by different coordination environments around central metal ions and the coordination modes of the carboxylate ligand (H_4 MDIP). Magnetic susceptibility measurements reveal dominant ferromagnetic interactions for the three complexes. The three compounds not only show an aesthetic diversity of coordinative chemistry, but also, for example, can be used for the design of magnetic materials. Our future work will focus on the synthesis of new functional coordination polymers by using other paramagnetic metals and the H_4 MDIP ligand.

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