

Diverse Ni(II) MOFs constructed from asymmetric semi-rigid V-shaped multicarboxylate ligands: structures and magnetic properties†

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Novel nickel(II) coordination polymers have been constructed from asymmetric semi-rigid V-shaped multicarboxylate ligands with the help of 4,4'-bipyridine (4,4'-bpy) ligand. The hydrothermal reaction between 3-(4-carboxy-phenoxy)-phthalic acid (H_3L^1) and $Ni(OAc)_2 \cdot 4H_2O$ led to the formation of $[Ni_3(L^1)_2(\mu-4,4'-bpy)_3(H_2O)_2]_n \cdot (4,4'-bpy)_n \cdot (H_2O)_{5n}$ (**1**). In contrast, the same reaction using 3-(2-carboxy-phenoxy)-phthalic acid (H_3L^2) as a starting material instead of H_3L^1 resulted in $[Ni_3(L^2)_2(H_2O)_4(\mu-4,4'-bpy)_3]_n \cdot (H_2O)_{2n}$ (**2**) and $[Ni_3(L^2)_2(H_2O)_4(\mu-4,4'-bpy)_4]_n \cdot (H_2O)_{2n}$ (**3**) at 120 and 150 °C, respectively, revealing the effect of reaction temperature on the structure of the coordination polymer formed from the semi-rigid V-shaped ligand of L^2 . Single-crystal X-ray diffraction analysis reveals that complex **1** shows a 3D framework structure assembled from right- and left-handed helices together with isolated tubes. This compound represents the first metal–organic hybrid tube constructed from an asymmetric semi-rigid V-shaped multicarboxylate ligand. Compound **2** also exhibits a 3D network composed of discontinuous trinuclear Ni(II) clusters, while the 3D architecture of **3** consisting of isolated Ni(II) ions separated in a long distance is constructed by two kinds of 2D (6,3) networks. Magnetic studies reveal the overall antiferromagnetic interaction between the neighbouring Ni(II) ions in **1–3**.

Introduction

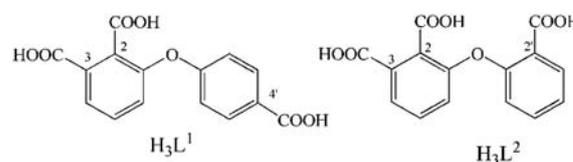
As an important branch in the field of supramolecular chemistry and crystal engineering, the design and assembly of metal–organic coordination frameworks (MOFs) with appealing structures and properties have stimulated the interests of chemists over the past few decades.^{1,2} Recently, considerable progress has been achieved in the preparation of metal–organic tubular compounds containing open pores with potential applications for gas storage and separation.³ However, only a few metal–organic hybrid tubular complexes with open or closed pores have been reported.^{4,5} Accordingly, the progress in directional design and synthesis of functional metal–organic hybrid tubular complexes is retarded due to the limitation in establishing the correlation between the tube-like structure of complexes and organic ligand.

Quite recently, semi-rigid V-shaped multicarboxylate ligands with two benzene rings of central molecular framework bridged by a nonmetallic atom (C, O, S, and N atoms) have been utilized to construct MOFs, giving interesting framework

structures (including helices and interpenetrating networks) and potential applications in the field of separation, absorption, catalyst, and sensors.⁶

Among the above mentioned compounds, those with intriguing multi-stranded helix structures called multi-stranded molecular braids are usually obtained from semi-rigid V-shaped multicarboxylate ligands with two or four carboxylic substituents attached at symmetrical positions of the two benzene rings.⁷ As a result, the metal–organic hybrid tube-like complexes are expected to be obtained from multi-stranded helix motif by introducing coordination carboxylic groups at asymmetrical positions on the V-shaped central molecular framework of semi-rigid ligands to bind the neighbouring single helices. However, to the best of our knowledge, the metal–organic hybrid tubular complexes constructed from asymmetric semi-rigid V-shaped multicarboxylate with carboxylic groups attached at asymmetrical positions of the two benzene rings have not been reported thus far. It therefore worth trying to prepare novel metal–organic hybrid tubular complexes using such kind of asymmetric semi-rigid V-shaped multicarboxylate ligands.

In the present paper, two asymmetric multidentate O-donor ligands including 3-(4-carboxy-phenoxy)-phthalic acid (H_3L^1)



Scheme 1 Schematic molecular structure of H_3L^1 and H_3L^2 .

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† Electronic supplementary information (ESI) available: X-Ray crystallographic files (CIF), diagrams of the structures, selected bond distances, bond angles, and TGA curves of compounds **1–3**. CCDC reference numbers 745620, 709626, 739919 and 739920. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b917659d

and 3-(2-carboxy-phenoxy)-phthalic acid (H_3L^2) (Scheme 1) with three carboxylic groups attached at 2-, 3-, and 4'-positions and 2-, 2'-, and 3-positions of semi-rigid V-shaped central molecular framework, respectively, were employed to assemble Ni(II) ions into MOFs with the help of 4,4'-bpy as secondary ligand. Fortunately, a series of three novel Ni(II) MOFs with diverse 3D molecular structures $[\text{Ni}_3(\text{L}^1)_2(\mu\text{-}4,4'\text{-bpy})_3(\text{H}_2\text{O})_2]_n \cdot (4,4'\text{-bpy})_n \cdot (\text{H}_2\text{O})_{5n}$ (**1**), $[\text{Ni}_3(\text{L}^2)_2(\text{H}_2\text{O})_4(\mu\text{-}4,4'\text{-bpy})_3]_n \cdot (\text{H}_2\text{O})_{2n}$ (**2**), and $[\text{Ni}_3(\text{L}^2)_2(\text{H}_2\text{O})_4(\mu\text{-}4,4'\text{-bpy})_4]_n \cdot (\text{H}_2\text{O})_{2n}$ (**3**) have been obtained. Their single crystal structures as well as magnetic properties have been systematically investigated.

Experimental

All reagents and solvents involved in the present work were obtained from the commercial source and used directly without further purification. The two ligands H_3L^1 and H_3L^2 were synthesized according to the reported procedure.⁸

General synthesis procedure for complexes 1–3

The target complexes were prepared by employing hydrothermal method with the same stoichiometric ratio for the starting materials in the absence of any base. A Teflon-lined stainless steel container (25 mL) was utilized as reaction vessel containing all starting materials, which was heated to appropriate temperature and held for 48 h for **1–3**, then cooled to 50 °C at a descent rate of 10 °C per hour. Finally, the oven was cut off and kept for another 10 h, perfect crystals were isolated with high yield based on multicarboxylate ligand.

$[\text{Ni}_3(\text{L}^1)_2(\mu\text{-}4,4'\text{-bpy})_3(\text{H}_2\text{O})_2]_n \cdot (4,4'\text{-bpy})_n \cdot (\text{H}_2\text{O})_{5n}$ (**1**). The mixture of $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (0.0498 g, 0.2 mmol), 4,4'-bpy (0.0312 g, 0.2 mmol), H_3L^1 (0.0302 g, 0.1 mmol), and H_2O (15 mL) was sealed in 25 mL Teflon-lined stainless steel reactor and heated to 120 °C. Green block-shaped crystals suitable for X-ray diffraction analysis were separated by filtration with the yield of 0.0469 g, 63% (based on multicarboxylate ligand). Anal. calcd for $\text{C}_{70}\text{H}_{60}\text{N}_8\text{Ni}_3\text{O}_{21}$: C 55.12, H 3.96, N 7.35. Found: C 55.39, H 3.70, N 7.48. IR / cm^{-1} (KBr): 3447 (m), 3075 (m), 1605 (s), 1547 (s), 1475 (m), 1410 (s), 1239 (s), 1067 (m), 769 (m).

$[\text{Ni}_3(\text{L}^2)_2(\text{H}_2\text{O})_4(\mu\text{-}4,4'\text{-bpy})_3]_n \cdot (\text{H}_2\text{O})_{2n}$ (**2**). By employing the above-described procedure used to prepare **1** with H_3L^2 (0.0302 g, 0.1 mmol) instead of H_3L^1 (0.0302 g, 0.1 mmol) as starting material, green block-shaped crystals of compound **2** suitable for X-ray diffraction analysis were separated by filtration with the yield of 0.0440 g, 33% (based on multicarboxylate ligand). Anal. calcd for $\text{C}_{60}\text{H}_{50}\text{N}_6\text{Ni}_3\text{O}_{20}$: C 53.33, H 3.73, N 6.22. Found: C 54.04, H 3.60, N 6.28. IR / cm^{-1} (KBr): 3447 (m), 3070 (m), 1608 (s), 1551 (s), 1414 (m), 1389 (s), 1238 (s), 1070 (m), 816 (m).

$[\text{Ni}_3(\text{L}^2)_2(\text{H}_2\text{O})_4(\mu\text{-}4,4'\text{-bpy})_4]_n \cdot (\text{H}_2\text{O})_{2n}$ (**3**). By using the same procedure used to prepare **2** with reaction temperature at 150 °C instead of 120 °C, blue blocked crystals were obtained after the reactor was cooled to room temperature with the yield of 0.0709 g, 47% (based on multicarboxylate ligand). Anal. calcd for $\text{C}_{70}\text{H}_{58}\text{N}_8\text{Ni}_3\text{O}_{20}$: C 55.78, H 3.89, N 7.43. Found: C 55.74, H 3.68, N 7.40. IR / cm^{-1} (KBr): 3082 (m), 1606 (s), 1569 (s), 1416 (m), 1391 (s), 1244 (s), 1096 (m), 804 (m).

Physical measurements

Elemental analyses were carried out with an Elementary Vario El. The infrared spectroscopy on KBr pellets was performed on a Magna-IR 750 spectrophotometer in the region of 4000–400 cm^{-1} . Variable-temperature magnetic susceptibility measurements were performed on a Quantum Design MPMS SQUID magnetometer. The experimental susceptibilities were corrected for the diamagnetism of the constituent atoms (Pascal's tables). TGA was performed on a Perkin-Elmer TG-7 analyzer heated from 30–600 °C under nitrogen.

Single-crystal X-ray diffraction determination

Crystal data[†] for these three complexes were collected on a Bruker SMART APEXII CCD diffractometer with graphite monochromatic Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$) using the SMART and SAINT programs at 298 K, and the structures were solved by the direct method (SHELXS-97) and refined by full-matrix least-squares (SHELXL-97) on F^2 . Anisotropic thermal parameters were used for the non-hydrogen atoms and isotropic parameters for the hydrogen atoms. Hydrogen atoms were added geometrically and refined using a riding model. For **1**, the 'dfix' order was used to constrain the hydrogen atoms of water molecules with bond O–H = 0.85 Å and the bond angle H–O–H = 105°, and the free 4,4'-bpy was also restricted in a disorder model. This is also true for the hydrogen atoms of water molecules of **2** and **3**. Selected bond distances and bond angles with their estimated standard deviations are listed in ESI Table S1.†

Results and discussion

Synthesis of the complexes 1–3

In the present study, complexes **1–3** were prepared from the hydrothermal reaction between corresponding ligands and $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ together with 4,4'-bpy ligand in a molar ratio of 1 : 2 : 2. The reactions between corresponding multicarboxylate ligands and $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ salt without 4,4'-bpy ligand performed at different temperature, giving only some precipitates. However, when the N-donor ligand 4,4'-bpy was introduced, perfect single crystals of complexes were obtained. In detail, the hydrothermal reaction between H_3L^1 and $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ in the presence of 4,4'-bpy leads to the formation of compound **1** at

[†] **Crystallographic data for H_3L^2** : $\text{C}_{15}\text{H}_{10}\text{O}_7$, $M = 302.23$, monoclinic, space group $C2/c$, $a = 25.342(16) \text{ \AA}$, $b = 8.645(5) \text{ \AA}$, $c = 14.204(11) \text{ \AA}$, $\beta = 120.412(19)^\circ$, $V = 2684(3) \text{ \AA}^3$, $Z = 8$, $D_c = 1.496 \text{ g cm}^{-3}$, $\mu = 0.121 \text{ mm}^{-1}$, $F000 = 1248$, $R_1 = 0.0987$, $wR_2 = 0.2792$ ($I > 2\sigma$), $R_1 = 0.1347$, $wR_2 = 0.3021$ (for all). **Crystallographic data for **1****: $\text{C}_{70}\text{H}_{60}\text{N}_8\text{Ni}_3\text{O}_{21}$, $M = 1525.27$, monoclinic, space group $C2/c$, $a = 17.0025(14) \text{ \AA}$, $b = 36.907(3) \text{ \AA}$, $c = 11.2149(10) \text{ \AA}$, $\beta = 94.907(2)^\circ$, $V = 7011.7(10) \text{ \AA}^3$, $Z = 4$, $D_c = 1.445 \text{ g cm}^{-3}$, $\mu = 0.874 \text{ mm}^{-1}$, $F000 = 3072$, $R_1 = 0.0464$, $wR_2 = 0.1252$ ($I > 2\sigma$), $R_1 = 0.0663$, $wR_2 = 0.1356$ (for all). **Crystallographic data for **2****: $\text{C}_{60}\text{H}_{48}\text{N}_6\text{Ni}_3\text{O}_{20}$, $M = 1351.15$, monoclinic, space group Cc , $a = 11.336(3) \text{ \AA}$, $b = 19.518(6) \text{ \AA}$, $c = 27.059(8) \text{ \AA}$, $\beta = 98.092(5)^\circ$, $V = 5928(3) \text{ \AA}^3$, $Z = 4$, $D_c = 1.494 \text{ g cm}^{-3}$, $\mu = 1.023 \text{ mm}^{-1}$, $F000 = 2744$, $R_1 = 0.0768$, $wR_2 = 0.1986$ ($I > 2\sigma$), $R_1 = 0.0904$, $wR_2 = 0.2094$ (for all). **Crystallographic data for **3****: $\text{C}_{70}\text{H}_{58}\text{N}_8\text{Ni}_3\text{O}_{20}$, $M = 1507.31$, monoclinic, space group $P2_1/c$, $a = 9.990(3) \text{ \AA}$, $b = 22.497(7) \text{ \AA}$, $c = 14.764(5) \text{ \AA}$, $\beta = 100.521(5)^\circ$, $V = 3262.1(18) \text{ \AA}^3$, $Z = 2$, $D_c = 1.535 \text{ g cm}^{-3}$, $\mu = 0.942 \text{ mm}^{-1}$, $F000 = 1556$, $R_1 = 0.0621$, $wR_2 = 0.1234$ ($I > 2\sigma$), $R_1 = 0.0919$, $wR_2 = 0.1414$ (for all).

different temperature. In contrast, the same reaction utilizing H_3L^2 instead of H_3L^1 as starting material affords **2** and **3** at 120 and 150 °C, respectively, revealing the effect of reaction temperature on the coordination conformation of the semi-rigid V-shaped ligand of L^2 and therefore tuning the molecular structure of coordination polymers.^{2,9}

IR spectra

The absorption bands in the range of 1605–1608 cm^{-1} in the IR spectra of compounds **1–3** are attributed to the characteristic asymmetric stretching vibration of coordinated carboxylic groups due to the formation of Ni(II)–O coordination bond of carboxylic oxygen atom in these two ligands.

Crystal structure of H_3L^2 ligand

Fig. 1 shows the crystal structure of H_3L^2 . As can be seen, there exists intramolecular hydrogen bonding between the 2-carboxylic groups and the 3-carboxylic with $O(2)–O(6) = 2.615(2)$ Å. In addition, the two planes of aromatic ring linked by the ether oxygen atom are nearly perpendicular with the dihedral angle of $89.01(5)^\circ$, in line with that reported for the complexes constructed from similar symmetric V-shaped ligands, which is formed reasonably to minimize steric barrier effect between the two phenolic rings. It is worth noting that the H_3L^2 ligand adopts a *cis*-type conformation.

Crystal structure of complex **1**

Complex **1** crystallizes in the space group of $C2/c$, which displays a 3D covalent framework structure composed of isolated tubes

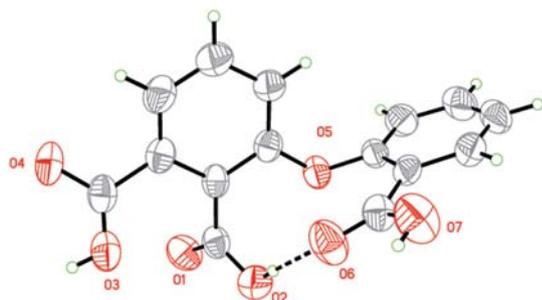


Fig. 1 ORTEP drawing of molecular structure for free H_3L^2 ligand.

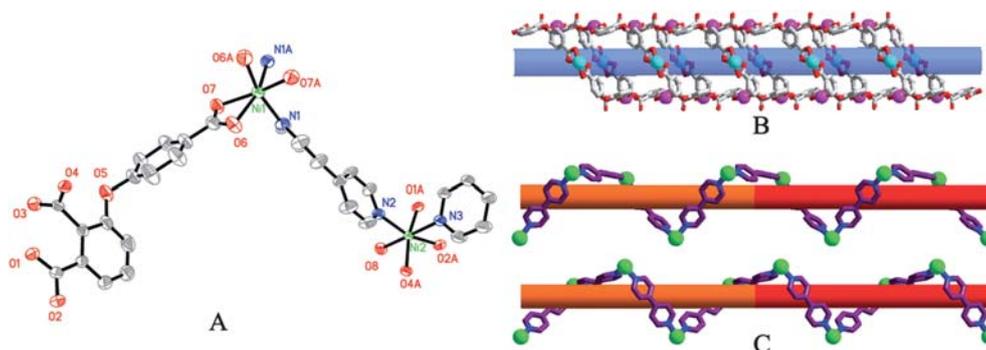


Fig. 2 ORTEP diagram of complex **1** (A), tube-like subunit (B), and left and right helix-like subunit (C top and bottom, respectively).

and helices as subunits, Fig. 2. The asymmetric unit of **1** is composed of one L^1 ligand, one and half coordinated 4,4'-bpy ligands, half uncoordinated 4,4'-bpy ligand, one and half Ni(II) ions, and three water molecules (one coordinated water molecule and two solvent water molecules). Two kinds of crystallographically independent Ni(II) ions both locate in the octahedral coordination geometry formed by four oxygen atoms and two nitrogen atoms of 4,4'-bpy ligands, Fig. 2A. However, the oxygen atoms coordinating to Ni1 ion come from two bidentate chelating carboxyl groups. For Ni2 ion, those coordinated oxygen atoms come from one bidentate chelating carboxyl group, one monodentate binding carboxyl group, and one water molecule. The length of Ni–O bonds is in the range of 2.050(3) to 2.085(4) Å, and the distance of Ni–N bonds spans from 2.031(3) to 2.160(3) Å, which are consistent with those reported for complexes containing N–Ni–O segment.¹⁰

As shown in ESI Fig. S1,† a 50-membered ring is first formed by four Ni(II) ions (two Ni1 and two Ni2 ions) bridged with four L^1 ligands in *cis*-coordination conformation. The remaining four carboxylic groups of these four tricarboxylate ligands bind other four Ni(II) ions in two direction, forming rare discrete metal–organic hybrid tube,¹¹ Fig. 2B and ESI Fig. S2.† In comparison with the helices based on symmetric semi-rigid V-shaped ligand with two or four carboxylic substituents reported previously, the metal–organic hybrid tube might be a necessary product associated with the *cis*-coordination conformation of the three asymmetric coordination substituents of L^1 ligand. In addition, these crystallographically independent Ni(II) ions are also connected by 4,4'-bpy ligands, leading to two kinds of interesting helices, namely left- and right-handed helices, Fig. 2C. To the best of our knowledge, there appear only two examples for helices made of sole 4,4'-bpy ligands reported thus far.¹² From the perspective view, the helix-like subunits construct a beautiful star-like diagram, Fig. 3A. The coordinated and uncoordinated 4,4'-bpy ligands are filled in the cavities of the coordination tube to stabilize the molecular structure of **1**, Fig. 3B. It is worth noting that the formation of discrete tube-like subunit is attributed to the semi-rigid V-shaped nature of L^1 ligand and template function of the secondary ligand.

Crystal structure of complex **2**

Complex **2** crystallizes in the non-centrosymmetric space group Cc and features a complicated 3D covalent framework, Fig. 4.

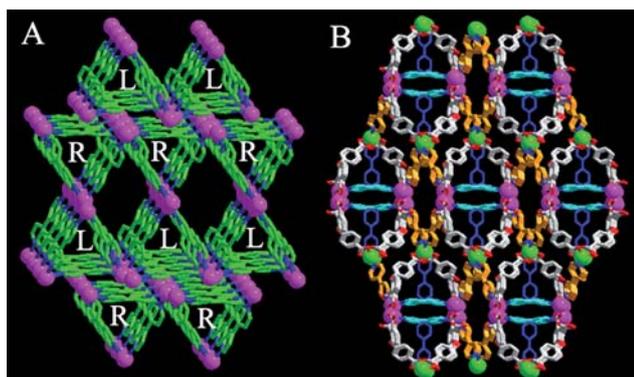


Fig. 3 Perspective diagram of helix subunits (A) and packing drawing of complex **1** along the *c* axis (B), water molecules are omitted for clarity.

This compound contains three crystallographically independent Ni(II) ions, two kinds of L² ligands, and three types of 4,4'-bpy ligands, Fig. 4A. These three kinds of Ni(II) ions all possess octahedral coordination environments completed by four oxygen atoms at equatorial position and two nitrogen atoms of 4,4'-bpy ligands occupying the axis positions. Differently, the oxygen atoms coordinating to Ni1 ion come from one bidentate chelating carboxylic group, one monodentate coordinated carboxylic group, and one water molecule. For Ni2 ion, those coordinated oxygen atoms are from one monodentate carboxylic substituent, two carboxylic groups in *syn-anti* coordination mode, and one etheric oxygen atom. For Ni3 ion, the four oxygen atoms bound to Ni3 are associated with three water molecules and a single carboxylic acid group coordinated in

a *syn-anti* coordination fashion. It is noteworthy that coordination polymers of semi-rigid V-shaped ligands containing metal ion bound by bridged atom between two benzene rings have never been reported, to the best of our knowledge. The length of Ni–O bonds amounts from 1.984(8) to 2.144(9) Å, and the distance of Ni–N bonds spans the range of 2.089(10) to 2.137(9) Å. These bond distances are corresponding with those reported for complexes containing Ni–O and Ni–N bonds.¹⁰ As shown in Fig. 4A, the Ni(II) trimer is formed by three Ni(II) ions (namely Ni1, Ni2 and Ni3 ions) linked by two carboxylic groups in a *syn-anti* coordination mode of one L² ligand exhibiting *cis*-coordination configuration. The distance of Ni1–Ni2 and Ni2–Ni3 bonds is 5.070(8) and 5.167(9) Å, respectively. These trinuclear clusters are further connected by L² ligands in a *trans*-coordination conformation, generating a 1D infinite zigzag chain, Fig. 4B. These zigzag chains are linked by 4,4'-bpy binding to only Ni1 ion, leading to a 2D layered network in *a* × *c* plane, ESI Fig. S3.† In addition, there is a ladder-like subunit composed of 4,4'-bpy ligand linking to Ni2 and Ni3 ions as two rails, with the carboxylic O–C–O group as rungs, ESI Fig. S4.† These 2D layered motifs are further connected by the 4,4'-bpy linkers in ladder-like subunits *via* Ni2 and Ni3 ions as node, giving a complicated 3D framework structure, Fig. 4C.

Crystal structure of complex 3

Complex **3** belongs to the monoclinic system with *P2₁/c* space group, which consists of two kinds of crystallographically different Ni(II) ions. Ni1 ion is six-coordinated with a distorted octahedral geometry formed by a *trans*-position from two

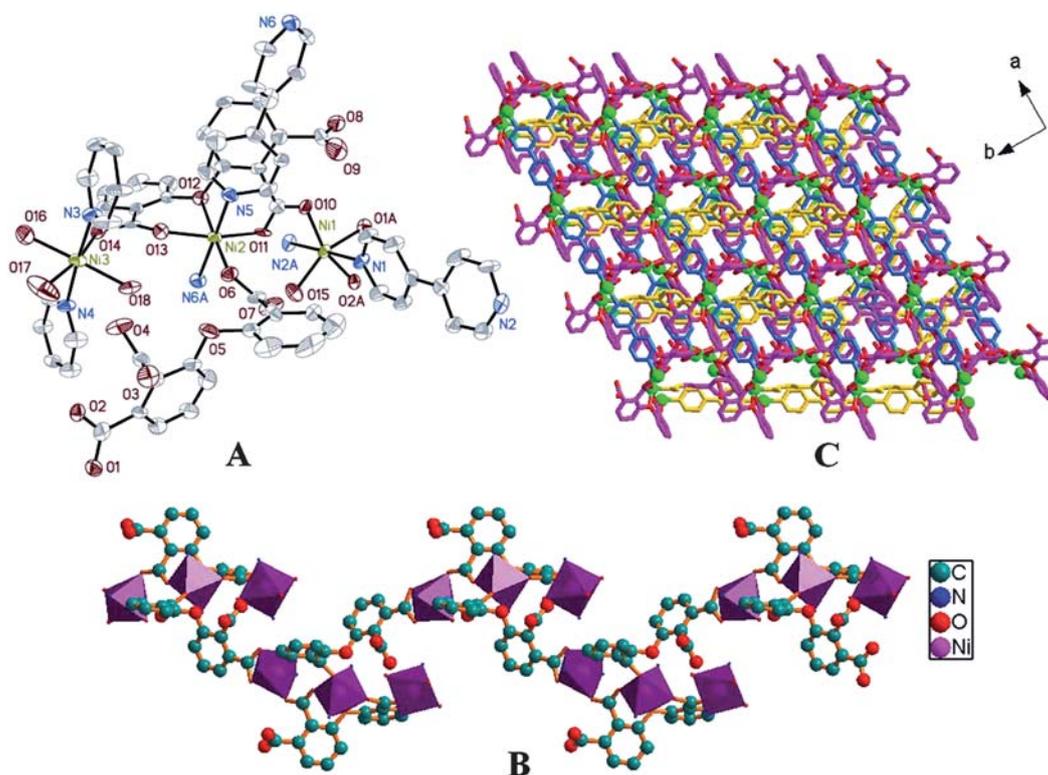


Fig. 4 ORTEP diagram of complex **2** (A), a 1D wavy chain (B), and 3D complicated network in the *a* × *b* plane (C).

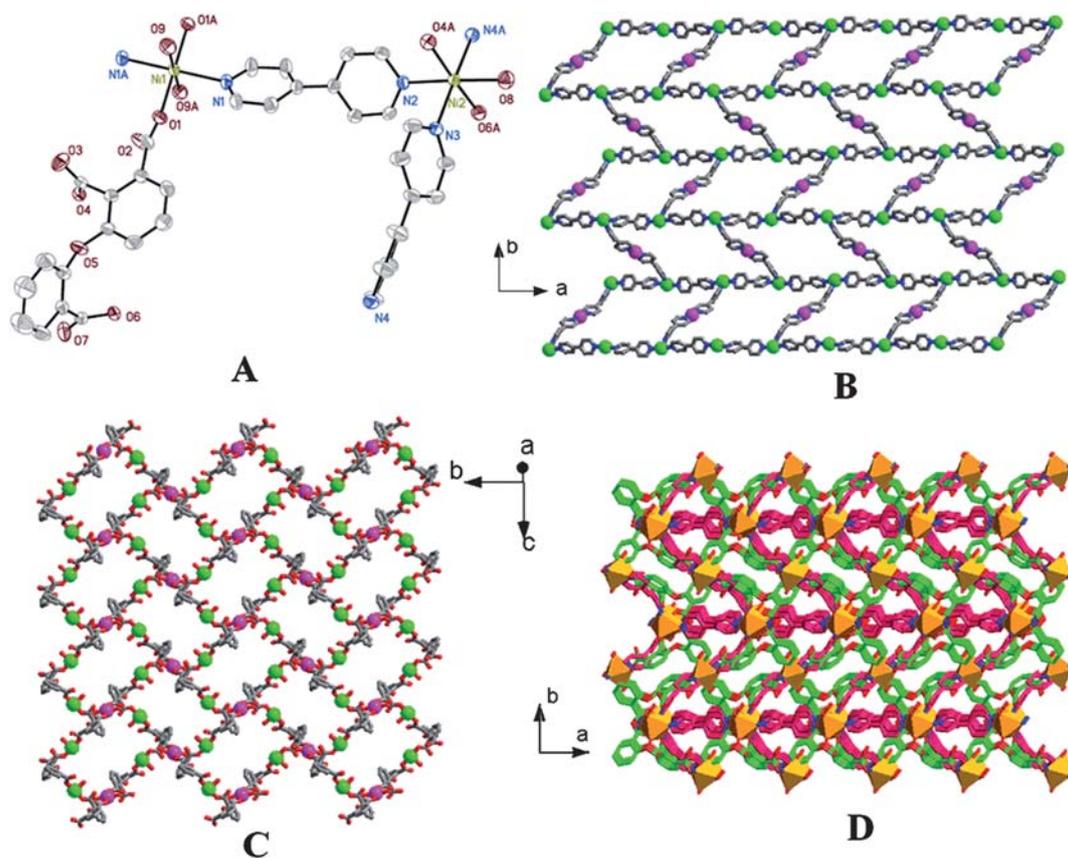


Fig. 5 ORTEP diagram of complex 3 (A), a 2D wavy (6,3) network (B), a herringbone motif (C), and a 3D complicated network in the $a \times b$ plane (D).

oxygen atoms of water molecules, two oxygen atoms of two monodentate coordinated carboxylic groups from different L^2 ligands, and two nitrogen atoms from 4,4'-bpy ligands, Fig. 5A. Ni2 ion possesses a distorted octahedral coordination sphere completed by two oxygen atoms of monodentate carboxylic groups, one oxygen atom from water molecule, and three nitrogen atoms of 4,4'-bpy ligands. Ni1 and Ni2 ions are linked only by 4,4'-bpy ligands, giving a wavy layered network in $a \times b$ plane, Fig. 5B. In case that the Ni1 and Ni2 ions are treated as 3-connected nodes, topological analysis reveals that the wavy layered motif is a (6,3) network. Apart from this linkage by 4,4'-bpy ligand, Ni1 and Ni2 ions are also bridged by L^2 ligands in a *trans*-type coordination conformation, leading to a herringbone motif in the $b \times c$ plane, Fig. 5C. If the L^2 ligand is considered as a 3-connected node, the herringbone motifs are also revealed as a (6,3) network, ESI Fig. S5.† The two different directional networks are compiled by the Ni(II) ions, forming a complicated 3D framework, Fig. 5D.

The coordination modes of multicarboxylate ligands L^1 and L^2

The organic multicarboxylates as important O-donor ligands have been widely employed to assemble MOFs not only due to their diversely coordination modes but also due to their inherent nature of forming supramolecular structure *via* hydrogen bond interactions. As a consequence, it seems necessary to understand and compare the difference of the coordination modes between these two asymmetric semi-rigid V-shaped multicarboxylate

ligands H_3L^1 and H_3L^2 containing 2-, 3-, and 4'-carboxylic groups and 2-, 2', and 3-carboxylic groups, respectively, for the purpose of directional design and synthesis of functional materials with open pores. As can be seen in Fig. 6, there are four types of different coordination modes and two kinds of coordination configurations for these two ligands. For 1, L^1 ligand shows a *cis*-coordination configuration with μ_3 -bridging mode, 2-carboxylic group displays a monodentate coordination mode, 3- and 4'-carboxylic groups exhibit bidentate chelating mode, Fig. 6A. For 2, there are two kinds of binding conformation for L^2 ligand, including a *cis*- and *trans*-typed

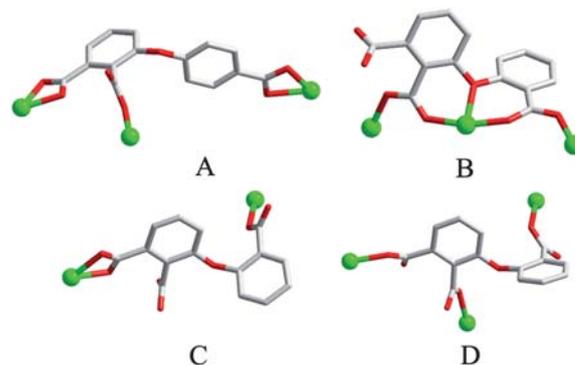


Fig. 6 Coordination modes of semi-rigid asymmetric ligands in complexes 1–3 (A for 1, B and C for 2, and D for 3).

conformation, Fig. 6B and 6C. The L² ligand of **3** displays a *trans*-coordination configuration in a μ₃-bridging mode with each carboxylic group in a monodentate coordination mode, Fig. 6D. In comparison with *trans*-typed mode of semi-rigid V-shaped tricarboxylate ligands in **2** and **3**, the *cis*-coordination configuration supports the formation of 1D metal–organic hybrid tube-like subunit of complex **1** in cooperation with the three asymmetrically attached coordination substituents of L¹ ligand, namely 2-, 3-, and 4'-carboxylic groups. In addition, in comparison with the *cis*-coordination configuration of the free ligand H₃L², Fig. 1, the *trans*-coordination conformation of L² in **2** and **3** is considered as the necessary product since the free rotating benzene rings around the central non-metallic bridged atoms of L² ligand are constrained and locked due to the ligand coordinating to Ni(II) atoms as bridge.¹³ The different conformation of L² ligand in **2** and **3** indicates the dependence of coordination configuration of this asymmetric semi-rigid V-shaped tricarboxylate ligand on the reaction temperature. At the end of this section, it is worth noting that the 4,4'-bpy as the secondary ligand with abundant coordination modes plays an important role in the formation of these coordination polymers **1–3**, which expands the low dimensional subunits into 3D framework structures. In addition, the uncoordinated and coordinated 4,4'-bpy ligands filled in the cavities of the subunits of **1** might function as template to support the formation of the isolated coordination tube-like subunit.¹³

Magnetic properties of complexes **1–3**

The magnetic properties of compounds **1–3** were investigated in the temperature range of 2.0–300.0 K under an outer field of 2000 Oe. As shown in Fig. 7 and ESI Fig. S6,[†] the changing tendency

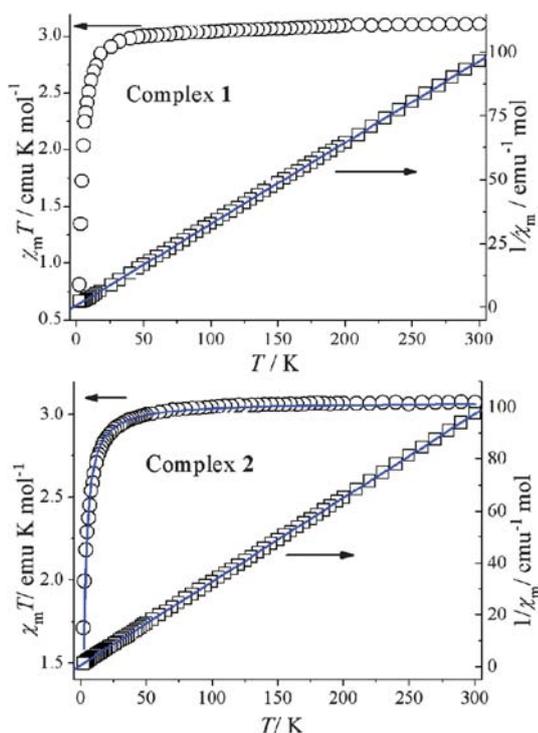


Fig. 7 Temperature dependence of $\chi_m T$ for **1** and **2**. The blue solid lines represent the best fitting in the temperature range of 2–300 K.

for temperature dependence of magnetic susceptibility for these three complexes is similar. As for the room temperature value of $\chi_m T$ 3.108, 3.075, and 3.145 emu K mol⁻¹ for **1–3**, respectively, these values are close to the expected value 3.00 emu K mol⁻¹ (for three isolated spin Ni(II) ions $S = 1$) with $g = 2.0$. When the temperature is lowered, $\chi_m T$ value decreases slowly until about 30 K, then decreasing quickly to 0.815, 1.711, and 1.084 emu K mol⁻¹ at 2 K for **1–3**, respectively. These results reveal the overall antiferromagnetic interaction between neighbouring Ni(II) ions in these two complexes. The magnetic susceptibilities obey Curie–Weiss law in the whole temperature range measured for these two complexes, giving negative Weiss constants $\theta = -1.693$ K and Curie constant $C = 3.135$ emu K mol⁻¹ for **1**, Weiss constants $\theta = -2.015$ K and Curie constant $C = 3.093$ emu K mol⁻¹ for **2** as well as Weiss constants $\theta = -1.248$ K, and Curie constant $C = 3.156$ emu K mol⁻¹ for **3**, confirming again the antiferromagnetic interaction exhibiting in these three complexes. On the basis of the analysis over the crystal structures for **1–3**, the superexchange magnetic coupling through OC–C–C–CO bridge of L¹ ligand in **1** and 4,4'-bpy linker in **3** is responsible for the weak antiferromagnetic interaction between the neighbouring Ni(II) ions.¹³ Compound **2** possesses a discrete trinuclear magnetic topology with neighbouring Ni(II) atoms bridged by the carboxylic O–C–O group in a *syn-anti* mode. The magnetic susceptibilities of **2** can be fitted by the following polynomial expression in eqn (1) deduced from the spin Hamiltonian $\hat{H} = -2J(\hat{S}_1\hat{S}_2 + \hat{S}_2\hat{S}_3)$.¹⁴

$$\chi_m = \frac{Ng^2\beta^2}{\kappa T} \times (28\exp(4J/KT) + 12\exp(-2J/KT) + 2\exp(-6J/KT) + 10\exp(2J/KT) + 2)/(7\exp(4J/KT) + 8\exp(-2J/KT) + 3\exp(-6J/KT) + 5\exp(2J/KT) + \exp(-4J/KT) + 3)$$

The best-fit parameters obtained are $J = -0.56$ cm⁻¹, $g = 2.03$. The magnetic coupling constant J is slightly smaller than that of similar complexes containing same carboxylic bridges linking to metal ions. The negative coupling constant J confirms the weak antiferromagnetic interaction between the neighbouring Ni(II) ions in **2**.¹⁵

Thermal analysis

The thermal behaviour for compounds **1–3** was investigated to reveal their thermal stability. TGA experiments were performed on pure single crystal samples of **1–3** under N₂ atmosphere with a heating rate of 10 °C per minute in the temperature range of 30–600 °C. The thermal curves are exhibited in ESI Fig. S7.[†] The TGA curve of complex **1** indicates that the water molecules are lost firstly followed by uncoordinated 4,4'-bpy ligands in the range of 30–320 °C, obsd 16.24%, calcd 16.51%. For **2**, TGA curve shows that the water molecules are lost in the temperature range of 30–165 °C, obsd 2.72%, calcd 2.70%. For **3**, the TGA curve reveals that the lattice water molecules are lost from room temperature to 205 °C, obsd 6.81%, calcd 7.17%. The residual composition of this complex is then decomposed in the temperature range of 331–519 °C.

Conclusion

In summary, two asymmetric semi-rigid V-shaped multicarboxylate ligands have been utilized for the first time to construct Ni(II) coordination polymers with the help of 4,4'-bpy as the secondary ligand. Structural investigation reveals that the framework structure of coordination polymers could be tuned by changing the positions of carboxylic groups at the V-shaped central molecular framework of asymmetric tricarboxylate ligands as well as reaction temperature. In addition, complex **1** represents the first metal–organic hybrid tube built from an asymmetric semi-rigid V-shaped tricarboxylate ligand. Magnetic studies indicate the overall antiferromagnetic interactions in **1–3**. Further systematic work towards fabricating more MOFs with interesting structures and functionalities using asymmetric ligands is in progress.

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