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Syntheses, characterization, and magnetic properties of novel divalent Co/Ni coordination polymers based on a V-shaped pyridine ligand and dicarboxylate acids

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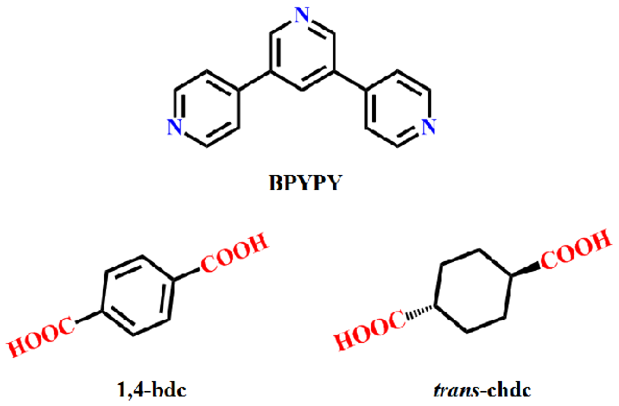
Solvothermal reactions of 3,5-bis(4-pyridyl)-pyridine (BPYPY) with 1,4-benzenedicarboxylate (1,4-bdc) and *trans*-1,4-cyclohexanedicarboxylic acid (*trans*-chdc) in the presence of Co(II) and Ni(II) salts in DMF/H_2O or DMA/CH_3CN/H_2O produced three new compounds, namely, $\{[Co_3(BPYPY)_2(1,4\text{-bdc})_3(H_2O)_6]\}_n$ (**1**), $\{[Ni_3(BPYPY)_2(1,4\text{-bdc})_3(H_2O)_6]\}_n$ (**2**), $\{[Co(BPYPY)(\text{trans-chdc})_{0.5}(NO_3)]\cdot(H_2O)\}_n$ (**3**). These compounds were characterized by elemental analysis, IR spectroscopy, and X-ray single-crystal diffraction. Compounds **1** and **2** are isomorphous and present 3,4-connected 3-fold interpenetrating **tfz** network with a point symbol of $\{6^3\}_2\{6^4\cdot8\cdot10\}_3$. Compound **3** exists binuclear Co clusters which are linked by BPYPY and *trans*-chdc to generate a 4-connected **cds** network with the point symbol of $\{6^5\cdot8\}$ and displays antiferromagnetic character. In addition, the thermal stabilities of these new compounds also have been discussed in detail.

1. Introduction

The design and systhesis of metal-organic frameworks (MOFs) from various molecular building blocks connected by coordination bond, supramolecular contacts, has been of intense interest, because of their intriguing aesthetic structures and topological features,[1] as well as their promising applications such as gas adsorption,[2] catalysis,[3] fluorescence,[4] drug delivery,[5] ion exchange,[6] and molecular magnetism.[7] The use of multidentate organic ligands and suitable metal salts to construct MOFs has been a major strategy of supramolecular chemistry in recent years.[8] And also, a large number of mixed-ligand MOFs have been reported,[9] revealing that the combination of different ligands can result in greater tunability of structural frameworks than single ligands. Therefore, mixed ligands are a good choice for the construction of new polymeric structures.

Herein, two carboxylate ligands, namely, 1,4-benzenedicarboxylate (1,4-bdc) and *trans*-1,4-cyclohexanedicarboxylic acid (*trans*-chdc) (Scheme 1), were used as coligands to react with 3,5-bis(4-pyridyl)-pyridine (BPYPY) and Co(II)/Ni(II) salts. Then, three new compounds were obtained, namely, $\{[Co_3(BPYPY)_2(1,4\text{-bdc})_3(H_2O)_6]\}_n$ (**1**), $\{[Ni_3(BPYPY)_2(1,4\text{-bdc})_3(H_2O)_6]\}_n$ (**2**), $\{[Co(BPYPY)(\textit{trans}\text{-chdc})_{0.5}(NO_3)]\cdot(H_2O)\}_n$ (**3**), and the details of their syntheses, structures, and properties were investigated below.



Scheme 1. Structures of the BPYPY ligand and carboxylic acid ligands in this work.

2. Experimental

2.1 Materials and methods

The reagents and solvents employed were purchased from commercial sources and used without further purification. BPYPY was prepared by literature methods.[10] Powder X-ray diffraction (PXRD) patterns were collected in the $2\theta = 5\text{-}50\ °$ range with a scan speed of 0.2 deg s^{-1} on a Bruker D8 Advance instrument using Mo Kα radiation at room temperature, in which the X-ray tube was operated at 40 kV and 40 mA. Fourier Transform Infrared (FT-IR) spectra of these compounds were obtained on a Bruker Vector 22 FT-IR spectrophotometer by using KBr pellets. Thermogravimetric analyses (TGA) were performed on a Perkin-Elmer thermal analyzer with a heating rate of 20 °C min^{-1} under a nitrogen atmosphere from room temperature to 800 °C. Solid-state UV-vis diffuse reflectance spectra were obtained at room temperature using Shimadzu UV-3600 double monochromator spectrophotometer, and $BaSO_4$ was used as a 100% reflectance standard for all materials. The temperature-dependent magnetic susceptibility was measured on a MPMS XL-7 SQUID magnetometer under an applied field of 2000 Oe over the temperature range of 1.8-300 K.

2.2 Synthesis of $\{[Co_3(BPYPY)_2(1,4\text{-bdc})_3(H_2O)_6]\}_n$ (1)

A mixture of $Co(NO_3)_2{\cdot}6H_2O$ (29 mg, 0.1 mmol), BPYPY (23 mg, 0.1 mmol) and 1,4-bdc (16.6 mg, 0.1 mmol) was dissolved in 5 mL of DMF/H_2O (1:1, v/v). The final mixture was placed in a Parr Teflon-lined stainless steel vessel (15 mL) under autogenous pressure and heated at 90 °C for 3 days. Orange-block crystals were obtained. The yield of the reaction was ca. 74% based on BPYPY ligand. Calcd for $C_{54}H_{46}Co_3N_6O_{18}$: C, 52.10%; H, 3.70%; N, 6.75%. Found: C, 52.07%; H, 3.72%; N, 6.73%. IR (KBr, cm^{-1}): 3362(vs), 3046(s), 2967(m), 2353(w), 1618(s), 1551(vs), 1496(m), 1380(vs), 1222(m), 1161(w), 1094(w), 1009(w), 876(w), 821(w), 796(m), 748(s), 711(w), 644(w), 535(w), 511(w).

2.3 Synthesis of $\{[Ni_3(BPYPY)_2(1,4\text{-bdc})_3(H_2O)_6]\}_n$ (2)

A mixture of $Ni(NO_3)_2{\cdot}6H_2O$ (29 mg, 0.1 mmol), BPYPY (23 mg, 0.1 mmol) and 1,4-bdc (16.6 mg, 0.1 mmol) was dissolved in 5 mL of DMF/H_2O (1:1, v/v). The final mixture was placed in a Parr Teflon-lined stainless steel vessel (15 mL) under autogenous pressure and heated at 90 °C for 3 days. Green-block crystals were obtained. The yield of the reaction was ca. 77% based on BPYPY ligand. Calcd for $C_{54}H_{46}Ni_3N_6O_{18}$: C, 52.13%; H, 3.70%; N, 6.76%. Found: C, 52.11%; H, 3.74%; N, 6.79%. IR (KBr, cm^{-1}): 3375(s), 3077(m), 2973(m), 2359(w), 1630(m), 1557(vs), 1496(m), 1374(vs), 1210(m), 1161(w), 1094(w), 1009(w), 918(w), 888(w), 803(s), 754(s), 705(m), 638(m), 535(m), 512(w).

2.4 Synthesis of {[Co(BPYPY)(*trans*-chdc)$_{0.5}$(NO$_3$)]·(H$_2$O)}$_n$ (3)

A mixture of $Co(NO_3)_2\cdot 6H_2O$ (29 mg, 0.1 mmol), BPYPY (23 mg, 0.1 mmol) and *trans*-chdc (17.2 mg, 0.1 mmol) was dissolved in 5 mL of DMA/CH_3CN/H_2O (1:3:1, v/v/v). The final mixture was placed in a Parr Teflon-lined stainless steel vessel (15 mL) under autogenous pressure and heated at 95 °C for 3 days. Orange-block crystals were obtained. The yield of the reaction was ca. 67% based on BPYPY ligand. Calcd for $C_{19}H_{18}CoN_4O_6$: C, 49.86%; H, 3.94%; N, 12.25%. Found: C, 49.87%; H, 3.92%; N, 12.23%. IR (KBr, cm^{-1}): 3411(vs), 3064(w), 2931(w), 2845(w), 1612(vs), 1453(m), 1423(s), 1399(s), 1301(m), 1222(w), 1174(w), 1070(w), 1021(w), 827(m), 711(w), 638(m), 547(m).

3. X-ray crystallography

Crystallographic data of **1-3** were collected on a Bruker Smart Apex CCD diffractometer with graphite monochromated Mo Kα radiation (λ = 0.71073 Å) using the ω-scan technique. The linear absorption coefficients, scattering factors for the atoms, and the anomalous dispersion corrections were referred to from the International Tables for X-ray Crystallography. Semiempirical absorption correction was carried by using the SADABS program.[11] The structures were solved by direct methods, and all non-hydrogen atoms were refined anisotropically on F^2 by the full-matrix least-squares technique using the SHELXL-97 crystallographic software.[12] The hydrogen atom positions were fixed geometrically at calculated distances and allowed to ride on the parent atoms. The relevant crystallographic data are presented in Table 1, while the selected bond lengths and angles are given in Table S1-S3 in the Supporting Information. The topological analysis and some diagrams were produced using the TOPOS program.[13]

4. Results and discussion

4.1 Crystal structures

4.1.1 $\{[Co_3(BPYPY)_2(1,4\text{-bdc})_3(H_2O)_6]\}_n$ (1) and $\{[Ni_3(BPYPY)_2(1,4\text{-bdc})_3(H_2O)_6]\}_n$ (2). Single-crystal structure analysis reveals that **1** and **2** are isomorphous and crystallize in the monoclinic crystal system with $P2_1/c$ space group. Hence, only the structure of **1** is described in detail and the structure of compound **2** can be found in the Supporting Information (Fig. S5). The asymmetric unit of **1** contains one and a half Co atoms, one BPYPY ligand, one and a half 1,4-bdc ligands and three coordinated water molecules. The Co(II) sites in distorted octahedral geometry, defined by two nitrogen atoms and four oxygen atoms. The axial positions are occupied by two nitrogen atoms from two BPYPY ligands while the equatorial plane consists of four oxygen atoms from two coordinated water molecules and two 1,4-bdc ligands (Fig. 1a). The Co-O bond distances vary in the range of 2.0163(14)-2.1475(14) Å, and the Co-N bond distances are 2.1442(17) and 2.1648(17) Å, which are all similar to those found in other Co(II) compounds.[14] The pyridine groups of BPYPY ligand link Co atoms to form 2D wave-like layers, and the carboxylate groups of 1,4-bdc ligands link these 2D layers with vertical direction to form a 3D network (Fig. 1b). Better insight into the complicated 3D architecture can be achieved by topology analysis, so the resulting structure can be reduced to a 3,4-connected 3-fold interpenetrating **tfz** net with a point symbol of $\{6^3\}_2\{6^4\cdot 8\cdot 10\}_3$ by simplifying the BPYPY and 1,4-bdc as linkers. In order to minimize the large voids in the single net, three equivalent nets adopt 3-fold interpenetration (Fig.1c).

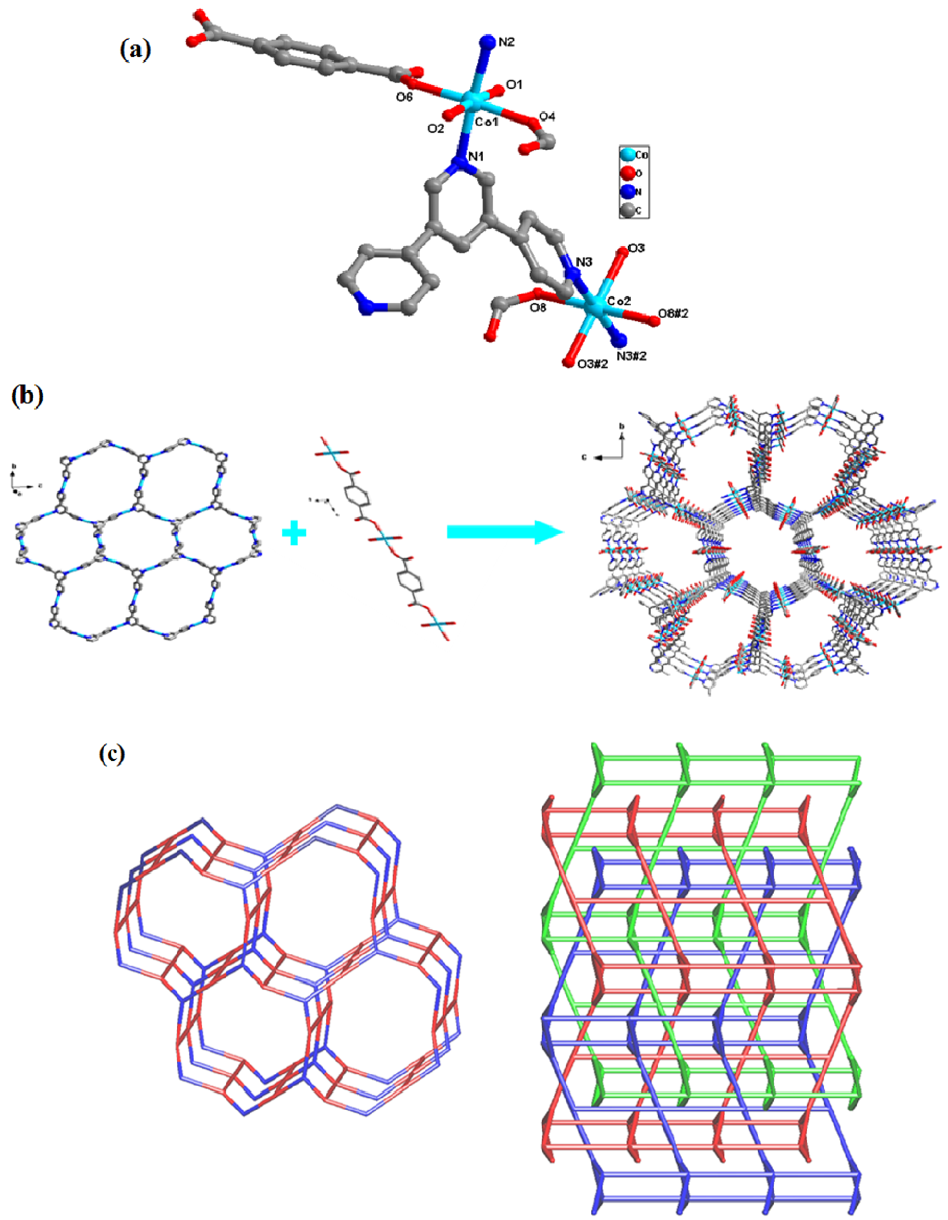


Fig. 1 (a) Coordination environment of the Co(II) cation in **1**. The hydrogen atoms are omitted for clarity. Symmetry codes: #1 = $-x+2, -y+2, -z$. (b) Left: a 2D wave-like layer formed by Co(II) atoms and BPYPY ligands. Middle: an infinite 1D linear chain constructed from 1,4-bdc ligands and Co(II) atoms. Right: 3D network of **1**. (c) Left: schematic representation of **tfz** topology of **1**. Right: 3-fold interpenetrating 3D framework of **1**.

4.1.2 {[Co(BPYPY)(*trans*-chdc)$_{0.5}$(NO$_3$)]·(H$_2$O)}$_n$ (3). Single crystal X-ray diffraction analysis reveals that the compound **3** is a 3D supramolecular structure and crystallizes in the monoclinic crystal system with *C*2/*c* space group. The asymmetric unit contains one Co atom, one BPYPY ligand, half a *trans*-chdc ligand, one coordinated nitrate anion and one lattice water molecule. The coordination environment around the Co(II) cation is exhibited in Fig. 2a. Each Co(II) is coordinated by four oxygen atoms from two *trans*-chdc ligands and one nitrate anion in a flat position, and two nitrogen atoms from two BPYPY ligands in the axial direction plane, which forms a distorted octahedral coordination mode. The Co-N bond distances are 2.143(3) and 2.155(4) Å, and the Co-O bond distances vary in the range of 1.991(3)-2.273(4) Å; the N-Co-O angles are from 84.80(14)° to 96.75(15)°, and the O-Co-O angles are in the range of 57.19(13)-147.63(13)°. These are similar to values found in other Co(II) compounds.[15] Two crystallographically equivalent Co(II) cations are bridged by two carboxylate groups adopting a bis-bidentate coordination mode to generate a dinuclear Co(II) secondary building unit (SBU) with a Co···Co distance of 4.0147 Å. Each $[Co_2(CO_2)_2]$ SBU bridges *trans*-chdc ligands to yield one infinite 1D chain. And, the other infinite 1D linear chain was generated by BPYPY ligands and the $[Co_2(CO_2)_2]$ SBUs. Due to the two *trans*-chdc ligands are not in the same plane and the stretching direction of BPYPY ligands are decided by $[Co_2(CO_2)_2]$ SBU, so there is no obvious layer in the whole structure. Actually, two *trans*-chdc ligands in a diagonal position of the $[Co_2(CO_2)_2]$ SBU connect upward and downward SBU respectively to form a chain structure, then those chains combine with the BPYPY ligands from vertical direction to construct 3D framework (Figs. 2b, 2c). In addition, there exist weak π···π stacking interactions (centroid-to-centroid distance of 3.7621(8) and 3.9345(8) Å) among adjacent pyridine cycles of BPYPY ligands (Fig. S6), which further stabilize the 3D network. It can be regarded the binuclear cobalt as a network node, and each node connects to four adjacent ones. Thus, the 3D coordination polymer lattice for compound **3** can be characterized as a 4-connected **cds** network with the point symbol of $\{6^5\cdot 8\}$ (Fig. 2d).

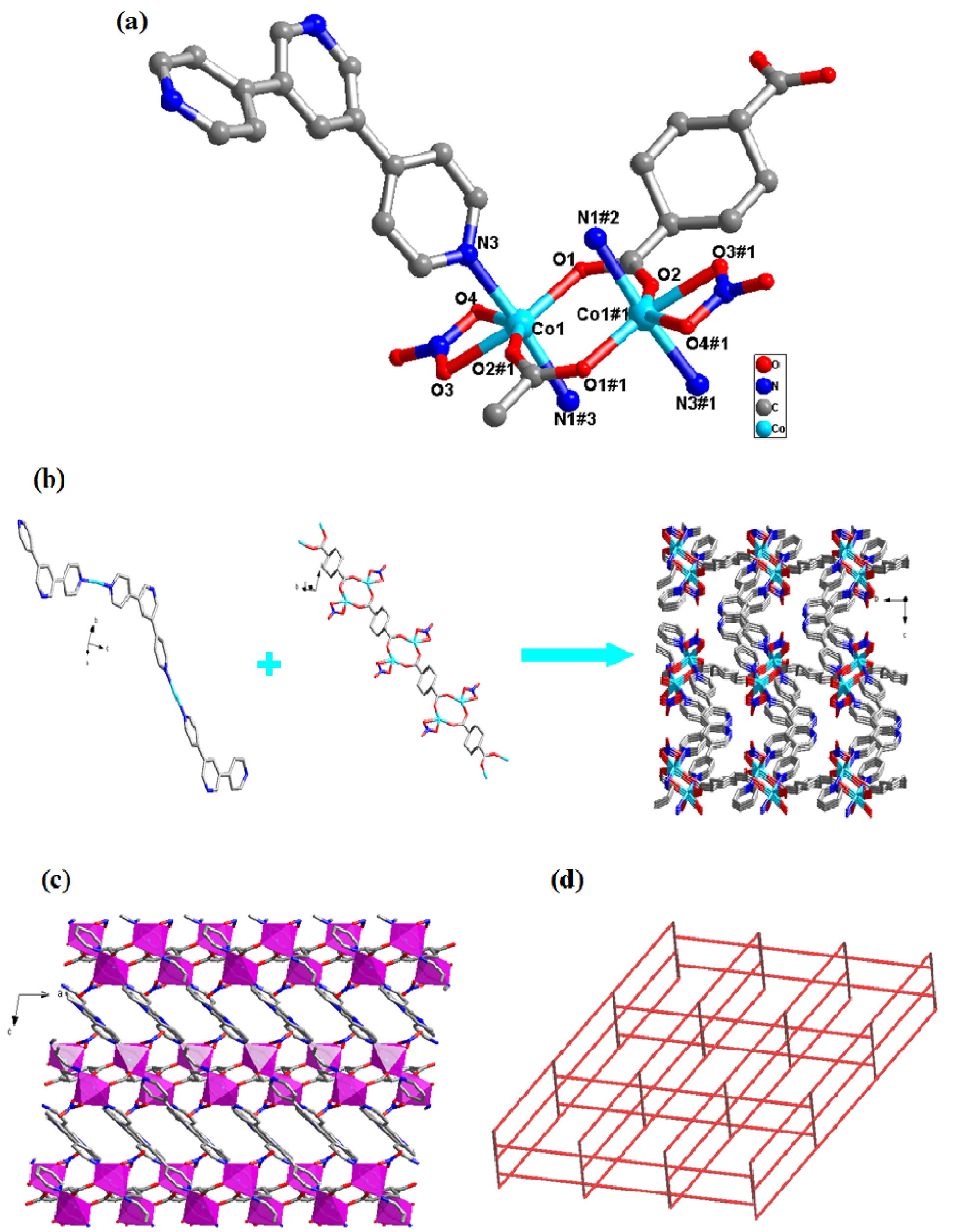


Fig. 2 (a) Views of the coordination mode for the dinuclear Co(II) in **3**. The hydrogen atoms are omitted for clarity. Symmetry codes: #1 = $-x+1$, $-y+2$, $-z+1$; #2 = $2-x$, y, $3/2-z$; #3 = $x-1$, $-y+2$, $z-1/2$. (b) Left: a 1D chain formed by Co(II) atoms and BPYPY ligands. Middle: an infinite 1D chain constructed from [$Co_2(CO_2)_2$] SBU and *trans*-chdc ligands. Right: 3D network of **3** from *a* axis. (c) View of the 3D framework from *b* axis. (d) Schematic representation of a 4-connected **cds** network of **3**.

4.2 X-ray powder diffraction results

From the PXRD patterns of compounds **1-3** (Supporting Information, Fig. S2-S4), the peak positions are in good agreement with their simulated ones, which indicates that the products have been successfully obtained as pure crystalline phases.

4.3 UV-visible spectra

The UV-vis absorption spectra of BPYPY, 1,4-bdc, *trans*-chdc and compounds **1-3** were carried out in the crystalline state at room temperature (Fig. 3). Compounds **1-3** show intensive bands in the UV range with a narrow absorption band in the range 200-330 nm, all of these peaks are due to the intraligand charge transfer transitions. In addition, for compounds **1** and **3**, we observe three additional peaks at 475 nm $[^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)]$ with a peak at 540 nm $[^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)]$ and 675 nm assigned to the $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$. Besides, two additional peaks are also observed for Ni(II) compound. The second peak centers at 350 nm $[^3T_{1g}(P) \rightarrow {}^3A_{2g}]$, and the third sites in 610 nm $[^3T_{1g}(F) \rightarrow {}^3A_{2g}]$, which is typical for octahedrally coordinated Ni(II) compounds.[16]

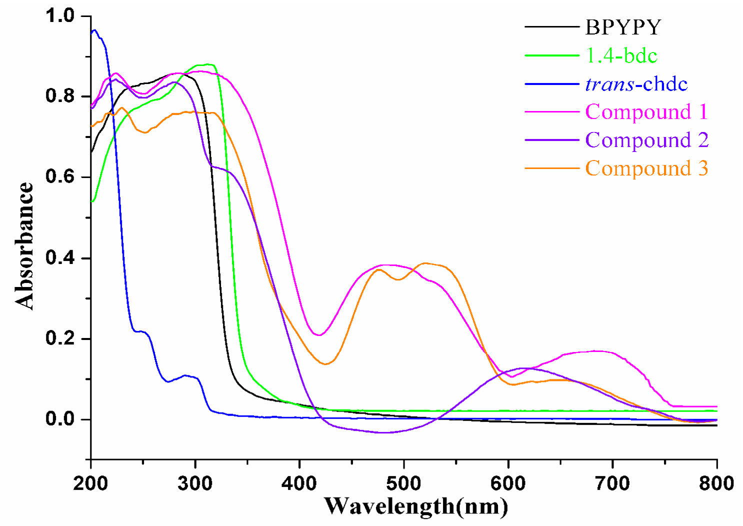


Fig. 3 UV-vis absorbance spectra.

4.4 Thermogravimetric analyses

To characterize the compounds more fully in terms of thermal stability, their thermal behaviors were studied by TGA (Fig. 4). For compound **1**, a weight loss of 8.57% from ambient temperature to 175 °C corresponds to the loss of six coordinated water molecules (calcd 8.68%). Then the TGA curve presents a platform and the framework starts to decompose at 335 °C. The TGA curve of compound **2** indicates that there is an initial weight loss of approximate 8.55% between 20 and 175 °C, corresponding to the loss of six coordinated water molecules (calcd 8.69%), and the framework collapses at 440 °C. In the case of compound **3**, a little weight loss is observed from ambient temperature to 160 °C due to the release of one lattice water molecule, with a weight loss of 3.26% (calcd 3.94%), furthermore, the decomposition of **3** occurs after 340 °C.

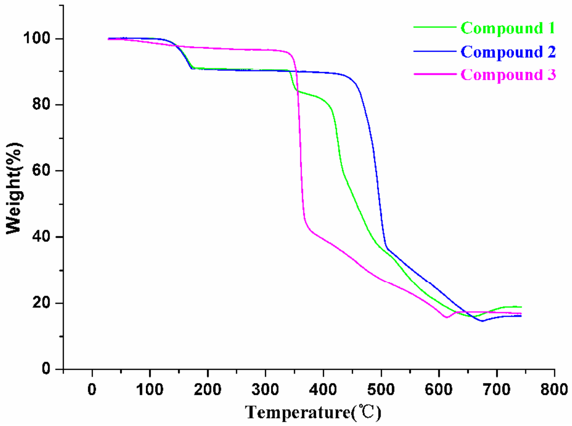


Fig. 4 The TGA curves of **1**-**3**.

4.5 Magnetic properties

The magnetic measurements were performed on polycrystalline samples of **3** using a SQUID magnetometer under an applied field of 2000 Oe over the temperature range of 1.8-300 K. The temperature dependence of magnetic susceptibility of **3** in the forms of $\chi_M T$ and χ_M versus T is displayed in Fig. 5, the experimental $\chi_M T$ value equal to 5.41 cm^3 K mol^{-1} at 300 K is greater than the expected value of 3.75 cm^3 K mol^{-1} for two isolated high-spin Co(II) ions (g = 2 and S = 3/2) per formula because of the prominent orbital contribution arising from the ${}^4T_{1g}$ ground state of Co(II).[17] Upon cooling, $\chi_M T$ continuously decreases and reaches 1.23 $cm^3\ K\ mol^{-1}$ at 1.8 K, possibly due to weak antiferromagnetic interactions and/or spin-orbital coupling.

The $1/\chi_M$ versus T plot in the temperature range from 1.8 to 300 K can be fitted by the Curie-Weiss law $\chi_M = C/(T-\theta)$, giving a Curie constant C = 5.5252 $cm^3\ K\ mol^{-1}$ and Weiss constant $\theta = -\ 9.1412$ K, which further confirms an overall antiferromagnetic interactions between the Co(II) ions (Fig. 5). Although this is observed at very low temperatures, where some anisotropy may be significant, Co(II) is expected to be Heisenberg-like in its magnetic behavior. The magnetic susceptibility data were fitted assuming that the carboxylate and oxygen bridges of the Co(II) ions form an isolated spin dimer system. The intermolecular magnetic coupling constants zj' were taken into account, and the magnetic susceptibility from 1.8 to 300 K was fitted with eq 1, which is deduced from the spin Hamiltonian, $H = -2JS_1S_2$:[18]

$$\hat{H} = -2J\hat{S}_1\hat{S}_2 = -J(\hat{S}_T^2 - \sum_{i=1}^{2}\hat{S}^2)$$

$$E(S_T) = -JS_T(S_T+1)$$

$$S_T = 0, 1, 2, 3$$

$$E(S_T) = 0, -2J, -6J, -12J$$

$$\chi_M = \frac{Ng^2\beta^2}{3kT} \times \frac{84e^{12J/kT} + 30e^{6J/kT} + 6e^{2J/kT}}{7e^{12J/kT} + 5e^{6J/kT} + 3e^{2J/kT} + 1}$$
$$= \frac{2Ng^2\beta^2}{kT} \times \frac{14e^{12J/kT} + 5e^{6J/kT} + e^{2J/kT}}{7e^{12J/kT} + 5e^{6J/kT} + 3e^{2J/kT} + 1} \quad (1)$$

An excellent fit was obtained with $J = -0.41\ cm^{-1}$, $zj' = -0.06\ cm^{-1}$, and $g = 2.02$ with an agreement factor $R = 8.5 \times 10^{-5}$. This result also indicates antiferromagnetic coupling between two Co(II) centers.

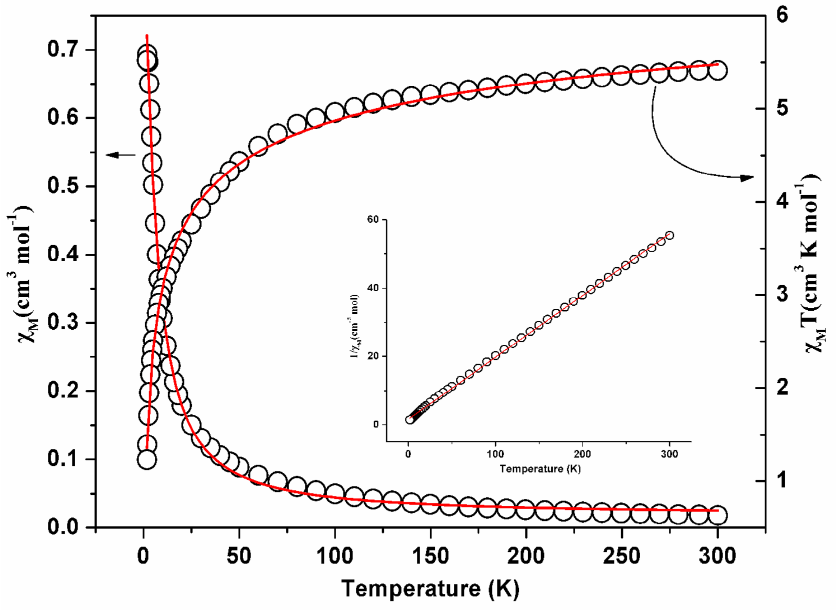


Fig. 5 (a) Experimental magnetic data plotted as χ_M and $\chi_M T$ versus T for **3**; (b) the inset showing $1/\chi_M$ versus T. The solid line results from a least-squares fit of the data to the theoretical equations.

5. Conclusions

In summary, three new compounds have been synthesized via the self-assembly of BPYPY, 1,4-bdc, and *trans*-1,4-cyclohexanedicarboxylic acid ligands under solvothermal conditions. All of these compounds get the 3D supramolecular structures through interligand interactions. The results show that those carboxylic acid ligands can take different conformations to meet the coordination nature of the metal cations. In addition, magnetism study of compound **3** indicates that there are antiferromagnetic interactions between Co(II) atoms in this systems.

Supplementary information

PXRD, IR, the selected bond lengths and angles. CCDC: 1401544-1401546 for **1-3**. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/

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Acknowledgements

This work was supported by grants from the Natural Science Foundation of China (Nos. 21371092, 91022011) and National Basic Research Program of China (2010CB923303).

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Table 1 Crystallographic data for compounds **1-3**.

	1	**2**	**3**
Formula	$C_{54}H_{46}Co_3N_6O_{18}$	$C_{54}H_{46}N_6Ni_3O_{18}$	$C_{19}H_{18}CoN_4O_6$
F_w	1243.76	1243.10	457.3
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	$C2/c$
a/Å	11.2930(14)	11.2710(18)	10.895(3)
b/Å	12.7554(15)	12.618(2)	17.520(4)
c/Å	19.524(2)	19.339(3)	20.545(6)
α/°	90	90	90
β/°	90.010	90.010	99.160
γ/°	90	90	90
V/Å^3	2812.4(6)	2750.3(8)	3871.8(17)
Z	2	2	8
D_c/g cm^{-3}	1.469	1.501	1.569
F(000)	1274	1280	1880
R(int)	0.0395	0.0262	0.0737
GOF on F^2	1.033	1.036	1.027
$R_1[I>2\sigma(I)]$	0.0366	0.0508	0.0503
wR_2 (all data)	0.0999	0.1402	0.1446

Graphical Abstract

Syntheses, characterization, and magnetic properties of novel divalent Co/Ni coordination polymers based on a V-shaped pyridine ligand and dicarboxylate acids

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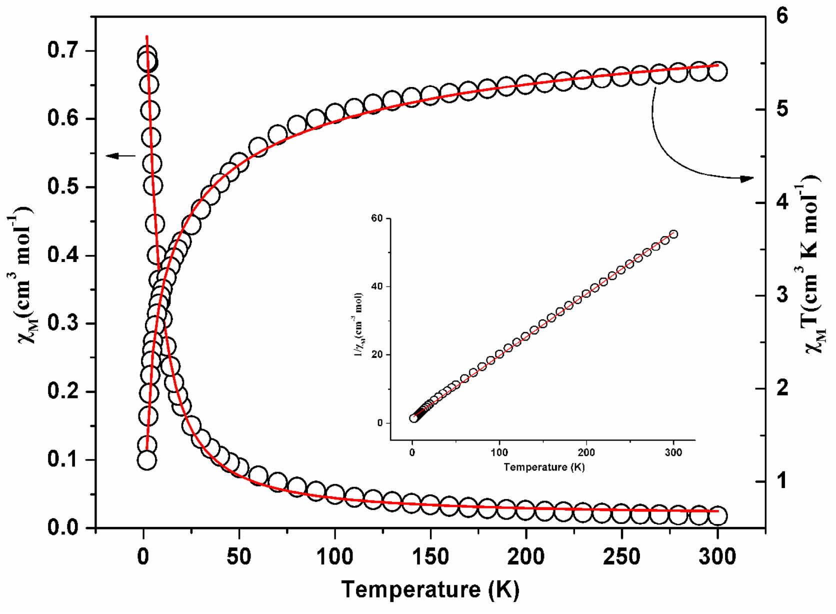

Syntheses, structures, and properties of compounds **1-3** were investigated in details. In addition, magnetism study of compound **3** indicates that there are antiferromagnetic interactions between Co atoms.