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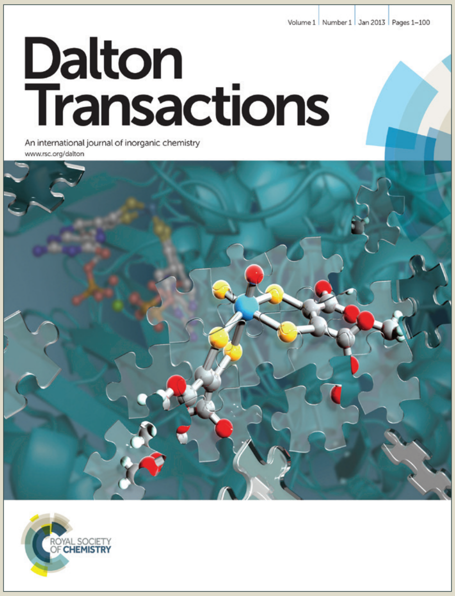

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Coligand-directed synthesis of five Co(II)/Ni(II) coordination polymers with neutral tetradentate ligand: syntheses, crystal structures, and properties†

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Dedicated to Professor Xin-Quan Xin on the occasion of his 80th birthday

The solvothermal reactions of 1,1'-oxybis[3,5-di-4-pyridine]-benzene (L) and transition metal cations (Co, Ni) afford five novel coordination polymers in the presence of flexible bridging ligands (4,4'-H_2nba = 4, 4'-dicarboxydiphenylamine, H_2cam = D-camphoric acid, 4,4'-H_2sdb = 4,4'-sulfonyldibenzoic acid, H_2chdc = 1,4-trans-cyclohexanedicarboxylic acid, namely, $\{[Co_2L_2(OH)_2(nba)]\cdot 2DMF\}_n$ (**1**), $\{[CoL(cam)(H_2O)]\}_n$ (**2**), $\{[Co_3(L)(4,4'\text{-sdb})_3(H_2O)]\cdot 1.5CH_3CN\cdot 4H_2O\}_n$ (**3**), $\{[Ni_3(L)(4,4'\text{-sdb})_3(H_2O)]\cdot 1.5CH_3CN\cdot 4H_2O\}_n$ (**4**), and $\{[Ni_2L_2(chdc)_2(H_2O)_2]\cdot(H_2O)_3\}_n$ (**5**) (DMF = N,N-dimethylformamide). Their structures have been determined by single-crystal X-ray diffraction analyses and further characterized by elemental analyses, IR spectra, and powder X-ray diffraction. Complex **1** reveals a 2-fold interpenetrating three-dimensional (3D) framework with the Schläfli symbol $\{4.8.10^4\}\{4.8.10\}$ topology. Compound **2** crystallizes in the achiral space group with D-camphorate ligand racemized. Compounds **3** and **4** reveal similar structure with $\{3.4^4.6\}\{3^2.4^8.5^9.6^9\}$ topology based on linear trinuclear building block $M_3(OOCR)_6$ (M = Co(II) or Ni(II)). Compound **5** is a wavy sheet, where both carboxylate and L ligands act as bidentate ligands. Moreover, UV-Visible

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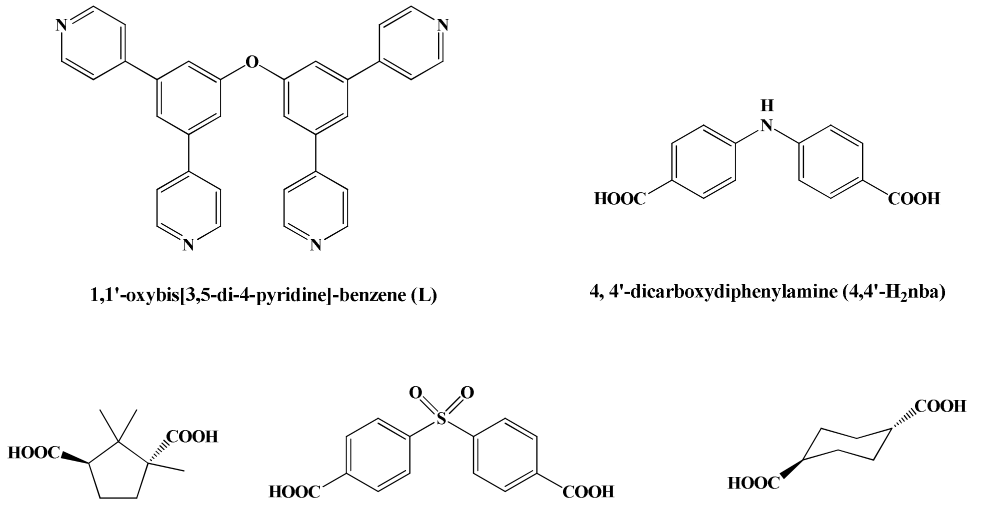
† Electronic supplementary information (ESI) available: IR, PXRD, Uv-vis, the selected bond lengths and angles. CCDC: 1002453 for **2**, 1002454 for **1**, 1002455 for **5**, 1002456 for **4**, 1002457 for **3**. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/

absorption spectra of complexes **1**-**3**, **5** and the magnetic properties for **3** have been investigated.

Introduction

The design and synthesis of coordination polymers (CPs) have attracted increasing interest not only because of their appealing structural and topological novelty but also owing to their tremendous potential applications as functional materials such as nonlinear optics,[1] molecular magnetism,[2] gas storage,[3] drug delivery,[4] ferroelectricity,[5] sensor,[6] and catalysis[7]. Generally, the structural diversity of such crystalline materials is dependent on many factors, such as metal ion,[8] templating agents,[9] temperature,[10] solvent,[11] counteranion[12] and organic ligands[13]. Among the strategies, the rational selection of organic ligands or coligands according to their length, rigidity, space and functional groups is important for the assembly of structural controllable coordinated polymers, based on this strategy, many significant works have been done.[14]

Recently, we reported a neutral tetradentate non-rigid ligand, 1,1'-oxybis[3,5-di-4-pyridine]-benzene (L) (Scheme 1).[15] By introduction of different co-ligands, 4, 4'-dicarboxydiphenylamine (H_2nba)[16], D-camphoric acid (H_2cam),[17] 4,4'-sulfonyldibenzoic acid (4,4'-H_2sdb),[18] *trans*-1,4-cyclohexanedicarboxylic acid (*trans*-H_2chdc)[19], a remarkable range of materials containing various architectures can be prepared, that is $\{[Co_2L_2(OH)_2(nba)]\cdot 2DMF\}_n$ (**1**), $\{[CoL(cam)(H_2O)]\}_n$ (**2**), $\{[Co_3(L)(4,4'\text{-sdb})_3(H_2O)]\cdot 1.5CH_3CN\cdot 4H_2O\}_n$ (**3**), $\{[Ni_3(L)(4,4'\text{-sdb})_3(H_2O)]\cdot 1.5CH_3CN\cdot 4H_2O\}_n$ (**4**), and $\{[Ni_2L_2(chdc)_2(H_2O)_2]\cdot (H_2O)_3\}_n$ (**5**). These compounds were synthesized under the same hydrothermal conditions. The coligand-directed synthesis has a great effect on the final structures.



1,1'-oxybis[3,5-di-4-pyridine]-benzene (L)

4, 4'-dicarboxydiphenylamine (4,4'-H_2nba)

D-camphoric acid (H_2cam)

4,4'-sulfonyldibenzoate (4,4'-H_2sdb)

trans-1,4-cyclohexanedicarboxylic acid (H_2chdc)

Scheme 1. Neutral tetradentate N-containing ligand and carboxylate co-ligands

Experimental section

Materials and measurements. Reagents and solvents employed were commercially available. L ligand was prepared by the literature methods. IR spectra of the compounds were recorded in the range of 400–4000 cm^{-1} on a Nicolet (Impact 410) spectrometer with KBr pellets. C, H and N analyses were carried out with a Perkin Elmer 240C elemental analyzer. Powder X-ray diffraction (PXRD) measurements were performed on a Bruker D8 Advance X-ray diffractometer using Mo-K_α radiation (λ = 0.71073 Å), in which the X-ray tube was operated at 40 kV and 40 mA. 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. Temperature dependent magnetic susceptibility data for polycrystalline complexes **3** was obtained on a SQUID magnetometer under an applied field of 2000 Oe over the temperature range of 1.8-300 K.

Synthetic procedure: Compounds **1-5** can be synthesized by a general step: a mixture of metal nitrate, L and dicarboxylic acid was dissolved in a DMF-H_2O-CH_3CN mixed solvent. The final mixture was placed in a Parr Teflon-lined stainless steel vessel (25 mL) under autogenous pressure and heated at 95°C for 3 days. The detailed information of synthesis and the main features are displayed in Table 1.

Table 1 Detailed synthesis information of compounds **1-5**.

Compound	Raw material	The amount (mmol)	Yield(%)	calcd.EA(%); Found(%)	Color
1	$Co(NO_3)_2 \cdot 6H_2O$+L+H_2nba	2-2-1	56	$C_{78}H_{55}Co_2N_9O_8(2C_3H_7NO)$ C 66.80, H 4.60, N 10.20; C 66.78, H 4.58, N 10.16	purple
2	$Co(NO_3)_2 \cdot 6H_2O$+L+ H_2cam	2-2-1	55	$C_{42}H_{38}CoN_4O_6$ C 66.93, H 5.08, N 7.43; C 66.96, H 5.06, N 7.45	pink
3	$Co(NO_3)_2 \cdot 6H_2O$ +L+ H_2sdb	2-2-1	70	$C_{74}H_{48}Co_3N_4O_{20}S_3(1.5CH_3CN, 4H_2O)$ C 53.78, H 3.55, N 4.48; C 53.82, H3.52, N 4.51	red
4	$Ni(NO_3)_2 \cdot 6H_2O$ + L+ H_2sdb	2-2-1	30	$C_{154}H_{105}N_{11}Ni_6O_{40}S_6(8H_2O)$ C 53.80, H 3.55, N 4.48; C 53.85, H 3.51, N 4.51	green
5	$Ni(NO_3)_2 \cdot 6H_2O$ + L+ H_2chdc	2-2-1	55	$C_{80}H_{74}N_8Ni_2O_{15}$ C 63.85, H 4.96, N 7.45; C 63.82, H 4.98, N 7.48	green

X-Ray crystallography. Single crystals of **1 - 5** were prepared by the methods described in the synthetic procedures. X-Ray crystallographic data of these compound **1 - 5** were collected on a Bruker Apex Smart CCD diffractometer with graphite-monochromated Mo K_α radiation (λ = 0.71073 Å). Structure solutions were solved by direct methods and the non-hydrogen atoms were located from the trial structure and then refined anisotropically with *SHELXTL* using full-matrix least-squares procedures based on F^2 values. A semiempirical absorption correction was applied using SADABS.[20]The hydrogen atom positions were fixed geometrically at calculated distances and allowed to ride on the parent atoms. The distributions of peaks in the channels of **1**, **3**, and **4** were chemically featureless to refine using conventional discrete-atom models. To resolve these issues, the contribution of the electron density by the remaining solvent molecule was removed by the SQUEEZE routine in PLATON.[21] The relevant crystallographic data are presented in Table 2, while the selected bond lengths and angles are given in the Supporting Information (Table S1). CCDC: 1002453 for **2**, 1002454 for **1**, 1002455 for **5**, 1002456 for **4**, 1002457 for **3**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Results and discussion

Crystal structure $\{[Co_2L_2(OH)_2(nba)]\cdot 2DMF\}_n$ (1). Compound **1** crystallizes in the tetragonal crystal system in the space group $I4_1/acd$ (no. 142). The asymmetric unit consists of two L ligands, one nba^{2-} ligand, two OH^- anions. Each Co (II) ion exhibits a distorted octahedral configuration coordinated by two oxygen atoms from one chelating carboxylate group, three nitrogen atoms from L ligand and one OH^- anion (Fig.1a). Both Co-O (2.046(2)-2.162(2) Å) and Co-N (2.109(2)-2.219(2) Å) bond lengths are in the normal range reported for cobalt complexes.[22]

Each L ligand links three Co(II) ions resulting in a 2D layer as shown in Fig.1b, the fourth pyridine groups does not involve in coordination. The nba^{2-} ligands connect the 2D layers to form a three dimensional net (Fig.1c). A better insight into the nature of this intricate framework is provided by a TOPOS analysis software,[23] reducing multidimensional structures to simple nodes and connection nets. The L ligands and metal cations can be regarded as a 3 and 4-connected node, respectively. Therefore, the whole structure can be represented as a 3, 4 -connected topology net with the Schläfli symbol $\{4.8.10^4\}\{4.8.10\}$ (Fig. 1d). The nets are mutually interpenetration to generate the 2-fold interpenetration (Fig. 1e).

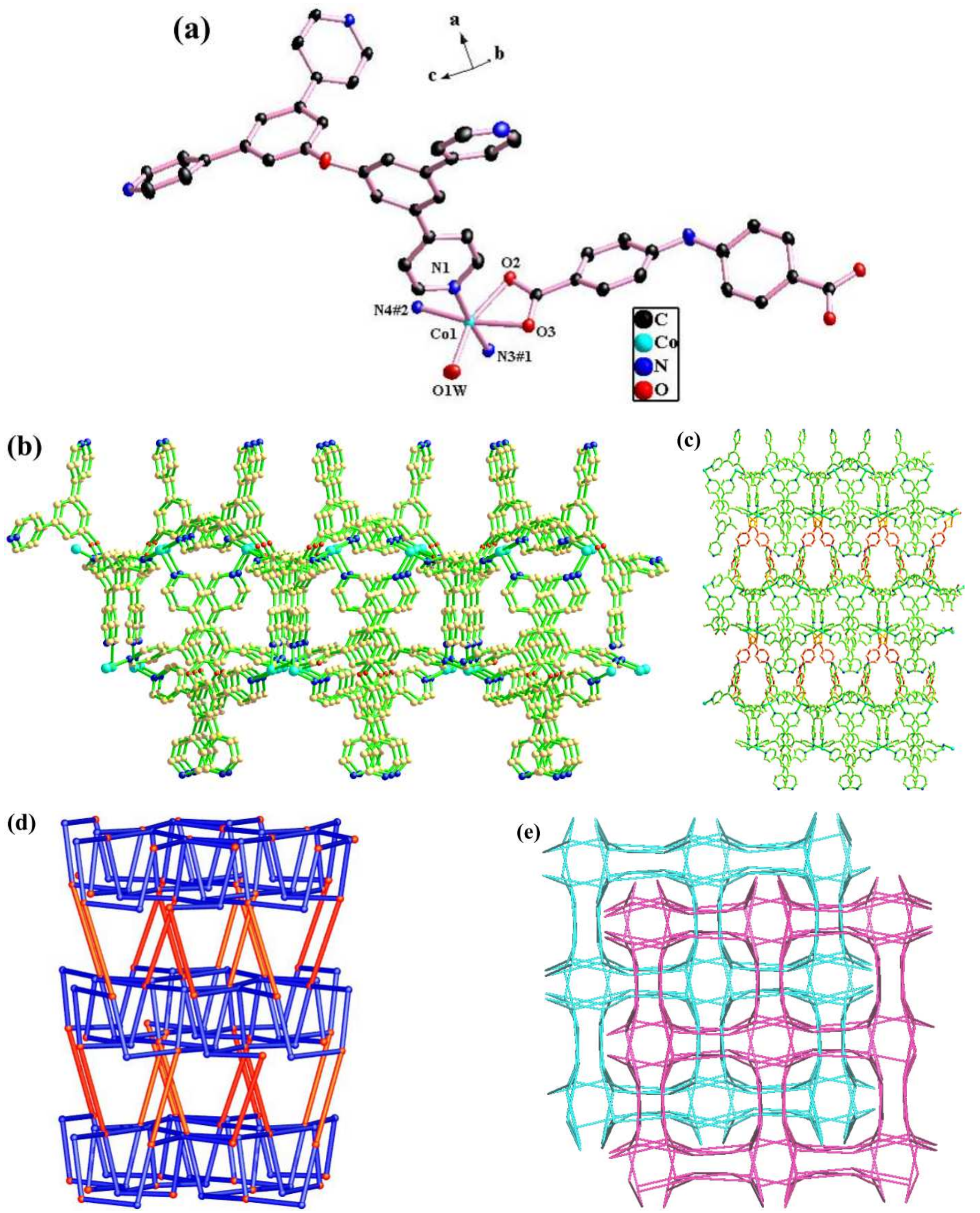


Fig. 1. (a) Coordination environment of the Co(II) ion in **1**. The hydrogen atoms are omitted for clarity (30% ellipsoid probability). Symmetry codes: #1 = -0.5 + *x*, 1 - *y*, *z*; #2 = -0.25 + y, 0.25 + *x*, 0.25 - *z*. (b) Views of the 2D network connected by the L ligands and Co (II) ions; (c) Views of the 3D network generated by the mixed ligands and metal centers (green represent L ligand, red represent nba^{2-} ligand); (d) Views of the topology of **1**; (e) Schematic view of the 2-fold interpenetrating structure **1**.

Crystal structure {[CoL(cam)(H_2O)]}$_n$ (2). D-Camphoric acid is a cyclopentane derivative with two carboxylate groups functionalized on the 1,3-carbon atoms, of which 1-carbon atom has a further methyl group, and two methyl occupies at 2-carbon atom, therefore, being an enantiopure ditopic organic linker. Compound **2** crystallizes in the achiral space group with the chiral D-camphorate ligand racemized. The asymmetry unit of **2** contains one Co(II) atom, one L, one cam^{2-} ligand and two water molecules. As depicted in Fig. 2a, the camphorate ligands are always inherently disordered over two positions. Each Co(II) atom is six-coordinated to two pyridyl nitrogen atoms from L ligands, three oxygen atoms of cam^{2-} ligands, and one water molecule giving a distorted [CoN_2O_4] octahedral geometry. The equatorial plane is completed by the coordination of N2, O2, O3, and O4 atoms. The axial positions are occupied by N1 and O1w atoms with a N1-Co1-O1w bond angle of 178.77(13)°. The Co-O bond distances vary from 2.051(3) to 2.230(3) Å, and the average Co-N bond distance is 2.118 Å. The D-H_2cam is completely deprotonated. The cam^{2-} ligands coordinate to Co1 ions via a chelating carboxyl group and a monodentate carboxyl group and result in the formation of a 1D chain, which are connected by the L ligand to form a 2D layer, as shown in Fig. 2b.

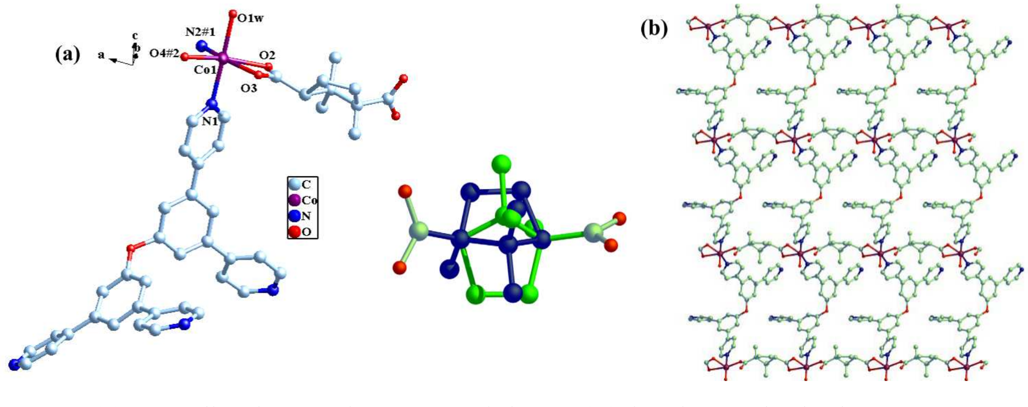
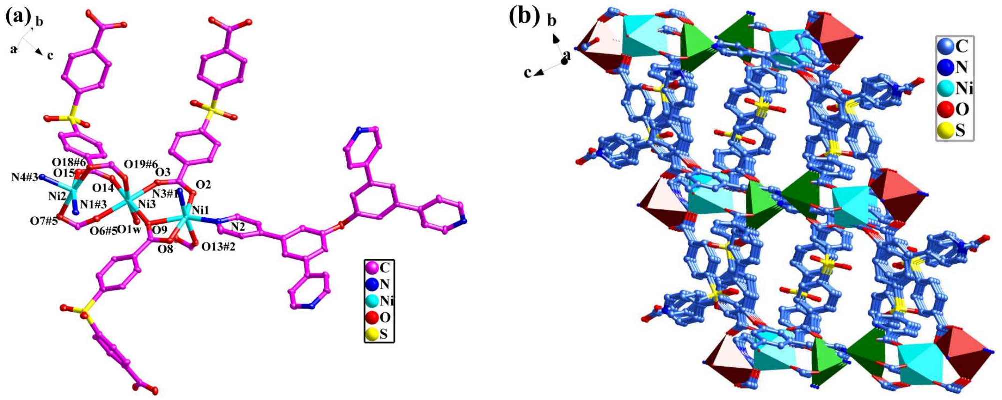


Fig. 2. (a) Coordination environment of the Co(II) ion in **2**. The hydrogen atoms are omitted for clarity (30% ellipsoid probability). Symmetry codes: #1 = x, y, 1 + z; #2 = 1 + x, y, z. right: Schematic drawing of a typical structure of disorder for cam^{2-} over two positions (green and blue). (b) Views of the 2D network connected by the L, cam ligand and Co (II) ions (only one position of the disordered camphorate anion is shown).

Crystal structures {[Co_3(L)(4,4'-sdb)$_3$(H_2O)]·1.5CH_3CN·4H_2O}$_n$ (3) and {[Ni_3(L)(4,4'-sdb)$_3$(H_2O)]·1.5CH_3CN·4H_2O}$_n$ (4). The X-ray crystallographic analysis reveals that compounds **3** and **4** are similar structures. Thus only the structure of **4** is discussed here in detail. There are three crystallographically independent Ni(II) ions in **4** as shown in Fig. 3a. Ni1 is coordinated in an octahedral geometry by four carboxylate oxygen atoms from three 4,4'-sdb anions and two nitrogen atoms from two L molecules on the axial positions. Ni3 is coordinated by five 4,4'-sdb anions and one water oxygen. However, Ni2 is coordinated in a tetragonal pyramid geometry by three carboxylate groups of three 4,4'-sdb anions and two nitrogen atoms from two L molecules. Each independent Ni3 center bridged one adjacent Ni2 ion via three carboxylate groups in a *syn*-*syn* fashion and one Ni1 cation via two carboxylate groups in *syn*-*syn* fashion and chelating/bridging mode, which generates a linear trinuclear building block $Ni_3(OOCR)_6$ with a Ni1 ··· Ni3 distance of 3.8168(7) Å and a Ni2 ··· Ni3 distance of 3.5270(7) Å. Such a building block is further linked to eight neighboring trinuclear units, leading to a three-dimensional framework (Fig. 3b). The overall structure of the 3D network can be described as a 4,8-connected net (Fig. 3c), which can be further specified by the Schläfli symbol $\{3.4^4.6\}\{3^2.4^8.5^9.6^9\}$.



(c)

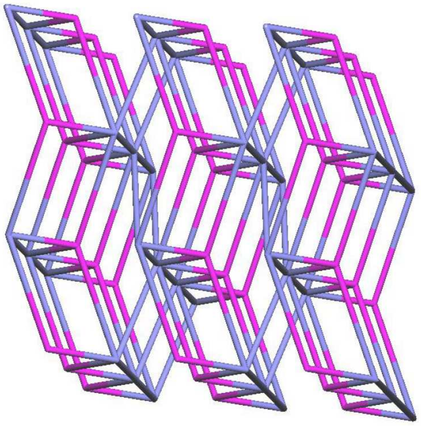


Fig. 3. (a) Coordination environment of **4** with 30% ellipsoid probability (hydrogen atoms and DMF molecules are omitted for clarity). Symmetry code: #1 = - *x*, 1 - *y*, 1 - *z*; #2 = 2 - *x*, - *y* , 1 - *z*; #3 = 1 - *x*, - *y* , 1 - *z*; #4 = 1 + *x*, -1 + *y* , -1 + *z*; #5 = 1 + *x*, -1 + *y* , *z*; #6 = 1 - *x*, 1 - *y* , - *z*. (b) Schematic representation of 3D framework of compound **4**: Ni1 polyhedrons shown in red, Ni2 shown in green, and Ni3 shown in turquoise. (c) Views of the 4,8-c topology of **4**.

Crystal structure $\{[Ni_2L_2(chdc)_2(H_2O)_2]\cdot(H_2O)_3\}_n$ (5). Single-crystal X-ray diffraction analysis reveals that compound **5** crystallizes in the monoclinic space group $P\bar{1}$. The asymmetric unit contained one Ni^{2+} center connected to the L ligand, one $chdc^{2-}$ ligand, and one coordinated water molecule together with guest water molecules (Fig. 4a). Each Ni (II) ion shows a distorted octahedral configuration coordinated by three oxygen atoms from one chelating and one monodentate carboxylate groups, two nitrogen atoms from L ligands and one water molecule. As shown in Fig. 4b, both carboxylate and L ligands act as bidentate ligands combined with Ni atoms to form a wavy sheet (Fig. 4b). When considering the H-bonds interaction (O6-H2W···N4), one of the uncoordinated N atoms of the A layer interacts the uncoordinated carboxylate oxygen atoms of the B layer to form a rare binodal 3,5-coordinated 3D architecture with a $\{6^3\}\{6^9.8\}$ *hms* topology (Fig. 4c). The nets are mutually interpenetration to generate the 2-fold interpenetration (Fig. 4d).

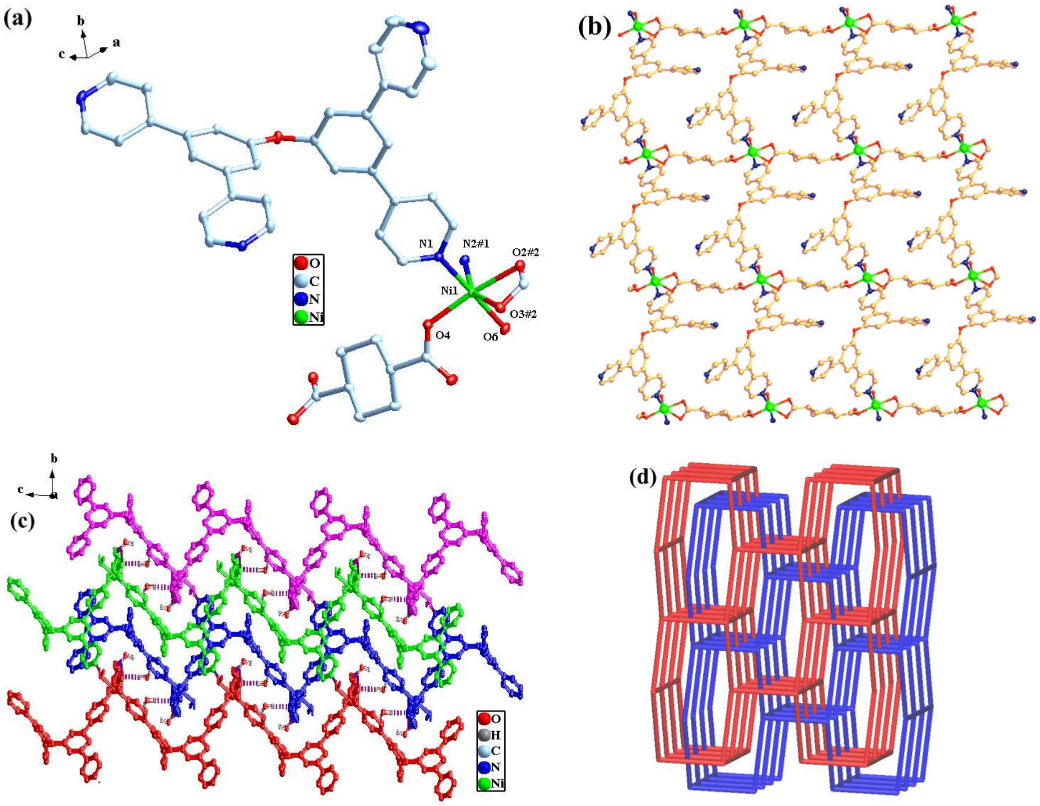


Fig. 4. (a) Coordination environment of the Ni(II) ion in **5**. The hydrogen atoms and lattice water molecules are omitted for clarity (30% ellipsoid probability). Symmetry codes: #1 = *x*, *y*, -1 + *z*; #2 = 1 + *x*, *y*, *z*. (b) Views of the 2D wavy network connected by the L, chdc ligand and Ni(II) ions. (c) Schematic view of 3D structure considering the H-bonds interaction. (d) Schematic views of two fold interpenetrating framework with *hms* topology.

Magnetic properties. Temperature-dependent magnetic susceptibility measurements for compound **3** was performed on the polycrystalline sample in the temperature range of 1.8-300 K in a fixed magnetic field 2 kOe, and the magnetic behaviours in the form of χ_mT and χ_m versus T plots were depicted in Fig. 5. Direct-current (dc) magnetic susceptibility studies reveal a room-temperature χ_MT value of 8.14 cm^{3}·K·mol^{-1}, larger than that for three free S = 3/2 spins (χ_MT = 5.625 cm^{3}Kmol^{-1} and g = 2) for three high-spin Co(II) atoms in each Co3 unit per formula. The larger experimental value than corresponding spin only value can be assigned to the unquenched orbital-moment as a result of spin-orbit coupling in the distorted octahedral coordinated Co(II) ions.[24] The χ_MT product gradually decreases with lowering temperature, reaching a value of 7.44 cm^{3}·K·mol^{-1} at 100 K, then decreases quickly to minimum value of 4.3 cm^{3}Kmol^{-1} at 1.8 K. The result at the high temperature region reveals the antiferromagnetic interaction between neighboring Co(II) ions. The decrease at low temperature was due mainly to antiferromagnetic coupling interaction between neighboring Co(II) ions and contribution of the orbital momentum of the single Co(II) ion. The magnetic susceptibilities obey the Curie-Weiss law in the temperature range above 30 K, giving a negative Weiss constant θ = - 14.79 K and Curie constant C = 8.57 emu·K·mol^{-1}.

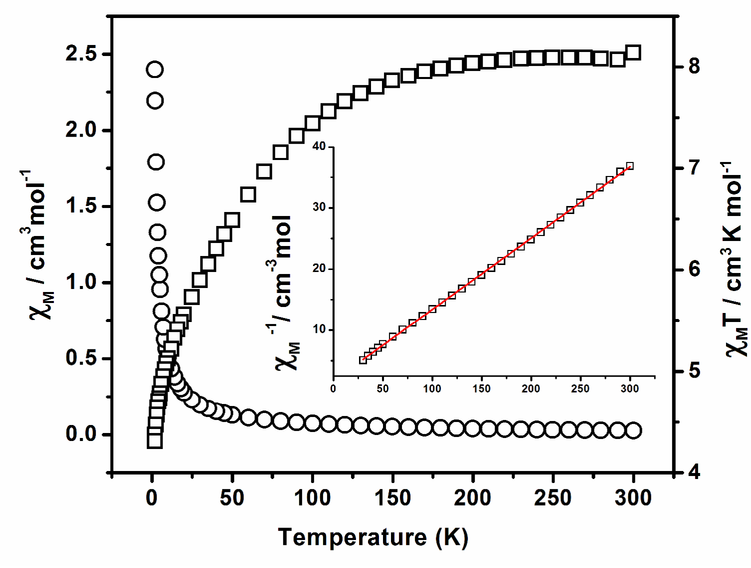


Fig. 5. Plot of $\chi_M T$ and χ_M vs T for **3**. Inset: Plot of χ_M^{-1} vs T (The solid lines represent the magnetic susceptibilities obey the Curie - Weiss law in the temperature range above 30 K).

UV-Visible spectra and PXRD analyses. As can be seen in the UV-vis absorbance spectra (Fig S5), The L ligand shows intense absorption peaks respectively at 250-290 nm, which can be ascribed to π-π* transitions of the ligands. The compounds **1-3** show two broad bands in the UV range at 350-400nm, and visible region at 450-550nm. The higher energy bands (in the UV range) are assigned as metal-to-ligand charge transfer (MLCT) transitions, while the lower energy bands arise from d-d transitions. In the visible region, we observe one additional peak at 460 nm [$^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$] with a shoulder at 550 nm [$^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$] transitions. Besides, one additional peak is observed for Ni(II) compound **5**, which sites in 630 nm [$^3T_{1g}(F) \rightarrow {}^3A_{2g}$]^{25}. Phase purity of the bulk materials was confirmed by the comparison of their powder diffraction (PXRD) patterns with those calculated from single-crystal X-ray diffraction studies (Figs S6-S9).

Conclusion

In summary, we successfully synthesized five coordination polymers, which were constructed from 1,1'-oxybis[3,5-di-4-pyridine]-benzene in the presence of different carboxylic acids co-ligands under the same hydrothermal conditions. Complex **1** reveals a 2-fold interpenetrating 3D net where three nitrogen atoms of L ligands involved in coordination. Complexes **2** and **5** have similar structures, and feature a 2D undulated (4,4)-layer structure in which only two nitrogen atoms of L ligands involved in coordination. Compounds **3** and **4** reveal 3D frameworks based on linear trinuclear building block with the four nitrogen atoms involved in coordination.

■ Acknowledgments

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Table 2. Crystal data and structure refinements parameters of complexes 1-5

Complex	**1**[a]	**2**	**3**[a]	**4**[a]	**5**
Formula	$C_{78}H_{55}Co_2N_9O_8$	$C_{42}H_{38}CoN_4O_6$	$C_{74}H_{48}Co_3N_4O_{20}$	$C_{154}H_{105}N_{11}Ni_6$	$C_{80}H_{74}N_8Ni_2O_{15}$
M_r	1364.17	753.69	1586.13	3294.11	1504.89
Cryst syst	tetragonal	triclinic	triclinic	triclinic	triclinic
Space group	$I4(1)/acd$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a (Å)	24.8128(14)	10.1215(13)	14.2269(18)	14.0905(15)	10.7106(19)
b (Å)	24.8128(14)	13.6526(17)	14.7692(11)	14.6762(17)	12.991(2)
c (Å)	44.811(5)	14.0503(18)	21.6912(19)	21.5858(14)	13.191(2)
α (°)	90.00	88.059(2)	90.391(2)	89.937(2)	86.517(2)
β (°)	90.00	86.639(2)	94.357(3)	85.402(3)	87.155(2)
γ (°)	90.00	78.294(2)	118.233(2)	61.994(2)	78.985(2)
V (Å^3)	27589(4)	1897.4(4)	3999.2(7)	3925.0(7)	1796.9(5)
Z	16	2	2	1	1
ρ_{caled} (g cm^{-3})	1.314	1.319	1.317	1.394	1.391
μ (mm^{-1})	0.544	0.505	0.762	0.865	0.598
F (000)	11264	786	1618	1690	786
rflns collected	73876	10398	28024	22907	16304
Uniq. rflns	6084	6552	14993	15116	8124
R(int)	0.0720	0.0682	0.0112	0.0170	0.0413
GOF(F^2)	1.059	1.102	1.019	1.017	1.011
R_1[I>2σ(I)][b]	0.0512	0.0697	0.0547	0.0530	0.0457
wR_2[I>2σ(I)][c]	0.1463	0.1733	0.1315	0.1019	0.1394
Min. and max resd dens (e ·Å^{-3})	-0.350, 0.824	-0.993, 1.328	-0.388, 0.787	-0.359, 0.319	-0.533, 0.597

[a] The residual electron densities were flattened by using the SQUEEZE option of PLATON.

[b] $R1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$.

[c] $wR2 = \{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$; where $w=1/[\sigma^2(F_o^2)+(aP)^2+bP], P=(F_o^2+2F_c^2)/3$.

Coligand-directed synthesis of five Co(II)/Ni(II) coordination polymers with neutral tetradentate ligand: syntheses, crystal structures, and properties†

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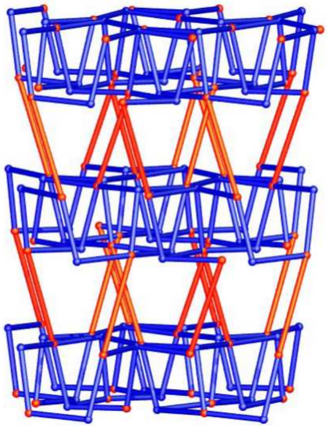

The solvothermal reactions afford five coordination polymers with different coligand, the coligand-directed synthesis has a great effect on the final structures.

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† Electronic supplementary information (ESI) available: IR, PXRD, Uv-vis, the selected bond lengths and angles. CCDC: 1002453 for **2**, 1002454 for **1**, 1002455 for **5**, 1002456 for **4**, 1002457 for **3**. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/