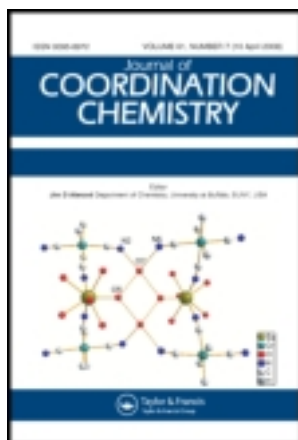


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Journal of Coordination Chemistry

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/gcoo20>

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Published online: 12 Aug 2011.

To cite this article: Zhi-Fang Jia, Jin Yang, Ying-Ying Liu & Jian-Fang Ma (2011) Syntheses, structures, and luminescence of coordination compounds based on N-containing polycarboxylates, *Journal of Coordination Chemistry*, 64:16, 2899-2911, DOI: [10.1080/00958972.2011.608427](https://doi.org/10.1080/00958972.2011.608427)

To link to this article: <http://dx.doi.org/10.1080/00958972.2011.608427>

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Syntheses, structures, and luminescence of coordination compounds based on N-containing polycarboxylates

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(Received 25 March 2011; in final form 28 June 2011)

Six coordination compounds constructed by two structurally related flexible nitrogen-containing polycarboxylate ligands 2,2'-(2,2'-(ethane-1,2-diylbis(oxy))bis(2,1-phenylene))bis(methylene)bis(azanediyl)dibenzoic acid (H₂L1) and 5,5'-(2,2'-(ethane-1,2-diylbis(oxy))bis(2,1-phenylene))bis(methylene)bis(azanediyl)diisophthalic acid (H₄L2) have been synthesized: [Ni(H₂O)₆]·L1·(C₂H₅OH)_{0.5}·H₂O (1), [Co(L1)(L3)]·CH₃OH (2), [Ni(L1)(L3)]·CH₃OH (3), [Zn(L1)(L3)]·CH₃OH (4), [Cd(L1)(L3)]·CH₃OH (5), and [Zn(L2)_{0.5}(phen)]·C₂H₅OH (6), where L3 = 3,4:9,10:17,18:23,24-tetrabenzo-1,12,15,26-tetraaza-5,8,19,22-tetraoxacyclooctacosan and phen = 1,10-phenanthroline. The crystal structures have been determined by single-crystal X-ray diffraction. Compound 1 displays a discrete structure, which is further linked by hydrogen bonds to form a 2-D supramolecular layer. Compounds 2–5 display similar structures. These compounds possess 1-D *meso*-chain structures linked by L1 and metals. The C–H···π interactions from neighboring chains extend the chains in different directions, giving a 3-D plywood network. Compound 6 possesses 2-D layers, which are further linked by hydrogen-bonding interactions to generate a 3-D supramolecular architecture.

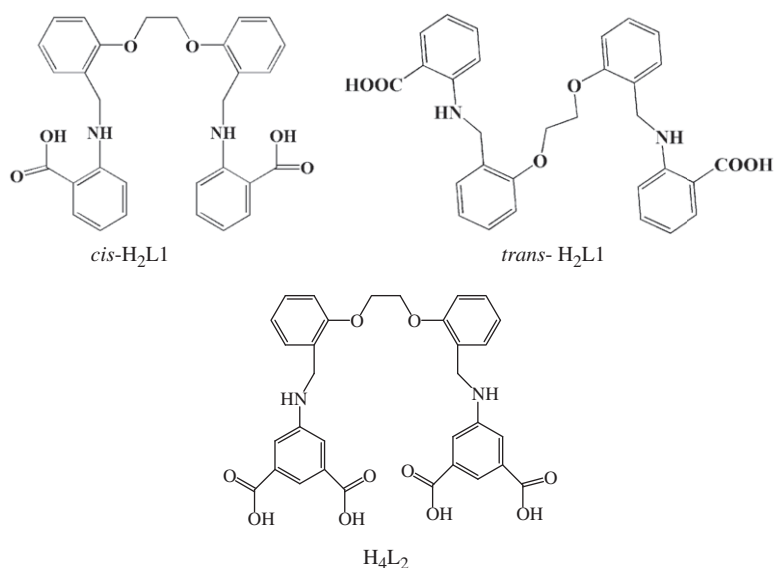
Keywords: Coordination polymers; N-containing polycarboxylate; Crystal structure

1. Introduction

Crystal engineering based on coordination frameworks continues to attract interest for their intriguing topologies and potential applications in molecular magnetism, catalysis, gas sorption, fluorescent sensing, and microelectronics [1]. Studies in this field have focused on the design and construction of coordination frameworks and the relationships between their structures and properties [2]. The molecular architecture depends on the coordination of the metal, ligand structures, counterions, hydrogen bonds, etc. Noncovalent interactions such as hydrogen bonds and C–H···π interactions play a very important role in crystal design and properties [3].

Strong hydrogen-bonding interactions between the hydroxyl of carboxylic acid and heterocyclic nitrogens have proved to be a powerful organizing force utilized for the

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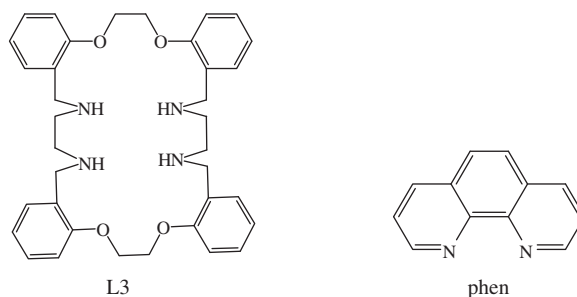
Scheme 1. The Polycarboxylate ligands used in this work.

formation of supramolecules. Rigid polycarboxylates [4], such as terephthalic acid and 1,3,5-benzenetricarboxylic acid [5], have been extensively employed in the construction of a variety of architectures. The polycarboxylates display various coordination modes [6], resulting from complete or partial deprotonation, and are hydrogen-bond acceptors and donors to assemble intriguing supramolecular structures [7]. However, investigation on nitrogen-containing flexible polycarboxylates is relatively scarce. In this article, two new nitrogen-containing flexible polycarboxylates: 2,2'-(2,2'-(ethane-1,2-diylbis(oxy))bis(2,1-phenylene))bis(methylene)bis(azanediyl)dibenzoic acid ($\text{H}_2\text{L1}$) and 5,5'-(2,2'-(ethane-1,2-diylbis(oxy))bis(2,1-phenylene)) bis(methylene)bis(azanediyl)diiisophthalic acid ($\text{H}_4\text{L2}$) (scheme 1), and six coordination polymers, $[\text{Ni}(\text{H}_2\text{O})_6] \cdot \text{L1} \cdot (\text{C}_2\text{H}_5\text{OH})_{0.5} \cdot \text{H}_2\text{O}$ (**1**), $[\text{Co}(\text{L1})(\text{L3})] \cdot \text{CH}_3\text{OH}$ (**2**), $[\text{Ni}(\text{L1})(\text{L3})] \cdot \text{CH}_3\text{OH}$ (**3**), $[\text{Zn}(\text{L1})(\text{L3})] \cdot \text{CH}_3\text{OH}$ (**4**), $[\text{Cd}(\text{L1})(\text{L3})] \cdot \text{CH}_3\text{OH}$ (**5**), and $[\text{Zn}(\text{L2})_{0.5}(\text{phen})] \cdot \text{C}_2\text{H}_5\text{OH}$ (**6**), have been synthesized through solution or solvothermal methods ($\text{L3} = 3,4:9,10:17,18:23,24$ -tetrabenzo-1,12,15,26-tetraaza-5,8,19,22-tetraoxacyclooctacosan and phen = 1,10-phenanthroline) (scheme 2). To the best of our knowledge, the coordination chemistry of $\text{H}_2\text{L1}$ and $\text{H}_4\text{L2}$ has never been studied [8]. The compounds are characterized by elemental analysis, IR spectra, and X-ray crystallography. The luminescence of the compounds were also investigated.

2. Experimental

2.1. Preparation

All chemicals were obtained commercially and used as received. L3 was prepared according to the literature [9, 10].



Scheme 2. The secondary ligands used in this work.

2.1.1. Synthesis of H₂L1. To salicylaldehyde (24.4 g, 0.2 mol) in ethanol (20 mL) sodium hydroxide (8.0 g, 0.2 mol) in water (400 mL) was added. The mixture was warmed and 1,2-dibromoethane (18.4 g, 0.1 mol) was added. Alcohol (300 mL) was then added. The solution was refluxed under nitrogen for 44 h and then cooled and let stand at 0°C. The cream-colored crystals produced were washed with water. Re-crystallization was performed using an ether–chloroform mixture.

To a stirred, warm solution of the above cream-colored crystals (2.70 g, 0.01 mol) in dry methanol (200 mL) 2-aminobenzoic acid (2.74 g, 0.02 mol) in dry methanol (50 mL) was slowly added. After addition of borax (1.0 g), sodium borohydride (2.0 g) was slowly added. The solution was stirred 10 h, dried *in vacuo*, and then poured into 200 mL of water. A yellow solid of H₂L1 formed immediately (yield: 2.34 g) when pH = 5.

2.1.2. Synthesis of H₄L2. H₄L2 was prepared in the same way as H₂L1 by using 5-aminobenzene-1,3-dioic acid (3.62 g, 0.02 mol) instead of 2-aminobenzoic acid.

2.1.3. Synthesis of [Ni(H₂O)₆] · [(L1)(C₂H₅OH)_{0.5} · H₂O] (1). A mixture of NiCO₃ (0.012 g, 0.10 mmol), H₂L1 (0.051 g, 0.10 mmol), ethanol (3.5 mL), and water (3.5 mL) was placed in a Teflon reactor (15 mL). The mixture was heated at 120°C for 4 days and then gradually cooled to room temperature at 10°C h⁻¹. Green crystals of **1** were obtained. Yield: 42% based on NiCO₃. Anal. Calcd for C₃₁H₄₃N₂O_{13.5}Ni (*M_r* = 718.38): C, 51.83; H, 6.03; N, 3.90. Found: C, 51.89; H, 6.11; N, 3.94. IR (cm⁻¹): 3736 (w), 3215 (w), 2940 (w), 2863 (w), 1691 (w), 1614 (s), 1499 (m), 1040 (m), 955 (w), 751 (s).

2.1.4. Synthesis of [Co(L1)(L3)] · CH₃OH (2). A mixture of CoCO₃ (0.012 g, 0.10 mmol), H₂L1 (0.051 g, 0.10 mmol), L3 (0.060 g, 0.10 mol) and methanol (7 mL) was placed in a Teflon reactor (15 mL). The mixture was heated at 120°C for 4 days and then gradually cooled to room temperature at 10°C h⁻¹. Yellow crystals of **2** were obtained. Yield: 34% based on CoCO₃. Anal. Calcd for C₆₇H₇₄N₆O₁₁Co (*M_r* = 1198.25): C, 67.16; H, 6.22; N, 7.01. Found: C, 67.20; H, 6.14; N, 7.04. IR (cm⁻¹): 3742 (m), 3220 (w), 2938 (w), 2868 (w), 1693 (w), 1611 (s), 1497 (s), 1382 (m), 1229 (s), 1047 (s), 941 (w), 752 (s).

2.1.5. Synthesis of [Ni(L1)(L3)]·CH₃OH (3). A mixture of NiCO₃ (0.012 g, 0.10 mmol), H₂L1 (0.051 g, 0.10 mmol), L3 (0.060 g, 0.10 mol), and methanol (7 mL) was placed in a Teflon reactor (15 mL). The mixture was heated at 120°C for 4 days and then gradually cooled to room temperature at 10°C h⁻¹. Green crystals of **3** were obtained. Yield: 41% based on NiCO₃. Anal. Calcd for C₆₇H₇₄N₆O₁₁Ni (*M_r* = 1198.03): C, 67.17; H, 6.23; N, 7.01. Found: C, 67.10; H, 6.19; N, 7.10. IR (cm⁻¹): 3742 (w), 3219 (w), 2943 (w), 2868 (w), 1693 (w), 1610 (s), 1495 (m), 1231 (m), 1048 (m), 942 (w), 753 (s).

2.1.6. Synthesis of [Zn(L1)(L3)]·CH₃OH (4). A mixture of ZnCO₃ (0.013 g, 0.10 mmol), L1 (0.051 g, 0.10 mmol), L3 (0.060 g, 0.10 mol), and methanol (7 mL) was placed in a Teflon reactor (15 mL). The mixture was heated at 120°C for 4 days and then gradually cooled to room temperature at 10°C h⁻¹. Colorless crystals of **4** were obtained. Yield: 56% based on ZnCO₃. Anal. Calcd for C₆₇H₇₄N₆O₁₁Zn (*M_r* = 1204.73): C, 66.79; H, 6.23; N, 7.02. Found: C, 66.91; H, 6.21; N, 7.07. IR (cm⁻¹): 3740 (m), 3212 (w), 2935 (w), 2869 (w), 1694 (w), 1612 (s), 1498 (s), 1229 (s), 1045 (m), 943 (w), 752 (m).

2.1.7. Synthesis of [Cd(L1)(L3)]·CH₃OH (5). A mixture of Cd(OH)₂ (0.013 g, 0.10 mmol), H₂L1 (0.051 g, 0.10 mmol), L3 (0.060 g, 0.10 mol), and methanol (7 mL) was placed in a Teflon reactor (15 mL). The mixture was heated at 120°C for 4 days and then gradually cooled to room temperature at 10°C h⁻¹. Colorless crystals of **5** were obtained. Yield: 56% based on Cd(OH)₂. Anal. Calcd for C₆₇H₇₄N₆O₁₁Cd (*M_r* = 1251.7): C, 64.29; H, 5.96; N, 6.97. Found: C, 64.35; H, 6.03; N, 7.07. IR (cm⁻¹): 3216 (w), 2933 (w), 1695 (m), 1610 (m), 1454 (m), 1372 (m), 1227 (s), 1047 (s), 750 (m).

2.1.8. Synthesis of [Zn(L2)_{0.5}(phen)]·C₂H₅OH (6). A mixture of ZnCO₃ (0.013 g, 0.10 mmol), H₄L2 (0.060 g, 0.10 mmol), phen (0.018 g, 0.10 mol) and ethanol (7 mL) was placed in a Teflon reactor (15 mL). The mixture was heated at 120°C for 4 days and then gradually cooled to room temperature at 10°C h⁻¹. Colorless crystals of **6** were obtained. Yield: 56% based on ZnCO₃. Anal. Calcd for C₃₀H₂₆N₃O₆Zn (*M_r* = 589.93): C, 61.08; H, 4.44; N, 7.12. Found: C, 61.21; H, 4.37; N, 7.04. IR (cm⁻¹): 3334 (m), 3063 (w), 2937 (w), 2876 (w), 1695 (m), 1551 (s), 1424 (s), 1368 (m), 1230 (m), 1047 (m), 844 (m), 724 (w).

2.2. Physical measurements and X-ray crystallography

C, H, and N elemental analyses were conducted on a Perkin-Elmer 240 C elemental analyzer. IR spectra were recorded from KBr pellets from 4000 to 400 cm⁻¹ on a Mattson Alpha-Centauri spectrometer. The photoluminescent properties were measured on an FLSP920 Edinburgh Fluorescence Spectrometer.

Single-crystal X-ray diffraction data for **1–4** and **6** were collected on a Rigaku RAXIS-RAPID single-crystal diffractometer with Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$) at 293 K. Compound **5** was collected on an Oxford Diffraction Gemini R Ultra single-crystal diffractometer with Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$) at 293 K.

Absorption corrections were applied using the multi-scan technique. All structures were solved by the Direct Methods of SHELXS-97 [11] and refined by full-matrix least-squares using SHELXL-97 [12]. Nonhydrogen atoms were refined with anisotropic temperature parameters. Hydrogens attached to carbons were generated geometrically; the water hydrogens were located from difference Fourier maps and refined with isotropic displacement parameters.

The detailed crystallographic data and structure refinement parameters for **1–6** are summarized in table 1. Selected hydrogen-bonding parameters are listed in table 2. Selected bond distances and angles for all compounds are listed in tables S1–S6 (see Supplementary material).

3. Results and discussion

3.1. Crystal structure

3.1.1. Structure of $[\text{Ni}(\text{H}_2\text{O})_6] \cdot \text{L1} \cdot (\text{C}_2\text{H}_5\text{OH})_{0.5} \cdot \text{H}_2\text{O}$ (1**).** Single-crystal X-ray structural analysis revealed that $[\text{Ni}(\text{H}_2\text{O})_6] \cdot [(\text{L1})(\text{C}_2\text{H}_5\text{OH})_{0.5}\text{H}_2\text{O}]$ (**1**) crystallized in the triclinic space group $P\bar{1}$ and consists of 1-D *meso*-helical chains. As shown in figure 1(a), the asymmetric unit consists of one crystallographically independent Ni^{II} , one L1, and six water molecules with Ni^{II} coordinated by six oxygens from six water molecules in a distorted octahedral geometry. The uncoordinated L1 anion exhibits *cis*-configuration with dihedral angles between the two pairs of benzene rings being 16.1° . The Ni–O bond lengths range from 2.107(5) to 2.14(2) Å, which are in the normal range [13].

The Ni^{II} s are linked by L1 into left- and right-handed helical chains through $\text{O2W} \cdots \text{H2WB} \cdots \text{O1}^{\#2}$ ($\#2$: $-x, -y + 1, -z + 2$) and $\text{O3W} \cdots \text{H3WA} \cdots \text{O6}^{\#1}$ ($\#1$: $-x + 1, -y + 2, -z + 2$) hydrogen bonds (figure 1b and c). The pitch of the helices is 13.6(0) Å. A left-handed helical chain linked an adjacent right-helical chain to give a *meso*-helical chain through the $\text{O2W} \cdots \text{H2WA} \cdots \text{O2}$ hydrogen-bonding interactions (figure 1d). The most interesting structural feature of **1**, however, is that the *meso*-helical chains are further linked through the $\text{O} \cdots \text{H} \cdots \text{O}$ hydrogen bonds to result in a 2-D supramolecular layer (figure 1e [14]).

3.1.2. Structures of **2–5.** Single-crystal X-ray structural analysis shows that **2–5** have the same 1-D *meso*-helical chain structures. Illustrated by $[\text{Co}(\text{L1})(\text{L3})] \cdot \text{CH}_3\text{OH}$ (**2**), each Co(II) is six-coordinate by four nitrogens from L3 and two carboxylate oxygens from L1 in a distorted octahedral geometry (figure 2a). Each carboxylate of L1 bridges Co(II)s in an *exo*-bidentate chelating mode, resulting in a linear coordination polymer of **2** (figure 2b). L1 shows a twisted *trans*-conformation with dihedral angles between the two pairs of benzene rings being 61.02° . The dihedral angle between the carboxylate plane and the secondary amine planes is 79.4° . Intramolecular hydrogen-bonding interactions exist between the uncoordinate oxygens of carboxylate and the secondary amines of L1, which form the stable six-membered ring ($\text{N3} \cdots \text{H3N} \cdots \text{O4} = 2.630(4)$ Å).

L1 links Co(II)s to generate an interesting *meso*-helical chain with $\text{Co} \cdots \text{Co}$ distance of 12.673(2) Å (figure 2c) [15]. As schematized by the rod-packing of figure 2(d),

Table 1. Crystal data and structure refinements for 1-6.

	1	2	3	4	5	6
Empirical formula	C ₃₁ H ₄₃ O _{13.5} N ₂ Ni	C ₆₇ H ₇₄ O ₁₁ N ₆ Co	C ₆₇ H ₇₄ O ₁₁ N ₆ Ni	C ₆₇ H ₇₄ N ₆ O ₁₁ Zn	C ₆₇ H ₇₄ N ₆ O ₁₁ Cd	C ₃₀ H ₂₆ N ₃ O ₆ Zn
Formula weight	718.39	1198.25	1198.03	1204.69	1251.72	589.91
Crystal system	Triclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	<i>P</i> $\bar{1}$	<i>C2/c</i>	<i>C2/c</i>	<i>C2/c</i>	<i>C2/c</i>	<i>P2₁/n</i>
Unit cell dimensions (Å, °)						
<i>a</i>	7.906(3)	20.588(4)	20.596(6)	20.536(4)	20.597 (1)	11.719(4)
<i>b</i>	11.640(5)	14.782(5)	14.692(6)	14.852(3)	14.763(6)	16.680(7)
<i>c</i>	20.488(10)	20.559(8)	20.506(7)	20.730(6)	20.613(1)	13.377(4)
α	99.025(16)	90.000	90.000	90.000	90.000	90.000
β	91.813(15)	91.167(16)	90.981(14)	91.373(19)	91.086(4)	96.587(11)
γ	94.207(14)	90.000	90.000	90.000	90.000	90.000
Volume (Å ³), <i>Z</i>	1855.3(14), 1	6255(3), 4	6204(4), 4	6321(3), 4	6266(3), 4	2597.6(16), 4
Calculated density (Mg cm ⁻³)	1.286	1.272	1.283	1.266	1.327	1.508
<i>F</i> (0 0 0)	758	2532	2536	2544	2616	1220
Reflections collected/unique	17,809/8176	29,075/7150	28,761/7080	30,400/7198	14,206/7265	24,105/5815
Goodness-of-fit on <i>F</i> ²	1.193	1.193	1.188	1.181	1.071	1.034
<i>R</i> ₁ ^a [<i>I</i> > 2σ(<i>I</i>)]	0.0948	0.846	0.0793	0.0770	0.1001	0.0600
<i>wR</i> ₂ ^b	0.1666	0.1768	0.1704	0.2146	0.2948	0.1444

^a*R*₁ = Σ||*F*_o| - |*F*_c||/Σ|*F*_o|. ^b*wR*₂ = [Σ*w*(|*F*_o|² - |*F*_c|²)/Σ|*w*(*F*_o)²]^{1/2}.

Table 2. Selected hydrogen-bonding geometry (in Å and °).

D–H...A	<i>d</i> (D–H)	<i>d</i> (H...A)	<i>d</i> (D...A)	∠(D–H...A)
Compound 1				
N(1)–H(1N)...O(2)	0.86(4)	1.91(4)	2.634(6)	141(5)
N(2)–H(2N)...O(5)	0.86(4)	2.06(4)	2.651(5)	125(4)
O(2W)–H(2WA)...O(2)	0.87(4)	1.83(2)	2.685(5)	171(5)
O(3W)–H(3WB)...O(7W)	0.89(4)	2.02(3)	2.844(9)	154(6)
O(5W)–H(5WB)...O(4W)	0.862(19)	2.59(5)	2.978(9)	109(4)
O(3W)–H(3WA)...O(6) ^{#1}	0.89(4)	1.97(2)	2.840(6)	172(5)
O(4W)–H(4WA)...O(6) ^{#1}	0.88(5)	2.40(3)	3.161(7)	145(4)
O(7W)–H(7WB)...O(5W) ^{#2}	0.88(4)	2.39(5)	3.097(8)	139(6)
O(2W)–H(2WB)...O(1) ^{#2}	0.83(6)	1.93(6)	2.724(7)	161(7)
Compound 2				
N(1)–H(1N)...O(4) ^{#1}	0.854(18)	2.16(3)	2.914(4)	147(4)
N(2)–H(2N)...O(2) ^{#1}	0.845(18)	2.30(3)	2.915(4)	129(3)
N(3)–H(3N)...O(4)	0.864(19)	1.93(4)	2.630(4)	137(4)
C(22)–H(22)...π ^{#2}	0.93	2.94(3)	3.82(2)	159(2)
Compound 3				
N(1)–H(1N)...O(3)	0.852(18)	2.17(3)	2.894(4)	143(4)
N(2)–H(2N)...O(1)	0.855(18)	2.31(3)	2.913(5)	128(3)
N(3)–H(3N)...O(3)	0.859(17)	1.96(4)	2.630(4)	134(4)
C(23)–H(23)...π ^{#3}	0.93	2.94(4)	3.82(6)	160(2)
C(30)–H(23)...π ^{#4}	0.93	2.99(3)	3.86(1)	158(2)
Compound 4				
N(2)–H(2N)...O(4) ^{#1}	0.836(1)	2.16(2)	2.952(5)	157(4)
N(3)–H(3N)...O(4)	0.844(1)	1.94(4)	2.642(5)	140(5)
C(22)–H(22)...π ^{#3}	0.93	2.95(3)	3.81(2)	154(2)
Compound 5				
N(1)–H(1N)...O(5)	0.81(2)	2.19(3)	2.923(6)	151(5)
C(23)–H(23)...π ^{#4}	0.93	2.94(4)	3.810(8)	157(2)
Compound 6				
O(6)–H(6O)...O(1) ^{#4}	0.88(2)	1.94(4)	2.788(7)	162(10)
N(3)–H(3N)...O(6)	0.847(19)	2.15(3)	2.930(6)	153(4)

Symmetry codes for **1**: ^{#1} $-x+1, -y+2, -z+2$; ^{#2} $-x, -y+1, -z+2$. **2**: ^{#1} $-x+1, -y+1, -z+2$; ^{#2} $-x, -y+1, -z+2$. **3**: ^{#3} $-x+1/2, y+1/2, -z+1/2$; ^{#4} $1-x, -y, 1-z$. **4**: ^{#1} $-x+1, -y+1, -z+1$; ^{#3} $-x+3/2, y-1/2, -z+3/2$. **5**: ^{#4} $-x+3/2, y+1/2, -z+3/2$. **6**: ^{#4} $x-1/2, -y+3/2, z-1/2$.

there are two series of 1-D *meso*-helical chains, extending in different directions, rotated by 71.36° on passing from one level to the next. These chains seem to be independent of one another. However, a careful examination leads to the finding that the different series of chains are interconnected by C–H...π interactions (H...π 2.94 Å and C–H...π 159°) between carbons of benzene belonging to one series of chains and benzene rings belonging to another series of chains, yielding a 3-D network (figure 2e) [16]. Methanols are placed in the framework cavities created by the two different series of chains. In contrast to those in **2**, **4**, and **5**, chains of **3** line up in layers, in which each chain is interconnected, resulting in the formation of the 3-D network of **3** (figure 2f). The structures of **2–5** are entirely different from the related compound [Cd₂(bptc)(bpimb)(H₂O)]·2H₂O (H₄bptc = biphenyl-1,3',4,4'-tetracarboxylic acid and bpimb = 1,3-bis((2-(pyridin-2-yl)-1Himidazol-1-yl)methyl)benzene) [16b]. In that reported compound, the bptc anions and bpimb ligands bridge Cd(II)'s to form a 3-D (3,8)-connected framework with tfz-d notation.

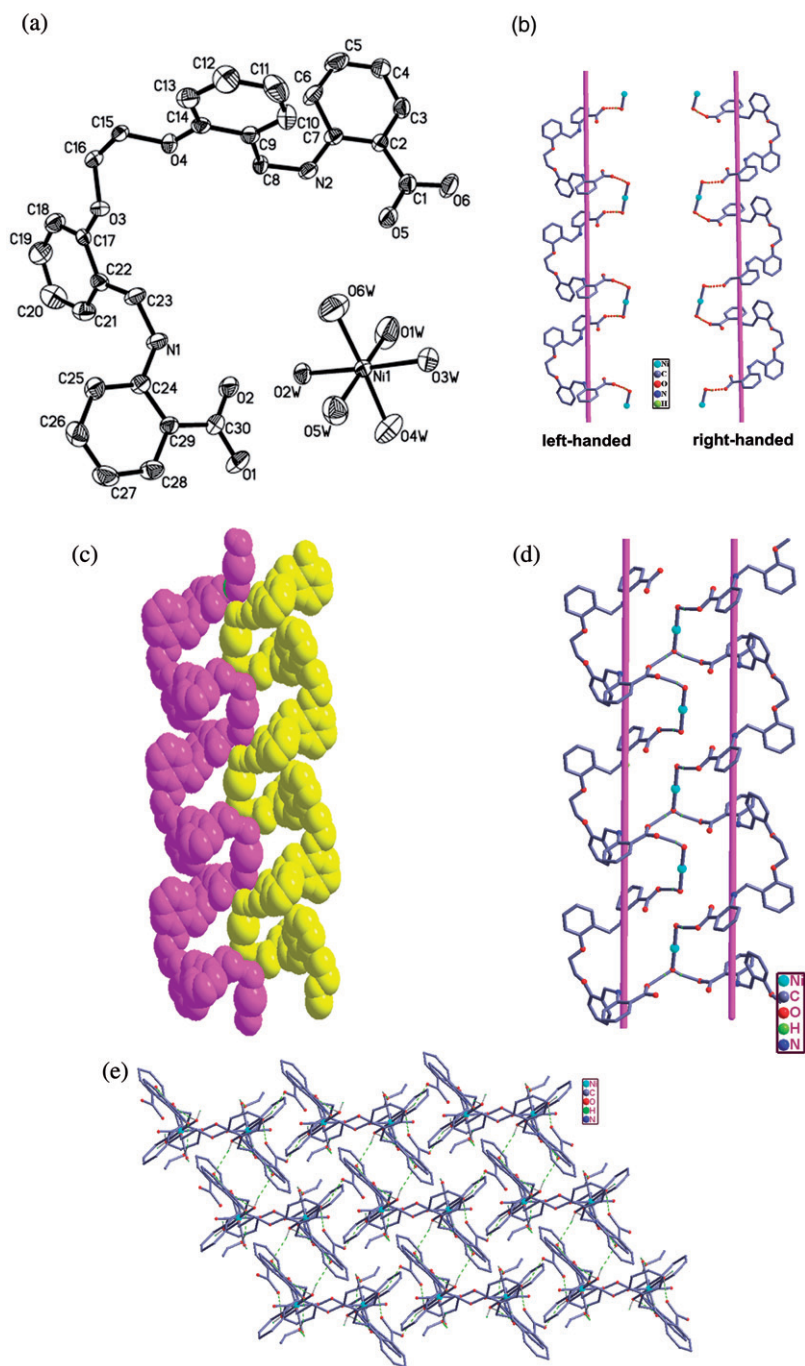


Figure 1. (a) ORTEP diagram showing the coordination environment of Ni^{II} in **1**. The uncoordinated water and all hydrogens are omitted for clarity. (b) The infinite left-handed and right-handed helical chains (H-bonds: dashed lines). (c) Packing diagram of the infinite 1-D helical chain. (d) The infinite 1-D *meso*-helical structure. (e) View of the 2-D layer (H-bonds: dashed lines).

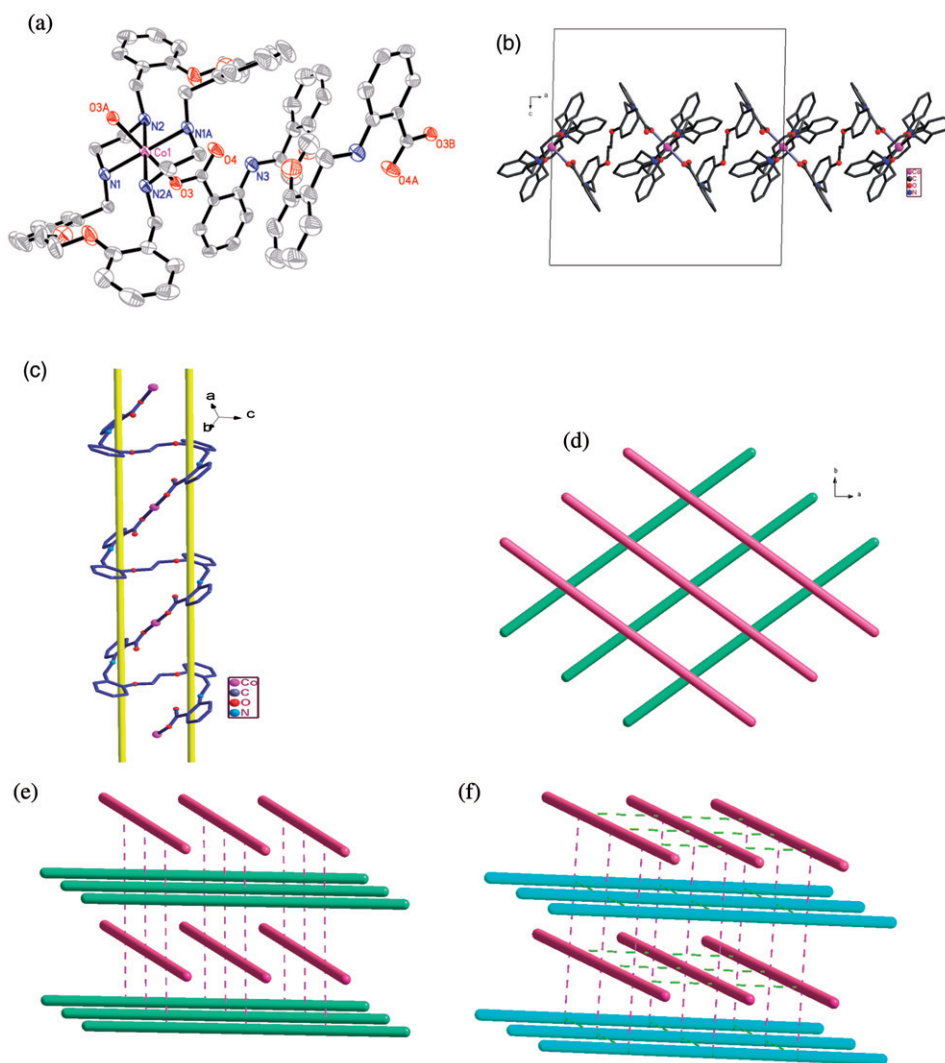


Figure 2. (a) ORTEP diagram showing the coordination environment for Co^{II} in **2**. Methanols and hydrogens are omitted for clarity. (b) Infinite chain formed by L1, L3, and Co^{II} . (c) Infinite *meso*-helical chain formed by L1 and Co^{II} . (d) The rod-packing modes of two series of 1-D *meso*-helical chains. (e) Schematic diagram showing how a 3-D network is constructed by 1-D chains. A rod represents a 1-D polymer chain. Dashed lines indicate $\text{C-H}\cdots\pi$ interactions between 1-D chains. (f) Schematic diagram showing how a 3-D network is constructed by 1-D chains in **3**. A rod represents a 1-D coordination polymer. Dashed lines indicate $\text{C-H}\cdots\pi$ interactions between 1-D chains.

3.1.3. Structure of $[\text{Zn}(\text{L}2)_{0.5}(\text{phen})] \cdot \text{C}_2\text{H}_5\text{OH}$ (6**).** Single-crystal X-ray structural analysis reveals that **6** is a 2-D network with quadrate grids, significantly different from the structures discussed above. As shown in figure 3(a), each $\text{Zn}(\text{II})$ is five-coordinate in a distorted square-pyramidal coordination sphere, $\{\text{ZnN}_2\text{O}_3\}$, defined by three oxygens from two carboxylates ($\text{Zn-O} = 1.947(3)\text{--}2.246(3)\text{ \AA}$) and two nitrogens from a phen ($\text{Zn-N} = 2.064(4)\text{--}2.095(4)\text{ \AA}$). Four carboxylates of L2 are deprotonated and exhibit

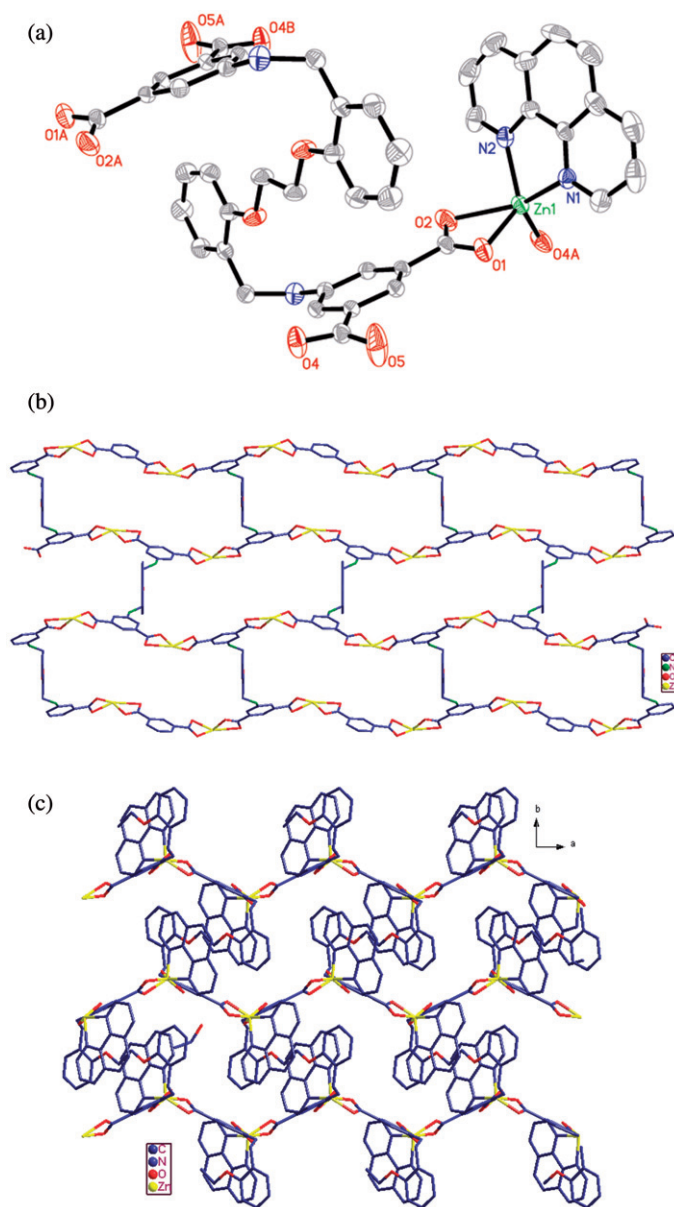


Figure 3. (a) ORTEP diagram showing the coordination environment for Zn^{II} in **6**. All hydrogens are omitted for clarity. (b) The [Zn₂(L₂)₂] network with the quadrat grids. (c) View of the 2-D network along the *c*-axis.

hexadentate coordination. Thus, each L₂ anion bridges four Zn(II) centers, forming an unusual quadrat grid with dimensions of $7.77 \times 16.77 \text{ \AA}^2$ (figure 3b). The 2-D grids are further linked through $\text{O}(6)\text{-H}(6\text{O})\cdots\text{O}(1)^{\#4}$ ($\#4x-1/2, -y+3/2, z-1/2$) hydrogen-bonding interactions, generating a 3-D supramolecular framework (figure 3c).

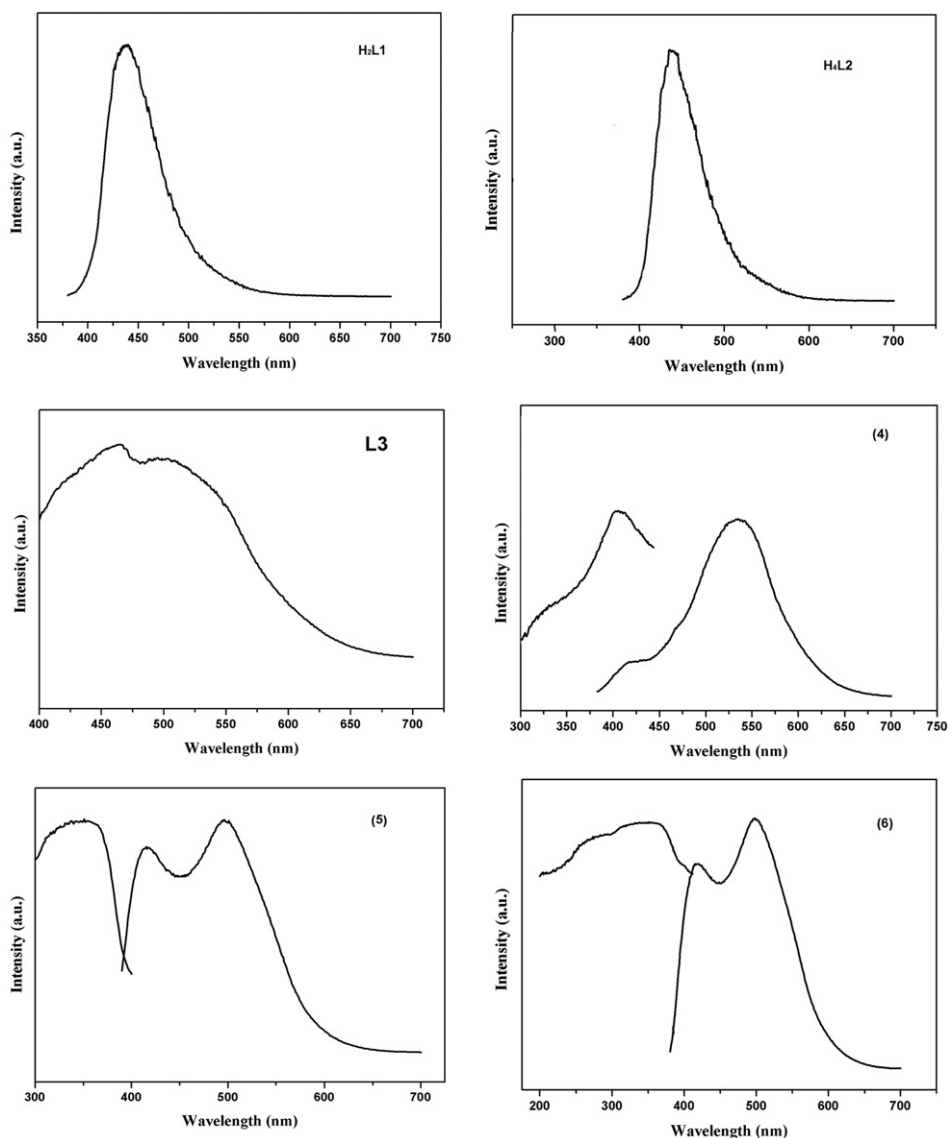


Figure 4. Solid-state photoluminescent spectra of H_2L1 , H_4L2 , $L3$, and **4–6** at room temperature.

The structure of **6** is completely different from $[Zn(H_2butca)(phen)(H_2O)]_n \cdot nH_2O$ (H_4butca = 1,2,3,4-butane-tetracarboxylic acid) [16c], $[Zn(H_2btc)(4,4'-bpy)_2]_n$ (H_4btc = biphenyl-2,2',4,4'-tetracarboxylic acid and 4,4'-bpy = 4,4'-bipyridine) [16d], and $\{[Zn_2(bim)_4(btec)] \cdot DMF\}_n$ (H_4btec = 1,2,4,5-benzenetetracarboxylic acid, bim = benzimidazole and DMF = N,N'-dimethylformamide) [16e]. In those compounds, tetracarboxylates link Zn(II)'s to form chain structures. The adjacent 1-D chains are further extended into 2-D or 3-D supramolecular architectures through inter-chain hydrogen bonds and π - π interactions.

3.2. Luminescent properties

Compounds of zinc or cadmium attract intense interest because of their potential applications in chemical sensors, photochemistry, and electroluminescent displays [17]. In this study, the solid-state photoluminescence of H₂L1, H₄L2, L3, and **4–6** have been studied in the solid state at room temperature.

The photoluminescence spectra of H₂L1, H₄L2, and L3 show emission maxima at 435 nm ($\lambda_{\text{ex}} = 320$ nm), 450 nm ($\lambda_{\text{ex}} = 325$ nm), and 456 nm ($\lambda_{\text{ex}} = 350$ nm), respectively (figure 4). The emission bands of these free ligands are attributable to $\pi^* \rightarrow n$ or $\pi^* \rightarrow \pi$ transition [17]. On complexation with Zn(II) and Cd(II), the emissions arising from the free ligands were not observed. Emission spectra for **4** show a main peak at 530 nm ($\lambda_{\text{ex}} = 330$ nm) that red-shifts (95 and 74 nm) with respect to the band shown by H₂L1 and L3, respectively. Compared with free H₂L1 and L3 ligands, **5** exhibits a broad emission at 496 nm ($\lambda_{\text{ex}} = 350$ nm), which shows red-shifts of 61 and 40 nm, respectively. According to the literature, phen shows emission peaks at 420 and 440 nm [18]. For **6**, the emission band appears at 500 nm ($\lambda_{\text{ex}} = 355$ nm), which red-shifted by 50, 60, and 80 nm from H₄L2 and phen. All emission peaks of **4–6** red-shift with respect to the free ligands. These emissions are neither ligand-to-metal charge transfer nor metal-to-ligand charge transfer because Zn(II) and Cd(II) are difficult to oxidize or to reduce due to their d¹⁰ configuration [19]. In comparison with free H₂L1 and H₄L2, replacement of the hydrogen proton by Zn(II) or Cd(II) in **4–6** decreases the $\pi^* \rightarrow n$ or $\pi^* \rightarrow \pi$ gap of the carboxylate ligands, resulting in red-shifts of the emission peaks [19]. As a result, the emission can be assigned to chelating of the carboxylates to the metal. The emission discrepancies of **4** and **5** may be due to changes from Zn(II) ion to Cd(II) ion, because the emission behavior is closely associated with the metal [20]. The photoluminescent result indicates that these three compounds may be good candidates for photoactive materials.

4. Conclusion

Six coordination compounds based on H₂L1 and H₄L2 have been synthesized and characterized. The results of this study illustrate that the ligands play an important role in the construction of coordination polymers, as do the coordination modes of anions, the coordination behavior of metal ions, and hydrogen–bond interactions. More metal complexes containing flexible divergent ligands and carboxylates with interesting structures as well as physical properties will be synthesized.

Supplementary material

X-ray crystallographic files in CIF format for **1–6** have been deposited at the Cambridge Crystallographic Data Center with the deposition numbers CCDC 817685–817690. Copies of the data can be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 IEZ, UK (Fax: +44-1223-336033; Email: deposit@ccdc.cam.ac.uk).

Acknowledgments

We thank the National Natural Science Foundation of China (grant nos 21071028, 21001023), the Science Foundation of Jilin Province (20090137), the Fundamental Research Funds for the Central Universities, the Specialized Research Fund for the Doctoral Program of Higher Education, the China Postdoctoral Science Foundation (20080431050 and 200801352), the Training Fund of NENU's Scientific Innovation Project, and the Analysis and Testing Foundation of Northeast Normal University for support.

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