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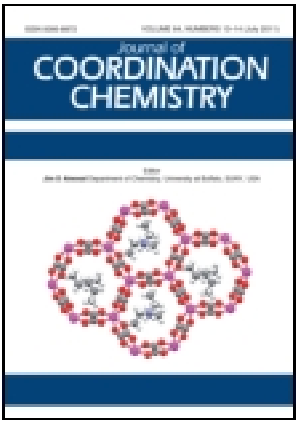

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Syntheses, crystal structures, and characterization of seven coordination compounds based on flexible 1,1′-(1,4-butanediyl)bis(3-carboxyl-2-oxidopyridinium)

Yu-Lan Chen [a], Jin Yang [a] & Jian-Fang Ma [a]
[a] Key Lab of Polyoxometalate Science, Department of Chemistry, Northeast Normal University, Changchun 130024, People's Republic of China

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Syntheses, crystal structures, and characterization of seven coordination compounds based on flexible 1,1′-(1,4-butanediyl)bis(3-carboxyl-2-oxidopyridinium)

YU-LAN CHEN, JIN YANG and JIAN-FANG MA*

Key Lab of Polyoxometalate Science, Department of Chemistry, Northeast Normal University, Changchun 130024, People's Republic of China

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Seven coordination compounds based on 1,1′-(1,4-butanediyl)bis(3-carboxyl-2-oxidopyridinium), $[CoNa(L)_{1.5}(C_2H_5OH)_3]$ (**1**), $[Zn(L)(OH)_2]\cdot 4H_2O$ (**2**), $[Co(L)(OH)_2]\cdot 2H_2O$ (**3**), $[Co(L)(H_2O)]$ (**4**), $[Zn(L)(H_2O)]$ (**5**), $[Ni(L)(H_2O)]$ (**6**), and $[Mn(L)(H_2O)]$ (**7**), have been synthesized and crystal structures have been determined by single-crystal X-ray diffraction. Compound **1** exhibits a 0-D molecular structure. Compound **2** shows a 1-D "Z" chain structure. Neighboring chains are further linked by hydrogen-bonding interactions into a 2-D supramolecular layer. Compound **3** features a 1-D "Z" chain structure. The chains are further extended into a 2-D supramolecular structure by hydrogen-bonding interactions. Compounds **4**–**7** are isomorphous and display 2-D (4^4)-**SQL** networks. These compounds are further characterized by infrared spectra, elemental analyses, and X-ray powder diffraction. The luminescent properties of the compounds were also investigated.

Keywords: Coordination compounds; Crystal structures; Luminescent properties

1. Introduction

Assembly of ordered coordination compounds is of interest in supramolecular chemistry and crystal engineering owing to intriguing structures and potential applications in host–guest chemistry, catalysis, and electrical conductivity [1]. Work has been done toward design and synthesis of coordination compounds based on coordination bonds yet non-covalent interactions, such as hydrogen-bonding, can play important roles in determining structure. Rigid polycarboxylates [2], for example, terephthalic acid and 1,3,5-benzenetricarboxylic acid, have been widely investigated in the construction of coordination polymers [3]. The polycarboxylates exhibit various coordination modes and produce intriguing supramolecular structures based on hydrogen-bonding interactions [4–6]. Studies on N-containing flexible polycarboxylate ligands are still lacking [7–9]. The flexible ligand 1,1′-(1,4-butanediyl)bis(3-carboxyl-2-oxidopyridinium) (H_2L) (scheme 1) contains hydroxyl and carboxyl groups, leading to a

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*Corresponding author. Email: jianfangma@yahoo.com.cn

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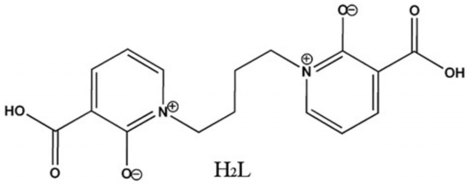
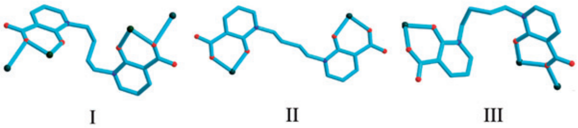


Scheme 1. Structure of H_2L.



Scheme 2. Coordination modes of L^{2-} anion.

variety of coordination modes (scheme 2). The two 3-carboxyl-2-oxidopyridinium rings can freely twist around the flexible $-CH_2-$ spacer to meet requirements of coordination geometries of metal cations in the assembly process. In this article, seven coordination compounds based on H_2L, $[CoNa(L)_{1.5}(EtOH)_3]$ (**1**), $[Zn(L)(OH)_2]\cdot 4H_2O$ (**2**), $[Co(L)(OH)_2]\cdot 2H_2O$ (**3**), $[Co(L)(H_2O)]$ (**4**), $[Zn(L)(H_2O)]$ (**5**), $[Ni(L)(H_2O)]$ (**6**), and $[Mn(L)(H_2O)]$ (**7**), have been synthesized. The crystal structures are described and luminescent properties for **2**, **5**, and H_2L have been studied in the solid state at room temperature.

2. Experimental

2.1. *Preparation*

Chemicals were obtained commercially and used as received.

2.1.1. Synthesis of H_2L. A mixture of 2-hydroxynicotinic acid (100 mmol, 13.9 g) and ethanol (300 mL) was stirred at 60°C for 1 h and then concentrated sulfuric acid (6.4 mL) was added. The solution was heated at reflux for 1 day. Most of the solvent was removed in a water bath and then 300 mL water was added. The mixture was adjusted with $NaHCO_3$ solid ($pH \approx 7$) and the resulting mixture was extracted with trichloromethane thrice. A white solid of ethyl 2-hydroxynicotinate was obtained after evaporation of the solvent. Ethyl 2-hydroxynicotinate (30 mmol, 5.01 g) and NaOH (30 mmol) in ethanol (200 mL) were stirred while heating until NaOH was dissolved, then 3.24 g 1,4-dibromobutane (15 mmol) was added. After stirring for 12 h, NaOH (120 mmol) aqueous solution was added. The solution was heated at reflux for 6 h then ethanol was removed by heating in a water bath and 100 mL water was added to the residue. The mixture was adjusted to a pH value of 1–2. The precipitate of H_2L was collected by filtration, washed with water, and dried in air. Yield: 68%.

2.1.2. Synthesis of [CoNa(L)$_{1.5}$(C$_2$H$_5$OH)$_3$] (1). A mixture of $Co(CH_3COO)_2 \cdot 6H_2O$ (0.014 g, 0.05 mmol), H_2L (0.017 g, 0.05 mmol), ethanol (8 mL), and NaOH (0.004 g, 0.1 mmol) was placed in a Teflon reactor (15 mL). The mixture was heated at 140°C for 3 days and then gradually cooled to room temperature. Pink crystals were obtained in 35% yield based on $Co(CH_3COO)_2 \cdot 6H_2O$. Anal. Calcd for $C_{30}H_{39}N_3O_{12}CoNa$ ($M_r = 715.6$): C, 50.36; H, 5.49; N, 5.87. Found: C, 50.21; H, 5.64; N, 5.75. Infrared (IR) data (KBr, cm^{-1}): 3403 (s), 3077 (s), 2946 (s), 1639 (w), 1595 (w), 1546 (w), 1449 (m), 1272 (m), 1135 (w), 996 (m), 948 (m), 934 (s), 915 (s), 878 (s), 857 (m), 827 (m), 782 (w), 733 (w), 652 (m), 584 (w), 542 (m), 483 (m).

2.1.3. Synthesis of [Zn(L)(OH)$_2$]•4H$_2$O (2). A mixture of $Zn(CH_3COO)_2 \cdot 2H_2O$ (0.022 g, 0.1 mmol), H_2L (0.034 g, 0.1 mmol), a few drops of NaOH solution (0.1 mol L^{-1}), ethanol (7.5 mL), and water (7.5 mL) was placed in a beaker. The mixture was stirred at room temperature and ammonia water added until all solids dissolved. The solution was filtered and colorless crystals were obtained by slow evaporation of the solution at room temperature for 30 days. Yield: 32% based on $Zn(CH_3COO)_2 \cdot 2H_2O$. Anal. Calcd for $C_{16}H_{24}N_2O_{12}Zn$ ($M_r = 501.8$): C, 38.30; H, 4.82; N, 5.58. Found: C, 38.21; H, 4.69; N, 5.25. IR data (KBr, cm^{-1}): 3419 (w), 2878 (m), 2238 (s), 1640 (w), 1554 (w), 1471 (w), 1439 (w), 1212 (s), 1360 (w), 1177 (m), 1126 (m), 1089 (s), 1069 (s), 1022 (s), 933 (s), 874 (s), 776 (w), 663 (m).

2.1.4. Synthesis of [Co(L)(OH)$_2$]•2H$_2$O (3). A mixture of $Co(CH_3COO)_2 \cdot 6H_2O$ (0.014 g, 0.05 mmol), H_2L (0.017 g, 0.05 mmol), a few drops of NaOH solution (0.1 mol L^{-1}), DMF (6 mL), and water (2 mL) was placed in a Teflon reactor (15 mL). The mixture was heated at 110°C for 3 days and then gradually cooled to room temperature. Pink crystals were obtained in 46% yield based on $Co(CH_3COO)_2 \cdot 6H_2O$. Anal. Calcd for $C_{16}H_{20}N_2O_{10}Co$ ($M_r = 459.3$): C, 41.84; H, 4.39; N, 6.10. Found: C, 40.17; H, 4.84; N, 5.88. IR data (KBr, cm^{-1}): 3745 (s), 3393 (w), 2923 (m), 1718 (m), 1641 (w), 1553 (w), 1458 (m), 1432 (w), 1276 (m), 1213 (s), 1180 (m), 1134 (m), 1073 (s), 980 (s), 936 (s), 915 (s), 875 (s), 783 (w), 660 (w), 584 (w), 542 (m), 483 (m).

2.1.5. Synthesis of [Co(L)(H$_2$O)] (4). A mixture of $Co(CH_3COO)_2 \cdot 6H_2O$ (0.014 g, 0.05 mmol) H_2L (0.034 g, 0.01 mmol), ethanol (4 mL), and water (4 mL) was sealed in a Teflon reactor (15 mL). The mixture was heated at 160°C for 3 days, cooled to room temperature and pink block crystals of **4** were collected in 43% yield based on $Co(CH_3COO)_2 \cdot 6H_2O$. Anal. Calcd for $CoC_{16}O_7N_2H_{16}$ ($M_r = 407.2$): C, 47.19; H, 3.96; N, 6.88. Found: C, 46.87; H, 4.14; N, 6.80. IR data (KBr, cm^{-1}): 3077 (m), 2987 (m), 2954 (m), 1965 (s), 1918 (s), 1893 (s), 1656 (w), 1544 (w), 1289 (w), 1231 (w), 1172 (w), 1137 (m), 1097 (w), 1072 (m), 1043 (m), 969 (s), 947 (s), 925 (s), 905 (m), 880 (s), 819 (s), 802 (s).

2.1.6. Synthesis of [Zn(L)(H$_2$O)] (5). A mixture of $Zn(CH_3COO)_2 \cdot 2H_2O$ (0.011 g, 0.05 mmol), H_2L (0.017 g, 0.05 mmol), DMF (2 mL), and water (6 mL) was sealed in a Teflon reactor (15 mL). The mixture was heated at 120°C for 3 days and then cooled to room temperature. Colorless crystals of **5** were obtained in 33% yield based on

$Zn(CH_3COO)_2 \cdot 2H_2O$. Anal. Calcd for $ZnC_{16}O_7N_2H_{16}$ ($M_r = 413.7$): C, 46.45; H, 3.90; N, 6.77. Found: C, 46.17; H, 4.16; N, 6.38. IR data (KBr, cm^{-1}): 3672 (s), 3647 (s), 3079 (w), 2923 (w), 2866 (m), 1644 (w), 1554 (w), 1469 (w), 1431 (w), 1276 (m), 1215 (m), 1134 (m), 1093 (s), 1072 (s), 877 (s), 780 (m), 659 (m), 584 (s), 542 (s), 473 (s).

2.1.7. Synthesis of [Ni(L)(H_2O)] (6). A mixture of $Zn(CH_3COO)_2 \cdot 4H_2O$ (0.013 g, 0.05 mmol), H_2L (0.017 g, 0.05 mmol), ethanol (5 mL), and water (5 mL) was placed in a Teflon reactor (15 mL). The mixture was heated at 140°C for 3 days and then gradually cooled to room temperature. Green crystals of **6** were obtained in 61% yield based on $Zn(CH_3COO)_2 \cdot 4H_2O$. Anal. Calcd for $NiC_{16}O_7N_2H_{16}$ ($M_r = 407.0$): C, 47.22; H, 3.96; N, 6.88. Found: C, 46.96; H, 4.33; N, 6.76. IR data (KBr, cm^{-1}): 3430 (m), 3079 (m), 2954 (m), 1655 (w), 1542 (w), 1470 (w), 1289 (w), 1231 (m), 1172 (w), 1137 (m), 1089 (m), 1071 (m), 969 (s), 946 (s), 926 (s), 905 (s), 881 (s), 778 (w), 651 (m), 589 (s), 550 (s).

2.1.8. Synthesis of [Mn(L)(H_2O)] (7). A mixture of $Mn(CH_3COO)_2$ (0.008 g, 0.05 mmol), H_2L (0.017 g, 0.05 mmol), ethanol (5 mL), and water (5 mL) was sealed in a Teflon reactor (15 mL). The mixture was heated at 170°C for 3 days and then cooled to room temperature. Brown crystals of **7** were collected in 57% yield based on $Mn(CH_3COO)_2$. Anal. Calcd for $C_{16}H_{16}N_2O_7Mn$ ($M_r = 403.3$): C, 47.66; H, 4.00; N, 6.95%. Found: C, 47.51; H, 4.46; N, 6.88%. IR data (KBr, cm^{-1}): 3444 (w), 3076 (m), 2952 (m), 1716 (m), 1653 (w), 1610 (w), 1544 (w), 1289 (w), 1247 (s), 1229 (m), 1172 (m), 1137 (m), 1100 (s), 1073 (s), 967 (s), 905 (s), 799 (s), 776 (w), 657 (s), 644 (m), 582 (s).

2.2. *Physical measurements and X-ray crystallography*

All materials were commercially available and used as received. FT-IR spectra were recorded as KBr pellets from 4000 to 400 cm^{-1} on a Mattson Alpha-Centauri spectrometer. C, H, and N elemental analyses were conducted on a Carlo Erba 1106 elemental analyzer. Solid-state emission/excitation spectra of **2** and **5** were recorded on an FLSP920 Edinburgh Fluorescence Spectrometer at room temperature.

Single-crystal X-ray diffraction data for **1**–**7** were recorded on an Oxford Diffraction Gemini R Ultra diffractometer with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) at 293 K. Absorption corrections were applied using multi-scan technique. All structures were solved by direct methods of SHELXS-97 and refined by full-matrix least-squares using the SHELXL-97 program [10, 11]. All non-hydrogen atoms were easily found from the Fourier difference maps and refined anisotropically. Hydrogen atoms attached to carbons and hydroxyl groups were generated geometrically. Hydrogen atoms of water were located from difference Fourier maps. Details of data collection and structure refinement parameters for **1**–**7** are summarized in table 1. Selected bond distances and angles for all compounds are listed in table S1 ("Supplementary material" section).

Table 1. Crystal data and structure refinements for **1–7**.

	1	**2**	**3**	**4**	**5**	**6**	**7**
Empirical formula	$C_{30}H_{39}N_3O_{12}CoNa$	$C_{16}H_{24}N_2O_{12}Zn$	$C_{16}H_{20}N_2O_{10}Co$	$C_{16}H_{16}N_2O_7Co$	$C_{16}H_{16}N_2O_7Zn$	$C_{16}H_{16}N_2O_7Ni$	$C_{16}H_{16}N_2O_7Mn$
Formula weight	715.6	501.7	459.3	407.2	413.7	407.0	403.3
Crystal system	Trigonal	Triclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$R\text{-}3c$	$P\bar{1}$	$C2/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$
Unit cell dimensions (Å, °)							
a	16.046(5)	4.822(6)	19.0900(18)	7.7480(3)	7.748(3)	7.745(3)	7.7510(2)
b	16.046(5)	10.070(14)	9.4014(5)	21.5230(9)	21.501(8)	21.369(7)	21.9450(6)
c	44.478(5)	11.053(5)	12.3839(11)	9.7620(4)	9.743(4)	9.773(4)	9.7380(3)
α	90	106.414(11)	90	90	90	90	90
β	90	91.042(10)	121.513(12)	105.533(4)	105.657(5)	105.887(5)	105.113(3)
γ	120	95.885(11)	90	90	90	90	90
Volume (Å^3), Z	9918(5), 12	511.5(11), 1	1894.8(3), 4	1568.46(11), 4	1562.9(11), 4	1555.7(13), 4	1599.10(8), 4
Calculated density (g cm^{-3})	1.438	1.629	1.610	1.725	1.758	1.738	1.675
$F(000)$	4488	260	948	836	848	840	828
Reflections collected/unique	18,832/1950	3186/1790	5580/1679	5741/2755	5894/2757	5846/2737	9833/2822
Goodness-of-fit on F^2	1.048	1.034	1.062	1.076	1.098	1.052	1.039
R_1[a] $[I > 2\sigma(I)]$	0.0422	0.0470	0.0501	0.0352	0.0279	0.0369	0.0347
wR_2[b]	0.1078	0.1099	0.1505	0.0933	0.0668	0.0945	0.0858

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = |\Sigma w(|F_o|^3 - |F_c|^3)|/\Sigma|w(F_o^3)^3|^{2/3}$.

3. Results and discussion

3.1. *Crystal structure*

3.1.1. Structure of [CoNa(L)$_{1.5}$(EtOH)$_3$] (1). As illustrated in figure 1(a), the asymmetric unit of **1** contains one-third of a Co(II) cation, one-third of an Na(I), half of an L anion, and one ethanol. Each Co(II) is six-coordinate with three carboxyl (Co–O2 = 2.0597(18), Co–O2$^{\#1}$ = 2.0597(18) and Co–O2$^{\#2}$ = 2.0597(18) Å) and three hydroxyl oxygen atoms from three L anions (Co–O1 = 2.0821(17), Co–O1$^{\#1}$ = 2.0821(17), and Co–O1$^{\#2}$ = 2.0821(17) Å) in a distorted octahedron. Each Na(I) is six-coordinate by three carboxyl oxygen atoms (Na–O2 = 2.524(2), Na–O2$^{\#1}$ = 2.524(2), and Na–O2$^{\#2}$ = 2.524(2) Å) from three L anions and three ethanols (Na–O4 = 2.390(2), Na–O4$^{\#1}$ = 2.390(2), and Na–O4$^{\#2}$ = 2.390(2) Å). In **1**, L adopts a μ_4-$\eta^0:\eta^2:\eta^1:\eta^1:\eta^2:\eta^0$ mode (mode I, scheme 2), bridging two Co(II) cations and two Na(I) cations to form a discrete structure (figure 1b).

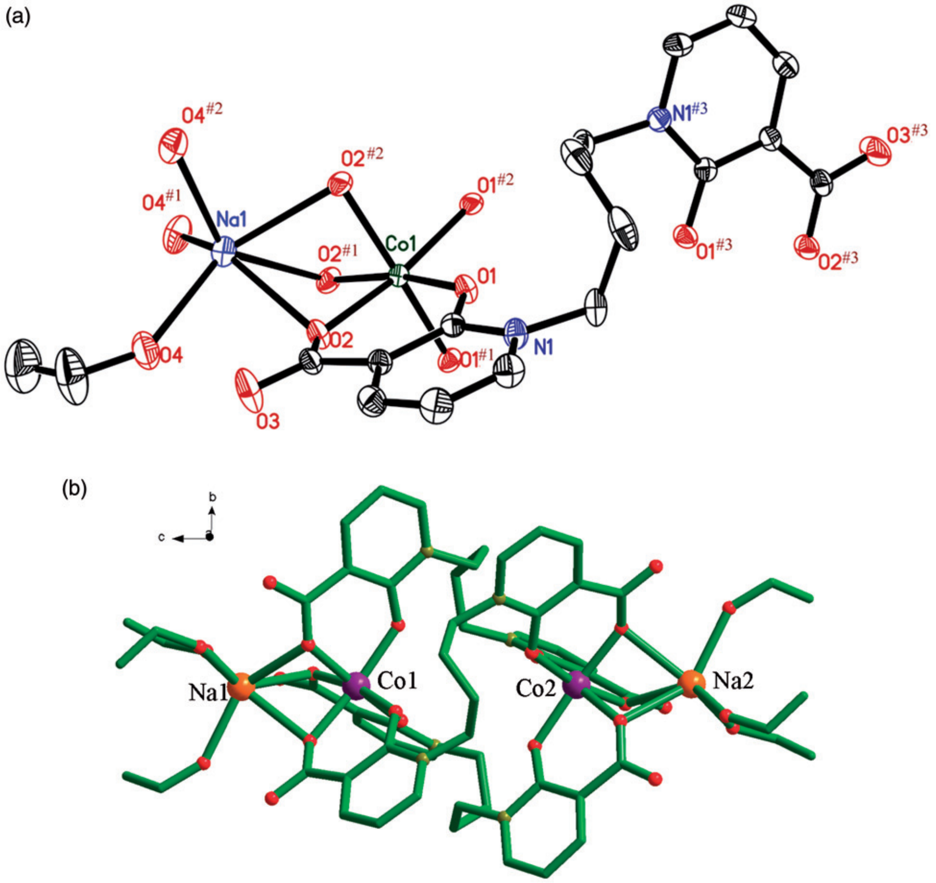


Figure 1. (a) ORTEP diagram showing the coordination environments for Co(II) and Na(I) cations in **1**. Symmetry codes: $^{\#1}$ $-x+y$, $-x$, z; $^{\#2}$ $-y$, $x-y$, z; $^{\#3}$ $-x$, $-x+y$, $-z+1/2$. All hydrogen atoms are omitted for clarity. (b) View of the discrete structure of **1** along the *a*-axis.

3.1.2. Structure of [Zn(L)(OH)$_2$]·4H$_2$O (2). As shown in figure 2(a), the asymmetric unit of **2** contains half a Zn(II) cation, half of an L anion, a hydroxyl, and two lattice water molecules. Each Zn(II) is six-coordinate with two carboxyl oxygen atoms from two L anions (Zn–O2 = 2.026(3) and Zn–O2$^{\#1}$ = 2.026(3) Å) and four hydroxyl

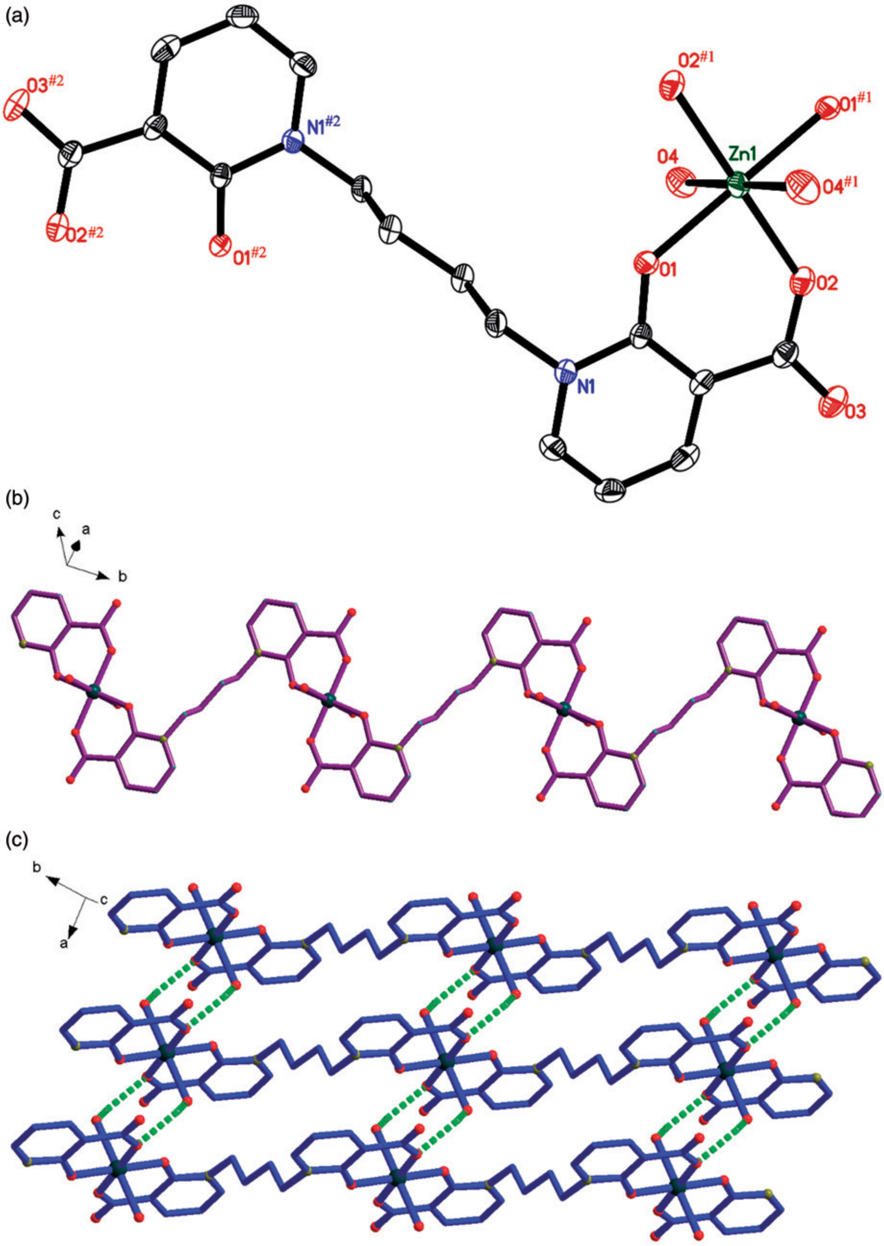


Figure 2. (a) ORTEP drawing of the asymmetric unit of **2**. All lattice water molecules and hydrogen atoms are omitted for clarity. Symmetry codes: $^{\#1}$ $-x$, $-y+1$, $-z$; $^{\#2}$ $-x-1$, $-y$, $-z$. (b) View of the 1-D chain of **2**. (c) The 2-D supramolecular layer constructed by hydrogen-bonding interactions (O4–H4A . . . O2) in **2**.

oxygen atoms (Zn–O1 = 2.065(2), Zn–O1$^{\#1}$ = 2.065(2), Zn–O4 = 2.160(3), and Zn–O4$^{\#1}$ = 2.160(3) Å), showing a distorted octahedral coordination. In **2**, L adopts a μ_4-$\eta^0:\eta^1:\eta^1:\eta^1:\eta^1:\eta^0$ mode (mode II, scheme 2), bridging Zn(II) cations to form a 1-D "Z" chain structure (figure 2b). Intermolecular hydrogen-bonding interaction (O4–H4A···O2) exists between hydroxyl and L. The chains are extended into a 2-D supramolecular layer by hydrogen-bonding interaction (figure 2c).

3.1.3. Structure of [Co(L)(OH)$_2$]·2H$_2$O (3).

The asymmetric unit of **3** consists of half a Co(II) cation, half of an L anion, a hydroxyl, and two half lattice water molecules. Each Co(II) is six-coordinate by two carboxyl oxygen atoms from two L (Co–O2 = 2.038(2) Å, Co–O2$^{\#1}$ = 2.038(2) Å) and four hydroxyl oxygen atoms (Co–O1 = 2.049(2) Å, Co–O1$^{\#1}$ = 2.049(2) Å, Co–O4 = 2.140(3) Å, and Co–O4$^{\#1}$ = 2.140(3) Å), showing a distorted octahedral coordination (figure 3a). Each L adopts a μ_4-$\eta^0:\eta^1:\eta^1:\eta^1:\eta^1:\eta^0$ mode (mode II, scheme 2), linking two Zn(II) cations to form a 1-D "Z" chain structure (figure 3b). The 1-D "Z" chain of **3** is similar to that of **2**, however, the packing mode of the chains is different. In **3**, the 1-D chains are arranged on parallel levels in different propagating directions to generate a plywood-like packing mode (figure 3c) [12]. Further, the 1-D chains are linked by intermolecular hydrogen-

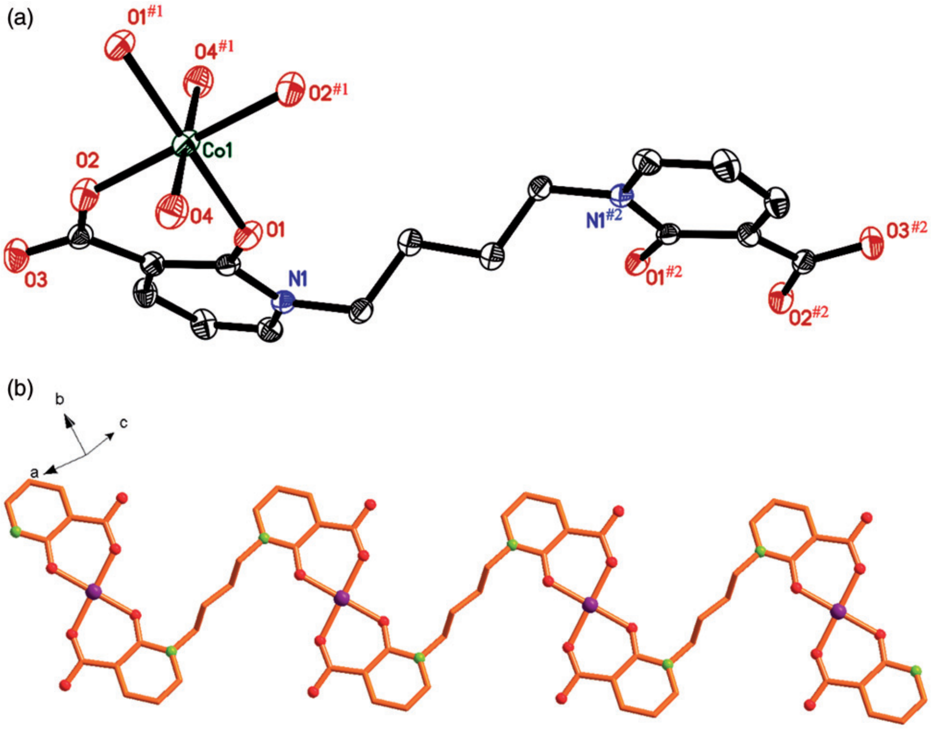


Figure 3. (a) Coordination environment of Co(II) cation in **3**. Symmetry codes: $^{\#1}$ $-x+1/2$, $-y+1/2$, $-z+1$; $^{\#2}$ $-x+1$, $-y+1$, $-z+1$. All lattice water molecules and hydrogen atoms are omitted for clarity. (b) The 1-D "Z" chain constructed by L anions and Co(II). (c) Schematic representation (left) and the plywood-like packing mode (right) of the 1-D chains (constructed by Co(II) and L anions) spanning two different directions. (d) Schematic representation of 2-D supramolecular structure constructed by hydrogen-bonding interactions.

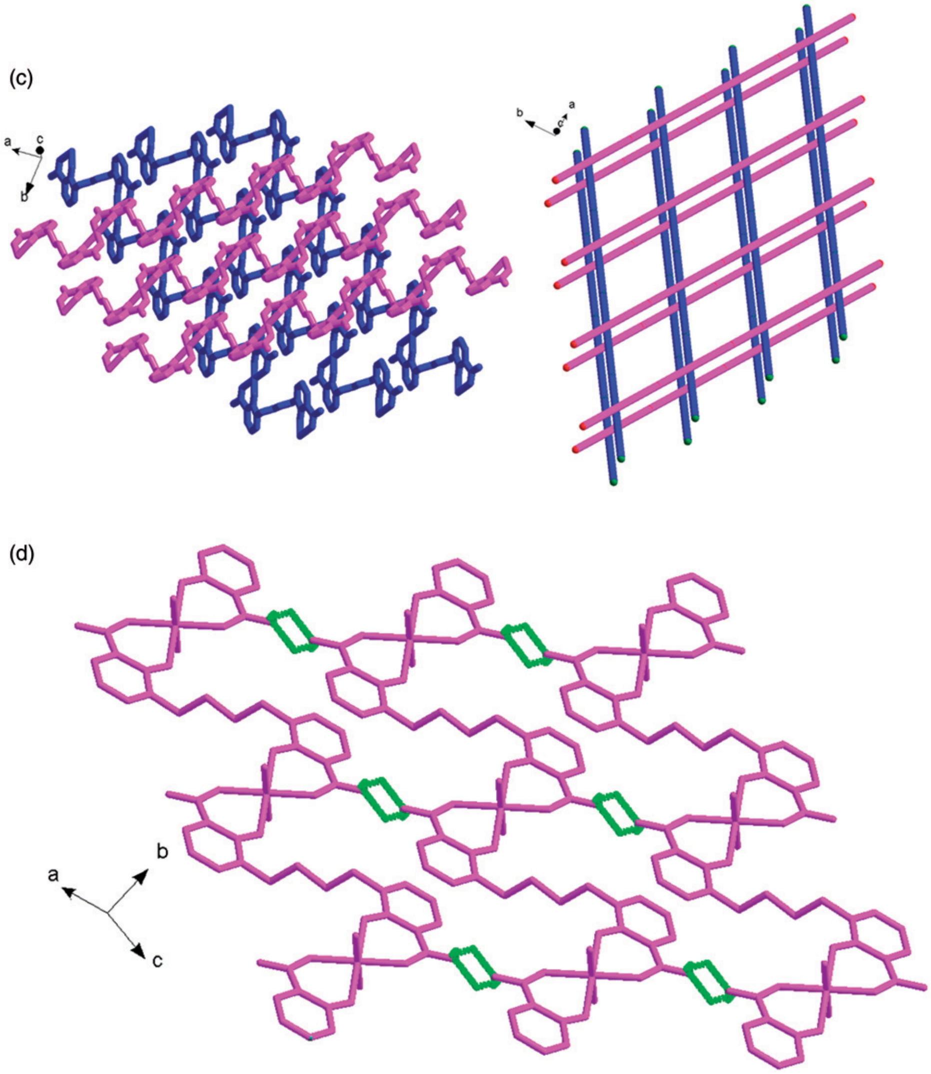


Figure 3. Continued.

bonding interactions (O1W–H1A···O3$^{\#3}$ and O1W–H1B···O3; $^{\#3}$ $-x$, $-y+1$, $-z+1$) into a 2-D supramolecular structure (figure 3d).

3.1.4. Structures of 4–7. Single-crystal X-ray structural analysis shows that **4**–**7** are isomorphous and have the same 2-D network structures. Illustrated by [Co(L)(H_2O)] (**4**), each Co(II) is six-coordinate with three carboxyl oxygen atoms from three L (Co–O2 = 2.0565(18), Co–O2$^{\#3}$ = 2.1302(17), and Co–O5$^{\#1}$ = 2.0853(18) Å), two hydroxyl oxygen atoms (Co–O1 = 2.0667(18) and Co–O4$^{\#1}$ = 2.0667(18) Å), and one water molecule (Co–O1W = 2.1440(19) Å) in an octahedral coordination (figure 4a). In **4**, each L bridges three Co(II) cations in a μ_4-$\eta^0:\eta^2:\eta^1:\eta^1:\eta^1:\eta^0$ coordination mode

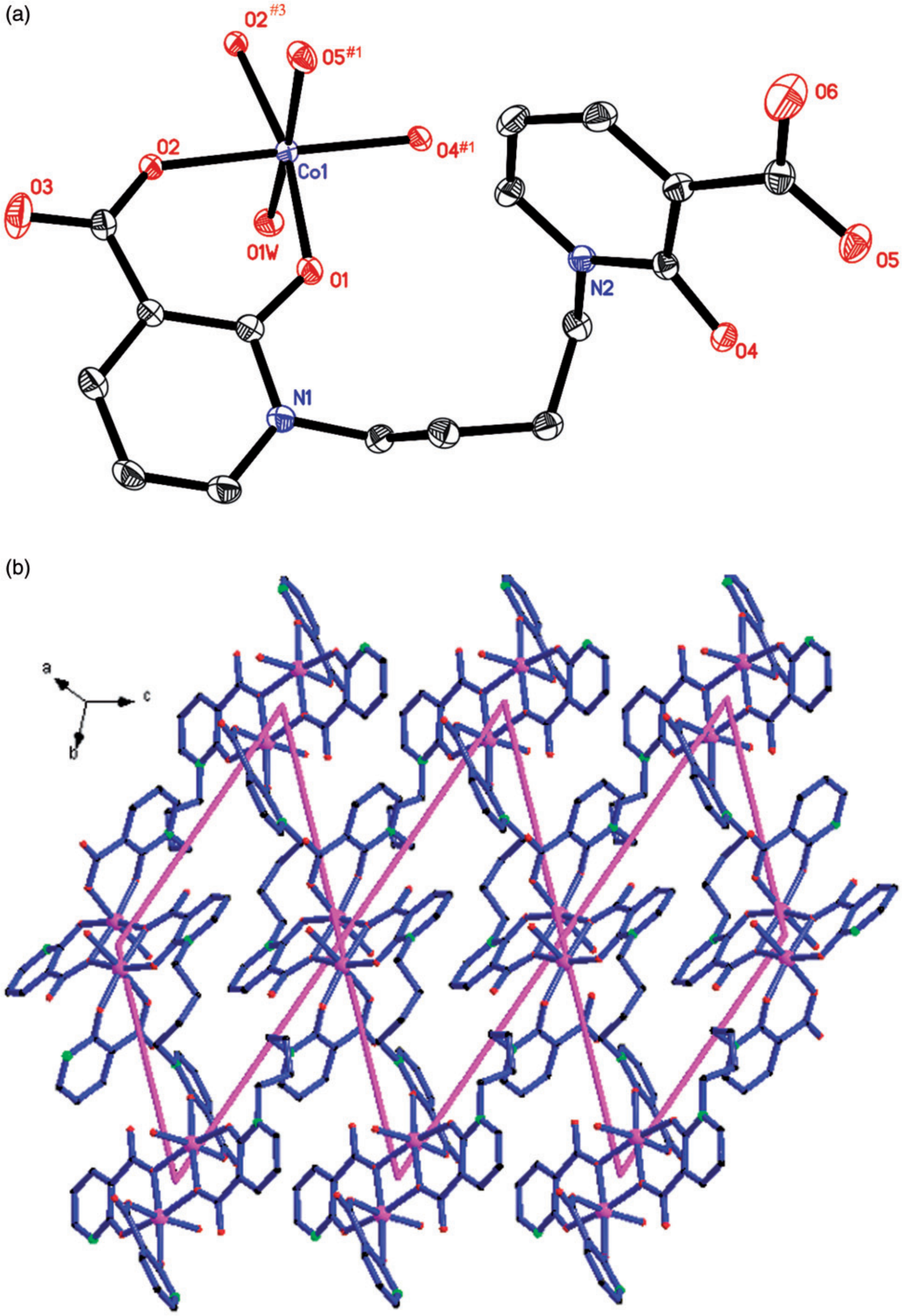


Figure 4. (a) Coordination environment of the Co(II) cation in **4**. Symmetry codes: $^{\#1}$ x, $-y+1/2$, $z-1/2$; $^{\#3}$ $-x$, $-y$, $-z$. All hydrogen atoms are omitted for clarity. (b) View of the 2-D (4^4)-**SQL** network constructed by L anions and Co(II) cations.

(mode III, scheme 2) to yield a 2-D grid structure. In the 2-D layer, two adjacent Co(II) cations are bridged by carboxyl oxygen atoms to generate a dinuclear Co(II) unit. From the topological view, if each (Co_2O_2) dimer is considered as a 4-connected node, the structure of **4** is a 2-D (4^4)-**SQL** network (figure 4b). The asymmetric units of **5**–**7** are shown in the "Supplementary material" (figures S1–S3) section.

3.2. *X-ray powder diffraction results*

To confirm whether the crystal structures are truly representative of the bulk materials, X-ray powder diffraction (XPRD) experiments were carried out for **1**–**7**. The experimental and computer-simulated XPRD patterns of the corresponding complexes are shown in the "Supplementary material" section. They show that the synthesized bulk materials and the measured single crystals are the same (figure S4).

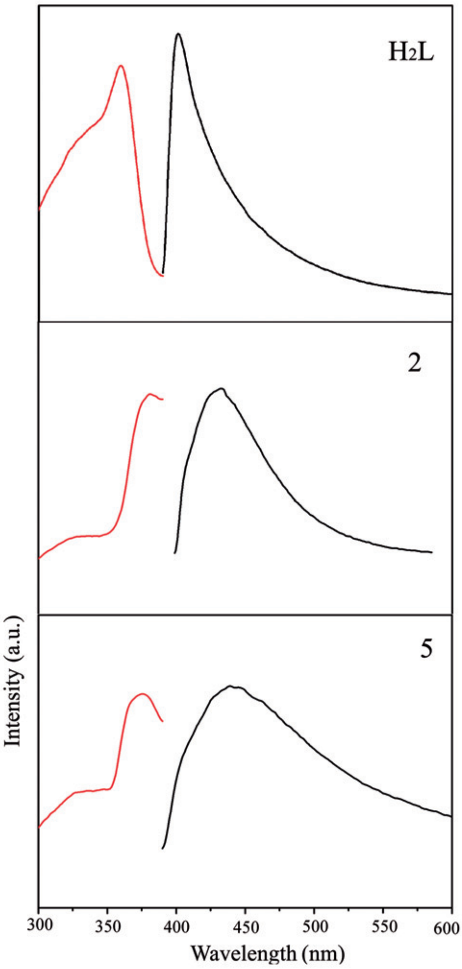


Figure 5. Solid-state photoluminescent spectra of free ligand H_2L, **2**, and **5** at room temperature.

3.3. *Luminescent properties*

Luminescent compounds have interest due to potential applications in chemical sensors, photochemistry, and electroluminescent displays [13]. Solid-state photoluminescent spectra of H_2L, **2**, and **5** have been studied at room temperature (figure 5). The emission maxima peak of H_2L is at 401 nm ($\lambda_{ex} = 360$ nm), attributed to $\pi^* \rightarrow n$ or $\pi^* \rightarrow \pi$ transitions as previously reported [14, 15]. The emission peaks of **2** and **5** are at 433 ($\lambda_{ex} = 382$ nm) and 439 nm ($\lambda_{ex} = 377$ nm), respectively, similar to that of free H_2L. Since the Zn(II) cations are difficult to oxidize or to reduce due to their d^{10} configuration, the emission peaks of **2** and **5** are neither metal-to-ligand charge transfer nor ligand-to-metal charge transfer [16]. For **2** and **5**, the emission peaks are red-shifted with respect to free H_2L because of the replacement of hydrogen atoms by Zn(II), which decreases the $\pi^* \rightarrow n$ or $\pi^* \rightarrow \pi$ gaps of the carboxylate ligand [17]. Therefore, the photoluminescence of **2** and **5** may be assigned to intraligand fluorescent emission of L anion [18].

4. Conclusion

Seven new coordination compounds based on H_2L have been isolated through varying the reaction conditions and metal cations. The compounds show 0-D, 1-D, and 2-D structures. The results demonstrate that the coordination modes of L and the metal cause structure variations. A number of coordination compounds with fascinating structures and potential applications will be constructed through using N-containing flexible polycarboxylate ligands.

Supplementary material

X-ray crystallographic files in CIF format for **1–3** have been deposited at the Cambridge Crystallographic Data Center with the deposition number CCDC 877 485–877491. Copies of the data can be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk).

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