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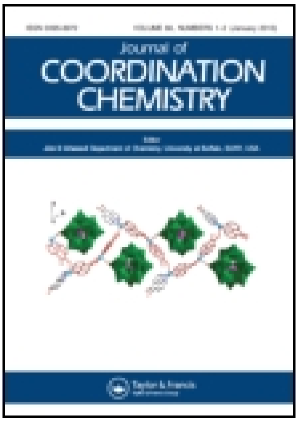

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Syntheses and structures of four transition metal coordination polymers constructed from 2,2′-bipyridyl-4,4′-dicarboxylate

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Syntheses and structures of four transition metal coordination polymers constructed from 2,2′-bipyridyl-4,4′-dicarboxylate

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Four transition metal(II) coordination polymers, $[Mn(bpdc)(H_2O)_2]_n$ (**1**), $\{Ni[(bpdc)(H_2O)_2].2H_2O\}_n$ (**2**), $[Ni(bpdc)(H_2O)_2]_n$ (**3**), and $[Cu(bpdc)H_2O)]_n$ (**4**) ($bpdc^{2-}$ = 2,2′-bipyridyl-4,4′-dicarboxylate), have been assembled from 2,2′-bipyridyl-4,4′-dicarboxylic acid and corresponding transition metal (II) salts under hydrothermal conditions. Single-crystal X-ray diffraction studies show that each metal ion in **1–3** is coordinated by two nitrogens of $bpdc^{2-}$, two carboxylate oxygens from $bpdc^{2-}$, and two waters to give a distorted octahedral geometry. Copper in **4** is coordinated by two nitrogens of $bpdc^{2-}$, two carboxylate oxygens from $bpdc^{2-}$, and one water to form a pyramid geometry. Compounds **1** and **3** are 3-D coordination polymers bridged by $bpdc^{2-}$, while **2** and **4** exhibit 2-D layer structures bridged by $bpdc^{2-}$; the layers are further assembled through hydrogen bonds to form 3-D supramolecular frameworks. Thermogravimetric analyzes of **1–4** show high thermal stability.

Keywords: Transition metal; 2,2′-Bipyridyl-4,4′-dicarboxylic acid; Chemical syntheses; Crystal structure

1. Introduction

Polymeric coordination compounds have relevance to construction of inorganic solid-state materials from molecular-bridging blocks [1] and potential applications to gas sorption, catalysis, ion exchange, non-linear optics, and molecular recognition [2–5]. To get designed frameworks and properties, studies are focused on coordination polymers with versatile ligands [6], in particular, ligands with carboxylates [7–13]. Among these ligands, 2,2′-bipyridyl-4,4′dicarboxylic acid, especially, is very good choice of O- and N-donor ligand [3, 14–17] because it possesses diverse coordination capabilities upon reacting with metal ions, and the overall framework architecture can be altered on the basis of coordination of metal ions [18–20]. Significant progress has been achieved in this area, for example, based on 2,2′-bipyridyl-4,4′-dicarboxylic acid (H_2bpdc) as ligand, many coordination polymers have been reported [4, 21–25]. However, to the best of our knowledge, reports on Mn(II), Ni(II), and Cu(II) coordination frameworks constructed from $bpdc^{2-}$ are rela-

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tively scarce [19, 26]. Herein, we report the syntheses and crystal structures of [Mn(bpdc)(H_2O)$_2$]$_n$ (**1**), {Ni[(bpdc)(H_2O)$_2$]·2H_2O}$_n$ (**2**), [Ni(bpdc)(H_2O)$_2$]$_n$ (**3**), and [Cu(bpdc)H_2O)]$_n$ (**4**). These compounds show high thermal stability.

2. Experimental

2.1. *General procedures*

All reagents used in the syntheses were purchased commercially and used without purification. Thermogravimetric (TG) analysis was conducted on a NETZSCH STA449C analyzer at 10 °C/min under nitrogen for all measurements. Elemental analyzes were performed on an Elementar Vario EL-III elemental analyzer. Infrared spectra were recorded on a Bruker Equinox 55 spectrometer from 4000 to 400 cm^{-1} using KBr pellets at room temperature under dry air. Crystallographic data were collected by a Bruker SMART-APEXIICCD diffractometer using graphite monochromated Mo Kα radiation ($\lambda = 0.7107$ Å).

2.2. *Synthesis of [Mn(bpdc)(H_2O)$_2$]$_n$ (1)*

The compound was synthesized under hydrothermal condition, placing reactants and solvent in a 25-mL beaker and stirring 0.5 h, transferring to a 25-mL polytetrafluoroethylene-lined stainless steel container, gradually heating the reaction mixture to 130 °C over 4 h, keeping the temperature for 4 days, gradually cooling the crude products over 24 h to room temperature, and compound **1** was obtained by filtering. The reacting components included 12.2 mg (0.05 mmol) 2,2′-bipyridyl-4,4′-dicarboxylic acid, 9.9 mg (0.05 mmol) $MnCl_2·4H_2O$, 7.8 mg (0.05 mmol) 4,4′-bipyridine, and 8 mL distilled water. The yield of the desired yellow crystalline product was 47% (7.8 mg). Anal. Calcd for [Mn(bpdc)(H_2O)$_2$]$_n$ (%): C, 43.24; H, 3.00; N, 8.41. Found: C, 43.52; H, 2.96; N, 8.44. IR (KBr, cm^{-1}): 3371 (b), 1606 (m), 1369 (s), 1294 (s), 1009 (w), 907 (w), 765 (m), 683 (m).

2.3. *Synthesis of {Ni[(bpdc)(H_2O)$_2$]·2H_2O}$_n$ (2)*

A mixture of 12.2 mg (0.05 mmol) 2,2′-bipyridyl-4,4′-dicarboxylic acid, 11.9 mg (0.05 mmol) $NiCl_2.6H_2O$, 7.8 mg (0.05 mmol), and 4,4′-bipyridine was dissolved in distilled water (8 mL) and stirred 0.5 h. Then, the mixture was added to a 25-mL polytetrafluoroethylene-lined stainless steel container. The container was gradually heated to 130 °C in 4 h and kept at that temperature for 4 days. The crude products were gradually cooled to room temperature over 24 h. The yield of the desired deep blue crystalline product was 32% (6.0 mg). Anal. Calcd for {Ni[(bpdc)(H_2O)$_2$]·2H_2O}$_n$ (%): C, 38.61; H, 3.75; N, 7.51. Found: C, 38.65; H, 3.73; N, 7.55. IR (KBr, cm^{-1}): 3407 (b), 1604 (s), 1550 (s), 1429 (m), 1381 (s), 1295 (w), 1239 (w), 780 (m), 705 (m).

2.4. *Synthesis of [Ni(bpdc)(H_2O)$_2$]$_n$ (3)*

A mixture of 12.2 mg (0.05 mmol) 2,2′-bipyridyl-4,4′-dicarboxylic acid, 11.9 mg (0.05 mmol) $NiCl_2.6H_2O$, and 8.3 mg (0.05 mmol) terephthalic acid was dissolved in distilled water (8 mL) and stirred 0.5 h, and then, mixture was added in a 25-mL polytetrafluoroethylene-lined stainless steel container. The container was gradually heated to 150 °C in 4 h and kept for 4 days; the products were gradually cooled to room temperature over 24 h, and crystalline products were obtained by filtering. The yield of the desired crystals was 62% (10.4 mg). Anal. Calcd for $[Ni(bpdc)(H_2O)_2]_n$ (%): C, 42.73; H, 2.97; N, 8.31. Found: C, 42.77; H, 2.92; N, 8.37. IR (KBr, cm^{-1}): 3420 (b), 1686 (s), 1616 (s), 1554 (s), 1425 (s), 1382 (s), 1291 (s), 779 (m), 732 (m), 651 (m).

2.5. *Synthesis of [Cu(bpdc)H$_2$O)]$_n$ (4)*

A mixture of 12.2 mg (0.05 mmol) 2,2′-bipyridyl-4,4′-dicarboxylic acid, 17.1 mg (0.10 mmol) $CuCl_2{\cdot}2H_2O$ and 6.2 mg (0.05 mmol) isonicotinic acid was dissolved in distilled water (8 mL) and stirred 0.5 h, added to a 25-ml polytetrafluoroethylene-lined stainless steel container, heated to 160 °C and kept for 3 days. Crude product was cooled to room temperature with yield of desired blue crystals of 54% (8.7 mg). Anal. Calcd for $[Cu(bpdc)(H_2O)]_n$ (%): C, 44.48; H, 2.47; N, 8.65. Found: C, 44.61; H, 2.42; N, 8.70. IR (KBr, cm^{-1}): 3425 (b), 1620 (s), 1552 (w), 1403 (m), 706 (w).

3. Results and discussion

3.1. *Synthesis*

Under hydrothermal conditions, **1–4** were synthesized. Auxiliary ligand (4,4′-bipyridine, 4,4′-bipyridine, terephthalic, and isonicotinic acids for **1**, **2**, **3,** and **4**, respectively) were added, but not found in crystals, indicating stronger coordination ability of $bpdc^{2-}$ than auxiliary ligand.

3.2. *IR spectra*

Comparing infrared spectra of free ligand to **1–4** gives information about coordination of the ligand. IR spectra (figure S1 in Supplementary material) of **1–4** show absorptions resulting from υ_s and υ_{as} of carboxylate at $1360-1490\,cm^{-1}$ and $1580-1635\,cm^{-1}$, respectively. Bands at $650-800\,cm^{-1}$ are assigned to C–H modes of pyridine. Absorptions of O–H of coordinated or lattice water of **1–4** are observed at $3400\,cm^{-1}$. In **1–4**, no band appears between 1700 and $1750\,cm^{-1}$, due to carboxylate of free ligand, indicating that carboxylate is coordinated.

3.3. *Crystallographic determination*

Crystallographic data for **1–4** were collected by a Bruker SMART-APEXIICCD diffractometer equipped with Mo Kα radiation ($\lambda = 0.7107$ Å) at 296 K. Crystal structures were solved by direct methods on SHELXL97 [27] and refined by Fourier full-matrix least-squares calculations using anisotropic displacement parameters for all non-hydrogen atoms [28–31].

3.4. *Structural description*

The crystallographic data of **1–4** are in table 1. Selected bond lengths and angles for **1–4** are given in tables S1−S5 (Supplementary material).

3.4.1. Structure of [Mn(bpdc)(H_2O)$_2$]$_n$ (1).

Single-crystal X-ray analysis reveals that **1** is in orthorhombic system $P2_12_12_1$ space group. As shown in figure 1(a), each Mn(II) is coordinated by two nitrogens (N1−Mn = 2.258(6), N2−Mn = 2.251(6) Å) of bpdc^{2-}, two carboxylate oxygens (O4A−Mn = 2.196(6), O1B−Mn = 2.161(5) Å) from two bpdc^{2-} and two waters (O2−Mn = 2.143(6), O3−Mn = 2.206(7) Å) to form a distorted octahedral coordination geometry (selected bond lengths and angles of **1** are given in table S1). Each bpdc^{2-} chelates one Mn(II) via two nitrogens and bridges two Mn(II) ions by using two oxygens from the same carboxylate.

The detailed structure analysis indicates that two oxygens of a carboxylate bind to the adjacent Mn(II), which gives a 1-D right-handed spiral coordination polymer (figure 1(b)). The chain shows the coordination modes of bpdc^{2-} and the configuration of Mn(II). Compared with the similar helical chains in previous reports [32–34], **1** has a different characteristic that all helical chains in **1** are right-handed spiral, while structures in reports have both right-handed and left-handed helical chains. The helical chains are further linked by oxygen of bpdc^{2-} to form a 3-D framework (figure 2).

3.4.2. Structure of {Ni[(bpdc)(H_2O)$_2$] 2H_2O}$_n$ (2).

X-ray crystallography analysis shows that **2** is in a monoclinic system, space group *Cc*. The asymmetric unit of **2** consists

Table 1. Crystal data and structure refinement parameters for **1–4**.

Compound	**1**	**2**	**3**	**4**
Empirical formula	$C_{12}H_{10}MnN_2O_6$	$C_{12}H_{14}N_2NiO_8$	$C_{12}H_{10}N_2NiO_6$	$C_{12}H_8CuN_2O_5$
Formula weight	333.16	372.96	336.93	323.74
Crystal system	Orthorhombic	Monoclinic	Trigonal	Monoclinic
Space group	$P2_12_12_1$	*Cc*	$P3_221$	*C2/c*
a (Å)	6.8689(12)	12.2269(16)	11.8620(12)	21.813(3)
b (Å)	13.2665(15)	9.1084(12)	11.8620(12)	8.8628(11)
c (Å)	13.290(2)	14.102(3)	8.2201(10)	13.6464(18)
α (°)	90	90	90	90
β (°)	90	110.3190(10)	90	126.1250(10)
γ (°)	90	90	120	90
V (Å^3)	1211.0(3)	1472.8(4)	1001.67(19)	2131.0(5)
Z	4	4	3	8
Dc (mg/cm^3)	1.827	1.682	1.676	2.018
T (K)	293(2)	296(2)	296(2)	296(2)
μ (MoKα) (mm^{-1})	1.122	1.362	1.482	2.074
Crystal size (mm)	0.32 × 0.24 × 0.19	0.35 × 0.24 × 0.21	0.32 × 0.29 × 0.25	0.32 × 0.21 × 0.19
F(000)	676	768	516	1304
GOF	1.044	1.083	0.861	1.082
θ Range for data	3.07–25.00	2.86–25.10	1.98–25.09	2.31–25.09
R_1 ($I > 2\sigma$)	$R_1 = 0.0614$	$R_1 = 0.0262$	$R_1 = 0.0352$	$R_1 = 0.0280$
wR_2 (I > 2σ)	$wR_2 = 0.1399$	$wR_2 = 0.0715$	$wR_2 = 0.0588$	$wR_2 = 0.0654$
R_1 (all data)	$R_1 = 0.0799$	$R_1 = 0.0299$	$R_1 = 0.0444$	$R_1 = 0.0339$
wR_2 (all data)	$wR_2 = 0.1509$	$wR_2 = 0.0927$	$wR_2 = 0.0610$	$wR_2 = 0.0689$

Note: $R_1 = \Sigma(|F_o|-|F_c|)/\Sigma|F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

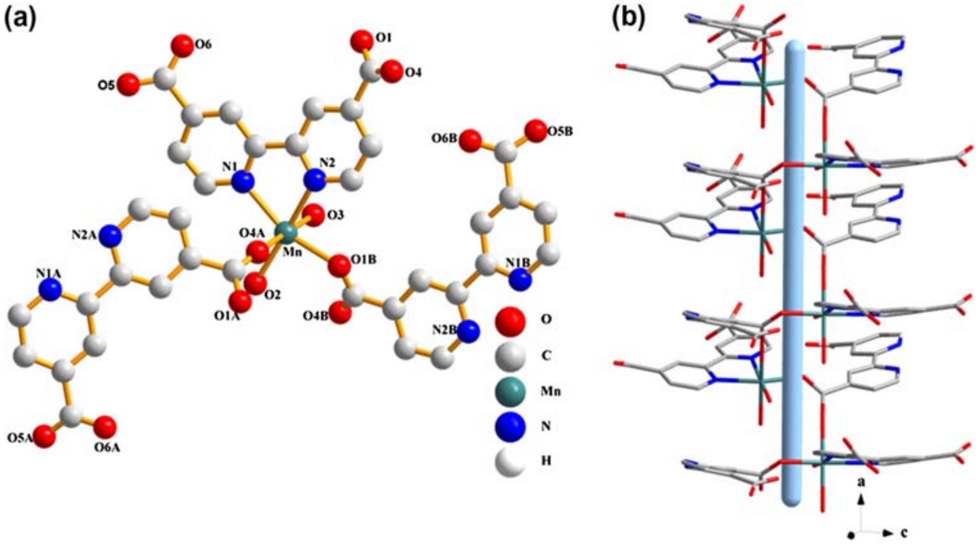


Figure 1. (a) The coordination environment of Mn(II). Symmetry codes: (A) $1-x$, $-0.5+y$, $0.5-z$; (B) $0.5-x$, $1-y$, $-0.5+z$ (hydrogens are omitted for clarity). (b) The right-handed helical chain formed by oxygens of a carboxylate and metal ions.

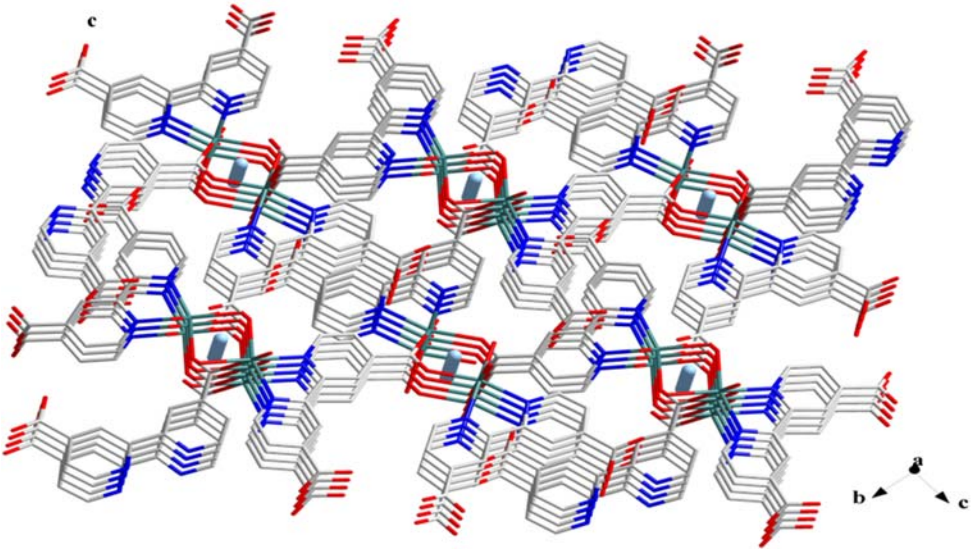


Figure 2. The 3-D structure network of **1** formed by helical chains.

of one Ni(II), one bpdc^{2-} and four waters (two coordinated and two lattice). Ni(II) displays a distorted octahedral environment (figure 3(a)). The equatorial plane consists of two nitrogens (N1–Ni1 = 2.032(4), N2–Ni1 = 2.062(4) Å) of a bpdc^{2-} ligand and two oxygens (O2A–Ni1 = 2.055(3), O3B–Ni1 = 2.067(3) Å) of bpdc^{2-} ligands. The axial positions are occupied by two waters (O5–Ni1 = 2.101(3) and O6–Ni = 2.123(3) Å)

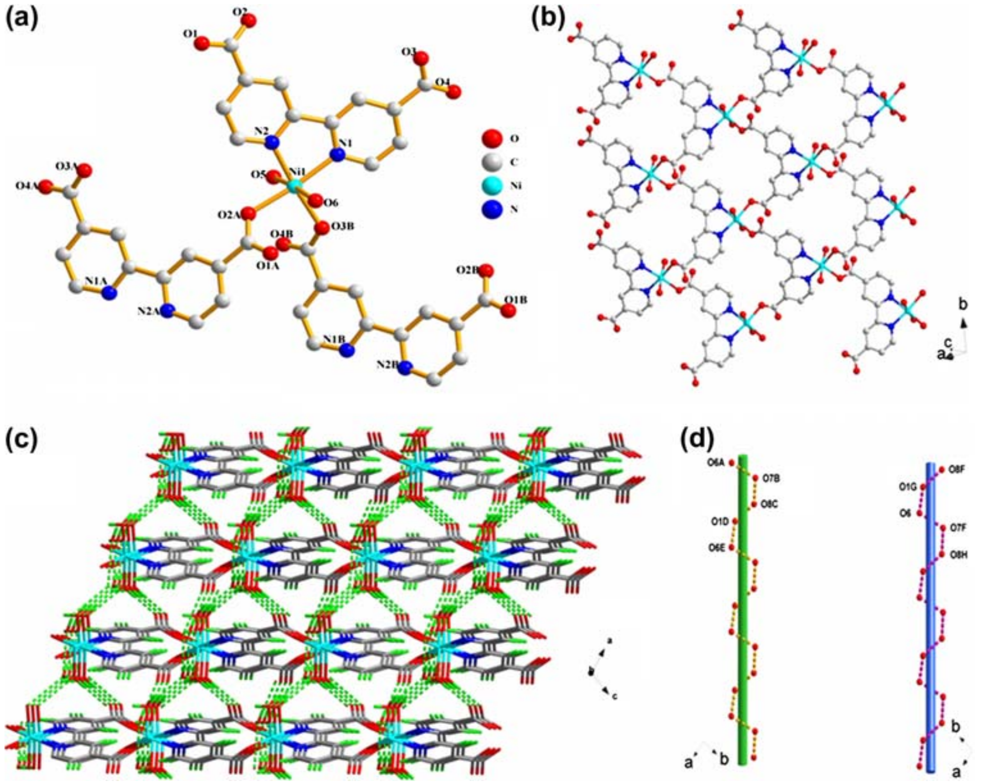


Figure 3. (a) The coordination environment of Ni(II). Symmetry codes: (A) $-0.5-x$, $0.5-y$, $-0.5+z$. (B) $-0.5+x$, $-0.5-y$, $-0.5+z$; (b) The 2-D layer constructed by O bridges of bpdc^{2-}. (c) The 3-D supramolecular structure of **2**; hydrogen-bonding interactions between the layers are indicated as green dotted line. (d) Helical chains of hydrogen bonds.

(table S2). Each bpdc^{2-} chelates one Ni(II) by nitrogens and connects another two Ni(II) ions via two oxygens from different carboxylates. Another oxygen of each carboxylate forms a hydrogen bond with neighboring coordinated water.

The Ni(II) ions are bridged by bpdc^{2-} to form a layer structure (shown in figure 3(b)). Adjacent layers are connected by two kinds of hydrogen bonds (O(6)−H(6B)···O(4)#6, −O1−O8−O7−O6−) (table S3), and thus, the 3-D supramolecular structure of **2** (figure 3c) is formed, similar to those in previous reports [35–38]. These hydrogen bond interactions give −O1−O8−O7−O6− left and right spiral structures (shown in figure 3(d)) which are similar to that reported [39].

3.4.3. Structure of [Ni(bpdc)(H$_2$O)$_2$]$_n$ (3).

Single-crystal X-ray analysis reveals that **3** is in trigonal system, *P3$_2$21* space group. Figure 4(a) depicts the coordination environment around Ni(II), coordinated by two nitrogens of a bpdc^{2-}, two oxygens from bpdc^{2-} ligands, and two waters. The bond length of N1−Ni1 is 2.069(4) Å, and the Ni1−O bond lengths are 2.064(3) to 2.067(3) Å (table S4).

The bpdc^{2-} chelates one Ni(II) by two nitrogens and bridges another two Ni(II) ions via two carboxylate oxygens in different directions to give a 3-D structure (figure 4(b)). This

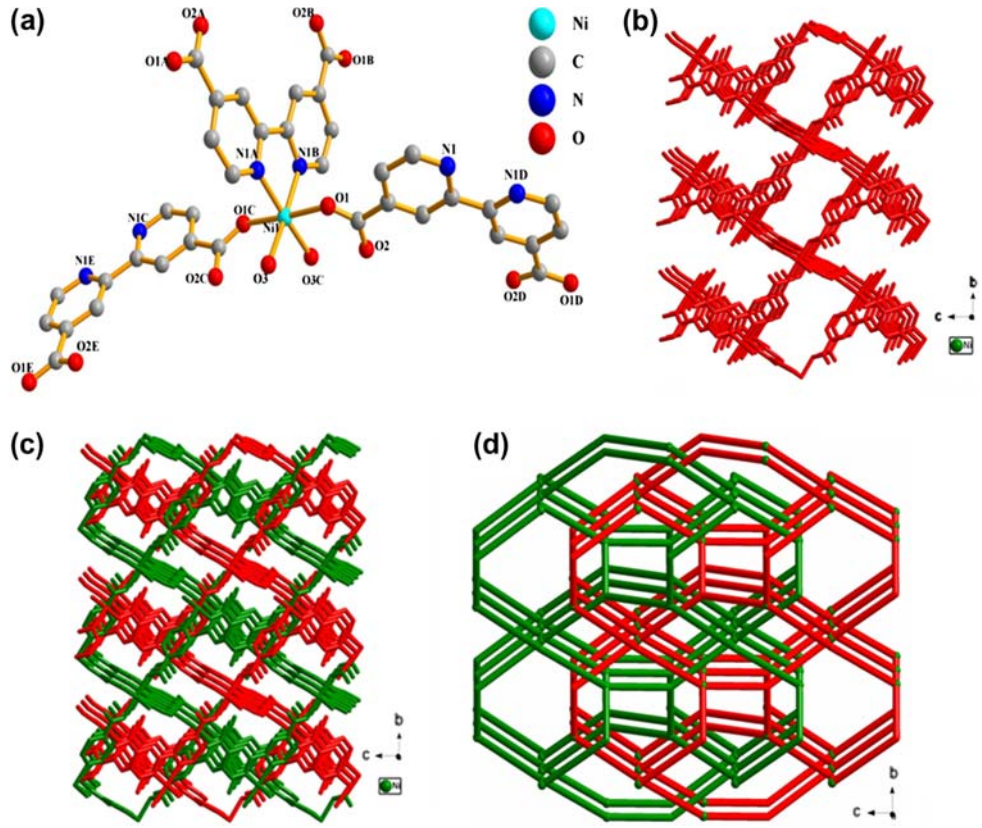


Figure 4. (a) The coordination environment of Ni(II) and 2,2′-bipyridyl-4,4′-dicarboxy. Symmetry codes: (A) $1-y$, $1+x+y$, $-0.66667+z$; (B) $1+x-y$, $1-y$, $-0.66667-z$; (C) y, x, $-z$; (D) $-x$, $-x+y$, $1.33333-z$; (E) $-x+y$, $-x$, $-1.3333+z$. (b) Structure formed by Ni and bpde^{2-}. (c) 2-Fold interpenetrating framework structure of **3**. (d) The topology of **3**.

structure can be regarded as a 3-D single net, and a pair of identical 3-D single nets are interlocked in parallel interpenetrating modes, thus directly leading to 2-fold interpenetrating frameworks (figure 4(c)). Further topological analysis suggests the *twt* framework for **3**, if we define the Ni(II) as a 3-connected node (figure 4(d)). Although coordination polymers based on topological substructures have been extensively studied [40], only a few cases exhibit 2-fold interpenetrating frameworks built by Ni(II).

3.4.4. Structure of $[Cu(bpdc)H_2O)]_n$ (4).

Single-crystal X-ray analysis reveals that **4** is in the monoclinic system *C2/c* space group. Cu(II) is coordinated by two nitrogens of a bpdc^{2-} (N1–Cu1 = 2.017(2), N2–Cu1 = 2.031(2) Å), two oxygens (O1A–Cu1 = 1.9409 (19), O3B–Cu1 = 1.9405(19) Å) from two bpdc^{2-} and one water (O5–Cu1 = 2.342(2) Å) (table S5) to form a pyramid coordination geometry (figure 5(a)).

Each bpdc^{2-} chelates one Cu(II) with two nitrogens and links two Cu(II) ions with two carboxylate oxygens, constructing a 2-D layer structure (figure 5(b)). Compared with the similar 2-D $[Er_2(bpdc)_3(phen)_2(H_2O)_2]_n$ [41], **4** has two different characteristics: (1) Both

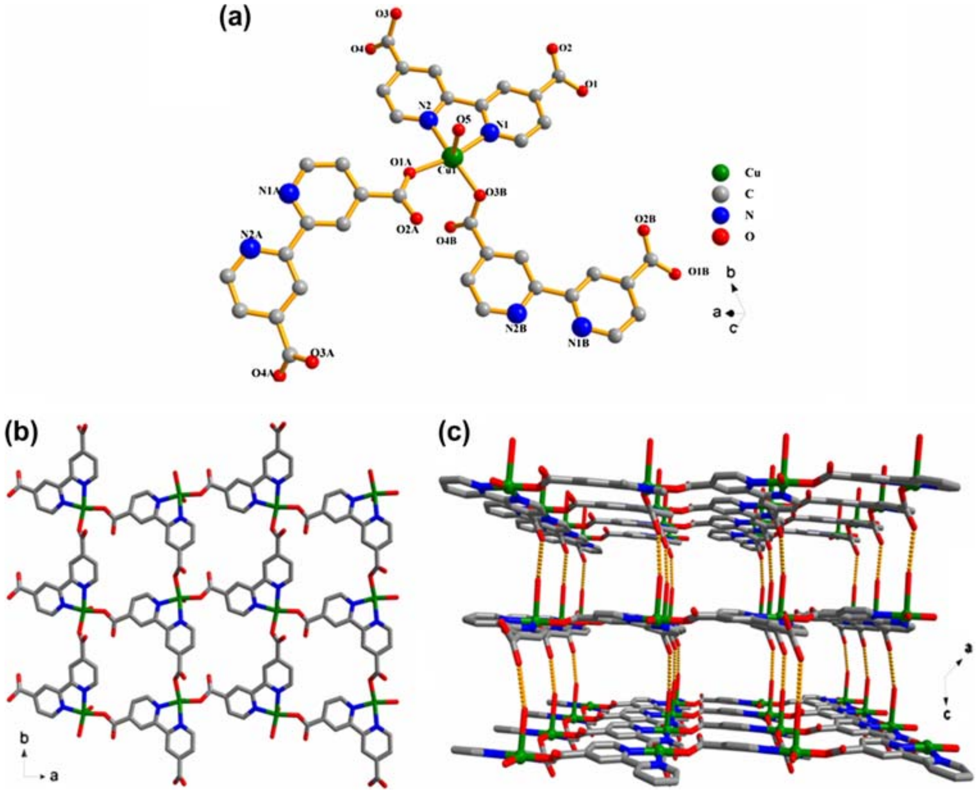


Figure 5. (a) The coordination environment of Cu(II) and 2,2′-bipyridyl-4,4′-dicarboxylic acid. Symmetry codes: (A) $0.5+x$, $0.5-y$, $0.5+z$; (B) x, $-1+y$, z. (b) The 2-D layer of **4** constructed by O bridges of bpdc^{2-}. (c) 3-D supramolecular structure of **4**.

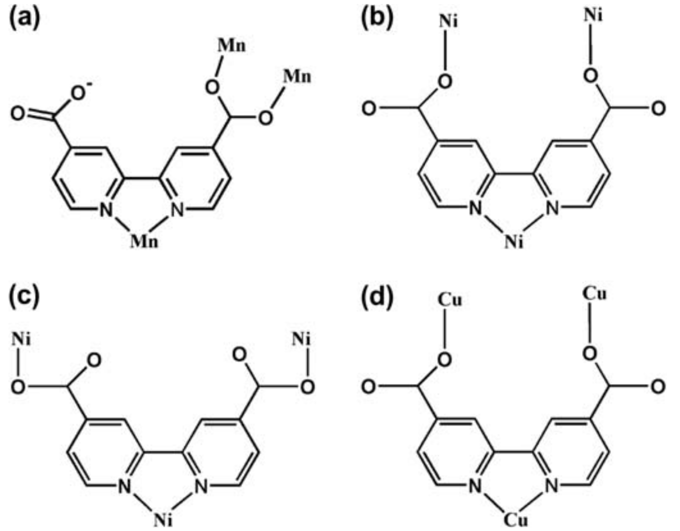
nitrogen and oxygen of bpdc^{2-} coordinate with Cu(II), while in [Er$_2$(bpdc)$_3$(phen)$_2$(H$_2$O)$_2$]$_n$, only oxygens of bpdc^{2-} coordinate with Er(III). (2) Each bpdc^{2-} in **4** connects three Cu(II) ions while that in [Er$_2$(bpdc)$_3$(phen)$_2$(H$_2$O)$_2$]$_n$ connects four Er(III) ions.

3-D supramolecular structure (figure 5(c)) can be formed taking into account hydrogen bond interactions between carboxylate oxygens and water (O···O distance = 2.809(3) Å) (table S6).

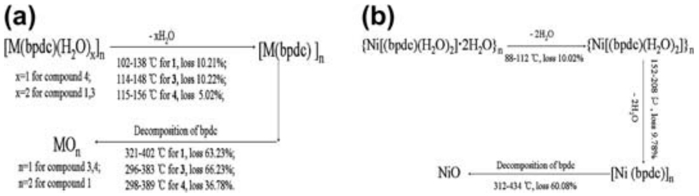
Comparison of coordination modes of bpdc^{2-} has been made [15, 42, 43], which shows some differences between the four compounds. In **1**, one carboxylate of bpdc^{2-} bridges two Mn(II) ions, while another carboxylate forms O–H···O hydrogen bond with coordinated water (scheme 1(a)). However, in **2**, **3** and **4** (shown in scheme 1(b)–(d)) the coordination of two carboxylates of bpdc^{2-} is similar with one oxygen of each carboxylate coordinating with a metal ion and another oxygen forming O–H···O hydrogen bond with coordinated water.

3.5. *Thermal gravimetric analysis*

Thermal gravimetric analyzes (TGA) of **1–4** were carried out under nitrogen with a heating rate of 10 °C/min. As shown in figure S2 (given in Supplementary material), **1**, **3**, and **4**



Scheme 1. Four coordination modes of 2,2′-bipyridyl-4,4′-dicarboxylic acid in **1–4**: (a) coordination mode of **1**; (b) coordination mode of **2**; (c) coordination mode of **3** and (d) coordination mode of **4**.



Scheme 2. (a) Thermal decomposition diagram of **1**, **3,** and **4**. (b) Thermal decomposition diagram of **2**.

show similar thermal behaviors, and the thermal behavior of **2** is obviously different from that of **1**, **3,** and **4**; only the thermal stability of **1** and **2** are discussed in detail. TGA trace of **1** (figure S2(a) in Supplementary material) shows an initial weight loss of 10.21% at 102−138 °C, corresponding to removal of coordinated water (cal. 10.81%). Significant weight loss of 63.23% from 321 to 402 °C is assigned to loss of bpdc^{2-} ligand (calcd 63.06%) (scheme 2(a)). The TGA curve of **2** (figure S2(b)) displays an initial weight loss at 88−112 °C of 10.02%, close to those of calculated values for the losses of two lattice waters (calcd 9.65%), the second weight loss step (9.78% of weight loss) between 152 and 208 °C corresponding to the loss of two coordinated waters (calcd 9.65%), the last weight loss step, losing 60.08% at 312−434 °C, is assigned to loss of bpdc^{2-} (scheme 2(b)). The TGA curves of **1–4** show a long plateau after loss of lattice water or coordinated water, indicating they are thermally stable.

4. Conclusion

[Mn(bpdc)(H_2O)$_2$]$_n$ (**1**), {Ni[(bpdc)(H_2O)$_2$]·2H_2O}$_n$ (**2**), [Ni(bpdc)(H_2O)$_2$]$_n$ (**3**), and [Cu (bpdc)H_2O)]$_n$ (**4**) have been synthesized from bpdc^{2-} and corresponding metal salts under hydrothermal conditions. Crystal structures indicate that **2** and **4** are 2-D layer structures, and the layers are further linked by hydrogen bonds to form 3-D supramolecular frameworks. Compounds **1** and **3** are 3-D coordination polymers bridged by bpdc^{2-}. TGA shows that **1–4** have high thermal stability.

Supplementary material

CCDC 894485 for **1**, 894488 for **2**, 894487 for **3**, and 894486 for **4** contain the supplementary crystallographic data. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

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