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# Three New Co(II)/Ni(II) Cordination Polymers Based on 3,3-biphenyl Dicarboxylic Acid and N-donor Co-ligands: Synthesis, Crystal Structures and Magnetic Properties[1]

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**Abstract**—Three new Co(II)/Ni(II) cordination polymers $[Co(Bpdc)(Bipy)]_n$ (**I**) and $[Co_2(Bpdc)_2(Dps)_2]_n$ (**II**) and $[Ni(Bpdc](Dps)]_n$ (**III**) ($H_2Bpdc$ = 3,3'-biphenyl dicarboxylic acid, Bipy = 2,2'-bipyridine, and Dps = 4,4'-dipyridyl sulfide) have been synthesized *via* hydrothermal method and characterized by elemental analysis, FT-IR, PXRD and single-crystal X-ray diffraction (CIF files CCDC nos. 994521 (**I**), 994522 (**II**), 1027995 (**III**)). Compound **I** is a 3D supremolecular structures extending through 1D double chain by the π···π stack interactions. However, compound **II** and **III** are topological isomorphic, which features a 3D four-fold interpenetrated neworks with 4-connected dia topology. Moreover, thermogravimetric analysis and magnetic properties of **I** and **II** were also discussed.

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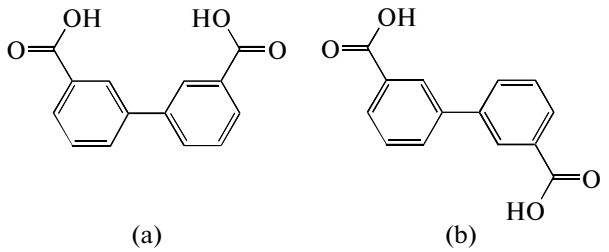
## INTRODUCTION

Recently, there are a great of interests which are focused on the synthesis, crystal structure and properties study of metal-organic frameworks for their potential application in the field of luminescence, magetism, catalyst and so on [1–9]. In this context, the rational design and synthesis diverse structural topologies with specific functions are always of great challenge for the chemists. In order to solve this problem, the action of organic building blocks with polytropic configurations has been investigated in the process of assembling MOFs. It is well known that the aromatic polycarboxylates are widely used in the construction of coordination polymers because of their diverse coordination modes [10–13]. Among these, 4,4'-biphenyl dicarboxylic acid, 3,4'-biphenyl dicarboxylic acid, and 3,3'-biphenyl dicarboxylic acid ($H_2Bpdc$), have extensively employed to construct many coordination polymers with different strutures and properties due to their flexible coordination modes [14–18]. Furthermore, the N-containing ligands, such as pyridine and imidazole derivatives, have supper coordinaition properitity on transition metal ions, and they have different function in the construction of MOFs [19–21].

In our privious work, two Zn(II) and Cd(II) coordination compounds based on $H_2Bpdc$ (Scheme 1) have been obtained and characterized [22]. Two possible geometrical configurations of $H_2Bpdc$ ligand: *cis*-configuration (a), *trans*-configuration (b) are in Scheme 1.




**Scheme 1.**

In order to do further investigation on the vertial coordination mode of $H_2Bpdc$ and the synergic action between the Bpdc ligand and bipyridyl derivates, herein, three new Co(II)/Ni(II) cordination polymers, namely $[Co(Bpdc)(Bipy)]_n$ (**I**), $[Co_2(Bpdc)_2(Dps)_2]_n$ (**II**), and $[Ni(Bpdc](Dps)]_n$ (**III**) (Bipy = 2,2'-bipyridine, Dps = 4,4'-dipyridyl sulfide) have been successfully synthesized and characterized. Moreover, the thermal stability and magnetic properties of compounds **I** and **II** has also been investigated.

## EXPERIMENTAL

**Materials and instrumentation.** The organic ligands employed were received from Alfa Aesar and other in-

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organic salt and solvents were received as reagent grade and used without any further purification. Elemental analyses were performed with a PerkinElmer 2400 Series II analyzer. The IR spectra were measured as KBr pellets with a FT-IR Nexus spectrophotometer from 4000 to 400 $cm^{-1}$. Powder X-ray diffractions (PXRD) patterns were recorded on a Rigaku Ultima IV diffractometer with Cu$K_\alpha$ radiation ($\lambda = 1.5406$ Å). The simulated powder patterns were calculated using Mercury 1.4. The purity and homogeneity of the bulk products were determined by comparison of the simulated and experimental X-ray powder diffraction patterns. Thermogravimetric analysis (**TGA**) was taken with a NETZSCH STA 449C microanalyzer in under an air atmosphere at a heating rate of 10°C $min^{-1}$. Variable-temperature magnetic measurements were carried out on a Quantum Design SQUID MPMS XL-7 instrument in the magnetic field of 1 kOe, and the diamagnetic corrections were evaluated using Pascal's constants.

**Synthesis of compound I.** A mixture of $Co(NO_3)_2 \cdot 6H_2O$ (29.7 mg, 0.10 mmol), 3,3'-$H_2$Bpdc (24.2 mg, 0.10 mmol), 2,2'-Bipy (15.6 mg, 0.10 mmol), and NaOH (8.0 mg, 0.20 mmol) in a solution of $H_2O$ (7 mL) were sealed into a 23 mL Teflon-lined stainless steel container under autogenous pressure, heated at 140°C for 3 days and cooled to room temperature for 24 h. Purple prismatic single crystals suitable for X-ray analyses were obtained. The yield was 67% (based on Co(II)).

For $C_{24}H_{16}N_2O_4Co$

| | | | |
|---|---|---|---|
| anal. calcd., %: | C, 63.31; | H, 3.54; | N, 6.15. |
| Found., %: | C, 63.22; | H, 3.49; | N, 6.23. |

IR (KBr pellet; ν, $cm^{-1}$): 2968 w, 1606 w, 1560 m, 1542 s, 1473 w, 1441 m, 1419 s, 1385 m, 1361 s, 1269 w, 1157 w, 1081w, 1022 w, 904 w, 863 w, 757 s.

**Synthesis of compound II** was carried out in a similar method used for **I** except that Bipy was rehlaced by Dps (18.8 mg, 0.10 mmol). The yield was 43% (based on Co(II)).

For $C_{48}H_{32}N_4O_8S_2Co_2$

| | | | |
|---|---|---|---|
| anal. calcd., %: | C, 59.14; | H, 3.31; | N, 5.75. |
| Found., %: | C, 59.35; | H, 3.53; | N, 5.83. |

IR (KBr pellet; ν, $cm^{-1}$): 3217 w, 1589 m, 1534 m, 1481 w,1413 s, 1372 m, 1266 w 1183 w, 1057 w, 1022 w, 862 w, 830 w, 812 w, 793 m, 760 s, 732 m.

**Synthesis of compound III** was carried out in a similar method to that of **II**. The yield was 38% (based on Ni(II)).

For $C_{24}H_{16}N_2O_4SNi$

| | | | |
|---|---|---|---|
| anal. calcd., %: | C, 59.17; | H, 3.31; | N, 5.75. |
| Found., %: | C, 59.25; | H, 3.27; | N, 5.93. |

IR (KBr pellet; ν, $cm^{-1}$): 3445 m, 2922 w, 2981 w, 1622 s, 1584 s, 1540 m, 1480 w, 1409 s, 1384 s, 1315 w, 1213 w, 828 w, 756 m.

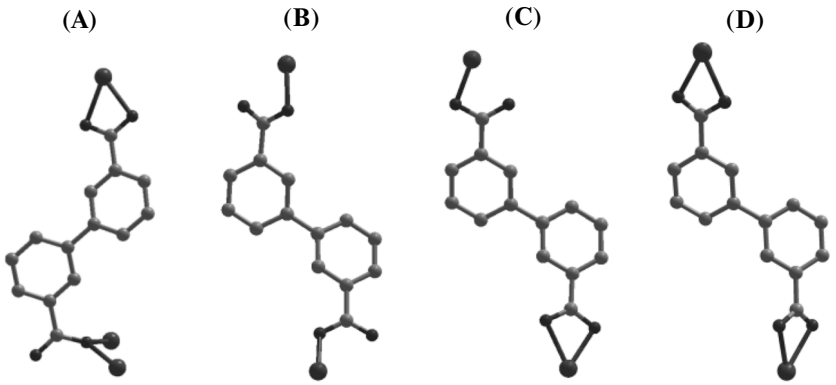
**X-ray structure determination.** Single crystal X-ray diffraction analysis of compounds **I**–**III** were carried out on a Rigaku XtaLAB mini diffractometer with graphite monochromated Mo$K_\alpha$ radiation ($\lambda = 0.71073$ Å). The collected data were reduced using the program CRYSTALCLEAR and an empirical absorption correction was applied [23]. The structure was solved by direct methods and refined based on $F^2$ by the full matrix least-squares methods using SHELXTL [24, 25]. The hydrogen atoms were assigned with common isotropic displacement factors and included in the nal renement by use of geometrical restrains. Generally, the positions of C/N-bound H atoms were generated by a riding model on idealized geometries. The crystallographic data for **I**–**III** are listed in Table 1 and selected bond lengths and angles are given in Table 2.

The supplementary crystallographic data for **I**–**III** been deposited the Cambridge Crystallographic Data Centre (CCDC nos. 994521 (**I**), 994522 (**II**), 1027995 (**III**); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

## RESULTS AND DISCUSSION

Single crystal structure analysis shows that the asymmetric unit of compound **I** consists of one $Co^{2+}$ ion, one Bpdc and one Bipy ligand. Each $Co^{2+}$ ion is six-coordinated by two nitrogen donors (N(1) and N(2)) from one bipy ligand and four carboxylate oxygen donors (O(1), O(2), O(3)$^{\#1}$ and O(3)$^{\#2}$, symmetry codes: $^{\#1}$ $x - 1, y, z + 1$; $^{\#2}$ $-x + 1, -y + 1, -z$) from three 3,3'-Bpdc ligands, thus generating an octhedral geometrical configuration (Fig. 1). The coordination Co–O/N bonds, varying from 2.344(3) to 2.608(3) Å, are within the reported results [26].

Four coordination modes of Bpdc in **I**–**III**: $\mu_3$-$\eta^1$:$\eta^1$:$\eta^2$ (**A**); $\mu_2$-$\eta^1$:$\eta^1$ (**B**); $\mu_2$-$\eta^1$:$\eta^1$:$\eta^1$ (**C**); $\mu_2$-$\eta^1$:$\eta^1$:$\eta^1$:$\eta^1$ (**D**) are given in Scheme 2:




**Scheme 2.**

**Table 1.** Crystallographic data and structure refinement information for compounds **I**–**III**

| Parameter | Value | | |
|---|---|---|---|
| | **I** | **II** | **III** |
| Formula weight | 455.32 | 974.76 | 487.16 |
| Temperature (K) | 296(2) | 296(2) | 296(2) |
| Crystal system | Triclinic | Monoclinic | Orthorhombic |
| Space group | $P\bar{1}$ | $P2_1/c$ | *Pbca* |
| Unit cell dimensions | | | |
| *a*, Å | 10.173(6) | 17.409(7) | 17.7833(3) |
| *b*, Å | 10.396(6) | 11.827(5) | 11.9359(2) |
| *c*, Å | 11.940(7) | 20.220(8) | 19.3104(3) |
| α, deg | 72.60(3) | 90 | 90 |
| β, deg | 66.70(3) | 92.757(6) | 90 |
| γ, deg | 61.04(3) | 90 | 90 |
| Volume, Å$^3$; *Z* | 1005.6(10); 2 | 4158(3); 4 | 4098.82; 8 |
| $\rho_{calcd}$, mg/m$^3$ | 1.504 | 1.557 | 1.579 |
| μ(Mo*K*α), mm$^{-1}$ | 0.888 | 0.961 | 1.085 |
| *F*(000) | 466 | 1992 | 2000 |
| θ Range, deg | 2.45–27.53 | 3.02–27.46 | 2.11–27.56 |
| Limiting indices | $-13 \le h \le 13$<br>$-13 \le k \le 13$<br>$-15 \le l \le 15$ | $-22 \le h \le 22$<br>$-15 \le k \le 15$<br>$-26 \le l \le 26$ | $-20 \le h \le 23$<br>$-15 \le k \le 13$<br>$-19 \le l \le 25$ |
| Crystal size, mm | 0.23 × 0.21 × 0.16 | 0.16 × 0.14 × 0.10 | 0.18 × 0.16 × 0.15 |
| Reections collected | 10724 | 43410 | 19106 |
| Independent reflection ($R_{int}$) | 4607 (0.0730) | 9496 (0.0894) | 4736 (0.0274) |
| Data/restraints/parameters | 4607/0/280 | 9496/0/577 | 4736/0/289 |
| Goodness-of-fit on $F^2$ | 1.011 | 1.098 | 1.021 |
| $R_1$*, $wR_2$** ($I > 2\sigma(I)$) | 0.0595, 0.1642 | 0.0538, 0.1114 | 0.0328, 0.0838 |
| $R_1$*, $wR_2$** (all data) | 0.0719, 0.1727 | 0.0750, 0.1219 | 0.0492, 0.0927 |
| $\Delta\rho_{max}/\Delta\rho_{min}$, *e* Å$^{-3}$ | 1.212/–0.880 | 0.549/–0.497 | 0.341/–0.428 |

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

**Table 2.** The selected bond lengths (Å) and bond angles(deg) for **I**–**III***

**I**

| Bond | *d*, Å | Bond | *d*, Å |
|---|---|---|---|
| Co(1)–O(3)$^{\#1}$ | 2.034(3) | Co(1)–N(1) | 2.130(3) |
| Co(1)–O(3)$^{\#2}$ | 2.117(2) | Co(1)–O(1) | 2.171(3) |
| Co(1)–N(2) | 2.129(3) | Co(1)–O(2) | 2.172(3) |
| Angle | ω, deg | Angle | ω, deg |
| O(3)$^{\#1}$Co(1)O(3)$^{\#2}$ | 79.24(10) | N(2)Co(1)O(1) | 90.82(12) |
| O(3)$^{\#1}$Co(1)N(2) | 96.90(11) | N(1)Co(1)O(1) | 153.31(11) |
| O(3)$^{\#2}$Co(1)N(2) | 172.40(10) | O(3)$^{\#1}$Co(1)O(2) | 159.91(10) |
| O(3)$^{\#1}$Co(1)N(1) | 102.75(11) | O(3)$^{\#2}$Co(1)O(2) | 91.34(10) |
| N(2)Co(1)N(1) | 76.60(12) | N(2)Co(1)O(2) | 94.29(12) |
| O(3)$^{\#1}$Co(1)O(1) | 102.07(10) | N(1)Co(1)O(2) | 96.04(11) |
| O(3)$^{\#2}$Co(1)O(1) | 96.38(11) | O(1)Co(1)O(2) | 61.05(10) |

**II**

| Bond | *d*, Å | Bond | *d*, Å |
|---|---|---|---|
| Co(1)–O(1) | 2.027(2) | Co(2)–O(3)$^{\#2}$ | 1.940(3) |
| Co(1)–N(2)$^{\#1}$ | 2.087(2) | Co(2)–O(7) | 2.000(2) |
| Co(1)–N(1) | 2.105(3) | Co(2)–N(3) | 2.051(3) |
| Co(1)–O(5) | 2.121(2) | Co(2)–N(4)$^{\#3}$ | 2.083(2) |
| Co(1)–O(6) | 2.189(2) | Co(1)–O(1) | 2.027(2) |
| Angle | ω, deg | Angle | ω, deg |
| O(1)Co(1)N(2)$^{\#1}$ | 106.97(10) | O(5)Co(1)O(6) | 61.00(9) |
| O(1)Co(1)N(1) | 92.57(10) | O(3)$^{\#2}$Co(2)O(7) | 121.85(12) |
| N(2)$^{\#1}$Co(1)N(1) | 101.94(10) | O(3)$^{\#2}$Co(2)N(3) | 100.06(12) |
| O(1)Co(1)O(5) | 141.15(9) | O(7)Co(2)N(3) | 116.08(10) |
| N(2)$^{\#1}$Co(1)O(5) | 97.82(9) | O(3)$^{\#2}$Co(2)N(4)$^{\#3}$ | 121.92(11) |
| N(1)Co(1)O(5) | 111.28(10) | O(7)Co(2)N(4)$^{\#3}$ | 93.17(10) |
| O(1)Co(1)O(6) | 90.30(10) | N(3)Co(2)N(4)$^{\#3}$ | 103.46(10) |
| N(2)$^{\#1}$Co(1)O(6) | 158.64(10) | N(2)$^{\#1}$Co(1)O(5) | 97.82(9) |
| N(1)Co(1)O(6) | 89.44(10) | | |

**III**

| Bond | *d*, Å | Bond | *d*, Å |
|---|---|---|---|
| Ni(1)–N(1) | 2.0512(15) | Ni(1)–O(1) | 2.0566(14) |
| Ni(1)–O(3)$^{\#1}$ | 2.0697(13) | Ni(1)–N(2)$^{\#2}$ | 2.0890(17) |
| Ni(1)–O(4)$^{\#1}$ | 2.1508(15) | Ni(1)–O(2) | 2.2250(15) |
| Angle | ω, deg | Angle | ω, deg |
| N(1)Ni(1)O(1) | 102.91(6) | N(1)Ni(1)O(3)$^{\#1}$ | 160.65(6) |
| O(1)Ni(1)O(3)$^{\#1}$ | 94.24(5) | N(1)Ni(1)N(2)$^{\#2}$ | 97.09(6) |
| O(1)Ni(1)N(2)$^{\#2}$ | 89.64(6) | O(3)$^{\#1}$Ni(1)N(2)$^{\#2}$ | 91.84(6) |
| N(1)Ni(1)O(4)$^{\#1}$ | 98.46(6) | O(1)Ni(1)O(4)$^{\#1}$ | 150.34(6) |
| O(3)$^{\#1}$Ni(1)O(4)$^{\#1}$ | 62.37(5) | N(2)$^{\#2}$Ni(1)O(4)$^{\#1}$ | 107.97(6) |
| N(1)Ni(1)O(2) | 91.28(6) | O(1)Ni(1)O(2) | 61.29(5) |
| O(3)$^{\#1}$Ni(1)O(2) | 89.15(6) | N(2)$^{\#2}$Ni(1)O(2) | 150.89(6) |
| O(4)$^{\#1}$Ni(1)O(2) | 98.21(6) | | |

* Symmetry codes: $^{\#1}$ $x-1, y, z+1$; $^{\#2}$ $-x+1, -y+1, -z$ (**I**); $^{\#1}$ $x, -y+1/2, z+1/2$; $^{\#2}$ $x+1, y, z$; $^{\#3}$ $x, -y+5/2, z-1/2$ (**II**); $^{\#1}$ $x-$ $-1/2, -y+3/2, -z$; $^{\#2}$ $x, -y+5/2, z-1/2$ (**III**).

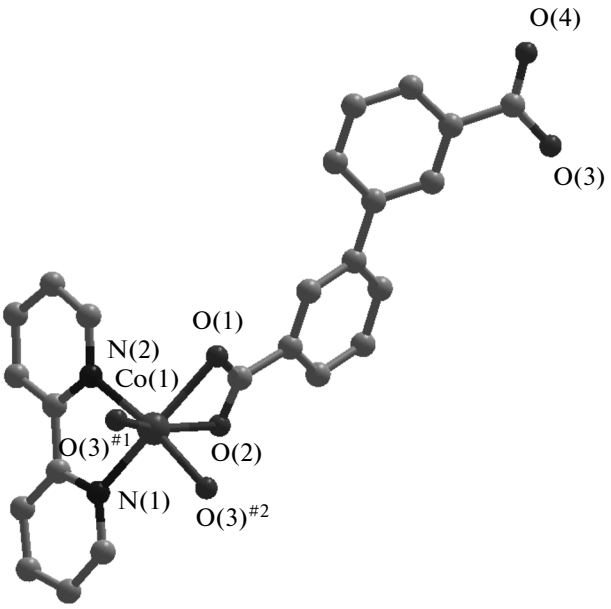



**Fig. 1.** The coordination enviroment center of Co(II) in **I**. Symmetry codes: #1 $x-1, y, z+1$; #2 $-x+1, -y+1, -z$.

In **I**, the adjacent $Co^{2+}$ ions are linked by two Bpdc ligands with the $\mu_3$-$\eta^1$:$\eta^1$:$\eta^2$ (type **A**; Scheme 2), wich result in the 1D double chain structures along the *z* axis (Fig. 2a). These chains extended into the 2D layer in the *xy* plane *via* the π···π stack interaction of pyridyl ring (centroid-to-centroid distance is 3.729 Å) (Fig. 2b). Furthermore, the 2D layers are linked into 3D supramolecular structure by the little weaker π···π interaction of aromatic rings of Bpdc ligands between adjacent layers (3.757 Å) (Fig. 2c and Fig. 2d).

Compounds **II** and **III** are topological isomorphic, which exhibits a 3D four-fold interpenetrated neworks with 4-connected **dia** topology. Structural analysis reveals that two complexes crystallize in different crystal system and space groups and display same 4-connected dia topological skeletons. The asymmetric unit of **II** contains two crystallographically unique $Co^{2+}$ ions, two $Bpdc^{2-}$ anions and two Dps ligands (Fig. 3a). The Co(1) ion shows a distorted octahedral coordination geometry [$CoN_2O_4$], which is completed by three carboxylate oxygen atoms (O(1), O(5) and O(6)) from two different $Bpdc^{2-}$ anions and two nitrogen atoms (N(1) and N(2)#1, symmetry codes: #1 $x$, $-y+1/2$,

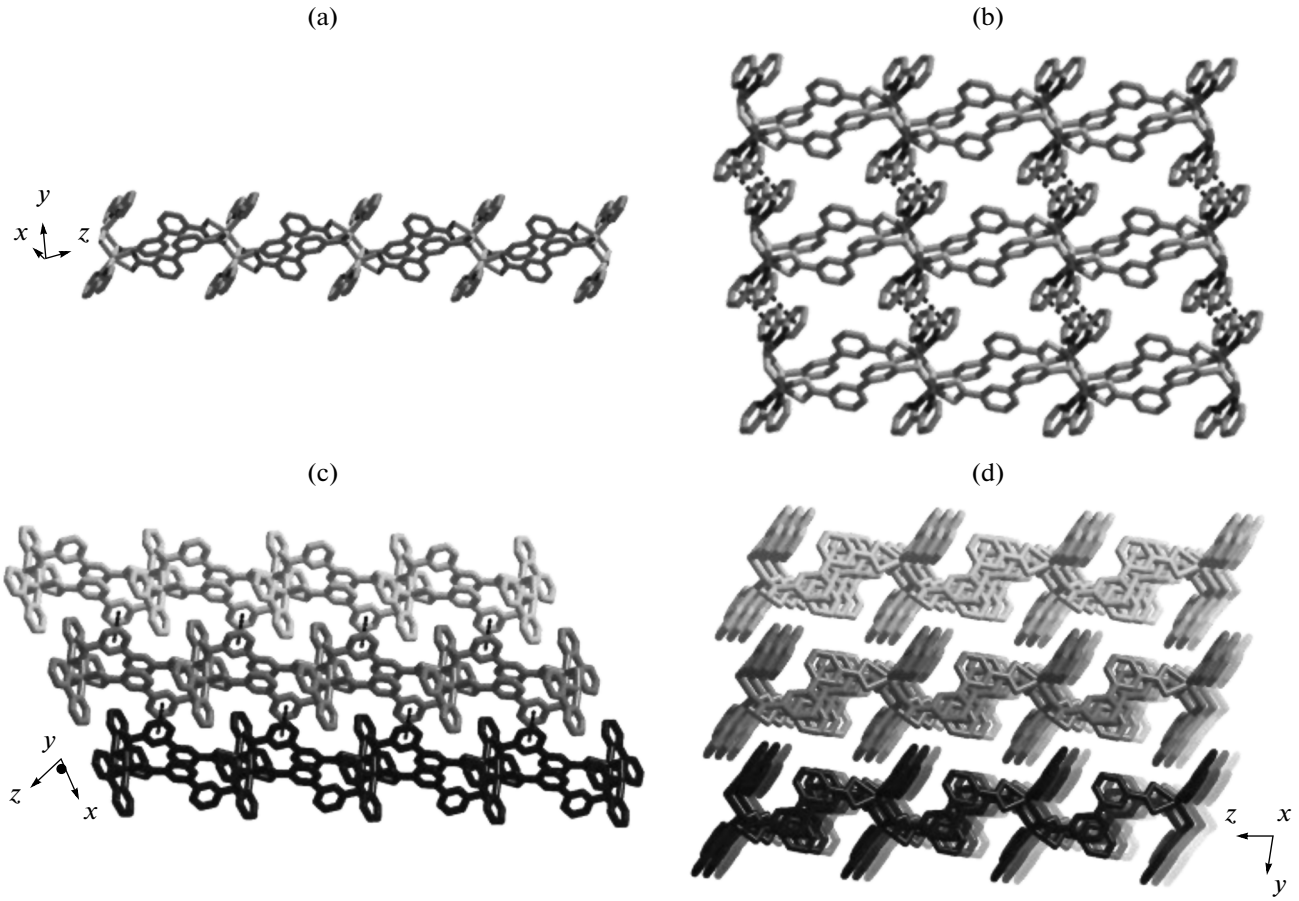



**Fig. 2.** View of the 1D double chain along the *z* axis (a); the 2D layer constructed by 1D double chain *via* the π···π interaction (b); the adjacent layers *via* the weak interaction (c); the packing 3D supramolecular structures of **I** (d).

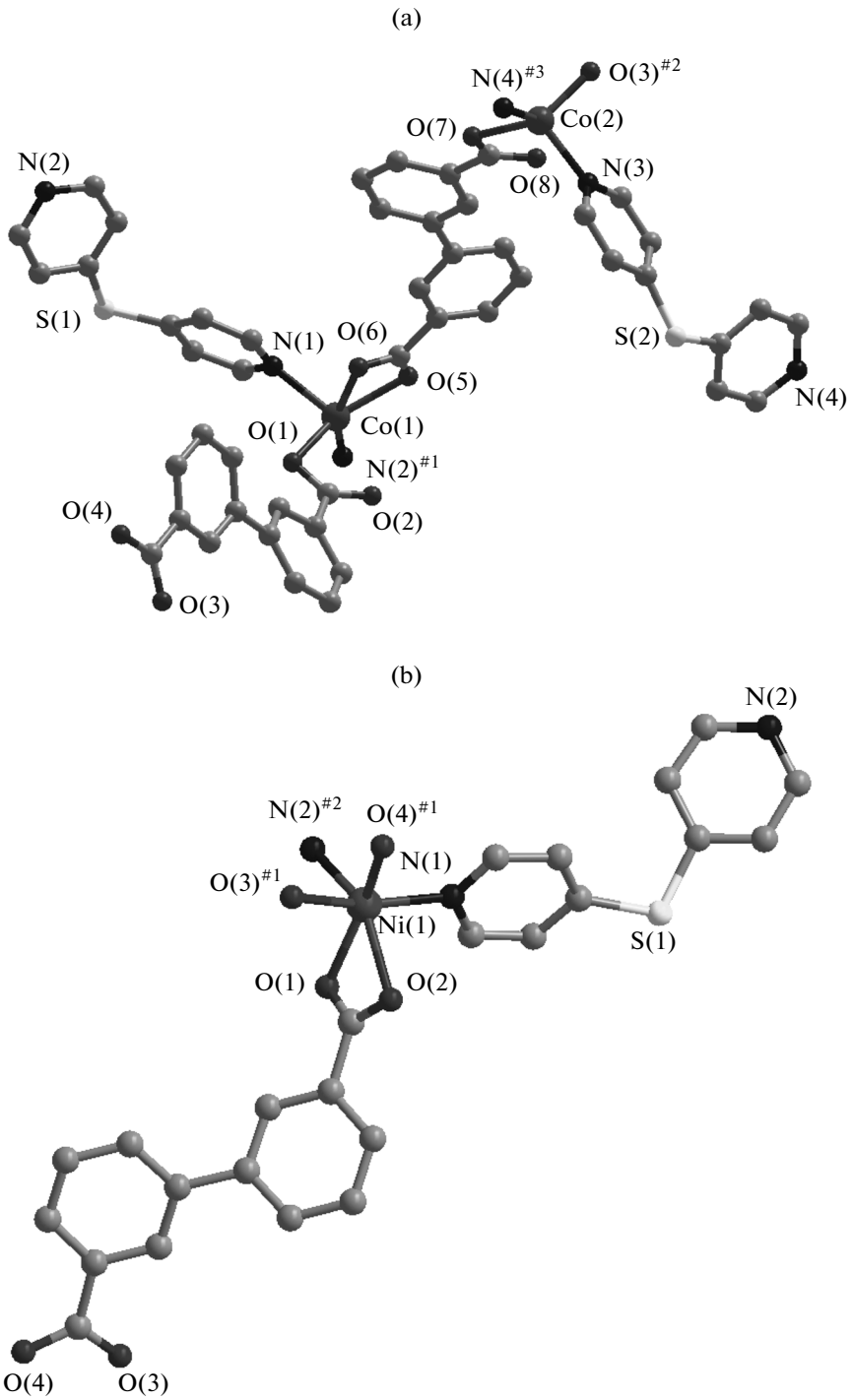



**Fig. 3.** The coordination enviroment center of Co(II) in **II** (a) and Ni(II) in **III** (b). Symmetry codes: #1 $x$, $-y + 1/2$, $z + 1/2$; #2 $x + 1$, $y$, $z$; #3 $x$, $-y + 5/2$, $z - 1/2$ (II); #1 $x - 1/2$, $-y + 3/2$, $-z$; #2 $x$, $-y + 5/2$, $z - 1/2$.

$z + 1/2$) from two different Dps molecules. The Co(2) ion is coordinated in a distorted tetrahedral geometry [$CoN_2O_2$] by two O atoms (O(3)#2 and O(7), symmetry codes: #2 $x + 1$, $y$, $z$) from the monodentate carboxylate groups of two $Bpdc^{2-}$ anions and two nitrogen atoms (N(3) and N(4)#3, symmetry codes: #3 $x$, $-y + 5/2$, $z - 1/2$) from two Dps molecules. Different from compound **I**, the asymmetric unit of **III** contains one crystallographically unique $Ni^{2+}$ ions, one $Bpdc^{2-}$ anions and one Dps ligand (Fig. 3b). The central $Ni^{2+}$ ion shows an obviously distorted octahedral coordination geometry [$NiN_2O_4$], which is ligated by four carboxy-

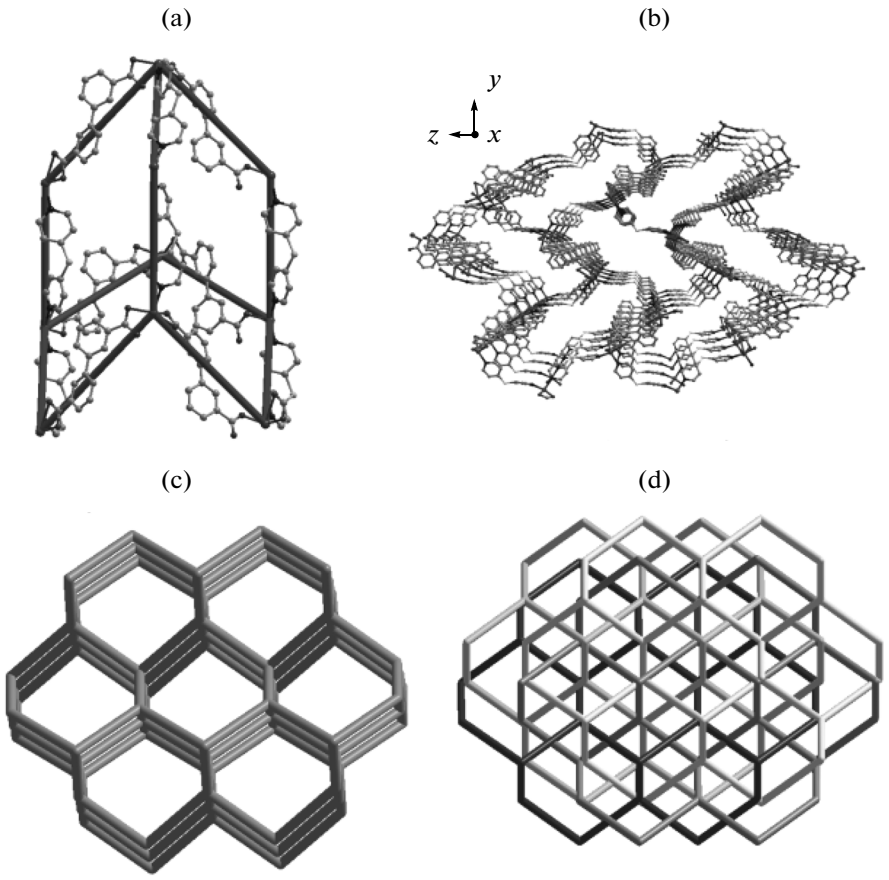



**Fig. 4.** Topological view showing the adamantane unit network in **II** (a); view of the complicated 3D frameworks containing 1D channels with the size of 22.67 × 11.65 Å$^2$ along the *x* axis (b); the single 3D net with dia topology (c); schematic description of *f*-fold interpenetrating topology net of **II** (d).

late oxygen atoms (O(1), O(2), O(3)$^{\#1}$ and O(4)$^{\#1}$, symmetry codes: $^{\#1}$ $x$ −1/2, $-y$ + 3/2, $-z$) from two different Bpdc$^{2-}$ anions and two nitrogen atoms (N(1) and N(2)$^{\#2}$, symmetry codes: $^{\#2}$ $x$, $-y$ + 5/2, $z$ − 1/2) from two different dps molecules. And the Co/Ni–O/N bond lengths and angles all are comparable with those reported in the Co/Ni-based compounds [27].

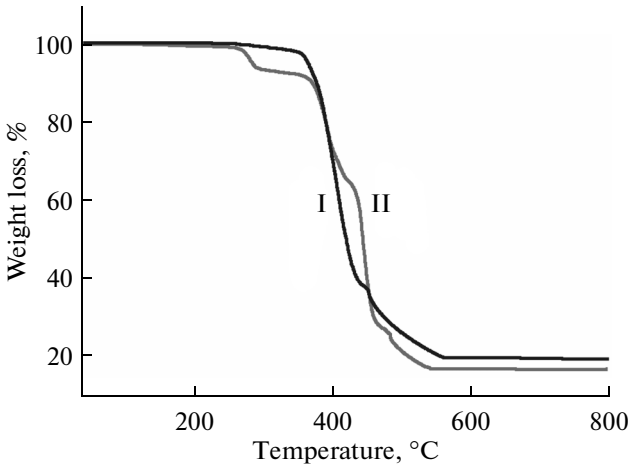



**Fig. 5.** The TG curves of compound **I** and **II**.

It is noted that the 3,3'-Bpda ligands display three different coordination modes: $\mu_2$-$\eta^1$:$\eta^1$ (Type **B**; Scheme 2 for **II**) and $\mu_2$-$\eta^1$:$\eta^1$:$\eta^1$ (Type **C**; Scheme 2 for **II**) and $\mu_2$-$\eta^1$:$\eta^1$:$\eta^1$:$\eta^1$ (Type **D**; Scheme 2 for **III**), respectively. Simultaneously, the dps ligands compensate for the need of metal coordination numbers as well as stabilize the resulting 3D network. Thus, the Co(II)/Ni(II) centers are connected by two types of spacers to generate a typical (6.3) net (Fig. 4a). The other 3,3'-Bpda$^{2-}$ anion further extends the (6.3) nets into a 3D dia framework (Fig. 4b and Fig. 4c). It has been well-known that diamond networks tend to interpenetrate to fill the voids within a single net. In **II** and **III**, notably, the (6.3) nets are pillared by the 3,3'-Bpda$^{2-}$ anions, thus resulting in a large hexagonal channel with the size 22.67 × 11.65 Å$^2$, which allows other four selfsame dia nets to penetrate and thus, affords a four-fold interpenetrating framework along the *y* axis (Fig. 4d).

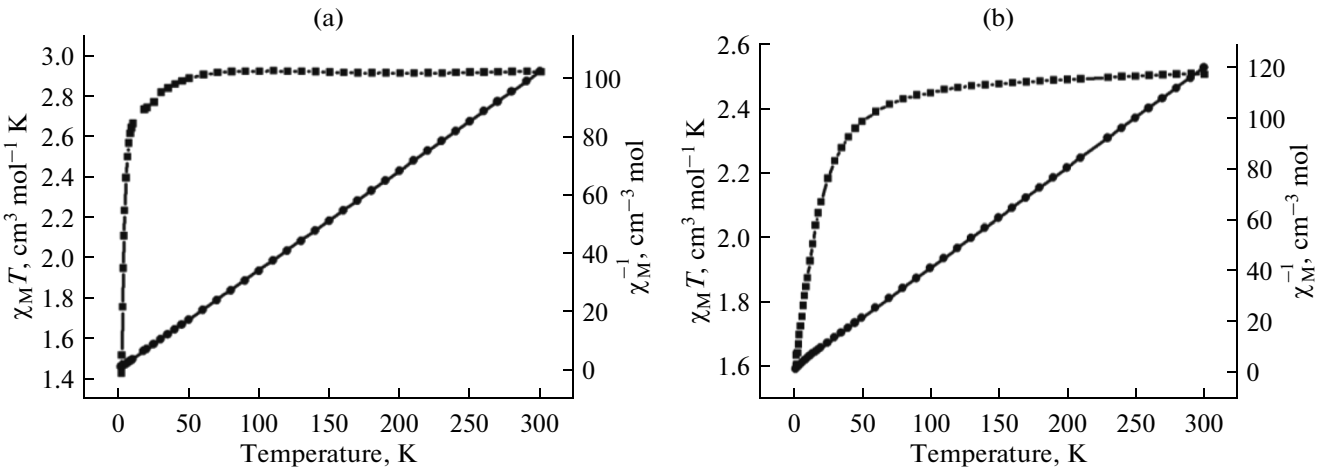



**Fig. 6.** Temperature dependence of the $\chi_M T$ and $\chi_M^{-1}$ curves of **I** (a) and **II** (b).

PXRD was used to check the purity of **I** and **II** at room temperature. All the peaks displayed in the measured patterns for each compound closely match those in the simulated patterns generated from single-crystal diffraction data, indicating that the single phases of **I** and **II** were formed. The TGA curves of **I**–**III** are similar and exhibit one main step of weight loss corresponding to the combustion of the organic groups. Therefore, only the patterns of **I** and **II** will be discussed as an example. As shown the Fig. 5, **I** and **II** are thermally stable to 350 and 270°C, respectively. Thereafter signicant weight loss occurs resulting in complete decomposition of the compounds. The residues indicate that the nal products are the metal oxides.

The variable-temperature magnetic susceptibility ($\chi_M$) data for **I** and **II** were collected over the temperature range of 2–300 K under an applied field of 1 kOe (Fig. 6). At room temperature, The $\chi_M T$ values of **I** and **II** at 300 K are 2.92 and 2.50 cm$^3$ mol$^{-1}$ K, which were slightly smaller than that of two isolated spin-only $Co^{2+}$ ions (3.75 cm$^3$ mol$^{-1}$ K) and larger than one isolated spin-only $Co^{2+}$ cations (1.88 cm$^3$ mol$^{-1}$ K) in the asymmetric unit, respectively. Upon cooling, the $\chi_M T$ value of **I** and **II** both decrease monotonically, reaching a minimum of 1.52 cm$^3$ mol$^{-1}$ K for **I** and 1.60 cm$^3$ mol$^{-1}$ K for **II** at 2 K, indicating overall antiferromagnetic interactions of **I** and **II**. The temperature dependence of the reciprocal susceptibility of ($1/\chi_M$) of **I** and **II** obey the Curie–Weiss law. Fitting the curve of **I** and **II** give parameters $\theta = -1.06$ K, $C = 2.93$ cm$^3$ K mol$^{-1}$ for **I** and $\theta = -3.04$ K, $C = 2.53$ cm$^3$ K mol$^{-1}$ for **II**. The negative $\theta$ value demonstrate that in both of **I** and **II** there exist antiferromagnetic interaction between the adjacent $Co^{2+}$ ions mediated through the carboxylate bridges, which is comparable to those reported for other similar Co(II) compounds [26, 28].

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