N-donor co-ligands driven two new Co(II)- coordination polymers with bi- and trinuclear units: Crystal structures, and magnetic properties

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Abstract: Two new Co(II) coordination polymers (CPs), namely $[\text{Co}_2(\text{bpe})_2(\text{Hbppc})]_n$ (**1**) and $[\text{Co}_3(\mu_3\text{-OH})(\text{bppc})(\text{bpm})(\text{H}_2\text{O})]\cdot 3\text{H}_2\text{O}$ (**2**) (H_5bppc = biphenyl-2,4,6,3',5'-pentacarboxylic acid, bpe = 1,2-bis(4-pyridyl)ethene, bpm = bis(4-pyridyl)amine), have been obtained and characterized by elemental analysis, single-crystal X-ray diffraction, powder X-ray diffraction (PXRD), IR spectra and thermogravimetric analysis (TGA). **1** shows a binodal (4,6)-connected **fsc** net with a $(4^4\cdot 6^{10}\cdot 8)(4^4\cdot 6^2)$ topology, while **2** shows a binodal (5,7)-connected 3D network based on trinuclear $[\text{Co}_3(\mu_3\text{-OH})]^{5+}$ units with unusual $(3\cdot 4^6\cdot 5^2\cdot 6)(3^2\cdot 4^6\cdot 5^7\cdot 6^5\cdot 7)$ topology. Variable-temperature magnetic susceptibility measurements reveals that complex **1** shows ferromagnetic interactions between the adjacent Co(II) ions, whereas **2** is a antiferromagnetic system.

Key words: Co^{II} -Cps; polynuclear unit; crystal structure; magnetic property

1. Introduction

Magnetic materials based on transition metal ions with polynuclear units, such as Co(II) and Mn(II), have received increasing attention, owing to its high spin ground state can be obtained from strong exchange interactions between 3d electrons [1-10]. Noted that, the development of coordination chemistry, many research efforts have been devoted to novel ways to fabricate, characterize and explore fundamental magnetic phenomena [11-23]. Coordination polymers (CPs) with polynuclear units based on Co(II) and Mn(II) have fascinating architectures and physical properties with widespread applications, such as catalysis, sorption, magnetism and electrical conductivity [24-30]. However, the final structures of coordination polymers are hardly controlled because the synthesis processes are influenced by many factors, such as the structural characteristics of the ligands, the coordination nature of metal ions, the solvent preference, the pH value of the solution, the reaction temperature and the metal/ligand ratios. Multicarboxylate ligands, which are widely employed to construct such extended architectures, not only bind several metal centers of specific coordination geometry to form polynuclear units but also can transmit the magnetic interaction [34-36]. Biphenyl-2,4,6,3',5'-pentacarboxylic acid (H_5bppc) is an important family of multidentate O-donor, which can be used as the mediators between the metal centers, because multicarboxylate groups have various coordination modes, which allowing

interesting structures with higher dimensionality. As well known, the multicarboxylate linkers have been extensively employed as the organic ligands to construct CPs [37-42].

In order to obtain Co-CPs with novel structures and functional properties, an useful strategy is introduced auxiliary N-donor ligands [43-46]. Using such tactics, our groups have reported some new Co(II)-cluster based mixed-ligand CPs with magnetism, gas adsorption and photocatalysis [5,8,20,47-51]. As part of our ongoing interest in understanding the ability of the multicarboxylate to direct the assembly of Co(II)-organic systems, herein, in this paper, H₅bppc with five carboxyl groups and different auxiliary N-donor spacers, 1,2-bis(4-pyridyl)ethene (bpe) with –CHCH– linker or bis(4-pyridyl)amine (bpm) with –NH– linker, are employed to induce Co^{II}-core aggregation and to tune the structures of polymetallic Co(II)-clusters, resulting in two coordination polymers containing bi- and tri-nuclear units, [Co₂(bpe)₂(Hbppc)]_n (**1**) and [Co₃(μ₃-OH)(bppc)(bpm)(H₂O)]·3H₂O (**2**). Moreover, their magnetic properties were also investigated and discussed.

2. Experimental

2.1 Materials and physical measurements: All solvents and reagents were available and were used as received. Elemental analysis for C, H and N was performed on a Flash 2000 organic elemental analyzer. Thermogravimetric analysis was performed on a NETZSCH STA 449C microanalyzer heated from 25 to 900°C in nitrogen atmosphere. Infrared spectra (4000~600 cm⁻¹) were recorded on a FT-IR Nexus spectrophotometer spectrometer. Powder X-ray diffraction (PXRD) patterns were taken on a Rigaku Ultima IV diffractometer (Cu Kα radiation, λ = 1.5406 Å), with a scan speed of 5 °/min and a step size of 0.02 ° in 2θ. Variable-temperature magnetic measurements were carried out on a Quantum Design SQUID MPMS XL-7 instrument (2~300 K) in the magnetic field of 1 KOe, and the diamagnetic corrections were evaluated by using Pascal's constants.

2.2 Preparation of complexes **1** and **2**.

[Co₂(bpe)₂(Hbppc)]_n (**1**). Co(NO₃)₂·6H₂O (0.2mmol, 58.2mg), H₅bppc (0.05 mmol, 18.7 mg), and bpe (0.1 mmol, 18.2 mg) were dissolved in EtOH-H₂O (1:1, 10 mL), and then NaOH (1 mL, 0.1 M) was added. The mixture was sealed in a Teflon-lined stainless steel vessel (25 mL), and

heated at 140 °C for 3 days, and then cooled to room temperature over 24 h. Violet prism crystals of **1** were obtained. Yield: 62% (based on Co(II)). Elemental analysis (%): calcd for $C_{41}H_{26}Co_2N_4O_{10}$ ($M_r = 852.52$): C 57.71, H 3.04, N 6.57 found: C 56.98, H 3.11, N 6.62; IR (cm^{-1}): 3409 (m), 1615(w), 1525(s), 1474(w), 1442(m), 1408(w), 1356(s), 1245(m), 1188(w), 1020(w), 762(m) (See Figure S1, Supplementary Information).

[Co₃(μ₃-OH)(bppc)(bpm)(H₂O)]·3H₂O (2). **2** was prepared by the similar method as that described for **1**, except that bpm (0.1 mmol, 17.1 mg) instead of bpe. Violet prism crystals of **2** were obtained. Yield: 54% (based on Co(II)). Elemental analysis (%): calcd for $C_{27}H_{27}N_3O_{15}Co_3$ ($M_r = 810.31$): C 39.98, H 3.33, N 5.18; found: C 40.15, H 3.36, N 5.21. IR (cm^{-1}): 3407 (s), 1598(s), 1516(w), 1432(w), 1359(s), 1213(m), 1019(m), 825(m), 766(m), 716(s) (See Figure S1, SI).

2.3 X-ray crystallography. Single crystal X-ray diffraction data for complexes **1** and **2** were collected on a Rigaku XtaLAB mini diffractometer equipped with a graphite monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) by using ϕ/ω scan technique. The structures were solved by direct methods and successive Fourier difference synthesis (SHELXS-97) [52], and refined by the full-matrix least-squares method on F^2 with anisotropic thermal parameters for all non-H atoms (SHELXL-97) [52]. H atoms were assigned with isotropic displacement factors and included in the final refinement with geometrical restraints. Further crystallographic data are shown in Table 1. Selected bond parameters for **1–2** are shown in Table S1, Supplementary Information. CCDC reference No: 1479782 for **1** and 1479783 for **2**.

Table 1. Crystallographic data and details of diffraction experiments for complexes **1** and **2**.

	1	2
Formula	C ₄₁ H ₂₆ Co ₂ N ₄ O ₁₀	C ₂₇ H ₂₇ Co ₃ N ₃ O ₁₅
<i>M</i> _r	852.52	810.31
<i>T</i> (K)	296(2)	296(2)
Crystal system	monoclinic	monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> (Å)	13.67(3)	11.545(4)
<i>b</i> (Å)	14.79(3)	20.225(6)
<i>c</i> (Å)	18.72(3)	14.390(4)
<i>β</i> (°)	97.78(2)	90.528(4)
<i>V</i> (Å ³)	3750(13)	3359.8(17)
<i>Z</i>	4	4
<i>ρ</i> (g cm ⁻³)	1.510	1.602
<i>F</i> (000)	1736	1644
<i>R</i> _{int}	0.1784	0.0655
<i>GOOF</i>	1.059	1.082
<i>R</i> [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0995 <i>wR</i> ₂ = 0.2300	<i>R</i> ₁ = 0.0480 <i>wR</i> ₂ = 0.1345 □
<i>R</i> (all data)	<i>R</i> ₁ = 0.1402 <i>wR</i> ₂ = 0.2604	<i>R</i> ₁ = 0.0567 <i>wR</i> ₂ = 0.144

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

3. Results and Discussion

3.1 Descriptions of Crystal Structures

[Co₂(bpe)₂(Hbppc)]_n (1). There are two crystallographic independent Co(II) atoms (Fig. 1a). Co1 is six-coordinated with a distorted octahedron geometry by four carboxylato-*O* from three Hbppc⁴⁻ ligand (O1, O5#2, O6#2, and O10#1) forming the equatorial plane, and two *cis* N atoms from two bpe (N3 and N4#3). Co2 is five coordinated with a distorted trigonal-bipyramidal coordination environment, in which three O atoms from three Hbppc⁴⁻ ligands (O2, O4#4, and O9#1) form the equatorial plane and the apical positions are occupied by two N atoms (N1 and N2#3) with N1-Co2-N2 angle of 177.0(2) °. In **1**, 4-carboxylic group of Hbppc⁴⁻ is protonated and free of coordination. The other four carboxylate groups of Hbppc⁴⁻ ligand adopt the (κ¹-κ¹)-(κ¹-κ¹)-(κ¹)-(κ¹-κ¹)-μ₆ coordination fashion to bridge three Co1 and three Co2 (Fig 1b). The Co1 and adjacent Co2 are bridged by two carboxyl groups in *syn,anti* fashion to generate a binuclear [Co₂(COO)₂]²⁺ unit with the Co···Co distance of 4.10 Å. Then the binuclear units are linked by Hbppc⁴⁻ ligands to form a 2D layer (Fig. 1c). Such 2D layers are further interlinked by

the bpe linkers to form a 3D network (Fig. 1d).

Analysis of the network topology of **1** reveals that binuclear $[\text{Co}_2(\text{COO})_2]^{2+}$ unit acts as a 6-connected node to connect six other binuclear units. And the Hbppc^{4-} ligand serves as the 4-connected nodes to join four binuclear units. Thus, the 3D structure of **1** is designated as a binodal (4,6)-connected **fsc** net with a $(4^4 \cdot 6^{10} \cdot 8)(4^4 \cdot 6^2)$ topology (Fig. 1e).

Fig. 1 Coordination environments of Co(II) ions in **1**. Symmetry codes for #1: $-x, y + 1/2, -z + 1/2$; #2: $-x, -y + 2, -z$; #3: $x - 1, y, z$; #4: $x, -y + 3/2, z + 1/2$. (b) Coordinated mode of Hbppc^{4-} ligand. (c) 2D layer constructed by Co(II) atoms and Hbppc^{4-} ligands. (d) 3D architecture. (e) Schematic representation of the (4,6)-connected **fsc** net.

$[\text{Co}_3(\mu_3\text{-OH})(\text{bpm})(\text{bppc})(\text{H}_2\text{O})] \cdot 3\text{H}_2\text{O}$ (2**).** Complex **2** has a 3D net with trinuclear $[\text{Co}_3(\mu_3\text{-OH})]^{5+}$ units. As illustrated in Fig. 2a, Co1 takes a distorted octahedral coordination geometry, defined by three carboxylic oxygen atoms (O1, O8#1, and O9#2) from three bppc^{5-} ligands, one nitrogen atom of a bpm and one oxygen atom (O11) from μ_3 -hydroxyl group as well as a coordinated aqua molecule. Co2 adopts a distorted trigonal-bipyramidal coordination

environment, in which three carboxylic oxygen atoms (O2, O4#4, and O7#1) from three bppc^{5-} ligands form the equatorial plane and the apical positions are occupied by O11 and N3#3 from a μ_3 -hydroxyl group and bpm ligand with O11-Co2-N3 angle of 156.01° . Co3 is four coordinated and resides in a distorted tetrahedral coordination environment with three carboxylic oxygen atoms (O3#4, O5#5, and O10#2) from three bppc^{5-} ligands, as well as one oxygen atom (O11) from μ_3 -hydroxyl group. The distances of Co...Co bridged by the μ_3 -hydroxyl group are 3.33, 3.43, and 3.51 Å, respectively. The five carboxylate groups of bppc^{5-} ligand display $(\kappa^1-\kappa^1)-(\kappa^1-\kappa^1)-(\kappa^1)-(\kappa^1-\kappa^1)-(\kappa^1-\kappa^1)-\mu_9$ binding fashion to link three Co1 atoms, three Co2 atoms and three Co3 atoms (Fig. 2b). The trinuclear $[\text{Co}_3(\mu_3\text{-OH})]^{5+}$ clusters are further bound by four carboxylate groups of different bppc^{5-} ligands in $(\kappa^1-\kappa^1)-\mu_2$ fashion. Each trinuclear unit is linked to adjacent trinuclear units through five bppc^{5-} ligands to generate a 5-connected 3D **bnn** network with a $(4^6 \cdot 6^4)$ (Fig. 2c and 2d). In addition, paired bpm ligands link the trinuclear units within the above **bnn** network to build a complicated 3D framework (Fig. 2e).

Analysis of the network topology of **2** reveals that each trinuclear $[\text{Co}_3(\mu_3\text{-OH})]^{5+}$ unit acts as a 7-connected node to connect five bppc^{5-} and two $[\text{Co}_3(\mu_3\text{-OH})]^{5+}$ units *via* two bpm spacers. And bppc^{5-} serves as 5-connected node to connect five $[\text{Co}_3(\mu_3\text{-OH})]^{5+}$ units. Thus, an unprecedented (5,7)-connected bi-nodal network with the Schläfli symbol of $(3 \cdot 4^6 \cdot 5^2 \cdot 6)(3^2 \cdot 4^6 \cdot 5^7 \cdot 6^5 \cdot 7)$ (Fig. 2f).

When the N-donor co-ligand isn't introduced the reaction system, $[\text{Co}(\text{H}_2\text{O})_6][\text{H}_3\text{O}] \cdot 3[\text{Co}_2(\text{bppc})(\text{H}_2\text{O})_2] \cdot 0.5\text{H}_2\text{O}$ (**3**) is obtained [53]. **3** is a 5-connected 3D **acs**- $4^4 \cdot 6^6$ net constructed from $[\text{Co}_2(\text{O}_2\text{C})_5(\text{H}_2\text{O})_2]^-$ dimer units and biphenyl-pentacarboxylate ligand with open hydrophilic channels, uniquely, the $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ and H_3O^+ as guest cations coexist in the channels. In **3**, The five carboxylate groups of bppc^{5-} ligand display $(\kappa^1-\kappa^2)-(\kappa^1-\kappa^1)-(\kappa^1)-(\kappa^1-\kappa^1)-(\kappa^1-\kappa^1)-\mu_8$ binding fashion to link eight Co(II) atoms. When bpe was employed as ancillary ligand, a (4,6)-connected **fsc** net with binuclear $[\text{Co}_2(\text{COO})_2]^{2+}$ unit **1** is formed. While bpe was replaced by bpm, a (5,7)-connected net with $[\text{Co}_3(\mu_3\text{-OH})]^{5+}$ trinuclear units **2** is obtained. In **1**, 4-carboxylic group of Hbppc^{4-} is protonated and free of coordination. The Hbppc^{4-} ligand adopt the $(\kappa^1-\kappa^1)-(\kappa^1-\kappa^1)-(\kappa^1)-(\kappa^1-\kappa^1)-\mu_6$ coordination fashion, while in **2**, the bppc^{5-} ligand display $(\kappa^1-\kappa^1)-(\kappa^1-\kappa^1)-(\kappa^1)-(\kappa^1-\kappa^1)-(\kappa^1-\kappa^1)-\mu_9$ binding fashion.

Fig. 2 (a) Coordination environment of Co(II) ions in **2**. Symmetry codes for #1: $-x + 1, -y, -z$; #2: $x - 1/2, -y + 1/2, z + 1/2$; #3: $x, y, z - 1$; #4: $x - 1/2, -y + 1/2, z - 1/2$; #5: $x - 1, y, z$. (b) Coordinated mode of bppc^{5-} ligand. (c) 3D net constructed by Co(II) atoms and bppc^{5-} ligands in **2**. (d) Schematic representation of the 3D **bnn** network constructed by Co(II) atoms and bppc^{5-} ligands. (e) 3D net of **2**. (f) Schematic representation of the 3D (5,7)-connected binodal network.

3.3 PXRD and Thermal Properties

To confirm the phase purity of the bulk materials, powder X-ray diffraction (PXRD) has been carried out. The PXRD experimental and computer-simulated patterns are in good agreement with each other, indicating that both **1** and **2** phase purity of the as-synthesized products (Figure S2, SI).

The TGA curves of the two compounds are shown in Figure S3, SI. For complex **1**, the first weight lost of 9.5% was observed from 100 °C to 270 °C corresponding to the lost of coordination water molecules (calcd. 8.7%). Then pyrolysis of the sample occurred from 330 to ~580 °C. Its

mass remnant of 18.4% corresponding to CoO (17.6% calcd). For complex **2**, in the temperature range of 55 to 165 °C, the weight loss of free and coordinated molecules is observed at 10.00% (calcd. 8.9%). Then a sharp weight-loss step was observed between 355 to 500 °C, representing the structure collapse.

3.4 Magnetic Properties

The temperature-dependent magnetic susceptibilities were measured on polycrystalline samples of **1** and **2** at 1000 Oe in the range of 2-300 K in Fig. 3. For complex **1**, the experimental $\chi_M T$ value at room temperature is $4.86 \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{K}$, which is larger than two isolated spin-only Co^{2+} cations ($3.75 \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{K}$ with $g = 2.0$). Upon cooling, the $\chi_M T$ value increases slightly, reaching a maximum value of $5.02 \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{K}$ at 152 K, and then decreases. The increases in $\chi_M T$ above 152 K are indicative of ferromagnetism between neighbouring Co ions [54]. According to previous literatures, the *syn*, *anti* carboxylate bridges can mediate ferromagnetic couplings [55]. The bridging mode of the carboxylate group is generally indication of ferromagnetic interactions. The magnetic susceptibilities data in 152-300 K can be well fitted to the Curie-Weiss law with a Weiss constant $\theta = -10.04 \text{ K}$ and Curie constant $C = 4.74 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$ for **1**, revealing weak ferromagnetic interactions between the adjacent Co(II) ions.

For complex **2**, the experimental $\chi_M T$ value at 300 K is $7.65 \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{K}$, which is larger than the spin-only value ($5.625 \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{K}$) expected for three magnetically isolated Co(II) ion. As the temperature is lowered, the $\chi_M T$ value decreases continuously. Among the superexchange pathways between the nearest neighbouring Co^{II} ions, the large Co–O–Co angle and the *syn*–*syn* bridging mode of the carboxylate group are indication of antiferromagnetic interactions [56]. In **2**, the antiferromagnetic interactions are found between Co^{II} ions in the trinuclear units relying on the effect of μ_3 -hydroxyl group (Co–O–Co 111.74, 112.30, 119.22 °) exchange pathway and *syn*–*syn* carboxylate exchange pathways. The magnetic susceptibilities data above 20 K can be well fitted to the Curie-Weiss law with $\theta = -69.84 \text{ K}$ and $C = 9.55 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$ for **2**, revealing weak antiferromagnetic interactions between the adjacent Co(II) ions.

Fig. 3 Temperature dependence of $\chi_M T$ and χ_M versus T for **1** (top) and **2** (bottom). Circle symbols represent $\chi_M T$ and square symbols represent χ_M .

4. Conclusion

In summary, two Co(II)-MOFs with bi- or tri-nuclear Secondary building units bridging by carboxylates have been prepared. The results reveal that the coordination frameworks can be well modulated by the different coordination modes of the carboxylic groups of multicarboxylate ligands with different degree of deprotonation and nature of N-donor auxiliary ligands. Magnetic studies indicate that **1** shows weak ferromagnetic interactions, while **2** exhibits weak antiferromagnetic interactions. The results demonstrate that such pentacarboxylic acid may be used as a versatile building block to construct novel coordination polymers with fascinating structures and properties, also, further synthesis, structures and properties studies of coordination frameworks with Co(II) based mixed-ligand coordination frameworks are under way in our lab.

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Graphical Abstract-Pictogram: