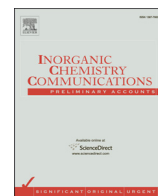




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Short communication

Structural and topological regulation on cobalt coordination polymers with mixed ligands

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ABSTRACT

Structural and topological regulation on a series of cobalt coordination polymers (CPs) built by V-shaped O-donor ligand, 4,4'-(hexafluoroisopropylidene)-bis(benzoic acid) (**H₂L**), and auxiliary N-donor ligands was reported. The introduction of secondary N-donor ligands (2,2'-bipyridine, **BPY**; 1,3-bis(4-pyridyl)propane, **BPP**) greatly affected the overall structures of cobalt CPs, due to the structural tailoring/directing effect of the neutral coordinating molecules **BPY** and **BPP**. The CPs were characterized by single crystal X-ray diffractions, infrared spectroscopy, thermogravimetry measurements, elemental analyses and X-ray powder diffractions. X-ray crystallography suggested the CPs possess 2-D covalent network structures, which identified versatile underlying topological structures. Moreover, magnetic properties of two complexes were also explored.

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The research on coordination polymers (CPs) has arisen revolutionary development over the past few decades due to their intriguing network architectures and potential applications as functional materials in the fields of catalysis [1,2], medicine [3,4], gas storage/separation [5–7], magnetism [8,9] etc. Various design strategies targeting on the structural modulation of CPs have been established so far, due to the advances of crystal engineering and self-assembly concepts [10–12]. Mixed-ligand CPs are typically assembled through the introduction of secondary ligands, either neutral or charged in need of charge balance, which require structural and topological matching with the primary ligands [13–15]. Of special note, a number of mixed-ligand CPs have shown distinctive structures and exceptional properties, as a result of the value-adding effect present in complementary coordination networks [16,17].

On the other hand, the employment of a secondary, or even a third, ligand in the self-assembly chemistry gives an extraordinary opportunity to adjust the structural flexibility and complexity in the resulting mixed-ligand CPs. Apart from the structural diversity shown by the mixed-ligand CPs, physicochemical property of the CPs materials turns sometimes remarkable, which also makes these systems more fascinating for contemporary research [18]. Despite the available strategies based on crystal engineering and reticular chemistry, structural

regulation of mixed-ligand CPs can be extremely challenging, in view of the multiple factors deciding the self-assembly processes i.e. pH, temperature, solvent system, cationic and anionic species, etc.

Our strategy for the systematic synthesis of mixed-ligand CPs is to modify the coordination fashion and rigidity/flexibility shown by the secondary/auxiliary ligands, as well as to interpret the underlying topological relation amongst various CPs [19,20]. Herein, the mixed-ligand system of a primary V-shaped dicarboxyl ligand (4,4'-(hexafluoroisopropylidene)-bis(benzoic acid); **H₂L**) has been regulated via the introduction of chelating/bridging auxiliary ligands (2,2'-bipyridine, **BPY**; 1,3-bis(4-pyridyl)propane, **BPP**), by which three cobalt CPs were synthesized and formulated as [Co(DMA)L]·2DMA (complex **1**), [Co₂(BPY)(L)₂] (complex **2**), and [Co₂(BPP)₂(HL)₂(L)] (complex **3**) (ESI). X-ray crystallography suggests the CPs possess 2-D covalent network structures, which identify versatile underlying topological structures [21].

Complex **1** crystallizes in Monoclinic, space group *P2₁/n* (Table S1; ESI). There are one crystallographically independent Co(II) center, one L²⁻ anion, one coordinated DMA, and two uncoordinated DMA molecules in the asymmetric unit. The L²⁻ anions adopt *bis*-chelating coordination mode to Co²⁺ cations, which display square-pyramidal geometry via binding to terminal DMA molecules. The Co—O bonds vary from 1.984 Å to 2.048 Å, which is in the normal range of Co—O bonds in cobalt CPs [22,23]. Two {CoO₅} units form a binuclear metal cluster and interconnect with L²⁻ anions into a 2-D layer structure (Fig. 1). The crystal structure and topology of complex **1** is common for CPs built by dicarboxyl ligands. However, the structures of complexes **2** and **3**, upon the introduction of auxiliary ligands, are somehow

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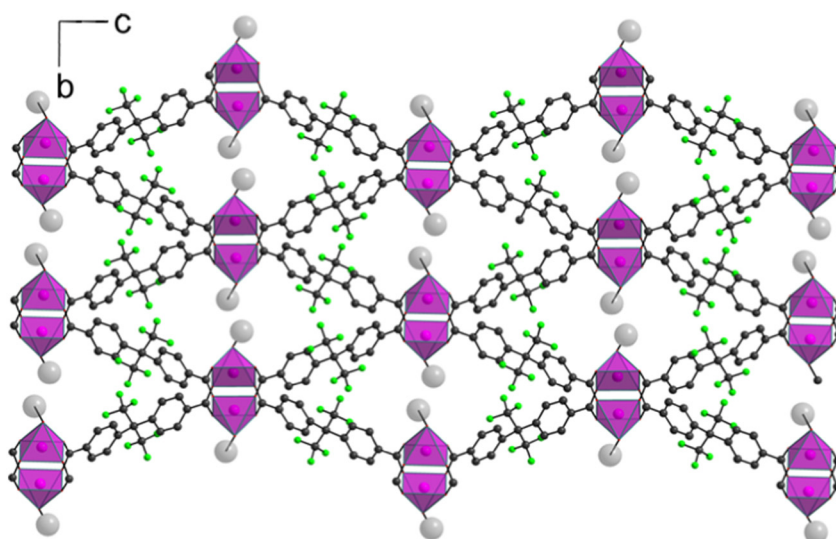


Fig. 1. A view of the 2-D layer subunit in complex 1. DMA molecules are shown as large light-gray balls. All hydrogen atoms are omitted for clarity (similarly hereinafter).

complex and interesting. Complex 2 crystallizes in Monoclinic, space group $C2/c$ (Table S1; ESI). X-ray crystallography indicates two Co(II) ions, two L^{2-} anions, and one BPY ligand exist in the asymmetric unit of 2. The Co(1) center shows tetrahedral coordination geometry accomplished by four carboxyl O atoms with an average Co—O bond of 1.934 Å; the Co(2) center adopts octahedral geometry by coordinating to four carboxyl O atoms and two N atoms from a BPY molecule. The Co—O bonds are in the range of 2.030 Å to 2.164 Å, while Co—N bonds are 2.136 Å and 3.105 Å, respectively. The tetrahedral and octahedral cobalt centers are bridged by carboxyl groups of L^{2-} anions into 1-D chain subunits (Fig. S1; ESI), which are extended into a 2-D layered structure through the interconnection of the skeleton of L^{2-} ligands (Fig. 2). The neutral BPY ligands locate on the octahedral cobalt centers, playing a role of geometry compensation. The BPY molecules are involved in interlayer $\pi \cdots \pi$ interactions (Fig. S2, insert; ESI), with distances between adjacent phenyl rings being ca. 3.589 Å, which extend the 2-D layers into a 3-D supramolecular network (Fig. S2; ESI).

Complex 3 crystallizes in Monoclinic, space group $C2/c$ (Table S1; ESI). One crystallographically independent Co(II) ion, one HL^- , half L^{2-} anion, and one BPP molecules lie in the asymmetric unit of 3. The cobalt center is five-coordinated with four carboxyl O atoms and one N atom from BPP to finish its square-pyramidal geometry, in which Co—O bonds range from 2.028 Å to 2.072 Å and Co—N bond is 2.088 Å. The partially deprotonated HL^- anion adopts 'end-on' coordination

mode, whereas the fully deprotonated L^{2-} anion exhibits *bis*-chelating coordination fashion. The cobalt centers are bridged by carboxyl groups from both HL^- and L^{2-} anions into cobalt oxide chain subunits along the *b* axis, which are further connected into 2-D layer through the backbone of L^{2-} anions (Fig. 3). The 'end-on' BPP molecules coordinate to Co atoms through each of the two pyridyl groups in a BPP, leaving the other pyridyl group uncoordinated (Fig. S3; ESI). The uncoordinated pyridyl group takes part in hydrogen bonding interactions with the protonated carboxyl groups in HL^- anions (N \cdots H—O distance of 2.612 Å), leading to an overall 3-D supramolecular network of complex 3 (Fig. S3, insert; ESI).

Topological analysis using *ToposPro* [21] indicates complex 1 contains 4^4 -*sql* (square layer) subunit, which is one of the most common topologies for 2-D layered structures with binuclear metal cluster units [24]. It should be noted that the solvent molecules occupying axial positions of the binuclear units are substitutable by coordinating molecules, in this case BPY and BPP. Upon the introduction of secondary ligands, the cobalt building units in complexes 2 and 3 are polymeric chain structures that are more interesting in terms of both topological study and magnetic property. Due to the chelating coordination modes of BPY molecules that normally prevent further connection of the building units, in-plane cobalt-oxygen chain structure is observed in complex 2. Moreover, BPY molecules form strong $\pi \cdots \pi$ interaction between the layer structures, which gives an overall Kagome-like rod-packing topology. The cobalt-oxygen chain structure in complex 3 is similar to the binuclear unit, viewing from the crystallographic *b* axis, connected by L^{2-} anions and HL^- /BPP into a hydrogen-bonded network, thanks to the interactions between HL^- and BPP, which results in a *pcu*-like rod-packing topology [25].

Due to the general research interest in magnetism of cobalt complexes [26,27], temperature dependence of the magnetic susceptibility of complexes 1 and 3 in the temperature range 2–300 K under a 1 kOe applied field were studied. Phase purity and homogeneity of complexes 1 and 3 were examined by means of powder X-ray diffractions (PXRD) prior to the magnetic susceptibility study. The experimental PXRD patterns match well with the calculated lines simulated from the single crystal data (Fig. S4; ESI). The magnetic data of complexes 1 and 3 are displayed in Fig. 4, plotted as the thermal variation of χ_m^{-1} and $\chi_m T$. The $\chi_m T$ value of $3.03 \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{K}$ at 300 K for complex 1 gradually decreases to a value of $1.57 \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{K}$ at 2 K (Fig. 4a). The magnetic data of complex 1 obeys the Curie–Weiss law between 2 K to 300 K and the fit of the χ_m^{-1} versus T curve in the temperature range of 30–300 K gives a Weiss constant $\theta = -13.44 \text{ K}$ and a Curie constant $C = 3.20 \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{K}$, which suggests the presence of antiferromagnetic

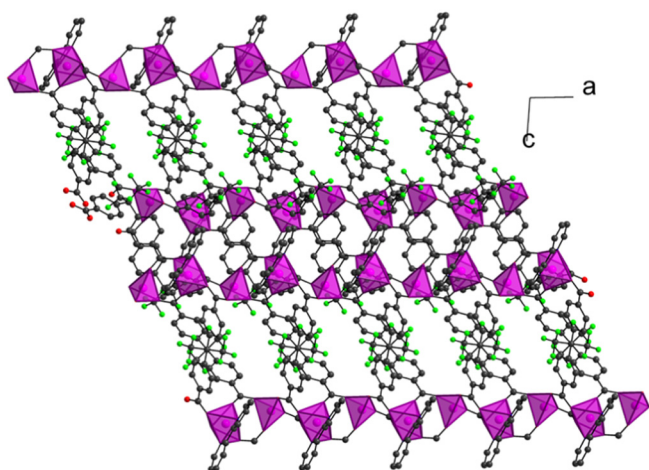


Fig. 2. A view of the 2-D layer subunit (e) in complex 2.

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