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Short communication

Effect of organic dicarboxylate on the self-assembly of ternary mixed-ligand cobalt(II) coordination polymers: Syntheses, fluorescence and catalytic properties

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ABSTRACT

Two Co(II) coordination polymers, formulated as $[Co(bix)(tbta)]_n$ (**1**) and $[Co(bix)_{0.5}(aip)(H_2O)]_n$ (**2**) (bix = 1,4-bis(imidazol-1-ylmethyl)benzene, H_2tbta = tetrabromoterephthalic acid, H_2aip = 5-aminoisophthalic acid) have been synthesized and structurally characterized by single crystal X-ray diffraction. Complex **1** features a 3D three-fold interpenetrating diamond framework. Complex **2** is a 2D (3,4) network with **3,4L83** topology and extend into an unusual (5,6)-connected 3D supramolecular framework *via* intermolecular hydrogen bonds. In addition, fluorescence and catalytic performances of complexes **1** and **2** for the degradation of Congo red dye in a photo-Fenton-like process were investigated.

The design, synthesis, structural characterization of metal organic coordination polymers (MOCPs) have been intensely investigated over the past two decades. These MOCPs can serve as stationary phases for ion exchange, luminescence sensors, heterogeneous catalysts, and gas storage [1]. The generation of intriguing and useful MOCPs is greatly influenced by metal ions, organic ligands, solvent system, pH value and non-covalent interactions such as H-bonding and π–π interactions [2]. Nevertheless, it is still a huge challenge to reasonably construct the expected architectures with unique properties. Selective suitable organic ligands are crucial for the formation of these novel coordination frameworks. In terms of the structural characteristics, the incorporation of polycarboxylates with flexible N-containing ligands is believed to furnish advantages for construction variety of MOCPs [3]. In especial, 1,4-bis(imidazol-1-ylmethyl)benzene (bix), a typical flexible bis(imidazole) derivative with arylaliphatic spacers, can selectively adjust the arrangements *via* rotation and/or bend on the backbone to construct the structural diversities of MOCPs [4]. Additionally, organic aromatic dicarboxylates can display diversiform bridging/chelating modes, which are beneficial for coordinating with metal centers in the construction of MOCPs [5]. Among of them, the inert halogen groups of terephthalic acid derivatives play a significant steric effect on their variety of coordination and supramolecular architectures [6]. Meanwhile, as a good rigid multidentate ligand, the 5-aminoisophthalic acid (H_2aip) can offer one amino group for the formation of hydrogen bond or coordination to the metal atoms, furnish various coordination modes *via* its two carboxylate groups [7]. For the construction of multidimensional coordination frameworks, the Co atom can present as four-, five- and six-coordinated geometries in the complex structures. To investigate the effect of different aromatic dicarboxylate on the self-assembly of ternary mixed-ligand cobalt(II) MOCPs, herein in this paper, we present two new Co(II) complexes: $[Co(bix)(tbta)]_n$ (**1**) and $[Co(bix)_{0.5}(aip)(H_2O)]_n$ (**2**) (H_2tbta = tetrabromoterephthalic acid) [Supplementary material]. Both complexes have been characterized by IR (Fig. S1), elemental analysis, XRPD, thermal analysis and fluorescence properties. Moreover, **1** and **2** display catalytic capacities for the degradation of the Congo red azo dye in a photo-Fenton-like process. The bix ligand prepared according to the previously literature [8].

The X-ray crystallographic study shows that complex **1** crystallizes in the monoclinic space group $C2/c$. The asymmetric unit comprises one half of a Co atom, one half of a bix ligand, and one half of a $tbta^{2-}$ ligand. As shown in Fig. 1a, the central Co^{II} atom is four-coordinated by two nitrogen atoms from two crystallographic symmetry bix ligands and two oxygen atoms originating from two symmetry related $tbta^{2-}$ ligands. The cobalt center shows a tetrahedral geometry with the τ parameter being 0.71 [9]. The Co–N bond distance (2.046(3) Å) and Co–O bond lengths (2.034(2) Å) are comparable to those observed in cobalt complexes [10].

The tbta ligand adopts bis-monodentate coordination mode to connect neighbor cobalt atoms forming $[Co(tbta)]_n$ zigzag chains along

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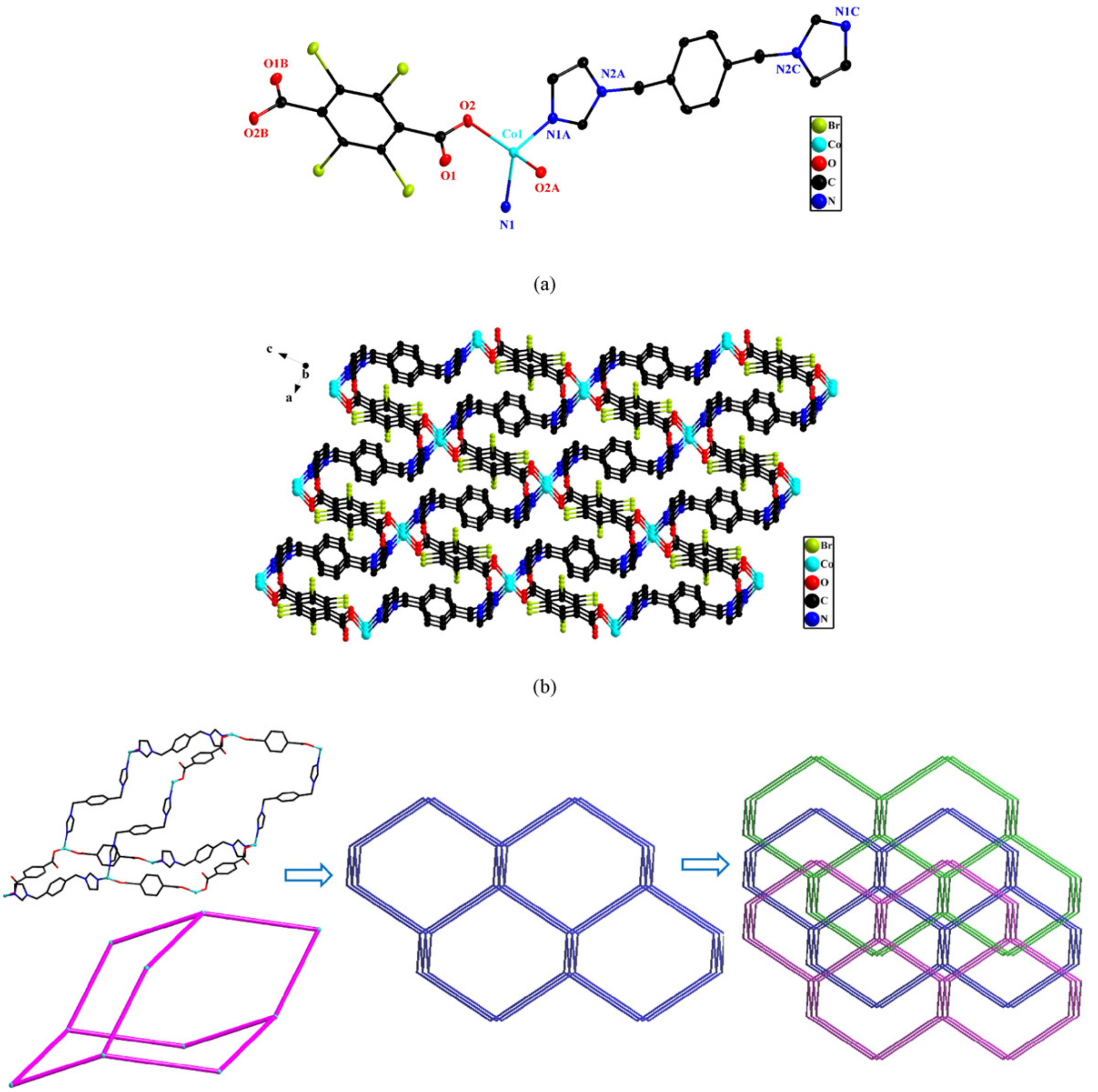

Fig. 1. (a) The coordination environment of Co(II). Symmetry codes: A: $-x, y, -z + 1/2$; (b) view of the 3D framework of **1**; (c) schematic illustration of the three-fold interpenetrating network in 1. All the nodes stand for Co atoms. Bromine atoms of the H_2tbta are omitted for clarity. Hydrogen atoms are omitted for clarity (30% ellipsoid probability).

the *c*-axis. Each bix ligand acts as a μ_2-bridging linker and adopt *anti* conformation with two imidazole rings being in a parallel fashion. The neutral 1D infinite $[Co(bix)]_n$ chains are constructed by bix ligands and Co(II) ions with a Co···Co separation of 14.069(5) Å. The interlaced connection of the two 1D chains give rise to a 3D coordination framework by sharing Co(II) ions (Fig. 1b). From the topological point of view, the Co atom connecting four neighboring Co atoms can be considered as 4-connected node, the bix and tbta^{2-} bridging ligands can be regarded as linkers. Accordingly, the 3D MOCP of **1** can be simplified as a 4-connected **dia** topology with the point symbol of 6^6, which is performed by the TOPOS4.0 software [11]. In order to avoid an extremely large void space, **1** exhibits a 3-fold interpenetrating structure (Fig. 1c). The three interpenetrated nets are related by a single translational vector (Class Ia) [12], with $Z_t = 3$ and $Z_n = 1$, where Z_t represents the number of interpenetrated nets related by translation, and Z_n denotes the number of interpenetrated nets related by crystallographic symmetry [13]. Intriguingly, a void volume of 100.6 Å^3 is also left after interpenetration and the pore volume ratio was calculated to be 4.1% by the PLATON program [14].

Complex **2** crystallizes in the triclinic space group $P\bar{1}$. The asymmetric unit consists of one Co atom, a half of bix ligand, one aip^{2-} ligand, and one coordination water molecule. The Co atom is six-coordinated by three oxygen atoms from two different aip^{2-} ligands [Co1–O1 = 2.124(2) Å, Co1–O2 = 2.261(2) Å, Co1–O3A = 2.016(2) Å, Symmetry code A: $x, y - 1, z$], an imidazolyl N atom from a bix ligand [Co1–N2 = 2.077(3) Å], one N atom belonging to the amino of aip ligand [Co1–N1B = 2.179(3) Å, Symmetry code B: $-x, -y + 1, -z$] [15], and one O atom from a coordination water molecule [Co1–O1W = 2.125(3) Å], completing the distorted octahedral geometry (Fig. 2a). In **2**, the aip^{2-} ligand exhibits a monodentate-monodentate-chelating coordination mode: one carboxyl group coordinates to one Co atom with a monodentate mode, the other one coordinates with another Co(II) center in a chelating coordination fashion, and the amino group also coordinates with one Co atom. So the aip^{2-} ligands link adjacent Co atoms forming folded ladder-like chains (Fig. S2a). The chains are further connected by the bix ligands with a μ_2-bridging mode to construct 2D sheets. From a topological view, if the Co atom is regarded as a 4-connected node, each aip^{2-} ligand is viewed as a 3-connected node, and the bix ligand is considered as a linear linker, the 2D network of **2** can be simplified as a 3,4-connected **3,4L83** topology with point symbol of $(4^2.6^3.8)(4^2.6)$, as shown in Fig. 2b. Furthermore, the 2D sheet is extended into a 3D supramolecular architecture by O–H···O