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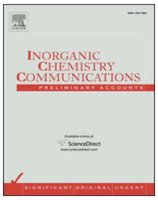

Short communication

# Two porous coordination polymers containing helix-based metal-organic nanotubes based on trigonal N-donor ligand

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ABSTRACT

Two isostructural 3D porous metal-organic frameworks (MOFs), namely $[Co_2(Htpim)_2(odpa)]\cdot 8H_2O$ **(1)** and $[Ni_2(Htpim)_2(odpa)]\cdot 8H_2O$ **(2)** (Htpim = 2,4,5-tri(4-pyridyl)-imidazole, odpa = 4,4′-oxydiphthalate), were prepared and characterized by elemental analyses, single crystal X-ray diffraction, powder X-ray diffraction, IR spectra and thermal analyses. The 3D architectures of compounds **1** and **2** are built from 1D metal-organic nanotubes (MONTs) which connect with each other by bridging ligands, and every 1D MONT is generated by linking the vertexes of helical chain with metal-organic fragments. In addition, the magnetic properties of **1** and **2** have also been studied.

Since the first discovery of carbon nanotubes (CNTs) [1], nanotubular materials have attracted widespread attention due to their intriguing architectures and potential applications in molecular capillaries, sieves, adsorption, and biological models [2]. Metal-organic frameworks (MOFs) have attracted much interest on account of their tunable well-defined structures and important applications in gas storage, separation, catalysis and drug delivery [3]. As a subfamily and new member of MOFs and nanotubular material, metal-organic nanotubes (MONTs) with MOF and nanotubular structural features are feasible to possess the merits of both to be further explored for some new applications in materials science and nanotechnology [4]. Even if the MONTs have arouse increasing concern for their structures and applications, the development of this realm is still in its infancy [5]. Therefore, further investigations are necessary to enrich this realm currently.

According to literature, connecting the vertexes of 1D helix via bridging ligands is regarded as a feasible route for the construction of MONTs [5b,6]. Recently, Hong et al. pointed out that some rigid pyridine- or carboxylate-based ligands might lead to helical structure when linked by appropriate connectors in assembly process [7]. Some examples of single-walled MONTs containing helical chains have been reported using linear rigid ligands as building blocks [8]. However, in contrast with linear rigid ligands, trigonal rigid N-donor ligands are rarely employed to build helix-based MONTs. In this work, the trigonal rigid N-donor ligand Htpim (Htpim = 2,4,5-tri(4-pyridyl)-imidazole) and odpa are simultaneously introduced to fabricate helix-containing MONTs for the following considerations: (i) The large trigonal Htpim ligand could generate large voids and thus favor the formation of hollow tubes. (ii) Htpim may act as V-shaped bridging ligand, which makes it possible to construct helix [9,7b]. (iii) Acting as rigid ligand, fixed conformation of Htpim ligand makes the ligand a good candidate to help rationally synthesize and predict the target compounds in some degree. (iv) Mixed-ligand synthetic strategy is confirmed to be effective to construct diverse coordination polymers [10].

Fortunately, by trial and error, two isostructural 3D porous MOFs containing single-walled MONTs have been successfully prepared, namely, $[Co_2(Htpim)_2(odpa)]\cdot 8H_2O$ **(1)** and $[Ni_2(Htpim)_2(odpa)]\cdot 8H_2O$ **(2)** (odpa = 4,4′-oxydiphthalate). Interestingly, each 1D MONT is constructed from helical chain, in which the vertexes are linked by metal-organic fragments.

Compounds **1** and **2** were obtained by reaction of $Co(Ac)_2\cdot 4H_2O$/$NiCl_2\cdot 6H_2O$, 2,4,5-tri(4-pyridyl)-imidazole, 4,4′-oxydiphthalic anhydride (see experimental section of supplementary information). They were characterized by elemental analyses, powder X-ray diffraction (Figs. S5 and S6), TG analyses (Figs. S7 and S8), IR spectra (Figs. S9 and S10) and single-crystal X-ray diffraction analyses. The crystal data and structure refinements of compounds **1** and **2** are summarized in Table S1. Selected bond lengths and angles for compounds **1** and **2** are listed in Table S2.

X-ray crystallography shows that compounds **1** and **2** are isostructural, since they crystallize in the same space group with almost identical cell parameters (Table S1), thus only the structure of **1** will be discussed in detail. Compound **1** is a tetranodal (3,4,4,6)-connected 3D

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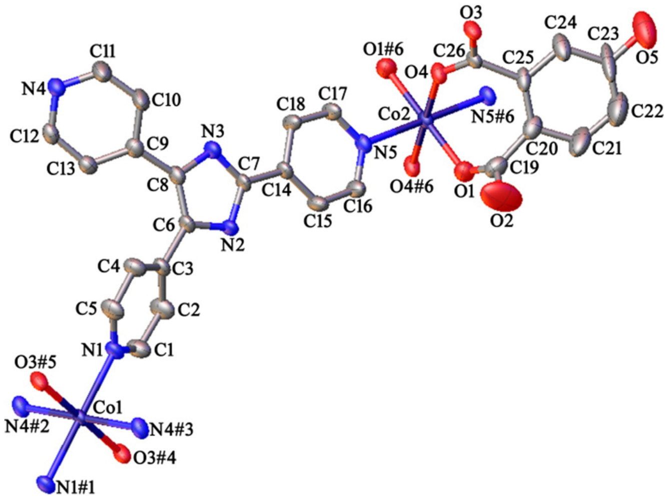

**Fig. 1.** Coordination environment of Co atoms in compound **1** (H atoms omitted for clarity; Symmetry codes: #1 1/2 − x, 1/2 − y, 1/2 − z. #2 1/2 − x, 1/2 + y, 1 − z. #3 + x, −y, −1/2 + z. #4 −1/2 + x, 1/2 + y, −1/2 + z. #5 1 − x, −y, 1 − z. #6 3/2 − x, 1/2 − y, 3/2 − z).

network with an unprecedented topology whose structure contains helix-based MONTs. As shown in Fig. 1, the asymmetric unit contains half of the formula, that is, two half Co(II) ions (half occupied Co1 and Co2) lying on inversion centers, one Htpim ligand and half an odpa ligand. Co1 atom is coordinated by four N atoms from four Htpim ligands (Co-N 2.197(3)–2.210(3) Å) and two O atoms from two odpa ligands (Co-O 2.075(2) Å), to yield a distorted octahedral geometry. Co2 center also displays a distorted octahedral geometry, being coordinated by two N atoms from two Htpim ligands (Co-N 2.187(3) Å) and four O atoms of two carboxylate ligands (Co-O 2.037(3)–2.102(2) Å). Every Htpim ligand acts as a tridentate ligand binding three Co(II) ions (Scheme S1a). In most cases, the Htpim ligands act as V-shaped ditopic linkers binding metal ions to form helical chains or voids [11,7b]. Interestingly, in this paper, three pyridine groups of Htpim ligand participate in coordination. In detail, 4- and 5-pyridine groups of Htpim ligands connect Co1 ions to generate helical chains (Fig. S2), and the 2-pyridine group bind Co2 ion. Each odpa ligand links four Co(II) ions with $\mu_2$-$\eta^1$:$\eta^0$:$\eta^1$:$\eta^1$ coordination mode (O1–O4) (Scheme S1b).

Based on these coordination modes, Co1 ions are linked by 4,5-di(4-pyridyl)-imidazole groups of Htpim ligands to generate a helical chain running along a crystallographic $2_1$ axis in the *b* direction with a pitch of 11.6075 Å (Fig. 2a). Notably, on the turning of helix, the Co1–imidazole–Co1 angle is 92.411° (Fig. S3), which leads to the helix coiling along the twofold screw axis. As depicted in Fig. S2, two $O_2C$-C-C-C-$CO_2$ groups of odpa ligands chelate Co2 ion to yield a $[Co(O_2C\text{-}C\text{-}C\text{-}C\text{-}CO_2)_2]$ metal-organic fragment. Then, the vertexes of helical chain are connected by $[Co(O_2C\text{-}C\text{-}C\text{-}C\text{-}CO_2)_2]$ metal-organic fragments to build a 1D MONT along the *b* axis (Figs. 2b and S2). Each 1D MONT is further linked to the adjacent MONTs through odpa ligands and 2-pyridine groups of Htpim ligands. On the basis of this way, these 1D MONTs

are regularly held together to give rise to a 3D microporous framework with unique nanotubular arrays (Fig. 2c). PLATON analysis showed that the effective free volume of **1** is 22.1% of the crystal volume (1147.9 Å$^3$ out of the 5204.2 Å$^3$ unit cell volumes) after all guest water molecules are removed [12].

From a topological perspective, Co1 center, surrounded by four N-donor ligands (Htpim) and two carboxylate ligands (odpa), can be simplified as a six-connected node; Co2 center, linked by two Htpim ligands and two odpa ligands, can act as a four-connected node; each odpa ligand is simplified as a four-connected node bridging four Co(II) ions; every Htpim ligand connecting three Co(II) ions acts as a three-connected node (Fig. S3). Based on the above simplification principle, the resulting structure of **1** can be rationalized as a (3,4,4,6)-connected network (Fig. 2d). The Schläfli symbol for this topology is $(6^3)_2(6^5\cdot8)(6^6)(6^9\cdot8^4\cdot10^2)$ as determined by the TOPOS program [13].

The temperature dependence of magnetic susceptibility for compounds **1** and **2** were measured in the temperature range of 2–300 K at a direct current field of 1.0 kOe. All the magnetic susceptibility data were corrected from diamagnetic contributions estimated from Pascal's constants. As shown in Fig. 3, For compound **1**, the $\chi_M T$ value at 300 K is 6.250 cm$^3$ K mol$^{-1}$ (7.071 $\mu_B$), which is higher than the expected value (3.750 cm$^3$ K mol$^{-1}$, 5.477 $\mu_B$) of two isolated spin-only Co$^{II}$ ions ($S = 3/2$, $g = 2.0$), which can be ascribed to the orbital contribution to the magnetic moment of Co$^{II}$ centers [14,15]. In the octahedral coordination geometry of Co$^{II}$, the ground state is a $^4T_{1g}$ term for S = 3/2. Taking into account an axial distortion of the Co$^{II}$ ion, the triplet $^4T_{1g}$ ground state would split into $^4A_2$ and $^4E$ levels. For the low temperature state, Abraham and Price have found an effective $S = 1/2$ and a gav = 13/3, consistent with the EPR spectra of several cobalt salts [14]. The $\chi_M T$ gradually decreases as the temperature is lowed, which is attributed to the antiferromagnetic interaction between Co$^{II}$ ions and/or Zero-Field Splitting (ZFS) effect. At 2 K, the $\chi_M T$ value is 3.326 cm$^3$ K mol$^{-1}$, which is in agreement with two Co$^{II}$ ions with effective $S = 1/2$ and a gav = 13/3 (3.520 cm$^3$ K mol$^{-1}$). The fit of the curve for $1/\chi_M$ versus $T$ plot to the Curie-Weiss law gives a good result in the temperature of 2–300 K with $C = 6.320$ cm$^3$ K mol$^{-1}$ and $\theta = -11.249$ K.

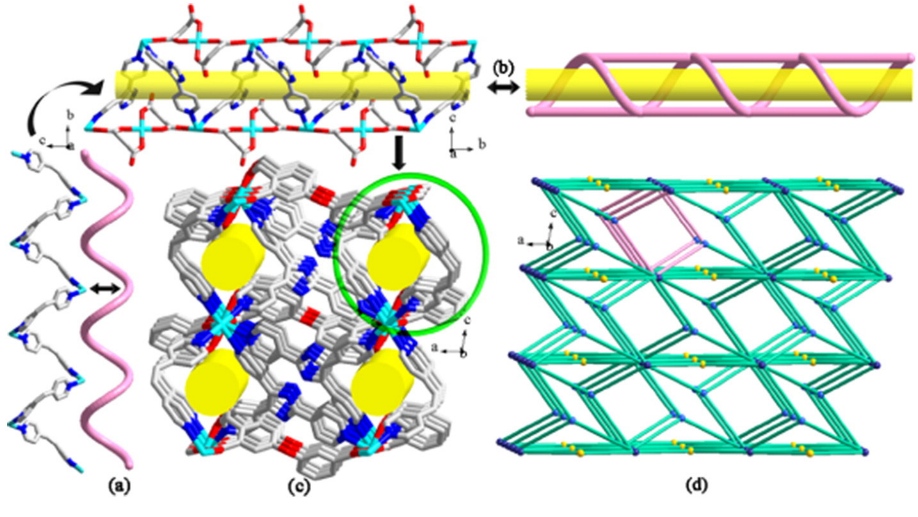

**Fig. 2.** (a) Perspective and schematic view of helical chain in **1**. (b) 1D nanotube of **1** viewed along *b* axis. (c) Perspective view of 3D framework in **1**. (d) Schematic view of the (3,4,4,6)-connected net with $(6^3)_2(6^5\cdot8)(6^6)(6^9\cdot8^4\cdot10^2)$ topology.