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## A High-connected Cobalt(II) Pyromellitate MOF Displaying An Uncommon Decadentate Coordination Mode

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### Introduction

Metal–organic frameworks (MOFs) from organic ligands and transition metals have become a field of quick growth in supramolecular and material chemistry due to their intriguing structural diversity and potential applications in several aspects such as gas adsorption/separation, catalysis, optics, magnetism, and molecular recognition.<sup>1</sup> In particular, topology focuses on the coordination network connectivity generated *via* the reduction of periodic nets into node-and linker/vertex-and-edge representations, which helps greatly the understanding of the significance of MOFs for theoretical crystal chemistry consists in close relations between their composition, physical properties and topology of the corresponding atomic net. To date, thousands of new MOFs have been synthesized.<sup>2,3</sup> In these reported coordination networks, the majority are commonly uninodal- and low connected (< 7) nodes, trinodal networks containing highly connected nodes such as (3,4,6)-, (3,4,7)-, (3,6,10)-, (3,8,10)-, (4,4,7)- and (4,8,16)-connected MOFs are relatively rare.<sup>4,5</sup> The formation of the highly connected MOFs is greatly affected by the organic ligands, the nature of the metal ions, the counterions, and other factors. Among the reported research, organic ligands with carboxylate groups are especially interesting in the field of crystal engineering and coordination chemistry. Pyromellitic acid (H<sub>4</sub>pm) as an outstanding organic ligand containing four exo-carboxyl groups around the benzene ring, shows diverse coordination modes and bridges central metal atoms to assemble multidimensional architectures.<sup>6,7</sup> Therefore, a number of highly connected MOFs based on H<sub>4</sub>pm have been synthesized and presented by our group and others during the past several years.<sup>8</sup> Based on H<sub>4</sub>pm, and mixed with bis(pyridyl)-1,2,4-triazolate ligands, two novel 3D zinc(II) coordination polymers were synthesized and characterized by Yu and his co-workers, the topological analysis results reveal the two MOFs can be simplified to a trinodal (3,4,10) and (3,4,5)-connected topology, respectively. Very recently, we found that introduction of rod-like neutral *N,N'*-donor btx (1,4-bis(1,2,4-triazol-1-ylmethyl)-benzene) ligands into the Co-pm system can generate novel compound {[Co<sub>5</sub>(pm)<sub>2</sub>(btx)(μ<sub>3</sub>-OH)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]}<sub>n</sub>·2H<sub>2</sub>O, which is an unusual 3D binodal (4,10)-connected MOF.<sup>9</sup> In

continuation of our exploratory research toward developing new coordination polymers constructed from H<sub>4</sub>pm with secondary bridging flexible two-connector *N*-containing co-ligands,<sup>8c</sup> herein, we report the synthesis, crystal structure and characterization of an unique trinodal (4,4,7)-connected 3D MOF, formulated as [Co<sub>2</sub>(pm)(bib)<sub>0.5</sub>(H<sub>2</sub>O)<sub>0.5</sub>]<sub>n</sub> (**1**) (bib = 1,4-bis(2-methyl-imidazol-1-yl)butane) with a Schläfli symbol of (4<sup>2</sup>.5<sup>2</sup>.6.7)(4<sup>4</sup>.6<sup>2</sup>)(4<sup>9</sup>.5<sup>6</sup>.6<sup>6</sup>), in which pyromellitate anions show an unprecedented decadentate coordination mode. In addition, TGA, XRPD and fluorescence spectra determinations were performed for **1**.

### Experimental

**Materials and Characterization Methods.** All reagents were purchased commercially and used without further purification. The *N*-containing ligand bib was synthesized in accordance with previously reported literature.<sup>10</sup> The elemental analyses (C, H, and N) were performed on a Perkin-Elmer 240C analyzer. Thermal analysis was performed on a Netzsch TG 209 thermal analyzer from room temperature to 800 °C under N<sub>2</sub> at a heating rate of 10 °C/min. FT-IR spectrum was recorded from KBr pellets in the range of 4000–400 cm<sup>-1</sup> on an Avatar 360 (Nicolet) spectrophotometer. The luminescence spectra for the powdered solid samples were measured at room temperature on a Hitachi F-7000 fluorescence spectrophotometer. The X-ray powder diffraction (XRPD) pattern was recorded on a Rigaku D/Max-2500 diffractometer at 40 kV, 100 mA for a Cu-target tube and a graphite monochromator.

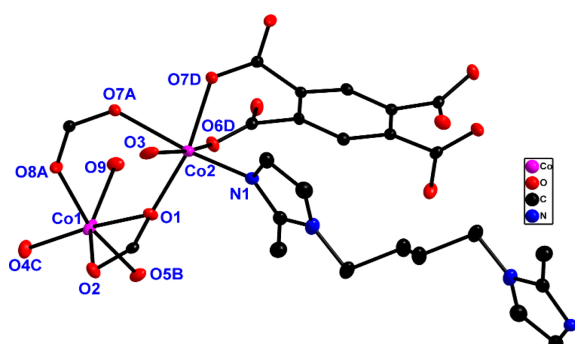
**Synthesis of [Co<sub>2</sub>(pm)(bib)<sub>0.5</sub>(H<sub>2</sub>O)<sub>0.5</sub>]<sub>n</sub>.** A mixture of CoCl<sub>2</sub>·6H<sub>2</sub>O (0.1 mmol, 23.8 mg), H<sub>4</sub>pm (0.1 mmol, 25.0 mg), bib (0.1 mmol, 22.0 mg), methanol (5 mL) and H<sub>2</sub>O (10 mL) was placed in a Teflon-lined stainless steel vessel and then, the pH value was adjusted to 6.5 by NaOH (0.1 M). The mixture was sealed and heated at 140 °C for 3 days under autogenous pressure. After the mixture cooled to room temperature at a rate of 5 °C/h, purple block single crystals of the complex, suitable for X-ray diffraction, were collected by filtration. Yield: 58% (based on Co). Anal. Calc. for C<sub>32</sub>H<sub>24</sub>Co<sub>4</sub>N<sub>4</sub>O<sub>17</sub> (%): C, 39.53; H, 2.49; N, 5.76%. Found: C, 39.68; H, 2.31; N, 5.52%. IR (KBr, cm<sup>-1</sup>): 3435s, 2923w,

1615s, 1565s, 1448s, 1390m, 1272m, 878w, 773w, 696m.

**Crystallography.** Single crystal X-ray diffraction analysis of the titled compound was carried out on a Bruker Smart 1000 CCD diffractometer with Mo- $K\alpha$  radiation ( $\lambda = 0.71073$  Å) and  $\omega$ - $2\theta$  scan mode at room temperature. The intensities were corrected for Lorentz and polarization effects as well as for empirical absorption based on multiscan techniques; the structure of the complex was solved by direct methods and refined by full-matrix least-squares fitting on  $F^2$  by SHELXL-97.<sup>11</sup> Multi-scan absorption corrections were applied to the data using the SADABS program.<sup>12</sup> All non-hydrogen atoms were located in difference Fourier maps and refined anisotropically. The H-atoms of organic ligands were generated theoretically onto the specific atoms and refined isotropically. The complex showed disorder in N1, N2, C11-C16 of the bib ligands; these atoms were refined with a split model with site occupation factor 0.63, SADI for restraining distances with related disordered atoms. The O9 atom is too close to a 2-fold axis, that means, by a 2 symmetry operation, an O9A that are 1.24 angstrom from O9 will be generated (A:  $-x+1/2, y-1/2, z$ ). So the SOF (site occupation factor) of O9 has to be 0.5. CCDC-993735 contains the supplementary crystallographic data. The crystallographic data is summarized in Table S1 (Supporting Information), and the selected bond lengths and angles are listed in Table S2 for the complex.

## Results and Discussion

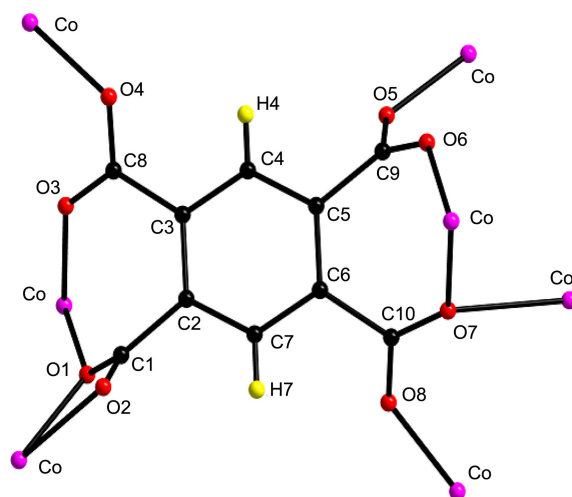
Single-crystal X-ray diffraction analysis reveals that the complex crystallizes in the orthorhombic group  $Pbcn$ . The coordination environment of the compound is depicted in Figure 1, wherein two crystallographically unique Co(II) cations coexist in the asymmetric unit. The asymmetry unit itself contains two independent cobalt atoms, one  $pm^4$  ligand, half of a coordinated water molecule and half of a neutral bib ligand. Both of the Co(II) centers are hexacoordinated, displaying a distorted octahedral geometry. The Co(1) center is coordinated by six oxygen atoms (O1, O2, O4C, O5B, O8A and O9). A:  $-x+1/2, y-1/2, z$ ; B:  $-x+1/2,$



**Figure 1.** Coordination environment of the two Co(II) centers in **1**. Thermal ellipsoids are drawn at the 30% probability level (All H atoms are omitted for clarity. Symmetry codes: A:  $-x+1/2, y-1/2, z$ ; B:  $-x+1/2, -y+1/2, z-1/2$ ; C:  $x, -y, z-1/2$ ; D:  $x-1/2, -y+1/2, -z+1$ ).

$-y+1/2, z-1/2$ ; C:  $x, -y, z-1/2$ ). Three of these oxygen atoms (O1, O2 and O4C), originating from two carboxylates of two  $pm^4$  ligands, and one coordinated water molecule (O9) are in the equatorial positions, whereas two oxygen atoms (O5B, O8A), deriving from two symmetry-equivalent  $pm^4$  anions, are in the apical positions (the coordination angle O8A–Co1–O5B is  $165.24(9)^\circ$ ). Co(2) is ligated to one nitrogen atom (N1) of the bib ligand and one oxygen atom (O7A) from one  $pm^4$  in the apical positions, four carboxyl oxygen atoms (O1, O6D, O7D, and O3. D:  $x-1/2, -y+1/2, -z+1$ ) from four carboxyl groups of two  $pm^4$  ligands in the equatorial positions (O7A–Co2–N1 of  $169.15(15)^\circ$ ). The Co–N bond distance is  $2.103(5)$  Å and the Co–O bond lengths are in the range of  $1.982(2)$ – $2.364(3)$  Å, which are both within acceptable ranges of those observed in other cobalt complexes.<sup>13</sup>

In **1**, the  $pm^4$  ligands take a rare decadentate coordination mode, acting as a  $\mu_7-\eta^3:\eta^3:\eta^2:\eta^2$  linker to connect seven  $Co^{2+}$  ions and the dihedral angles between the carboxylic groups and the aromatic ring are  $36.03(2)^\circ$ ,  $41.22(1)^\circ$ ,  $57.28(2)^\circ$ , and  $69.60(2)^\circ$ , respectively (Figure 2). When searching the Cambridge Structural Database (version 5.35, May 2014)<sup>13b</sup> for coordination modes of anionic pm ligands, no structures were found, featuring this decadentate coordination mode (Scheme S1 (supporting Information) illustrates the reported versatile coordination modes of the  $pm^4$  ligand). The bib and decadentate  $pm^4$  ligands interconnect the two types of Co atoms into a complicated 3D network with a high density value ( $1.996$  g  $cm^{-3}$ ) (Figure 3). Calculations from the X-ray structure data of **1** using PLATON<sup>14</sup> program show that this framework contains no residual solvent accessible void. From the topological point of view, the overall topology can be described as a trinodal high-connected network. The  $pm^4$  ligands can be regarded as topologically 7-connected nodes, which connect three Co2 and four Co1 nodes. Each Co1 node links four  $pm^4$  ligands by oxygen atoms of carboxyl groups of  $pm^4$ . As a result, the Co1 center can be simplified as a 4-connected node. The Co2 node fastens another neigh-



**Figure 2.** The rare decadentate coordination mode of the  $pm^4$  ligand in **1**.

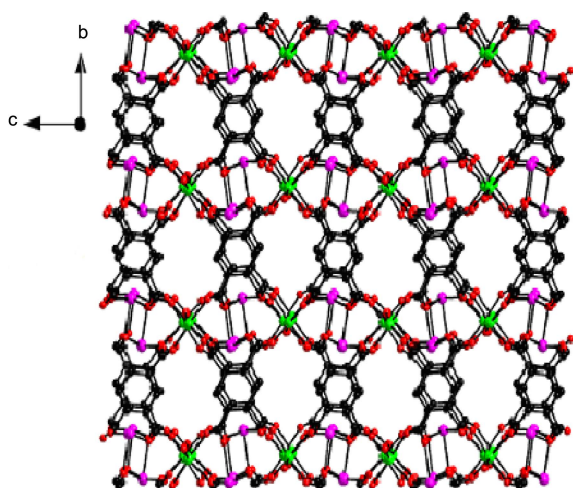


Figure 3. The 3D network of complex 1.

bouring  $\text{Co}^{2+}$  via a bridging bib ligand, and three  $\text{pm}^{4-}$  ligands, and can be regarded as a 4-connected node. The bib ligand is a linker (Figure S1 showing three types of nodes). Thus, the 3D high-connected MOF can be simplified as unique mixed nodes, a trinodal (4,4,7)-connected network with a Schläfli symbol of  $(4^2.5^2.6.7)(4^4.6^2)(4^9.5^6.6^6)$  analyzed by the TOPOS 4.0 program<sup>15</sup> (Figure 4). To the best of our knowledge, the topology of this net has not appeared in MOF chemistry, according to the reticular Chemistry Structure Resource Database.<sup>16</sup>

**IR Spectrum and XRPD Pattern.** The IR spectrum displays characteristic absorption band for water molecule, carboxyl groups of  $\text{pm}^{4-}$ , and bib ligand. There is no absorption peak between  $1730$  and  $1690\text{ cm}^{-1}$ , indicating that all carboxyl groups of the organic moieties are deprotonated.<sup>17</sup> The infrared spectra of the title complex represents a broad band centered at *ca.*  $3435\text{ cm}^{-1}$  which is due to the O-H stretching vibration of water molecules involved in extensive hydrogen bonding interactions or the coordinated water molecule. The bands at  $2923\text{ cm}^{-1}$  and  $1272\text{ cm}^{-1}$  are related to  $\nu_{\text{C-H3}}$  and  $\nu_{\text{C-N}}$  of the bib ligand, respectively. The splitting of  $\text{COO}^-$  bands suggests the different coordination mode of carboxylate groups from the  $\text{pm}^{4-}$  ligands.<sup>18</sup> This is also in agreement with the crystal structure of the complex.

The simulated and experimental XRPD patterns of compound, obtained at room temperature, are shown in Figure S2. Their peak positions are in good consistency with each other, indicating the phase purity of the as-synthesized samples.

**Thermal Analysis.** Thermogravimetric analysis (TGA) was performed on a sample of **1** under  $\text{N}_2$  atmosphere with a heating rate of  $10.0\text{ }^\circ\text{C}/\text{min}$ . As shown in Figure S3, the complex possessed a two-step weight-loss process. The first step occurred from  $110.0\text{ }^\circ\text{C}$  to  $147.0\text{ }^\circ\text{C}$ , with a weight-loss of  $2.0\%$ , which can be attributed to the loss of coordinated water molecules (calcd:  $1.9\%$ ). Furthermore, there is almost no weight loss from  $148.0\text{ }^\circ\text{C}$  to  $358.0\text{ }^\circ\text{C}$ . The second step with a weight-loss of  $24.9\%$  occurred in a temperature range from  $359.0\text{ }^\circ\text{C}$  to  $579.0\text{ }^\circ\text{C}$ , corresponding to the decomposi-

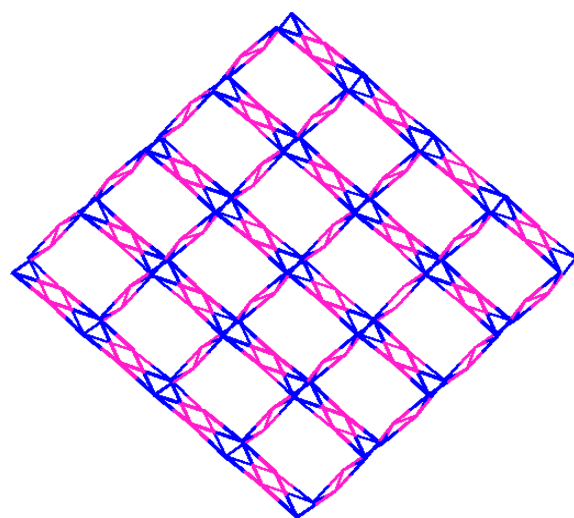


Figure 4. The 3D trinodal (4,4,7)-connected net of complex 1.

tion of the organic ligands. And finally, the remnants are  $29.8\%$ , which should be  $\text{CoO}$  (calcd.  $30.9\%$ ).

**Luminescence Properties.** The solid-state photoluminescence spectrum of compound **1** was measured at room temperature, and the result is depicted in Figure S4. The complex exhibits a fluorescent emission band with maximum at  $384\text{ nm}$  upon excitation at  $235\text{ nm}$ . The main emission peak of  $\text{H}_4\text{pm}$  is at  $342\text{ nm}$  ( $\lambda_{\text{ex}} = 308\text{ nm}$ ),<sup>19</sup> while the free bib ligand displays very weak fluorescent emission centered at  $465\text{ nm}$  ( $\lambda_{\text{ex}} = 280\text{ nm}$ ).<sup>20</sup> When comparing the title complex with the  $\text{H}_4\text{pm}$  ligand, the emission band of the complex is  $42\text{ nm}$  red-shifted, which can be assigned according to intraligand  $n-\pi^*$  transitions.<sup>21</sup>

## Conclusion

In summary, we present an unusual trinodal (4,4,7)-connected MOF with an uncommon coordination model of  $\text{pm}^{4-}$  ligand. The results clearly reveal that the  $\text{H}_4\text{pm}$  ligand acts as a rich library of tectons in designing and construction of highly-connected MOFs. Furthermore, the bib ligand may influence the functional properties of these coordination polymers.

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**Supplementary Material.** CCDC number: 993735 for the complex. The data can be obtained free of charge via [https://services.ccdc.cam.ac.uk/structure\\_deposit](https://services.ccdc.cam.ac.uk/structure_deposit) (or from the Cambridge Cryst allographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (44)1223-336-033(44); or [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)).

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