

# Synthesis and Crystal Structure of a Puckered Rhombus Grid-like Coordination Polymer with Bridging Ligand Containing Sulfanyl Linker

HAN, Lei(韩磊) LUO, Jun-Hua(罗军华) HONG, Mao-Chun\*(洪茂椿)  
WANG, Rui-Hu(王瑞虎) LIN, Zheng-Zhong(林郑忠) CAO, Rong(曹荣)

State Key Laboratory of Structural Chemistry, Fujian Institute of the Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, China

A new coordination polymer with sulfide moieties,  $[\text{Co}(\text{ptmb})_2] \cdot 0.25\text{H}_2\text{O}$  (ptmb=4-(4-pyridylthiomethyl)benzoate), was synthesized by self-assembly of  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  with Hptmb under solvothermal conditions. X-ray single crystal diffraction study shows that it is a 2D layer structure consisting of puckered rhombus grid with dimensions  $1.175 \text{ nm} \times 1.110 \text{ nm}$ .

**Keywords** crystal structure, coordination polymer, solvothermal synthesis, sulfide moiety

## Introduction

The design and construction of metal-organic frameworks (MOFs), obtained by metal-directed self-assembly from labile metal centers and multidentate bridging ligands, is a rapidly developing area of supramolecular chemistry.<sup>1-3</sup> Besides the aesthetic structural and fascinating functional motifs, they are of interest both for understanding the mechanisms of the assembly process and for the host-guest chemistry associated with their large central cavities.<sup>4-13</sup> It has been documented that the choice of ligand plays an important role in the structure of the open framework complexes. Although both length and flexibility of organic ligand have great impact on structural topology, studies on the influence of flexibility attract less attention. Recently, we have developed a convenient method for synthesis of flexible thioether-heterocyclic ligands and a series of interesting structures has been obtained, such as nanometer-sized metallosupramolecular cube, tube, single-stranded helical chain, and two-dimensional lamellar network structures.<sup>14-16</sup> The success prompted us to extend our work on flexible ligands with oxygen donor atoms.<sup>17</sup> As part of our systematic work, in this paper we report the synthesis and characterization of a novel flexible monoanionic ligand with hybrid pyridyl and benzoic carboxylate moieties, namely 4-(4-pyridylthiomethyl)benzoic acid (Hptmb), and its cobalt polymer  $[\text{Co}(\text{ptmb})_2] \cdot 0.25\text{H}_2\text{O}$  (**1**) which possesses a 2D layer structure consisting of puckered rhombus grid with dimensions  $1.175 \text{ nm} \times 1.110 \text{ nm}$ .

## Experimental

### Materials and measurements

4-Mercaptopyridine and  $\alpha$ -bromo-*p*-toluic acid were purchased from Acros Organics, other reagents were purchased from Shanghai reagent Co. All reagents were of analytical grade and used without further purification. Elemental analyses (C, H, N) were performed on a Perkin-Elmer model 240C automatic instrument. IR spectra were recorded on a Magna 750 FT-IR spectrophotometer with KBr pellet. <sup>1</sup>H NMR spectra were measured on a Bruker AM500 spectrometer with SiMe<sub>4</sub> as the internal reference. Thermogravimetric analysis was performed on a NETZSCH STA 449C thermal analyzer under flowing N<sub>2</sub> with a heating rate of 10 °C/min.

### Preparation of Hptmb

4-Mercaptopyridine (1.112 g, 10 mmol) was added to a stirred solution of NaOH (0.4 g, 10 mmol) in H<sub>2</sub>O (20 mL). The mixture was warmed to reflux, then  $\alpha$ -bromo-*p*-toluic acid (2.15 g, 10 mmol) was added and the mixture was refluxed for about 10 h with vigorous stirring. After being cooled, the mixture was left to stand overnight. The precipitate was filtered and washed with water, giving a fine white powder in 80% yield. <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>)  $\delta$ : 4.454 (s, 2H, CH<sub>2</sub>), 7.31 (d, *J*=4.5 Hz, 2H, C<sub>5</sub>H<sub>4</sub>N), 8.34 (d, *J*=4 Hz, 2H, C<sub>5</sub>H<sub>4</sub>), 7.56 (d, *J*=8 Hz, 2H, C<sub>6</sub>H<sub>4</sub>), 7.88 (d, *J*=8.5 Hz, 2H, C<sub>6</sub>H<sub>4</sub>); IR (KBr)  $\nu$ : 1630 (s), 1590 (vs), 1546 (s), 1385 (vs), 1110 (m), 1091 (m), 1018 (m), 799 (s), 746 (s), 635 (m), 536 (w), 492 (s) cm<sup>-1</sup>. Anal. calcd for C<sub>13</sub>H<sub>11</sub>NO<sub>2</sub>S:

\* E-mail: hmc@ms.fjirsm.ac.cn; Fax: +86-591-3714946

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C 63.65, H 4.52, N 5.71; found C 63.58, H 4.61, N 5.57.

### Preparation of [Co(ptmb)<sub>2</sub>] · 0.25H<sub>2</sub>O (**1**)

A mixture of Co(NO<sub>3</sub>)<sub>2</sub> · 6H<sub>2</sub>O (29 mg, 0.1 mmol) with Hptmb (49 mg, 0.2 mmol) in a metal-to-ligand ratio of 1 : 2 in 10 mL of CH<sub>3</sub>OH/H<sub>2</sub>O/Pyridine (500 : 500 : 1) was sealed in a stainless-steel reactor with a Teflon liner and heated at 110 °C for 72 h. A quantity of red, block crystals of **1** were obtained after the solution was cooled to room temperature. The yield of **1** was *ca.* 65% based on Hptmb. IR (KBr)  $\nu$ : 1595 (vs), 1537 (vs), 1485 (s), 1421 (vs), 1018 (m), 736 (s), 624 (m), 499 (s) cm<sup>-1</sup>. Anal. calcd for [Co(ptmb)<sub>2</sub>]: C 57.04, H 3.68, N 5.12; found C 56.78, H 3.92, N 4.97.

### Crystal structure determination

A red single crystal of the complex with approximate dimensions of 0.18 mm × 0.15 mm × 0.10 mm was mounted on a glass fiber and used for data collection. The intensity data were collected on a Bruker CCD diffractometer by  $\omega$  scan technique at room temperature using graphite-monochromated Mo K $\alpha$  ( $\lambda$ =0.071073 nm) radiation. The structure was solved by direct method using the SHELXTL-97 program package. All data were refined by full-matrix least-squares minimizations of  $\Sigma(F_o - F_c)^2$  with anisotropic thermal parameters for all non-hydrogen atoms except the O(5) atom. The positions of the H atoms were generated geometrically, assigned isotropic thermal parameters, and allowed to ride on their parent carbon before the final cycle of refinement. In Table 1 the important crystal data are summarized, and in Table 2 the selected bond lengths and angles for the complex are listed. Additional crystallographic details and complete listings of the complex have been deposited at the Cambridge Crystallographic Data Center (CCDC) as supplementary publications with reference number 213822.

**Table 1** Crystal data for **1**

Chemical formula	C <sub>26</sub> H <sub>20.50</sub> CoN <sub>2</sub> O <sub>4.25</sub> S <sub>2</sub>
Formula weight	551.99
Temperature	293(2) K
Wavelength	0.071073 nm
Crystal system	Triclinic
Space group	<i>P</i> -1
<i>a</i>	1.1102(2) nm
<i>b</i>	1.1207(2) nm
<i>c</i>	1.1749(2) nm
$\alpha$	63.60(3)°
$\beta$	80.07(3)°
$\gamma$	79.05(3)°
<i>V</i>	1.2790(4) nm <sup>3</sup>
<i>Z</i>	2

Continued

<i>D</i> <sub>c</sub>	1.433 g · cm <sup>-3</sup>
$\mu$	0.870 mm <sup>-1</sup>
<i>F</i> (000)	567
Crystal size	0.18 mm × 0.15 mm × 0.10 mm
$\theta$ range for data collection	1.88° to 27.48°
Limiting indices	-14 ≤ <i>h</i> ≤ 14, -14 ≤ <i>k</i> ≤ 0, -15 ≤ <i>l</i> ≤ 13
Reflections collected/unique	5729/5729 [ <i>R</i> (int)=0.0000]
Completeness to $\theta$ =27.48	97.4%
Refinement method	Full-matrix least-squares on <i>F</i> <sup>2</sup>
Data/restraints/parameters	5729/0/320
Goodness-of-fit on <i>F</i> <sup>2</sup>	0.962
Final <i>R</i> indices [ <i>I</i> >2 $\sigma$ ( <i>I</i> )]	<i>R</i> <sub>1</sub> =0.0531, <i>wR</i> <sub>2</sub> =0.1534
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> =0.0884, <i>wR</i> <sub>2</sub> =0.1764
Largest diff. peak and hole	1.001 and -0.330 e · nm <sup>-3</sup>

**Table 2** Selected bond lengths (nm) and angles (°) for complex **1**

Co(1)—O(1)	0.2087(3)	Co(1)—O(2)	0.2221(3)
Co(1)—N(2)	0.2094(3)	S(1)—C(3)	0.1751(4)
Co(1)—N(1)#1	0.2116(3)	S(1)—C(6)	0.1810(5)
Co(1)—O(3)#2	0.2149(3)	S(2)—C(16)	0.1755(4)
Co(1)—O(4)#2	0.2170(3)	S(2)—C(19)	0.1805(4)
O(1)—Co(1)—N(2)	95.07(12)	O(1)—Co(1)—O(2)	60.85(10)
O(1)—Co(1)—N(1)#1	56(12)	N(2)—Co(1)—O(2)	154.72(12)
N(2)—Co(1)—N(1)#1	101.31(13)	N(1)#1—Co(1)—O(2)	88.63(12)
O(1)—Co(1)—O(3)#2	112.18(12)	O(3)#2—Co(1)—O(2)	88.03(11)
N(2)—Co(1)—O(3)#2	95.01(12)	O(4)#2—Co(1)—O(2)	110.26(10)
N(1)#1—Co(1)—O(3)#2	148.13(12)	C(3)—S(1)—C(6)	103.8(2)
O(1)—Co(1)—O(4)#2	169.82(11)	C(16)—S(2)—C(19)	104.03(19)
N(2)—Co(1)—O(4)#2	92.91(12)	C(7)—C(6)—S(1)	116.6(3)
N(1)#1—Co(1)—O(4)#2	91.05(11)	C(20)—C(19)—S(2)	116.6(3)
O(3)#2—Co(1)—O(4)#2	60.71(10)		

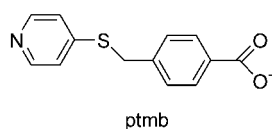
Symmetry transformations used to generate equivalent atoms: #1: *x*-1, *y*, *z*; #2: *x*, *y*, *z*-1; #3: *x*, *y*, *z*+1; #4: *x*+1, *y*, *z*.

## Results and discussion

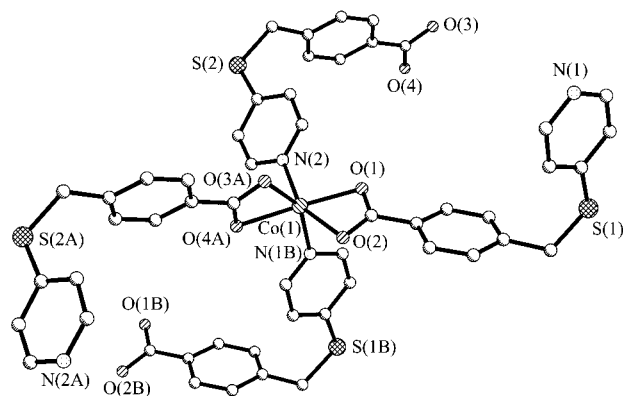
Attention has been paid on the sulfide group, a well-known functional group in organic chemistry, as reaction site. For the design of a new coordination polymer with sulfide moieties, we have synthesized a number of flexible organic ligands, such as 2,4,6-tri-[(4-pyridyl)methylsulfanyl]-1,3,5-triazine (tpst)<sup>14,15</sup> and 1,2-bis[(2-pyrimidinyl)sulfanylmethyl]-benzene (bpsb).<sup>16</sup> Here, the intriguing features of Hptmb arise from not only its flexibility but also the presence of hybrid pyridyl and benzoic carboxylate moieties that are con-

nected by a  $-\text{CH}_2\text{S}-$  spacer. As shown in Scheme 1, the ligand possesses four possible bonding sites, *i.e.*, the nitrogen atom, the sulfur atom, and the two oxygen atoms of the carboxylate group. Because the carboxylate group can adopt monodentate, chelating-bidentate, bridging-bidentate and bridging-multidentate modes, rich coordination modes of ptmb may be expected. If ptmb coordinates to metal ions through its carboxylate group and pyridyl nitrogen as well as the carboxylate group adopts a chelating-bidentate mode, it may be used as a mono-anionic singly bridging ligand. Accordingly, a grid-like structure may be expected by introducing metal ions favoring a hexa-coordination mode, with the advantage that no co-ligand is needed for saturating the coordination sphere of the metal ion owing to the chelating function of carboxylate. Thus ptmb was reacted with  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  in a metal-to-ligand ratio of 1 : 2 under solvothermal conditions. As expected, complex **1** containing puckered rhombus grids was obtained in high yield.

Scheme 1

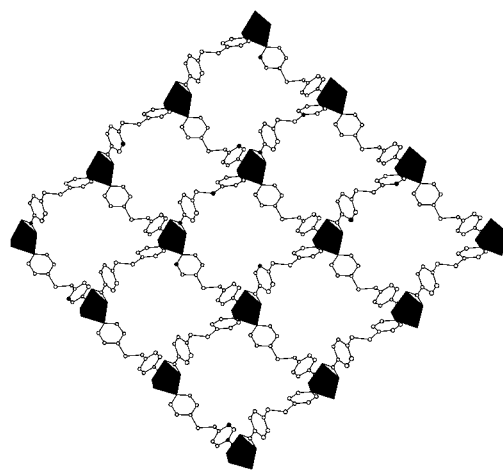
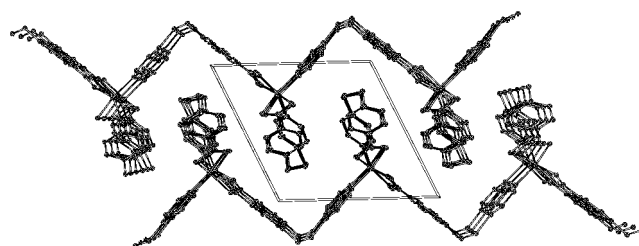


The crystallographic analysis reveals that complex **1** is a two-dimensional grid-like polymer. As shown in Figure 1, each cobalt ion is coordinated by two nitrogen atoms from two ligands and four oxygen atoms of the carboxylate groups from two other ligands in an highly distorted octahedral coordination geometry. One nitrogen atom [N(2)] and three oxygen atoms [O(1), O(2) and O(4A)] form the equatorial plane, while the axial positions are filled by one nitrogen atom [N(1B)] and one oxygen atom [O(3A)]. The Co—N and Co—O distances range from 0.2094(3) to 0.2116(3) and 0.2087(3) to 0.2221(3) nm (see Table 2), respectively.

Figure 1 Coordination environment of Co(II) in **1**.

Each ligand acts as a single bridge linking two cobalt ions through its nitrogen atom and carboxylate group, and each cobalt ion connects four ligands to form an

infinite two-dimensional structure. The grid-like  $\text{Co}_4(\text{ptmb})_4$  species can be viewed as the basic building block of the structure, in which the apices are occupied by cobalt ions and the sides are formed by ptmb ligands. Each four  $\text{Co}_4(\text{ptmb})_4$  grids are joined together through sharing the cobalt apices to give the final two-dimensional layer structure consisting of puckered rhombus grids with dimensions of  $1.175 \text{ nm} \times 1.110 \text{ nm}$  based on the metal-to-metal distances (Figure 2). The most intriguing feature of the structure is that the basic grid is puckered, different from previously reported grid-like structures in which the basic grids are usually coplanar or quasi-coplanar.<sup>18-20</sup> The puckered shape of the basic grid in **1** is understandable, because the  $\text{sp}^3$  configurations of C and S of the  $-\text{CH}_2\text{S}-$  spacer force the ptmb ligand to be non-linear, generating the non-linear grid sides and thereby the puckered grids. Actually, the C—C—S and C—S—C angles of ptmb in **1** range from  $116.7(3)^\circ$  to  $127.0(3)^\circ$  and  $103.8(2)^\circ$  to  $104.03(19)^\circ$ , respectively; the phenyl and pyridyl rings in each ligand are almost perpendicular to each other with an average dihedral angle of  $89.9^\circ$ . These structural data clearly depict the non-linear configuration of ptmb in **1**. It should be noted that the actual structure of the two-dimensional layer is wave-like, the convex surface of one layer is immersed into the concave surface of an adjacent layer to get a tightly packed structure (Figure 3). The lattice water molecules are wrapped in the middle of the adjacent layers.

Figure 2 Two-dimensional layer structure of **1**.Figure 3 Tightly packed structure of **1**, only two layers are shown for clarity.

In order to study the thermal stability of the compound **1**, thermogravimetric analysis (TGA) was performed on a polycrystalline sample. The result shows a release of 0.25 water molecules in the temperature range of 180–250 °C and no strikingly clear weight loss step occurred below 325 °C, indicating that **1** is stable up to this temperature (Figure 4).

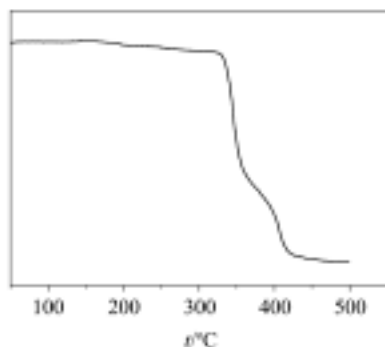


Figure 4 Thermogravimetric data for complex **1**.

## Conclusion

In summary, a novel flexible mono-anionic ligand (Hptmb) comprising hybrid pyridyl and benzoic carboxylate moieties linked by a  $-\text{CH}_2\text{S}-$  spacer was synthesized. The polymeric complex  $[\text{Co}(\text{ptmb})_2] \cdot 0.25\text{H}_2\text{O}$  (**1**) consisting of puckered rhombus grids with dimensions of 1.175 nm  $\times$  1.110 nm was obtained in the reaction of  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  with Hptmb under solvothermal conditions. The non-linear configuration of ptmb induces the puckered basic grid and the wave-like two-dimensional structure of **1**.

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