

# A tri-layer structure consisting of novel heptacobaltate clusters and single cobalt centers bridged by 5-*tert*-butyl isophthalate†

Li-Juan Chen,<sup>a,b</sup> Jiang-Bo Su,<sup>a</sup> Rong-Bin Huang,<sup>c</sup> Shen Lin,<sup>\*a,b</sup> Ming-Xing Yang<sup>a,b</sup> and Hua Huang<sup>a</sup>

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A 2D tri-layer compound  $\{[\text{Co}_8(\text{tbip})_6(\text{H}_2\text{O})_9(\text{OH})_4]\cdot 12(\text{H}_2\text{O})\}_n$  (**1**) ( $\text{H}_2\text{tbip}$  = 5-*tert*-butyl isophthalic acid) consisting of novel heptacobaltate clusters and single cobalt centers bridged by  $\text{tbip}^{2-}$  ligands has been hydrothermally synthesized. The complex represents a rare example of a homometallic coordination polymer built up from both heptanuclear metal clusters and single metal centers simultaneously. The magnetic investigation reveals that the complex exhibits the overall predominance of antiferromagnetic coupling between magnetic centers.

## Introduction

The rational design and preparation of metal–organic frameworks (MOFs) has become an increasingly popular field of research. This motive stems not only from the intriguing structural diversity but also from the demand for applications of functional materials in the fields of catalysis, porosity, luminescence, conductivity, sensing, optical and magnetic devices.<sup>1–4</sup> The construction of such extended architectures is mainly dependent on the selection of suitable organic ligands and inorganic secondary building units (SBUs).<sup>5</sup> Metallic clusters, which possess specific rigid geometries, various coordination advantages and potential to extend to high-dimensional structures with variable cavities or channels, have been proven to be fairly good candidates for the construction of porous coordination frameworks.<sup>6</sup> The versatile carboxylate ligands, such as benzenedicarboxylic acid, 1,3,5-benzenetricarboxylic acid, 1,2,4,5-benzenetetracarboxylic acid, and so on, have a strong tendency to form large, tightly bound metal clusters owing to their abundant carboxylate groups possessing high affinity to metal centers.<sup>7</sup> Therefore, organic aromatic polycarboxylates might act as effective linkers for the assembly of MOFs. In fact, numbers of novel metal–organic frameworks have been reported to be composed of metal clusters as nodes and di- or multi-carboxylate ligands as linkers.<sup>8</sup> In the view of development of synthetic strategies and functional materials, it will be valuable to construct extended frameworks based on single metal centers and metal

clusters owing to their excellent complementarity and tunability.<sup>9</sup> However, it is still a formidable challenge to chemists because of the presence of many subtle interactions during the assembling process and the difficulty in predicting the compositions or structures of the final products.

5-*tert*-Butyl isophthalic acid ( $\text{H}_2\text{tbip}$ ), with a 120° angle between the two carboxylic groups, may provide the potential to form unexpected, unpredictable, and interesting extended structures because the steric hindrance and electron-donating properties of the bulky *tert*-butyl may affect the coordination abilities and modes of the related carboxylic groups.<sup>10</sup> In the present work, by exploiting  $\text{H}_2\text{tbip}$  as the organic ligand and a cobalt(II) salt as the metal source, we obtained a 2D tri-layer structure consisting of heptanuclear cobalt(II) clusters and single cobalt(II) ions bridged by  $\text{tbip}^{2-}$ ,  $\{[\text{Co}_8(\text{tbip})_6(\text{H}_2\text{O})_9(\text{OH})_4]\cdot 12(\text{H}_2\text{O})\}_n$  (**1**). The heptanuclear cobalt(II) cluster included in compound **1** is unprecedented.

## Experimental section

All reagents for the synthesis were purchased from commercial sources and used as received. The title compound was synthesized in a poly(tetrafluoroethylene)-lined stainless steel autoclave under autogenous pressure. Elemental analyses of C, H and N were performed with an EA1110 CHNS-0 CE elemental analyzer. IR (KBr pellet) spectra were recorded on a Nicolet Magna 750FT-IR spectrometer. Thermogravimetric analysis was performed on a METTLER TGA/SDTA851 microanalyzer under a nitrogen atmosphere at a heating rate of 10 °C min<sup>-1</sup>. Magnetic studies were performed on a Quantum Design MPMS XL-7 magnetometer in the temperature range from 2 to 300 K.

## X-Ray crystallography

Single crystal X-ray diffraction analysis of **1** was carried out on a Rigaku Mercury CCD diffractometer equipped with graphite-monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å) at room

<sup>a</sup>College of Chemistry and Materials, Fujian Normal University, Fuzhou 35007, China. E-mail: shenlin@fjnu.edu.cn; Fax: +0086-591-83465393; Tel: +0086-591-22868191

<sup>b</sup>State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, the Chinese Academy of Sciences, Fuzhou, Fujian, 35002, China

<sup>c</sup>College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, People's Republic of China

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**Table 1** Crystallographic data for compound **1**

<b>1</b>	
Formula	C <sub>72</sub> H <sub>118</sub> Co <sub>8</sub> O <sub>49</sub>
<i>M<sub>r</sub></i>	2239.10
Crystal color	Red
Crystal system	Trigonal
Space group	<i>R</i> $\bar{3}$
<i>a</i> /Å	18.639(1)
<i>b</i> /Å	18.639(1)
<i>c</i> /Å	52.333(4)
$\alpha$ (°)	90
$\beta$ (°)	90
$\gamma$ (°)	120
<i>V</i> /Å <sup>3</sup>	15 744.80(12)
<i>D<sub>c</sub></i> /g cm <sup>-3</sup>	1.417
<i>Z</i>	6
<i>T</i> /K	296(2)
<i>F</i> (000)	6948
$\mu$ (Mo-K $\alpha$ )/mm <sup>-1</sup>	1.318
Reflections collected	29 832
Independent reflections	7978 ( <i>R</i> <sub>int</sub> = 0.0307)
Observed reflections	5968
GOF	1.048
<i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	0.0585, 0.1862

$R_1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$ ,  $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)]^{1/2}$ .

temperature. The structure was solved by direct methods and refined by full-matrix least-squares techniques on *F*<sup>2</sup> with the SHELX-97 program package.<sup>11</sup> All non-hydrogen atoms were located with successive Fourier difference syntheses and refined anisotropically. All hydrogen atoms of the organic ligands and coordinated waters were generated geometrically (C–H, 0.93 Å and O–H, 0.84 Å). Hydrogen atoms of isolated waters were neither found nor calculated. A summary of the crystallographic data and structure parameters for compound **1** is provided in Table 1, and the selected bond lengths and angles in Table 2. CCDC 816773 contains the supplementary crystallographic data for this paper.†

## Synthesis

{[Co<sub>8</sub>(tbp)<sub>6</sub>(H<sub>2</sub>O)<sub>9</sub>(OH)<sub>4</sub>·12H<sub>2</sub>O]}<sub>*n*</sub> (**1**). A mixture of 5-*tert*-butyl isophthalic acid (H<sub>2</sub>tbp, 0.032 g, 0.2 mmol), CoNO<sub>3</sub>·6H<sub>2</sub>O (0.102 g, 0.35 mmol), triethylamine (0.1 mL, 0.7 mmol), and H<sub>2</sub>O (5 mL) was placed in an 18 mL Teflon-lined Parr acid digestion bomb and heated for 5 days at 160 °C under autogenous pressure. Red prism crystals were singled out from the reaction mixture after slow cooling to room temperature (yield: 18 mg, 20% based on Co). Anal. calc. for C<sub>72</sub>H<sub>118</sub>Co<sub>8</sub>O<sub>49</sub>: C 38.62, H 5.31, O 35.01%. Found: C 38.37, H 6.16, O 35.66%. IR (solid KBr pellet,  $\nu$ /cm<sup>-1</sup>): 3436 (s), 2964 (m), 1614 (s), 1599 (s), 1437 (s), 1376 (vs), 1272 (w), 780 (m), 721 (m).

## Results and discussion

### Structural description

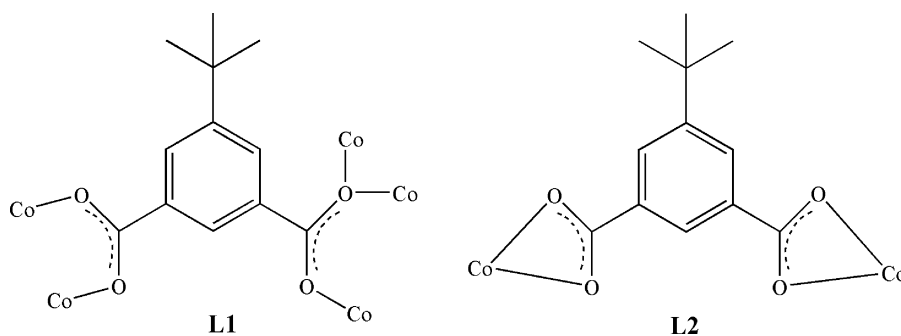
The architecture of 2D homometallic coordination polymers based on both a heptanuclear node and a mononuclear node is extremely rare. However, in compound **1**, the heptanuclear node [Co<sub>7</sub>( $\mu_3$ -OH)<sub>4</sub>]<sup>10+</sup> core and mononuclear node Co<sup>2+</sup> ion are simultaneously observed to be connected by tbp<sup>2-</sup> ligands, generating a 2D extended structure. As shown in Fig. 1 and Scheme 1, the tbp<sup>2-</sup>

**Table 2** Selected bond lengths (Å) and angles (°) for compound **1**

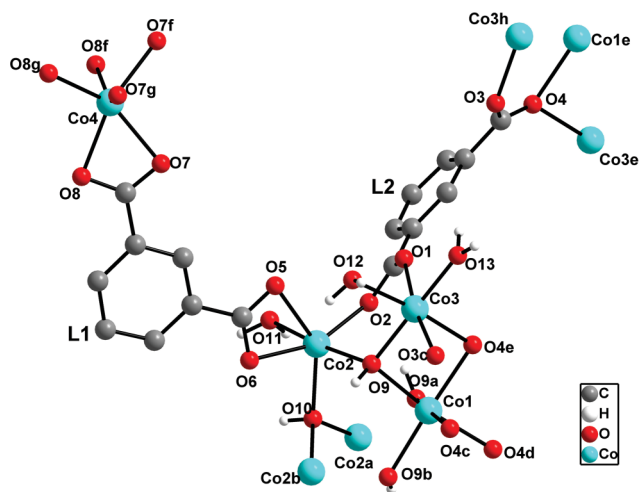
Co(1)–O(9)	2.093(3)	Co(3)–O(9)	2.032(3)
Co(1)–O(9a)	2.093(3)	Co(3)–O(1)	2.055(3)
Co(1)–O(9b)	2.093(3)	Co(3)–O(13)	2.058(4)
Co(1)–O(4c)	2.136(3)	Co(3)–O(3c)	2.083(3)
Co(1)–O(4d)	2.136(3)	Co(3)–O(12)	2.153(4)
Co(1)–O(4e)	2.136(3)	Co(3)–O(4e)	2.243(3)
Co(2)–O(9)	2.076(3)	Co(4)–O(7f)	2.170(4)
Co(2)–O(2)	2.090(3)	Co(4)–O(7g)	2.170(4)
Co(2)–O(10)	2.1086(12)	Co(4)–O(7)	2.170(4)
Co(2)–O(11)	2.128(3)	Co(4)–O(8f)	2.189(4)
Co(2)–O(6)	2.142(4)	Co(4)–O(8g)	2.189(4)
Co(2)–O(5)	2.397(4)	Co(4)–O(8)	2.189(4)
O(9)–Co(1)–O(9a)	96.35(11)	O(9)–Co(3)–O(1)	97.05(12)
O(9)–Co(1)–O(9b)	96.36(11)	O(9)–Co(3)–O(13)	175.29(14)
O(9a)–Co(1)–O(9b)	96.35(11)	O(1)–Co(3)–O(13)	87.19(15)
O(9)–Co(1)–O(4c)	91.47(11)	O(9)–Co(3)–O(3c)	89.50(13)
O(9a)–Co(1)–O(4c)	172.12(11)	O(1)–Co(3)–O(3c)	172.45(14)
O(9b)–Co(1)–O(4c)	83.58(12)	O(13)–Co(3)–O(3c)	86.41(16)
O(9)–Co(1)–O(4d)	172.12(11)	O(9)–Co(3)–O(12)	90.49(13)
O(9a)–Co(1)–O(4d)	83.58(12)	O(1)–Co(3)–O(12)	91.57(15)
O(9b)–Co(1)–O(4d)	91.48(11)	O(13)–Co(3)–O(12)	87.34(16)
O(4c)–Co(1)–O(4d)	88.55(13)	O(3c)–Co(3)–O(12)	92.14(15)
O(9)–Co(1)–O(4e)	83.58(12)	O(9)–Co(3)–O(4e)	82.33(11)
O(9a)–Co(1)–O(4e)	91.47(11)	O(1)–Co(3)–O(4e)	87.35(13)
O(9b)–Co(1)–O(4e)	172.12(11)	O(13)–Co(3)–O(4e)	99.96(14)
O(4c)–Co(1)–O(4e)	88.54(13)	O(3c)–Co(3)–O(4e)	89.81(12)
O(4d)–Co(1)–O(4e)	88.54(13)	O(12)–Co(3)–O(4e)	172.54(13)
O(9)–Co(2)–O(2)	89.64(12)	O(7f)–Co(4)–O(7g)	99.74(13)
O(9)–Co(2)–O(10)	88.72(15)	O(7f)–Co(4)–O(7)	99.74(13)
O(2)–Co(2)–O(10)	112.97(11)	O(7g)–Co(4)–O(7)	99.74(13)
O(9)–Co(2)–O(11)	170.94(13)	O(7f)–Co(4)–O(8f)	59.65(13)
O(2)–Co(2)–O(11)	81.69(13)	O(7g)–Co(4)–O(8f)	146.75(16)
O(10)–Co(2)–O(11)	92.24(15)	O(7)–Co(4)–O(8f)	108.90(17)
O(9)–Co(2)–O(6)	102.74(15)	O(7f)–Co(4)–O(8g)	108.90(17)
O(2)–Co(2)–O(6)	158.64(14)	O(7g)–Co(4)–O(8g)	59.65(13)
O(10)–Co(2)–O(6)	84.99(13)	O(7)–Co(4)–O(8g)	146.75(16)
O(11)–Co(2)–O(6)	86.31(15)	O(8f)–Co(4)–O(8g)	100.12(13)
O(9)–Co(2)–O(5)	96.46(13)	O(7f)–Co(4)–O(8)	146.75(16)
O(2)–Co(2)–O(5)	105.62(13)	O(7g)–Co(4)–O(8)	108.90(17)
O(10)–Co(2)–O(5)	141.10(12)	O(7)–Co(4)–O(8)	59.65(13)
O(11)–Co(2)–O(5)	88.44(14)	O(8f)–Co(4)–O(8)	100.12(13)
O(6)–Co(2)–O(5)	56.22(14)	O(8g)–Co(4)–O(8)	100.12(12)

Symmetry codes: a  $-y, x - y, z$ ; b  $-x + y, -x, z$ ; c  $x - y + 2/3, x + 1/3, -z + 1/3$ ; d  $y - 1/3, -x + y - 2/3, -z + 1/3$ ; e  $-x - 1/3, -y + 1/3, -z + 1/3$ ; f  $-x + y, -x + 1, z$ ; g  $-y + 1, x - y + 1, z$ .

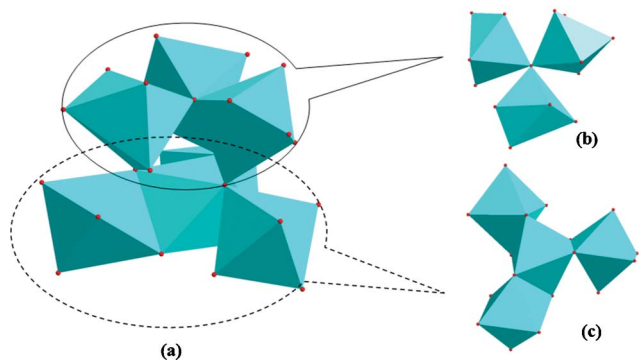
ligands exhibit two kinds of coordination modes. In the first mode, two carboxylate groups act as pentadentate ligands to bridge five Co atoms together (L1). In the second mode, two carboxylate groups act as chelating bis-bidentate ligands to bridge two Co atoms (L2). There are four crystallographic independent cobalt(II) atoms in **1**. All Co(II) centers are octahedrally coordinated, however, the detailed coordination environments among them are different. The Co1 ion is coordinated by three  $\mu_3$ -hydroxyl groups and three carboxylate oxygen atoms from three different L1 ligands. The Co2 ion is bound to two  $\mu_3$ -hydroxyl groups, one chelating carboxylate group from L2, one oxygen atom from L1 and one aqua ligand. The Co3 ion connects three carboxylate oxygen atoms from three different tbp<sup>2-</sup> ligands, two aqua ligands, and one  $\mu_3$ -hydroxyl group. The Co4 ion binds to six oxygen atoms from three chelating carboxylate groups of three different tbp<sup>2-</sup> ligands. On the basis of these connection modes, the Co1 ion and three symmetry-equivalent Co2 ions, as well as three symmetry-equivalent Co3 ions constitute the heptanuclear cluster node (Fig. 2), whereas Co4 acts as the mononuclear node.



**Scheme 1** The two coordination modes adopted by the  $\text{tbip}^{2-}$  ligands in **1**.



**Fig. 1** The coordination and linkage mode in **1**. The *tert*-butyl groups and all hydrogen atoms of the ligands are omitted for clarity. Symmetry codes: a  $-y, x - y, z$ ; b  $-x + y, -x, z$ ; c  $x - y + 2/3, x + 1/3, -z + 1/3$ ; d  $y - 1/3, -x + y - 2/3, -z + 1/3$ ; e  $-x - 1/3, -y + 1/3, -z + 1/3$ ; f  $-x + y, -x + 1, z$ ; g  $-y + 1, x - y + 1, z$ .



**Fig. 2** The  $\{\text{Co}_7\}$  cluster node (a) contained in **1**, and the  $\{\text{Co}_3\}$  (b) and  $\{\text{Co}_4\}$  (c) units that constitute the  $\{\text{Co}_7\}$  cluster.

As shown in Fig. 2, the heptacobaltate cluster in **1** may be considered to be composed of one  $\{\text{Co}_4\}$  cluster capped by a  $\{\text{Co}_3\}$  cluster. The  $\{\text{Co}_3\}$  unit is constructed from three  $[\text{CoO}_6]$  octahedra fused at one common corner, while the  $\{\text{Co}_4\}$  unit consists of one central  $[\text{CoO}_6]$  octahedron sharing its three edges with three symmetry-equivalent  $[\text{CoO}_6]$  octahedra in a *cis*-configuration. And then, the  $\{\text{Co}_3\}$  unit is capped on the  $\{\text{Co}_4\}$  unit to form the  $\{\text{Co}_7\}$  cluster node through sharing three corners, which reside on

the same face of the central  $[\text{CoO}_6]$  octahedron in the  $\{\text{Co}_4\}$  unit. Complexes containing heptanuclear cobalt clusters are rare, and the known  $\{\text{Co}_7\}$  clusters are wheel-shaped<sup>12</sup> where one cobalt occupies the center of the wheel and the other six on the rim, or in the form of corner-fused double cubanes.<sup>13</sup> The heptanuclear cobalt clusters of this type in **1** is unprecedented. The occurrence of the title compound may result from the suitable pH and size of the ligand used in the reaction.

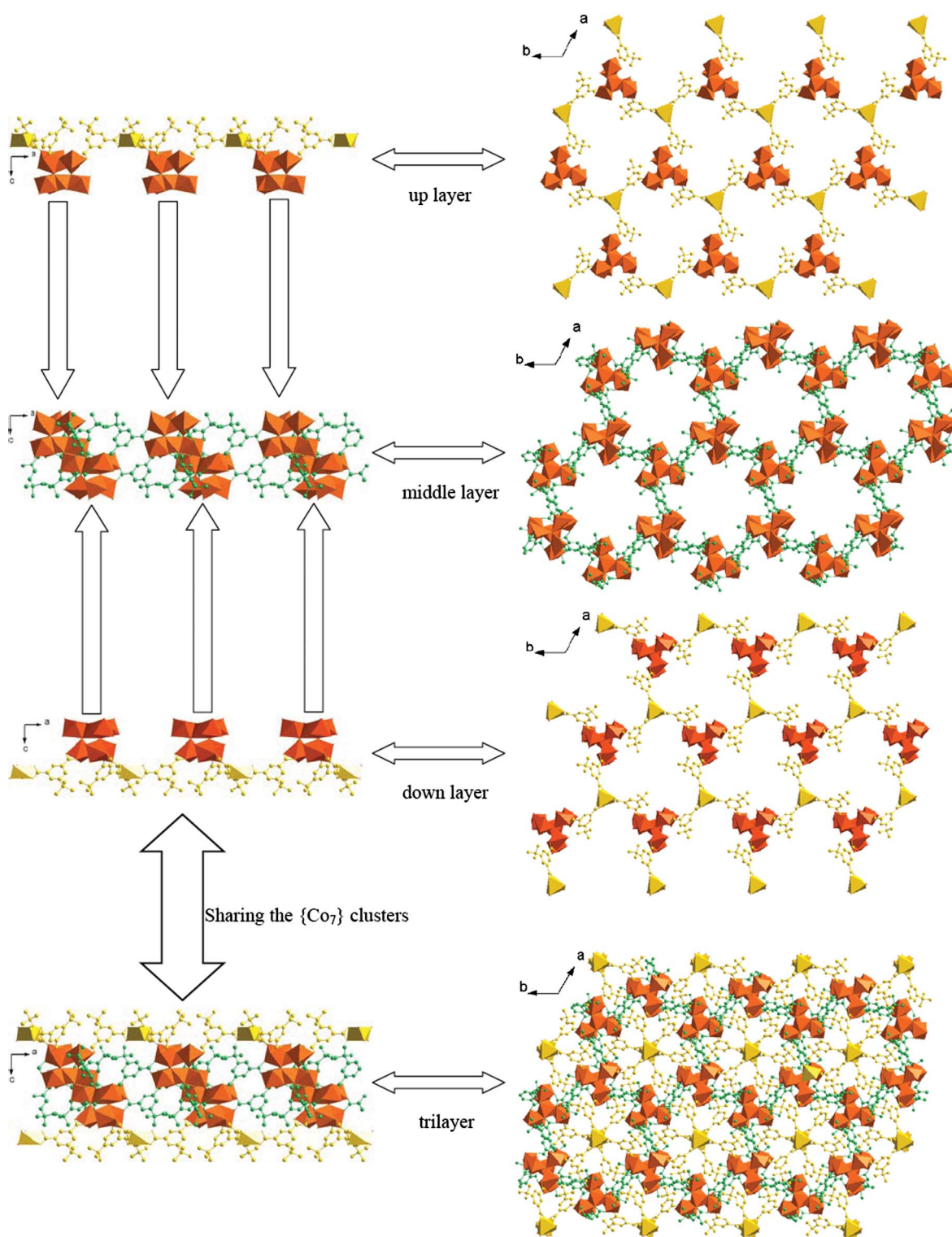
Each heptacobalt cluster node  $\{\text{Co}_7\}$  is connected to three neighboring  $\{\text{Co}_7\}$  through three pairs of L1 ligands, and three neighboring mononuclear node  $\text{Co}^{2+}$  through three L2 ligands. Consequently, a 2D tri-layer structure propagating along the *ab* plane is formed. To fully understand this tri-layer structure, we present the three layers separately in Fig. 3. The *tert*-butyl group of L2 is disordered over two sites. For clarity, only one of these sites is shown. The middle layer is built up from heptacobalt clusters bridged by pairs of L1 ligands to form the honeycomb network with its neighboring  $\{\text{Co}_7\}$  nodes directing away from each other, so that the  $\{\text{Co}_7\}$  nodes are arranged alternatively up and down along the *c* axis. While the layers above and below the middle-layer are constructed from  $\{\text{Co}_7\}$  clusters and mononuclear  $\text{Co}^{2+}$  centers linked by L2 ligands to shape the (6,3)-net, with the three-connected nodes defined by alternating  $\{\text{Co}_7\}$  clusters and  $\text{Co}^{2+}$  centers. The two layers are in a *trans*-configuration, and share their  $\{\text{Co}_7\}$  nodes with the middle-layer to afford a tri-layer structure. It is noteworthy that there are 1D channels along the *a* and *b* axes in the middle layer (Fig. 4), in which guest water solvates reside.

As shown in Fig. S1† and Table 3, there exist intra-trilayer hydrogen bonds among the coordinated aqua groups and the carboxylato groups in  $\text{tbip}^{2-}$  ligands ( $\text{O11} \cdots \text{O6a}$ , 2.681 Å;

**Table 3** Hydrogen bond geometries for compound **1** (Å and °)

D–H...A	D–H	H...A	D...A	∠DHA
O9–H9...O2 <sup>b</sup>	0.833	2.074	2.893	167.66
O11–H11D...O6 <sup>a</sup>	0.840	1.868	2.681	162.73
O11–H11E...O8 <sup>b</sup>	0.839	1.923	2.738	163.31
O12–H12D...O1W <sup>i</sup>	0.840	2.024	2.843	164.42
O12–H12E...O5	0.840	2.221	2.739	120.00
O13–H13A...O4W <sup>c</sup>	0.840	2.155	2.757	128.47
O13–H13B...O1W <sup>b</sup>	0.840	1.991	2.720	144.68

Symmetry codes: a  $-y, x - y, z$ ; b  $-x + y, -x, z$ ; c  $x - y + 2/3, x + 1/3, -z + 1/3$ ; h  $-x - 1/3, -y + 2/3, -z + 2/3$ ; i  $y + 2/3, -x + y + 1/3, -z + 1/3$ .



**Fig. 3** The middle-layer (constructed from heptacobaltate clusters bridged by L2) shares its heptacobaltate clusters with the top and bottom layers (constructed from L1 bridged heptacobaltate clusters and monocobalt centers) to form the tri-layer structure. View along the *b* axis (left) and *c* axis (right).

O12...O5, 2.739 Å, *a*  $-y, x - y, z$ ), between the hydroxyl group and the carboxylate group in  $\text{tbip}^{2-}$  ligands (O9...O2, 2.893 Å, *b*  $-x + y, -x, z$ ), and inter-trilayer hydrogen bonds between the coordinated water molecule and carboxylate oxygen atom (O11...O8h, 2.738 Å; *h*  $-x + 1/3, -y + 2/3, -z + 2/3$ ), as

well as hydrogen bonds among the coordinated aqua groups and free water molecules (O12...O1Wi, 2.843 Å; O13...O1Wb, 2.720 Å; O13...O4Wc, 2.757 Å; *b*  $-x + y, -x, z$ ; *c*  $x - y + 2/3, x + 1/3, -z + 1/3$ ; *i*  $y + 2/3, -x + y + 1/3, -z + 1/3$ ). In the solid state of the title compound, these 2D tri-layers

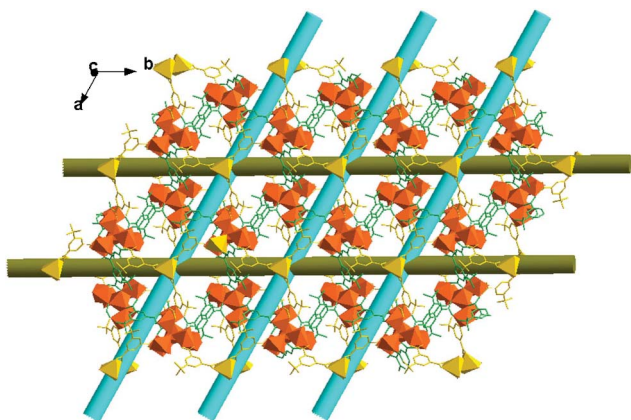


Fig. 4 One-dimensional channels reside in the tri-layer.

are stacked together in an ABCABC packing mode along the *c*-axis (Fig. S2).†

### Thermal and magnetic properties

Thermogravimetric studies of compound **1** were performed to explore its thermal stability. The TG curve is shown in Fig. S3.† The first weight loss of about 19.46% at 65–260 °C is attributed to the escape of the water molecules and the hydroxyl groups (calcd. 19.92%). The following weight loss of 59.71% at 260–507 °C might correspond to the elimination of the *tbip*<sup>2-</sup> ligands (calcd. 58.95%). And the collapse of the {Co<sub>7</sub>} clusters might happen at temperatures above 507 °C.

The magnetic susceptibility,  $\chi_M$ , of **1** was measured in the 2–300 K temperature range, and  $\chi_M T$  and  $\chi_M^{-1}$  versus *T* plots are shown in Fig. 5. The experimental  $\chi_M T$  value is 22.19 cm<sup>3</sup> K mol<sup>-1</sup> at 300 K, higher than the expected one for eight uncoupled Co<sup>2+</sup> ions, which indicates significant unquenched orbital contributions. As the temperature lowers, the  $\chi_M T$  value decreases gradually, suggesting an overall antiferromagnetic coupling between the adjacent Co<sup>2+</sup> ions.

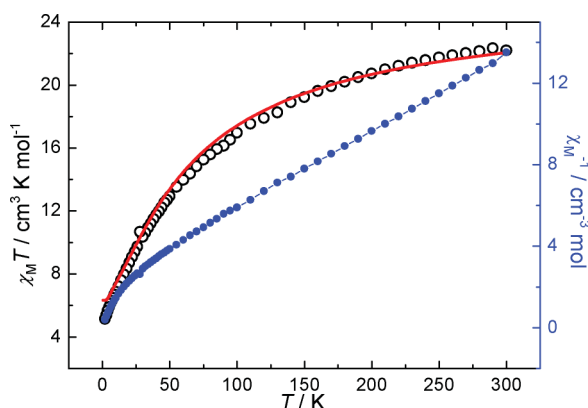


Fig. 5 Temperature dependence of  $\chi_M T$  and  $\chi_M^{-1}$  for **1**. The solid line is the best-fit obtained from the Hamiltonian given in the text.

Owing to the contribution from the spin–orbit coupling of octahedrally coordinated Co<sup>2+</sup> ions, the magnetic analyses for Co-containing compounds is rather complicated,<sup>10,14</sup> and some approximate methods are often applied to analyze magnetic interactions between Co<sup>2+</sup> ions. According to the structure of **1**, it could

be presumed that the main magnetic interactions might happen among the heptacobalt cluster, in which the coupling interactions might be transferred through  $\mu_3$ -OH and  $\mu_2$ -O(carboxylate). The exchange network of this Co(II) cluster is shown in Fig. 6. In this model, the exchange interaction between Co3...Co3 ions is ignored to avoid introducing too many parameters when modeling. On the other hand, the coupling constant between Co1...Co2 ions is assumed to be equal to that between Co2...Co2 centers, because of their nearly equal Co...Co separations (3.565(1) Å for Co1...Co2 and 3.564(1) Å for Co2...Co2). Thus, the magnetic susceptibility is simulated by the equation  $\chi_M = \chi_{\text{hepta}} + \chi_{\text{mono}}$ , where the Hamiltonian describing the exchange interactions within the {Co<sub>7</sub>} cluster can be written as

$$\begin{aligned} \bar{H} = & -2J_1(\bar{S}_1\bar{S}_2 + \bar{S}_1\bar{S}_3 + \bar{S}_1\bar{S}_4) \\ & -2J_2(\bar{S}_1\bar{S}_5 + \bar{S}_1\bar{S}_6 + \bar{S}_1\bar{S}_7 + \bar{S}_5\bar{S}_6 + \bar{S}_5\bar{S}_7 + \bar{S}_6\bar{S}_7) \\ & -2J_3(\bar{S}_2\bar{S}_5 + \bar{S}_3\bar{S}_6 + \bar{S}_4\bar{S}_7) + \mu_B g H \sum_i S_{iz} \end{aligned}$$

where  $S_1 = S_2 = S_3 = S_4 = S_5 = S_6 = S_7 = 3/2$ . The least-square fitting of magnetic susceptibilities with a fixed *g* value (2.60) led to  $J_1 = 0.20$  cm<sup>-1</sup>,  $J_2 = -4.40$  cm<sup>-1</sup> and  $J_3 = -7.60$  cm<sup>-1</sup>. The value of  $J_1$  indicates a weak ferromagnetic interaction between Co1...Co3. While the values of  $J_2$  and  $J_3$  suggest that the antiferromagnetic interactions between Co2...Co3, bridging through both  $\mu_3$ -OH and  $\mu_2$ -O(carboxylate), might be stronger than Co1...Co2 and Co2...Co2, bridging through  $\mu_3$ -OH only.

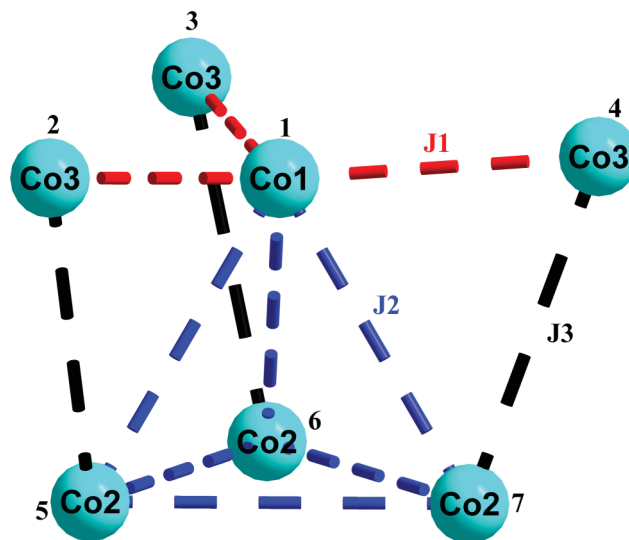


Fig. 6 Exchange scheme of magnetic cluster {Co<sub>7</sub>}. Distances (Å): Co1...Co3 = 3.115(1); Co1...Co2 ≈ Co2...Co2 = 3.565(1); Co2...Co3 = 3.511(1).

### Conclusions

In summary, a novel 2D tri-layer structure consisting of single cobalt centers and heptacobaltate clusters bridged by *tbip*<sup>2-</sup> ligands was hydrothermally synthesized by the reaction of 5-*tert*-butyl isophthalic acid (H<sub>2</sub>*tbip*) and CoNO<sub>3</sub>·6H<sub>2</sub>O. The title complex represents a rare example of a homometallic coordination polymer built up from heptanuclear metal clusters and single metal centers. The steric bulk of *tbip*<sup>2-</sup> might play an important role in

its construction. The investigation of its magnetic behavior reveals the overall predominance of antiferromagnetic coupling between magnetic centers.

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