

Xiang-Rong Hao,<sup>a,b</sup> Zhong-Min Su,<sup>a\*</sup> Ya-Hui Zhao,<sup>a</sup> Kui-Zhan Shao<sup>a</sup> and Yong Wang<sup>a</sup><sup>a</sup>Institute of Functional Materials Chemistry, Department of Chemistry, Northeast Normal University, Changchun 130024, People's Republic of China, and <sup>b</sup>Department of Chemistry, TongHua Teachers College, Tong Hua 134002, People's Republic of China

Correspondence e-mail: zmsu@nenu.edu.cn

## Key indicators

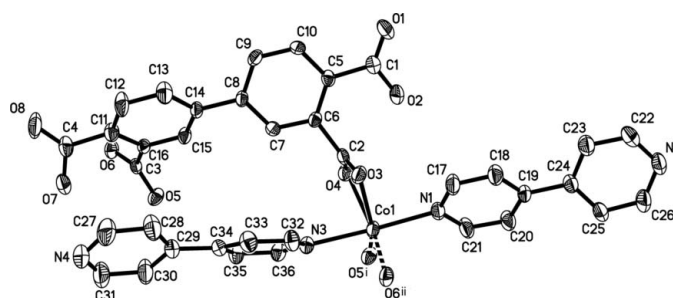
Single-crystal X-ray study  
 $T = 293$  K  
Mean  $\sigma(\text{C}-\text{C}) = 0.004$  Å  
 $R$  factor = 0.043  
 $wR$  factor = 0.101  
Data-to-parameter ratio = 15.5For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.Poly[bis(4,4'-bipyridine)( $\mu_3$ -4,4'-dicarboxy-biphenyl-3,3'-dicarboxylato)cobalt(II)]

The title cobalt(II) coordination polymer,  $[\text{Co}(\text{C}_{16}\text{H}_8\text{O}_8)(\text{C}_{10}\text{H}_8\text{N}_2)_2]_n$ , was obtained by the reaction of  $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$  (OAc is acetate), 4,4'-bipyridine (4,4'-bpy) and biphenyl-3,4,3',4'-tetracarboxylic acid ( $\text{H}_4\text{L}$ ) under hydrothermal conditions. Each  $\text{Co}^{\text{II}}$  atom lies at the centre of a distorted octahedron, coordinated by four O atoms from three  $\text{H}_2\text{L}^{2-}$  and two N atoms from two monodentate 4,4'-bpy ligands. Each  $\text{H}_2\text{L}^{2-}$  ligand coordinates to three  $\text{Co}^{\text{II}}$  centres through two carboxylate groups, one acting as a bridging bidentate group and the other in a chelating bidentate fashion. Two Co atoms, two  $\text{H}_2\text{L}^{2-}$  and four 4,4'-bpy ligands form a ring dimer node, and these nodes link into an extended broad chain along the  $c$  axis.

Received 4 August 2005  
Accepted 19 October 2005  
Online 5 November 2005

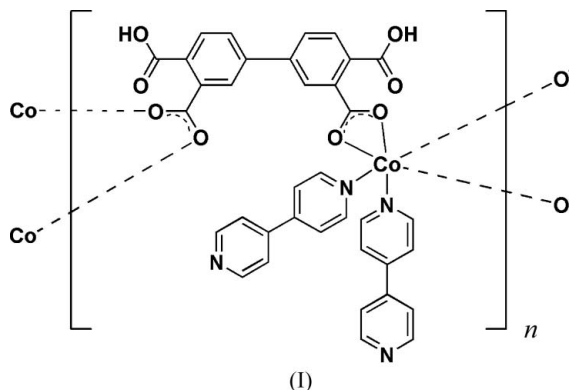
## Comment

Research on coordination polymers has been rapidly expanding because of their fascinating structural diversity and potential applications as functional materials (Batten & Robson, 1998; Moulton & Zaworotko, 2001). The synthesis and characterization of infinite one-, two- and three dimensional networks has been an area of rapid growth. Metal carboxylates have emerged as an important family (Rao *et al.*, 2004). Dicarboxylates and related species provide an effective means of designing novel hybrid structures which are porous, amongst other properties (Yaghi *et al.*, 2003; Kitagawa *et al.*, 2004). In some of these structures, the dicarboxylate acts as a linker between two inorganic units. Much of the work has so far been focused on coordination polymers with rigid ligands, such as terephthalate (Xu *et al.*, 2004), benzene-1,3,5-tricarboxylate (Rosi *et al.*, 2002; Li *et al.*, 1999; Millange *et al.*, 2002; Kepert & Rosseinsky, 1998), benzene-1,2,4,5-tetracarboxylate (Cao *et al.*, 2002; Hou *et al.*, 2004), biphenyl-4,4'-dicarboxylate (Pan *et al.*, 2003; Dai *et al.*, 2004; Mukherjee *et al.*, 2004; Shiu *et al.*, 2003) and their analogues. However, to the best of our



**Figure 1**  
A view of the local coordination of  $\text{Co}^{\text{II}}$  with the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms have been omitted. [Symmetry codes: (i)  $2 - x, -y, 2 - z$ , (ii)  $x, y, z - 1$ .]

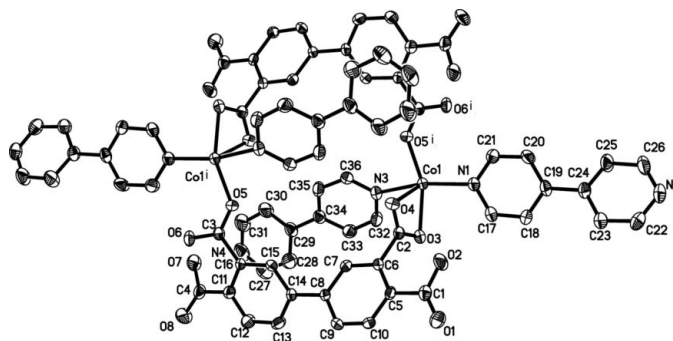
knowledge, the ligand  $H_4L$  (biphenyl-3,4,3',4'-tetracarboxylic acid) has not been used. We report here the preparation and crystal structure of a novel one-dimensional coordination polymer (I), formulated  $[Co(H_2L).2(4,4'-bpy)]_n$  (4,4'-bpy is 4,4'-bipyridine).



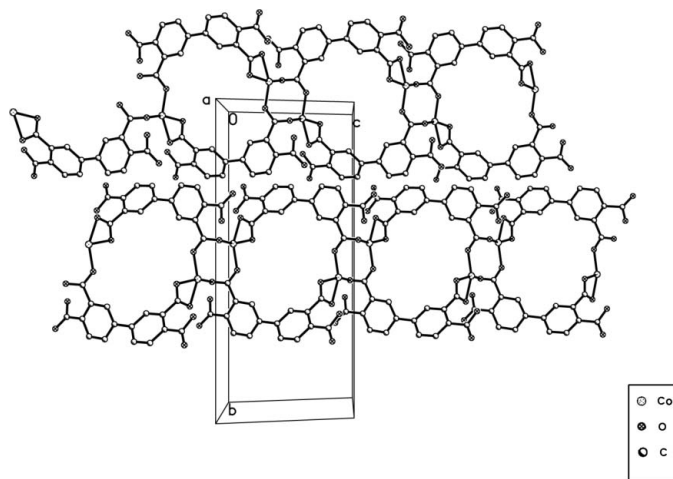
Single-crystal X-ray diffraction reveals that (I) is an extended one-dimensional chain based on ring dimer building blocks constructed by two Co atoms with two  $H_2L^{2-}$  and four 4,4'-bpy ligands. The cobalt centre is six-coordinate (see Fig. 1). Each  $Co^{II}$  atom is coordinated by two O atoms of one chelating bidentate  $H_2L^{2-}$  ligand, two O atoms from two different bridging bidentate  $H_2L^{2-}$  ligands and two N atoms [ $Co1-N1 = 2.177(2)$  Å and  $Co1-N3 = 2.214(2)$  Å] from two different 4,4'-bpy ligands, which unusually act as monodentate rather than bridging bidentate ligands. The four different carboxylate groups have Co–O distances in the range 2.0180 (17)–2.2769 (18) Å. The O–Co–O bond angles range from 59.55 (6) to 106.42 (7)°. Therefore, the Co centre displays a distorted octahedral coordination geometry (Table 1). The  $H_2L^{2-}$  ligand anions exhibit an interesting connection mode with three metal ions, as shown in the scheme. The four carboxylate groups display two different kinds of coordination mode, *viz.* the bidentate chelating and monodentate double-bridging modes. Each  $H_2L^{2-}$  ion acts as a four-connecting ligand by coordinating to three  $Co^{II}$  atoms. Additionally, the  $Co1 \cdots Co1^i$  distance [symmetry code: (i)  $2 - x - y - 2 - z$ ] of 4.375 (4) Å, which is longer than the sum of the van der Waals radii of Co (1.63 Å for Co), is too long to be considered a significant interaction. Two Co atoms with two  $H_2L^{2-}$  ions and four 4,4'-bpy ligands act as a ring dimer node (Fig. 2). These nodes connect to form an extended one-dimensional chain along the *c* axis (see Fig. 3). In the packing arrangement of (I) (Fig. 4), adjacent one-dimensional chains are parallel to each other and form a two-dimensional supramolecular framework *via* hydrogen bonds between 4,4'-bpy and the carboxylic acid groups of  $H_2L^{2-}$  ligands (Table 2).

## Experimental

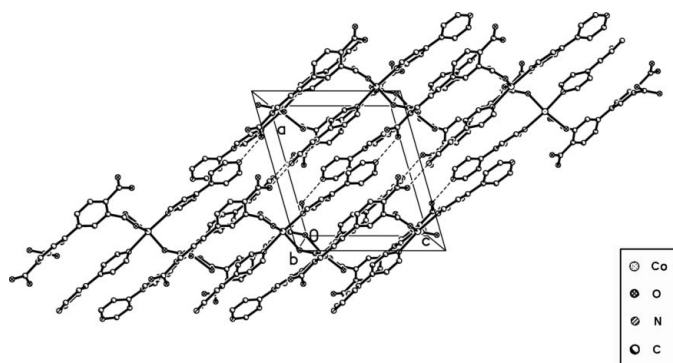
$H_4L$  was commercially purchased and used without further purification. The title compound was synthesized hydrothermally under autogenous pressure. A mixture of  $Co(OAc)_2 \cdot 4H_2O$  (0.258 g,



**Figure 2**  
View of the dimer node with the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms have been omitted. [Symmetry code: (i)  $2 - x - y - 2 - z$ .]



**Figure 3**  
The one-dimensional chain-like fragment along the *a* axis. 4,4'-bpy groups and H atoms have been omitted for clarity.



**Figure 4**  
Two-dimensional supramolecular framework showing C–OH...N hydrogen bonds along the *b* axis. H atoms have been omitted for clarity.

1 mmol),  $H_4L$  (0.330 g, 1 mmol), 4,4'-bpy (0.312 g, 2 mmol) and NaOH (0.080 g, 2 mmol) was stirred for 20 min and then sealed in a Parr Teflon-lined stainless steel vessel, which was heated to 443 K for 72 h. After slow cooling to ambient temperature, red block-like crystals of compound (I) were mechanically separated from the powder and washed with distilled water (yield *ca* 70% based on Co). The compound is insoluble in common organic solvents and water.

Analysis found: C 61.9, H 3.4, N 8.0%; C<sub>36</sub>H<sub>24</sub>N<sub>4</sub>O<sub>8</sub>Co requires: C 61.81, H 3.46, N 8.01%.

#### Crystal data

[Co(C <sub>16</sub> H <sub>8</sub> O <sub>8</sub> )(C <sub>10</sub> H <sub>8</sub> N <sub>2</sub> ) <sub>2</sub> ] <i>M<sub>r</sub></i> = 699.52	<i>D<sub>x</sub></i> = 1.564 Mg m <sup>-3</sup> Mo <i>K</i> α radiation
Monoclinic, <i>P</i> 2 <sub>1</sub> / <i>c</i>	Cell parameters from 18156 reflections
<i>a</i> = 11.9781 (10) Å	<i>θ</i> = 1.7–28.3°
<i>b</i> = 24.094 (2) Å	<i>μ</i> = 0.64 mm <sup>-1</sup>
<i>c</i> = 10.7056 (9) Å	<i>T</i> = 293 (2) K
<i>β</i> = 105.925 (2)°	Block, red
<i>V</i> = 2971.1 (4) Å <sup>3</sup>	0.24 × 0.23 × 0.11 mm
<i>Z</i> = 4	

#### Data collection

Rigaku R-Axis RAPID diffractometer	6985 independent reflections
<i>ω</i> scans	3983 reflections with <i>I</i> > 2σ( <i>I</i> )
Absorption correction: multi-scan (ABSCOR; Higashi, 1995)	<i>R</i> <sub>int</sub> = 0.049
<i>T</i> <sub>min</sub> = 0.812, <i>T</i> <sub>max</sub> = 0.896	<i>θ</i> <sub>max</sub> = 28.3°
18276 measured reflections	<i>h</i> = -13 → 15
	<i>k</i> = -31 → 28
	<i>l</i> = -14 → 12

#### Refinement

Refinement on <i>F</i> <sup>2</sup>	H atoms treated by a mixture of independent and constrained refinement
<i>R</i> [ <i>F</i> <sup>2</sup> > 2σ( <i>F</i> <sup>2</sup> )] = 0.043	<i>w</i> = 1/[σ <sup>2</sup> ( <i>F</i> <sub>o</sub> <sup>2</sup> ) + (0.0415 <i>P</i> ) <sup>2</sup> ]
<i>wR</i> ( <i>F</i> <sup>2</sup> ) = 0.101	where <i>P</i> = ( <i>F</i> <sub>o</sub> <sup>2</sup> + 2 <i>F</i> <sub>c</sub> <sup>2</sup> )/3
<i>S</i> = 0.97	(Δ/σ) <sub>max</sub> = 0.033
6985 reflections	Δρ <sub>max</sub> = 0.68 e Å <sup>-3</sup>
450 parameters	Δρ <sub>min</sub> = -0.46 e Å <sup>-3</sup>

**Table 1**

Selected geometric parameters (Å, °).

Co1—O6 <sup>ii</sup>	2.0180 (17)	Co1—N1	2.177 (2)
Co1—O5 <sup>i</sup>	2.0209 (16)	Co1—N3	2.214 (2)
Co1—O3	2.1333 (16)	Co1—O4	2.2769 (18)
O6 <sup>ii</sup> —Co1—O5 <sup>i</sup>	106.42 (7)	O5 <sup>i</sup> —Co1—N3	90.71 (7)
O6 <sup>ii</sup> —Co1—O3	104.71 (7)	O3—Co1—N3	82.94 (7)
O6 <sup>ii</sup> —Co1—N1	88.69 (7)	O5 <sup>i</sup> —Co1—O4	88.16 (6)
O5 <sup>i</sup> —Co1—N1	101.68 (7)	O3—Co1—O4	59.55 (6)
O3—Co1—N1	88.15 (7)	N1—Co1—O4	98.92 (7)
O6 <sup>ii</sup> —Co1—N3	84.75 (7)	N3—Co1—O4	84.46 (7)

Symmetry codes: (i)  $-x + 2, -y, -z + 2$ ; (ii)  $x, y, z - 1$ .

**Table 2**

Hydrogen-bond geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O7—H1...N2 <sup>iii</sup>	0.88 (4)	1.80 (4)	2.672 (4)	171 (5)
O2—H2...N4 <sup>iv</sup>	0.90 (3)	1.71 (4)	2.600 (3)	166 (4)

Symmetry codes: (iii)  $x + 1, y, z + 2$ ; (iv)  $x - 1, y, z - 1$ .

All H atoms on C atoms were positioned geometrically and refined as riding atoms, with C—H = 0.93 Å and *U*<sub>iso</sub>(H) = 1.2*U*<sub>eq</sub>(C). O-bound atoms H1 and H2 were located in an electron-density difference map and refined freely.

Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *PROCESS-AUTO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL-Plus* (Sheldrick, 1990); software used to prepare material for publication: *SHELXL97*.

We gratefully acknowledge financial support from the National Natural Science Foundation of China (project Nos. 20162005 and 20373009), the Youth Fund of Northeast Normal University (grant No. 111494017), the Trans-Century Training Programme Foundation for Talents by the State Education Commission, and Jilin Scientific Research Plan for Prominent Youngsters.

#### References

- Batten, S. R. & Robson, R. (1998). *Angew. Chem. Int. Ed. Engl.* **37**, 1461–1494.
- Cao, R., Sun, D. F., Liang, Y. C., Hong, M. C., Tatsumi, K. & Shi, Q. (2002). *Inorg. Chem.* **41**, 2087–2094.
- Dai, J. C., Wu, X. T., Hu, S. M., Fu, Z. Y., Zhang, J. J., Du, W. X., Zhang, H. H. & Sun, R. Q. (2004). *Eur. J. Inorg. Chem.* **40**, 2096–2106.
- Higashi, T. (1995). *ABSCOR*. Rigaku Corporation, Tokyo, Japan.
- Hou, Y., Wang, S. T., Shen, E. H., Wang, E. B., Xiao, D. R., Li, Y. G., Xu, L. & Hu, C. W. (2004). *Inorg. Chim. Acta*, **357**, 3155–3161.
- Keper, C. J. & Rosseinsky, M. J. (1998). *Chem. Commun.* pp. 31–32.
- Kitagawa, S., Kitaura, R. & Noro, S. (2004). *Angew. Chem. Int. Ed.* **43**, 2334–2375.
- Li, H., Eddaoudi, M., O'Keeffe, M. & Yaghi, O. M. (1999). *Nature (London)*, **402**, 276–279.
- Millange, F., Serre, C. & Ferey, G. (2002). *Chem. Commun.* pp. 822–823.
- Moulton, B. & Zaworotko, M. J. (2001). *Chem. Rev.* **101**, 1629–1658.
- Mukherjee, P. S., Das, N., Kryschenko, Y. K., Arif, A. M. & Stang, P. J. (2004). *J. Am. Chem. Soc.* **126**, 2464–2473.
- Pan, L., Liu, H. M., Lei, X. G., Huang, X. M., Olson, D. H., Turro, N. J. & Li, J. (2003). *Angew. Chem. Int. Ed.* **42**, 542–546.
- Rao, C. N. R., Natarajan, S. & Vaidyanathan, R. (2004). *Angew. Chem. Int. Ed.* **43**, 1466–1496.
- Rigaku (1998). *PROCESS-AUTO*. Rigaku Corporation, Tokyo, Japan.
- Rosi, N. L., Eddaoudi, M., Kim, J., O'Keeffe, M. & Yaghi, O. M. (2002). *Angew. Chem. Int. Ed.* **41**, 284–287.
- Sheldrick, G. M. (1990). *SHELXTL-Plus*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
- Shiu, K. B., Lee, H. C., Lee, G. H., Ko, B. T., Wang, Y. & Lin, C. C. (2003). *Angew. Chem. Int. Ed.* **42**, 2999–3001.
- Xu, H. B., Liang, Y. C., Su, Z. M., Zhao, Y. H., Shao, K. Z., Zhang, H. J. & Yue, S. M. (2004). *Acta Cryst.* **E60**, m142–m144.
- Yaghi, O. M., O'Keeffe, M., Ockwig, N. W., Chae, H. K., Eddaoudi, M. & Kim, J. (2003). *Nature (London)*, **423**, 705–714.