Poly[(μ4-biphenyl-3,3′,4,4′-tetra-carboxylato)bis[μ2-1,4-bis(imidazol-1-ylmethyl)benzene]dicobalt(II)]

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The asymmetric unit of the title two-dimensional coordination polymer, $[Co_2(C_{16}H_6O_8)(C_{14}H_{14}N_4)_2]_n$, contains one Co^{2+} ion, half of a biphenyl-3,3′,4,4′-tetracarboxylate (bptc) anion lying about an inversion centre and one 1,4-bis(imidazol-1-ylmethyl)-benzene (bix) ligand. The Co^{II} atom is coordinated by three carboxylate O atoms from two different bptc ligands and two N atoms from two bix ligands constructing a distorted square pyramid. Each Co^{2+} ion is interlinked by two bptc anions, while each bptc anion coordinates to four Co atoms as a hexadentate ligand so that four Co^{II} atoms and four bptc anions afford a larger 38-membered ring. These inorganic rings are further extended into a two-dimensional undulated network in the (10$\bar{1}$) plane. Two Co^{II} atoms in adjacent 38-membered rings are joined together by pairs of bix ligands forming a 26-membered $[Co_2(bix)_2]$ ring that is penetrated by a bptc anion; these components share a common inversion centre.

Comment

The rational design and synthesis of metal–organic frameworks have attracted considerable attention owing to the intriguing architectures of these frameworks, including various topologies, which have potential applications in the catalysis and gas storage fields (Eddaoudi et al., 2002; Belof et al., 2007). During the past decades, many metal–organic frameworks have been successfully synthesized and reported, in which polycarboxylates have been widely used as bridging ligands to assemble coordination polymers (Duan et al., 2007; Liu et al., 2008; Ghosh et al., 2009; Jiang et al., 2009; Xu et al., 2009; Li et al., 2009). Biphenyl-3,3′,4,4′-tetracarboxylic acid (H_4bptc) is a flexible ligand coordinating to transition metals [see modes (a)–(g) in the scheme], with four carboxylate groups that can supply eight potential O-donor atoms; in addition, the two benzene rings can be rotated around the C—C single bond. Only a few reports exist of coordination polymers related to H_4bptc (Wang et al., 2005, 2006; Wang, Gou et al., 2007; Wang,

Yang et al., 2007; Yang et al., 2007; Liu et al., 2009). We present here the title coordination polymer, $[Co_2(bptc)(bix)_2]_n$ [bix is 1,4-bis(imidazol-1-ylmethyl)benzene], (I).

(I)
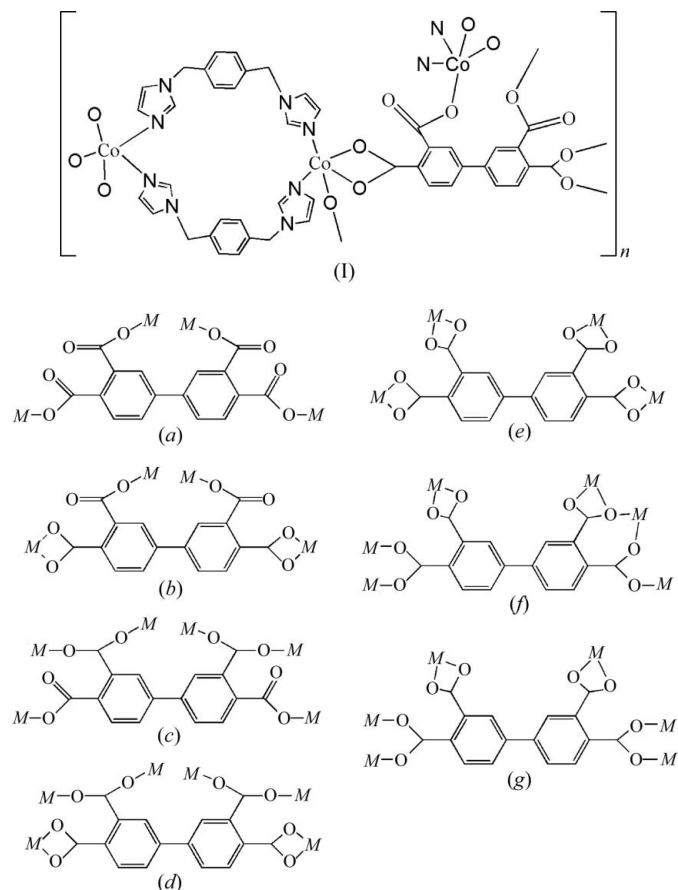
As shown in Fig. 1, the asymmetric unit of (I) contains one Co^{2+} ion and one bix ligand, both in general positions, as well as half of a bptc anion lying about an inversion centre chosen for convenience as $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. The Co^{2+} ion is coordinated by two N atoms (N1 and N4^{ii}; see Fig. 1) from two different bix ligands and three carboxylate O atoms (O1, O2 and O3^{i}) from two bptc anions. Three Co—O lengths range from 2.0212 (18) to 2.3411 (18) Å, and the Co—N distances are 2.048 (2) Å and 2.062 (2) Å (Table 1), similar to those in a cobalt–bptc coordination polymer (Liu et al., 2009). The Co atom exhibits an approximately square-pyramidal geometry with atoms O1,
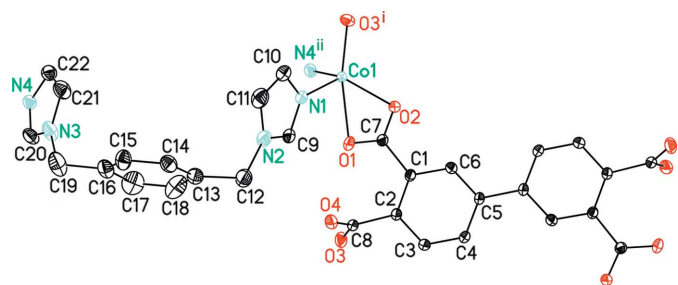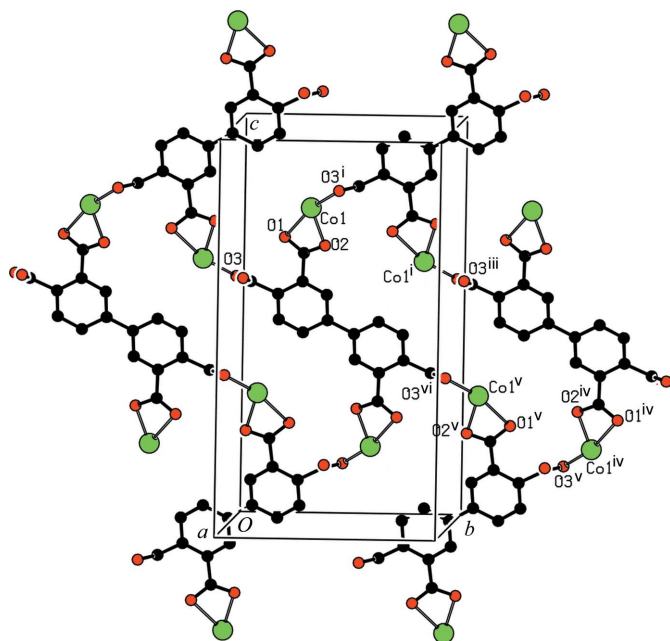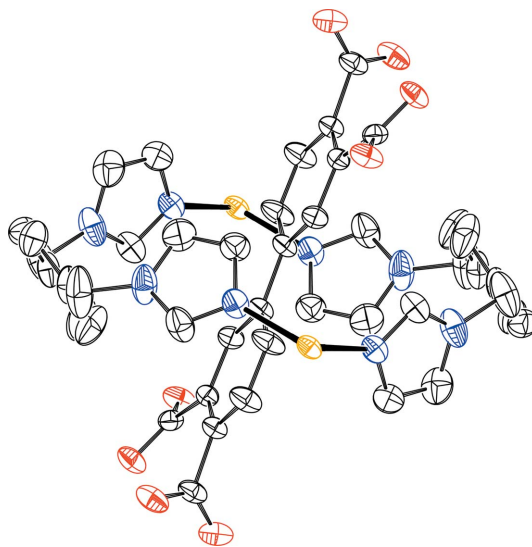

Figure 1
The molecular structure of (I), showing the asymmetric unit and key symmetry-related atoms. Displacement ellipsoids are drawn at the 30% probability level. [Symmetry codes: (i) $-x + \frac{3}{2}, y + \frac{1}{2}, -z + \frac{3}{2}$; (ii) $-x + 2, -y, -z + 2$.]

metal-organic compounds

Figure 2
View of the two-dimensional network in the $(10\bar{1})$ plane. [Symmetry codes: (i) $-x + \frac{3}{2}, y + \frac{1}{2}, -z + \frac{3}{2}$; (iii) $x, y + 1, z$; (iv) $-x + 1, -y + 2, -z + 1$; (v) $x - \frac{1}{2}, -y + \frac{3}{2}, z - \frac{1}{2}$; (vi) $-x + 1, -y + 1, -z + 1$.]

O2, O3^{i} and N4^{ii} in the equatorial plane (mean deviation from the plane = 0.0578 Å) and N1 in the apical position. For the bix ligand, two terminal imidazole groups assume a *cis* conformation and their planes are tilted 93.1 (3) and 74.9 (2)° with respect to the average plane of the benzene ring.

Each Co^{2+} ion is bonded to two bptc anions and each bptc anion coordinates to four Co atoms so that four Co atoms and four bptc anions give rise to a large 38-membered ring (Fig. 2) in which the bptc ligand acts as a hexadentate ligand. The carboxylate groups at the 3- and 3′-positions adopt monodentate bridging modes, while the carboxylate groups at the 4- and 4′-positions exhibit bidentate chelating modes [mode (*b*) in the scheme]. These inorganic rings are further extended into a two-dimensional undulated network parallel to the $(10\bar{1})$ plane. Two Co atoms in two adjacent 38-membered rings are linked by a pair of bix ligands forming a 26-membered [Co$_2$(bix)$_2$] ring lying about the inversion centre at (101) and this ring is penetrated by a bptc anion sharing the same inversion centre (Fig. 3). Metal–organic frameworks involving a loop have rarely been studied (Yang *et al.*, 2008). In [Co$_2$(1,3-bix)$_2$(bpea)$_2$]$_n$ (H$_2$bpea is biphenylethene-4,4′-dicarboxylic acid; Yang *et al.*, 2008), a Co$_2$(bix)$_2$ loop was formed, similar to that in (I). Adjacent Co$_2$(1,3-bix)$_2$ loops are joined by bpea ligands into a two-dimensional network and two identical networks interpenetrate each other. Notably, these loops are penetrated by bpea from an adjacent network, rather than the loops being penetrated by the bptc anion from the same network. Compound (I) is the first example reported of this latter interpenetration. A pair of bix ligands and a penetrated bptc anion are considered together as a node, which can be simplified to a {7^2,8}$_2${7^3,8} net (Blatov *et al.*, 2000) (Fig. 4). Each Co atom bridges three adjacent nodes and every node

Figure 3
A view showing the [Co$_2$(bix)$_2$] loop penetrated by the bptc anion in (I). Displacement ellipsoids are drawn at the 30% probability level.
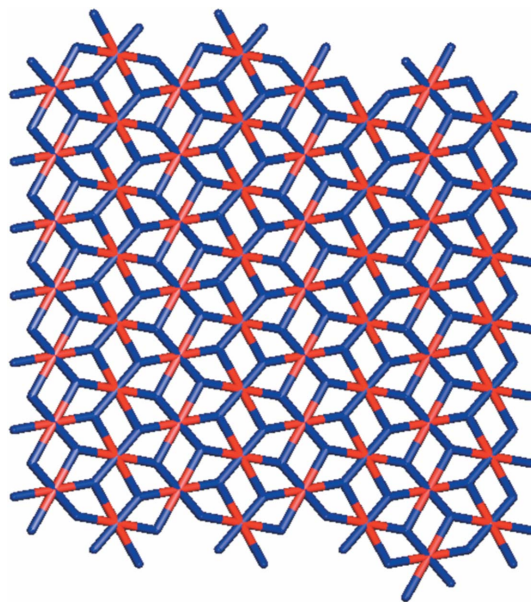
Figure 4
A view of the {7^2,8}$_2${7^3,8} net. (The colour key for the electronic version of the paper is: Co blue and node red.)

links six neighbouring Co atoms. Moreover, three nodes nearly form an equilateral triangle with the distances 11.61, 11.61 and 11.03 Å. Such a coordination mode for bptc has been reported in [Cu$_2$(bptc)(4,4′-bpy)(H$_2$O)$_2$]·2H$_2$O (4,4′-bpy is 4,4′-bipyridine; Yang *et al.*, 2007), in which bptc and 4,4′-bpy ligands bridge Cu atoms into a three-dimensional framework. In that structure, the Cu atom is also in a distorted square-pyramidal environment.

Experimental

A mixture of CoSO$_4$·7H$_2$O (0.5 mmol, 0.14 g), H$_4$bptc (0.5 mmol, 0.16 g), bix (0.5 mmol, 0.10 g), NaOH (2 mmol, 0.08 g) and H$_2$O

(15 ml) was placed in a Parr Teflon-lined stainless steel vessel (23 ml), which was sealed and heated at 393 K for 4 d. After that time, the mixture was cooled slowly to room temperature and red crystals of (I) were obtained.

Crystal data

$[Co_2(C_{16}H_6O_8)(C_{14}H_{14}N_4)_2]$	$V = 1998.6\ (4)$ Å³
$M_r = 460.33$	$Z = 4$
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation
$a = 9.3243\ (12)$ Å	$\mu = 0.90$ mm⁻¹
$b = 11.0261\ (14)$ Å	$T = 298$ K
$c = 19.675\ (3)$ Å	$0.16 \times 0.12 \times 0.10$ mm
$\beta = 98.872\ (2)°$	

Data collection

Bruker SMART APEX CCD area-detector diffractometer	16575 measured reflections
	4932 independent reflections
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)	3660 reflections with $I > 2\sigma(I)$
$T_{min} = 0.870$, $T_{max} = 0.916$	$R_{int} = 0.065$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.050$	280 parameters
$wR(F^2) = 0.101$	H-atom parameters constrained
$S = 1.00$	$\Delta\rho_{max} = 0.49$ e Å⁻³
4932 reflections	$\Delta\rho_{min} = -0.33$ e Å⁻³

Table 1
Selected geometric parameters (Å, °).

Co1—O3ⁱ	2.0212 (18)	Co1—N1	2.062 (2)
Co1—O2	2.0449 (17)	Co1—O1	2.3411 (18)
Co1—N4ⁱⁱ	2.048 (2)		
N2—C12—C13	112.0 (2)	N3—C19—C16	111.6 (3)

Symmetry codes: (i) $-x + \frac{3}{2}, y + \frac{1}{2}, -z + \frac{3}{2}$; (ii) $-x + 2, -y, -z + 2$.

All H atoms bound to C atoms were positioned geometrically and refined using a riding model, with C—H = 0.93 Å and $U_{iso}(H) = 1.2U_{eq}(C)$ for aromatic H atoms, and C—H = 0.97 Å and $U_{iso}(H) = 1.2U_{eq}$ for methylene H atoms.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SMART*; data reduction: *SAINT-Plus* (Bruker, 2001); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 2008) and *TOPOS* (Blatov *et al.*, 2000); software used to prepare material for publication: *PLATON* (Spek, 2009).

References

Belof, J. L., Stern, A. C., Eddaoudi, M. & Space, B. (2007). *J. Am. Chem. Soc.* **129**, 15202–15210.

Blatov, V. A., Shevchenko, A. P. & Serezhkin, V. N. (2000). *J. Appl. Cryst.* **33**, 1193.

Brandenburg, K. (2008). *DIAMOND*. Version 3.1f. Crystal Impact GbR, Bonn, Germany.

Bruker (2001). *SMART* (Version 5.628) and *SAINT-Plus* (Version 6.45). Bruker AXS Inc., Madison, Wisconsin, USA.

Duan, X. Y., Li, Y. Z., Su, Y., Zang, S. Q., Zhu, C. J. & Meng, Q. J. (2007). *CrystEngComm*, **9**, 758–766.

Eddaoudi, M., Kim, J., Rosi, N., Vodak, D., Wachter, J., O'Keeffe, M. & Yaghi, O. M. (2002). *Science*, **295**, 469–472.

Ghosh, S. K., Ribas, J. & Bharadwaj, P. K. (2009). *Cryst. Growth Des.* **5**, 623–629.

Jiang, Y. J., Huang, J., Kasumaj, B., Jeschke, G., Hunger, M., Mallat, T. & Baiker, A. (2009). *J. Am. Chem. Soc.* **131**, 2058–2059.

Li, X., Wu, B. L., Niu, C. Y., Niu, Y. Y. & Zhang, H. Y. (2009). *Cryst. Growth Des.* **9**, 3423–3431.

Liu, Y.-Y., Yang, J., Ma, J.-C. & Ma, J.-F. (2008). *Acta Cryst.* C**64**, m33–m36.

Liu, G. X., Zhu, K., Chen, H., Huang, R. Y. & Ren, X. M. (2009). *Z. Anorg. Allg. Chem.* **635**, 156–164.

Sheldrick, G. M. (2003). *SADABS*. Version 2.10. University of Göttingen, Germany.

Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.

Wang, J. J., Gou, L., Hu, H. M., Han, Z. X., Li, D. S., Xue, G. L., Yang, M. L. & Shi, Q. Z. (2007). *Cryst. Growth Des.* **7**, 1514–1521.

Wang, J. J., Yang, M. L., Hu, H. M., Xue, G. L., Li, D. S. & Shi, Q. Z. (2007). *Z. Anorg. Allg. Chem.* **633**, 341–345.

Wang, X. L., Qin, C. & Wang, E. B. (2006). *Cryst. Growth Des.* **6**, 439–443.

Wang, X. L., Qin, C., Wang, E. B. & Xu, L. (2005). *Eur. J. Inorg. Chem.* pp. 3418–3421.

Xu, Y., Luo, F., Che, Y. X. & Zheng, J. M. (2009). *Inorg. Chem. Commun.* **7**, 639–641.

Yang, G. P., Wang, Y. Y., Ma, L. F., Liu, J. Q., Wu, Y. P., Wu, W. P. & Shi, Q. Z. (2007). *Eur. J. Inorg. Chem.* pp. 3892–3898.

Yang, J., Ma, J. F., Batten, S. R. & Su, Z. M. (2008). *Chem. Commun.* pp. 2233–2235.