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A novel cobalt(II) coordination polymer with an unusual four-connected $4^2.6^3.8$ topology

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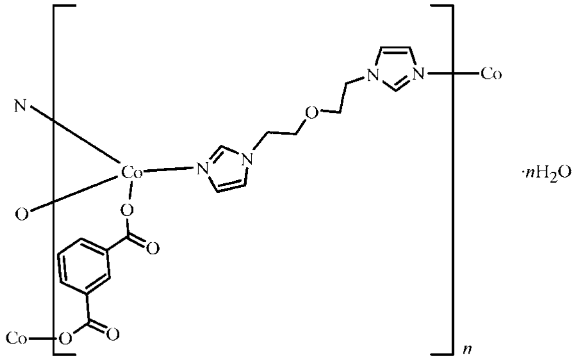
In the cobalt(II) coordination polymer poly[[(μ_2-benzene-1,3-dicarboxylato){μ_2-1,1′-[2,2′-oxybis(ethane-2,1-diyl)]di-1*H*-imidazole}cobalt(II)] monohydrate], $\{[Co(C_{10}H_{14}N_4O)(C_8H_4O_4)]\cdot H_2O\}_n$, two crystallographically distinct Co^{II} cations are four-coordinated by N_2O_2 donor sets in distorted tetrahedral geometries. The Co^{II} centers are connected by benzene-1,3-dicarboxylate (*m*-BDC) anions, giving two types of linear chains, which are further joined *via meso*-helical 1,1′-[2,2′-oxybis(ethane-2,1-diyl)]di-1*H*-imidazole ligands to yield a thick two-dimensional slab. The compound displays a two-dimensional four-connected $4^2.6^3.8$ topology, which is unprecedented in coordination polymers.

Comment

The design and synthesis of metal–organic coordination polymers are of great interest, not only because of their tremendous potential applications in nonlinear optics, catalysis, gas absorption, luminescence, magnetism and medicine, but also because of their intriguing variety of architectures and topologies (Wu *et al.*, 2005; Spencer *et al.*, 2006). The construction of coordination networks with different topological characteristics has attracted significant attention among chemists. By judicious choice of the organic spacers and the central metal atoms, it is possible to produce different types of coordination networks with novel topologies. So far, numerous fascinating archetypal topological structures, including diamond (6^6), $SrSi_2$ (10^3-a), α-$ThSi_2$ (10^3-b), SiO_2 (6^48^2-b) and PtS ($4^2.8^4$), have provided experimental examples of these theoretical topologies. In this regard, 4-connected networks are particularly interesting (Zhang *et al.*, 2005; Abrahams *et al.*, 1999; Carlucci *et al.*, 2002). The majority of 4-connected nets are constructed from tetrahedral or square-planar nodes. Typical 4-connected nets such as 6^6, $6^4.8^2$, $4^2.8^4$ and $7^5.9$ have been documented (Wells, 1984; Bregeaul & Herpin, 1970; Hawkins *et al.*, 1993; Qi *et al.*, 2008; Long *et al.*, 2004; Fang *et al.*, 2008; Bhogala *et al.*, 2004; Carlucci *et al.*, 1998).

We have reported several four-connected structures, such as the first square-planar four-connected 8^6 net made using the flexible 1,1′-(butane-1,4-diyl)bis(imidazole) ligand (Ma *et al.*, 2003, 2004; Yang *et al.*, 2005, 2006). In order to extend the study on topologies of coordination polymers with flexible ligands, a new flexible bis(imidazole) ligand, namely 1,1′-[2,2′-oxybis(ethane-2,1-diyl)]di-1*H*-imidazole (*L*), was used (Wei *et al.*, 2008). *L*, as a secondary *N*-donor bridging ligand, contains a heteroatom, oxygen, at the symmetric center of the molecule. Therefore, the two imidazole rings can twist freely around the oxy group to meet the requirements of the coordination geometries of metal atoms in the assembly process. Furthermore, owing to the presence of the flexible $-CH_2-$ spacer, the *L* ligand can exhibit more flexible conformations. In this contribution, *L* and deprotonated benzene-1,3-dicarboxylic acid (*m*-H_2BDC) were used as bridging ligands, and a new cobalt(II) coordination polymer, namely $\{[CoL(m\text{-}BDC)]\cdot H_2O\}_n$, (I), was obtained under hydrothermal conditions. Compound (I) is a rare example of a two-dimensional structure with a unique $4^2.6^3.8$ topology based solely on tetrahedral nodes.



(I)

The asymmetric unit of (I) contains two crystallographically distinct Co^{II} cations (Fig. 1), two unique *m*-BDC anions and two unique *L* ligands. Each Co^{II} ion has a distorted tetrahedral coordination environment formed by two carboxylate O atoms from two *m*-BDC anions [Co—O = 1.970 (3)–2.018 (3) Å] and two N atoms from two *L* ligands [Co—N = 2.018 (3)–2.035 (3) Å]. Each *m*-BDC anion coordinates to two Co^{II} centers in a bis-monodentate mode (see the scheme); the Co···Co distances through the *m*-BDC ligands are both 10.041 (1) Å, because both correspond to *C*-lattice translations. The two cobalt(II) cations are bridged by the crystallographically independent *m*-BDC anions to form two independent one-dimensional Co–*m*-BDC chains (Fig. 2). The Co2···Co2^{vi} chain propagates along [110] [symmetry code: (vi) $x + \frac{1}{2}, y + \frac{1}{2}, z$] in the plane $z = 0.127$, while the Co1···Co1^{v} chain propagates parallel to [1$\bar{1}$0] [symmetry code: (v) $x + \frac{1}{2}, y - \frac{1}{2}, z$] in the plane $z = 0.393$. Thus, the chains that run vertically in Fig. 2 are at a different elevation from those that run horizontally. The propagation vectors of the two Co–*m*-BDC polymer chains make an angle of 81.93 (5)° with one

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another (Fig. 2). The two crystallographically distinct *L* ligands exhibit similar conformations, and link atoms Co1 and Co2 to generate an interesting *meso*-helical chain (Han & Hong, 2005), with Co1$\cdots$Co2 distances of 8.211 (3) Å and Co1$\cdots$Co2^{iv} distances of 10.729 (5) Å [symmetry code: (iv) $x + 1, y, z$; Figs. 3 and 4]. The two imidazole rings of each *L* ligand are far from parallel [having dihedral angles of 81.1 (3)° between the N1- and N3-containing rings, 70.4 (4)° between the N5 and N7 rings, 79.3 (3)° between the N1 and N5 rings, and 87.3 (3)° between the N7 and N3^{iii} rings; symmetry code: (iii) $x - 1, y, z$; Fig. 3]. Obviously, these twists are important factors in forming the helical structure. The two independent *L* ligands link the nearly perpendicular Co–*m*-BDC chains into a slab (Fig. 5). Furthermore, these linear chains are connected by hydrogen-bonding bridges involving uncoordinated water molecules, which enhance the stability of the two-dimensional network. The adjacent two-dimensional slabs are stacked in a staggered pattern (–*ABAB*– sequence) along the *c* axis.

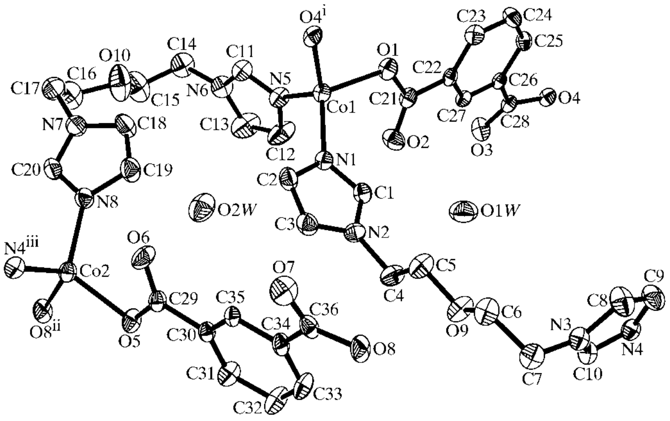

Figure 1
The local coordination of the Co^{II} cations in (I), showing the atom-numbering scheme. Displacement ellipsoids are shown at the 30% probability level. [Symmetry codes: (i) $x - \frac{1}{2}, y + \frac{1}{2}, z$; (ii) $x - \frac{1}{2}, y - \frac{1}{2}, z$; (iii) $x - 1, y, z$.]

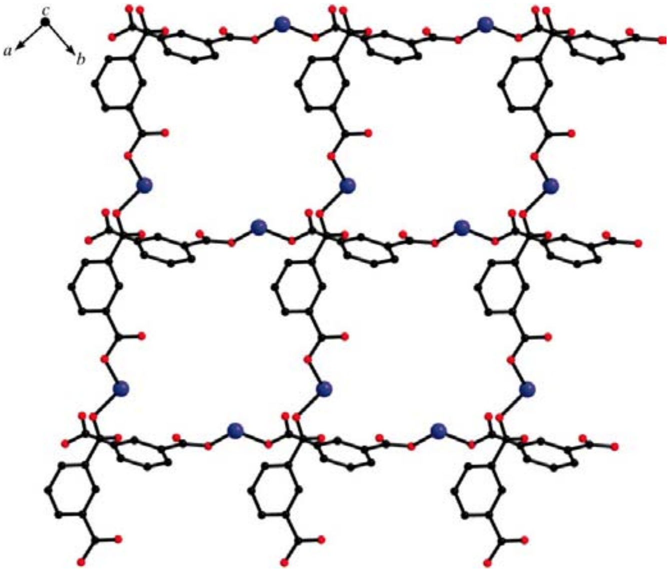

Figure 2
The perpendicular linear Co–*m*-BDC chains.

Better insight into the structure of (I) can be achieved by application of topological concepts, describing the multi-dimensional structure in terms of simple node-and-linker nets. The Co^{II} center is described as a tetrahedral four-connected node. The *m*-BDC and *L* ligands are bridges. With reference to Fig. 4, the Co1$^{i}\cdots$Co1$\cdots$Co1^{v} angle with links formed by the *m*-BDC ligand is 180° and the Co2$\cdots$Co1$\cdots$Co2^{iv} dihedral angle with links formed by the flexible *L* ligand is 81.93 (5)° [symmetry code: (i) $x - \frac{1}{2}, y + \frac{1}{2}, z$]. From a topological perspective, the resulting structure of (I) is a mononodal four-connected two-dimensional net with the short (Schläfli) vertex symbol $4^2.6^3.8$ and the long-form circuit symbol $4.4.6_2.6_2.6_4.8$ (Fig. 5) (Treacy *et al.*, 2006; *OLEX*; Dolomanov *et al.*, 2003). The topology of a single frame can be rationalized by considering that the shortest circuits starting and ending at each cobalt(II) cation are tetragons, hexagons and octagons in the ratio 2:3:1; that is, this is a $4^2.6^3.8$-net (Wells, 1979).

It is noteworthy that the $4^2.6^3.8$-net presented here is clearly different from the two-dimensional four-connected (4,4)-networks that have been widely reported. We are not aware of any previously reported coordination polymer with a two-dimensional four-connected structure with this topology. Polymer (I) appears to be the first example of a two-dimensional four-connected net with $4^2.6^3.8$ topology. The flexibility of the ligand *L* may play an important role in the formation of this unusual structure.

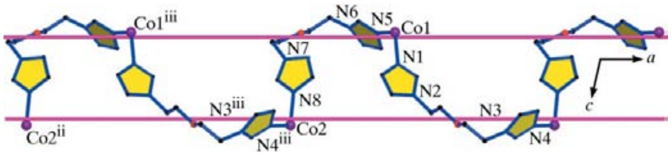

Figure 3
An infinite *meso*-helical chain formed by two types of *L* ligands.

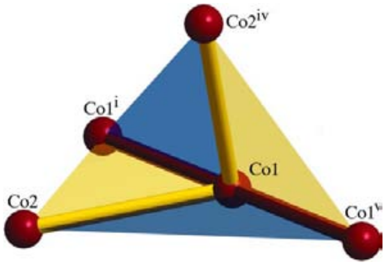

Figure 4
A schematic illustration of the distances and angles between topological nodes [Co1$\cdots$Co1^{i} = 10.041 (1) Å, Co1$\cdots$Co2 = 10.730 (1) Å, Co1$\cdots$Co2^{iv} = 8.211 (1) Å, Co1^{i}—Co1—Co2 = 123.35 (4)°, Co2—Co1—Co1^{v} = 56.65 (3)°, Co1^{v}—Co1—Co2^{iv} = 132.55 (5)° and Co2^{iv}—Co1—Co1^{i} = 47.45 (3)°] and two types of angles between adjacent nodes [Co2$\cdots$Co1$\cdots$ Co2^{iv} = 81.93 (5)° and Co1$^{i}\cdots$Co1$\cdots$Co1^{v} = 180°] in (I). [Symmetry codes: (i) $x - \frac{1}{2}, y + \frac{1}{2}, z$; (iv) $x + 1, y, z$; (v) $x + \frac{1}{2}, y - \frac{1}{2}, z$.]

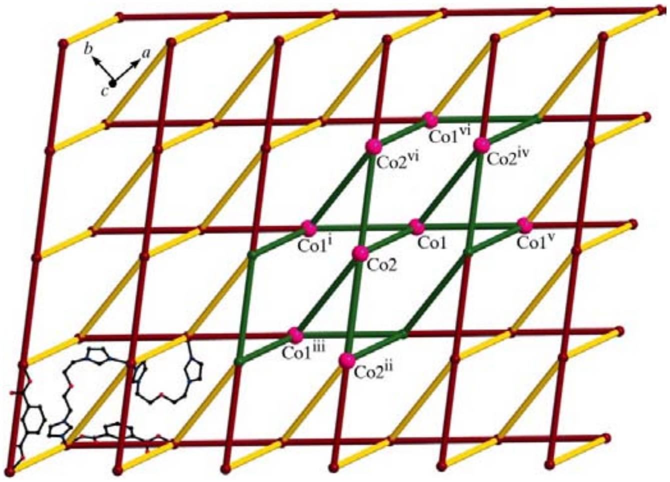

Figure 5
A schematic representation of the two-dimensional slab, with the $4^2.6^3.8$ topology of the two-dimensional four-connected network highlighted. [Symmetry codes: (i) $x - \frac{1}{2}, y + \frac{1}{2}, z$; (ii) $x - \frac{1}{2}, y - \frac{1}{2}, z$; (iii) $x - 1, y, z$; (iv) $x + 1, y, z$; (v) $x + \frac{1}{2}, y - \frac{1}{2}, z$; (vi) $x + \frac{1}{2}, y + \frac{1}{2}, z$.]

Table 1
Selected geometric parameters (Å, °).

Co1—O1	1.970 (3)	Co2—O8^{ii}	1.989 (3)
Co1—O4^{i}	2.011 (3)	Co2—O5	2.018 (3)
Co1—N5	2.018 (3)	Co2—N4^{iii}	2.029 (3)
Co1—N1	2.035 (3)	Co2—N8	2.033 (3)
O1—Co1—O4^{i}	94.52 (12)	O8^{ii}—Co2—O5	92.54 (12)
O1—Co1—N5	107.13 (14)	O8^{ii}—Co2—N4^{iii}	117.28 (13)
O4^{i}—Co1—N5	122.46 (13)	O5—Co2—N4^{iii}	114.84 (13)
O1—Co1—N1	113.96 (13)	O8^{ii}—Co2—N8	106.00 (13)
O4^{i}—Co1—N1	105.31 (12)	O5—Co2—N8	116.05 (13)
N5—Co1—N1	112.44 (14)	N4^{iii}—Co2—N8	109.23 (14)

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

Table 2
Hydrogen-bond geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O1W—H1$A\cdots$O2	1.00 (9)	1.87 (9)	2.830 (6)	158 (8)
O1W—H1$B\cdots$O6^{v}	0.83 (7)	1.99 (4)	2.773 (5)	157 (9)
O2W—H2$A\cdots$O7^{vii}	0.84 (9)	2.12 (9)	2.929 (6)	160 (9)

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

Experimental

A mixture of $Co(NO_3)_2 \cdot 6H_2O$ (29.1 mg, 0.10 mmol), *m*-H_2BDC (16.7 mg, 0.10 mmol), *L* (20.6 mg, 0.10 mmol) and water (7 ml) was sealed in a Teflon reactor (15 ml), which was heated at 453 K for 3 d and then cooled gradually to room temperature. Purple crystals of (I) were isolated using a cobalt(II)/*L*/*m*-H_2BDC molar ratio of 1:1:1 (yield 84% based on Co). Analysis calculated for $C_{36}H_{40}Co_2N_8O_{12}$ (M_r = 894.62): C 48.33, H 4.50, N 12.53%; found: C 48.34, H 4.50, N 12.52%. IR (cm^{-1}, KBr): 3110 (*s*), 3047 (*s*), 2915 (*vs*), 1605 (*vs*), 1391 (*s*), 1347 (*s*), 1106 (*s*), 753 (*s*), 656 (*s*).

Crystal data

$[Co(C_{10}H_{14}N_4O)(C_8H_4O_4)] \cdot H_2O$
M_r = 447.31
Monoclinic, *Cc*
a = 15.1641 (9) Å
b = 13.1653 (9) Å
c = 20.6761 (19) Å
β = 102.753 (1)°
V = 4025.9 (5) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 0.90 mm^{-1}
T = 293 (2) K
0.44 × 0.32 × 0.19 mm

Data collection

Bruker APEX CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.711, T_{max} = 0.841
10068 measured reflections
5554 independent reflections
4840 reflections with $I > 2\sigma(I)$
R_{int} = 0.037

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.035
$wR(F^2)$ = 0.081
S = 0.98
5554 reflections
535 parameters
4 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.46 e Å^{-3}
$\Delta\rho_{min}$ = −0.27 e Å^{-3}
Absolute structure: Flack (1983), 1999 Friedel pairs
Flack parameter: 0.007 (12)

H atoms bonded to C atoms were positioned geometrically (C—H = 0.93 and 0.97 Å) and refined as riding, with U_{iso}(H) values of $1.2U_{eq}$(C). Water H atoms were located in a difference Fourier map and were refined with O—H distance restraints of 0.85 (2) Å; their displacement parameters were tied to those of the parent atoms by a factor of 1.5.

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL-Plus* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FA3149). Services for accessing these data are described at the back of the journal.

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