

A new three-dimensional cobalt(II) coordination polymer with a 4-connected CdSO₄-like topology

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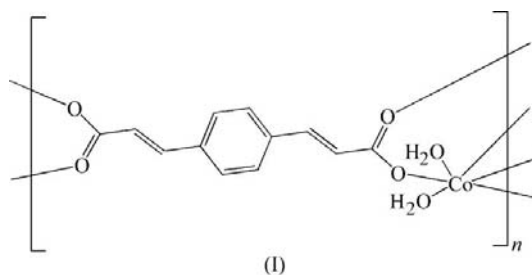
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The title cobalt(II) coordination polymer, poly[[diaquacobalt(II)]- μ_4 -3,3'-(*p*-phenylene)diacrylate], [Co(C₁₂H₈O₄)(H₂O)]_n, was obtained by reaction of Co(NO₃)₂·6H₂O and 3,3'-(*p*-phenylene)diacrylic acid (H₂L) under hydrothermal conditions. Each Co^{II} cation sits on a centre of inversion and is hexacoordinated by six O-atom donors in an octahedral geometry. The Co^{II} centres are connected by four centrosymmetric L²⁻ anions, resulting in a three-dimensional framework structure. The coordinated water molecules and carboxylate O atoms form hydrogen-bond interactions, stabilizing the structure of the three-dimensional framework. Topologically, the framework represents a rare example of the three-dimensional 4-connected CdSO₄ network type. The metal cations and the organic ligand both show in-plane coordination with respect to the extended structure.

Comment

Current interest in polymeric coordination networks is expanding rapidly, not only due to their potential applications in host-guest chemistry, ion exchange, gas storage and nonlinear optics, but also for their intriguing variety of topologies (Batten & Robson, 1998; Batten, 2001; Wu *et al.*, 2005; Spencer *et al.*, 2006). The construction of coordination networks with different topological characteristics has attracted significant attention from chemists (Barbour, 2001). It is well known that product topology can often be controlled and modified by selecting the coordination geometry preferred by the metal ion and the chemical structure of the organic ligand. The use of aromatic carboxylic acids in the synthesis of coordination polymers has aroused enormous interest due to their versatile coordination modes and variety of structural conformations (Yang *et al.*, 2008). Aromatic multicarboxylate ligands, such as benzene-1,2-dicarboxylic acid, benzene-1,3-dicarboxylic acid and benzene-1,4-dicar-

boxylic acid, are widely used to construct coordination polymers with interesting properties (Zhang *et al.*, 2005). In this regard, 3,3'-(*p*-phenylene)diacrylic acid (H₂L) is also a good ligand in coordination chemistry due to its strong coordination ability and versatile coordination modes, so much attention has been paid to it in recent years (Fang *et al.* 2007). In this contribution, H₂L was selected as a bridging ligand, and the title new cobalt(II) coordination polymer, poly[[diaquacobalt(II)]- μ_4 -3,3'-(*p*-phenylene)diacrylate], (I), was obtained under hydrothermal conditions. Compound (I) represents a rare example of a three-dimensional framework with a 4-connected CdSO₄-like topology based solely upon square-planar nodes.



Selected bond distances and angles are listed in Table 1. As shown in Fig. 1, the asymmetric unit of (I) contains one-half of a Co^{II} cation, one-half of an L anion and one water molecule. Each Co^{II} cation sits on a centre of inversion, has an octahedral coordination environment and is coordinated by four carboxylate O atoms from four different L anions (O1, O1ⁱ, O2ⁱⁱ and O2ⁱⁱⁱ; symmetry codes as in Fig. 1), which lie in a plane, while two water O atoms (O1W and O1Wⁱ) coordinate perpendicular to this plane. Each L anion is centrosymmetric and coordinates to four Co^{II} centres in a μ_4 -bridging mode (see scheme). This coordination forms a three-dimensional framework structure of (I) (Fig. 2), stabilized by hydrogen-bonding interactions between the coordinated water molecules and carboxylate O atoms (Table 2).

A better insight into the structure of (I) can be achieved by application of the topological approach, *i.e.* reducing multi-dimensional structures to simple node-and-linker nets. As discussed above, the Co^{II} centre is defined as a square-planar 4-connected node. The mean deviation of the non-H atoms of L from their mean plane is 0.222 Å. Thus, the ligand L can also

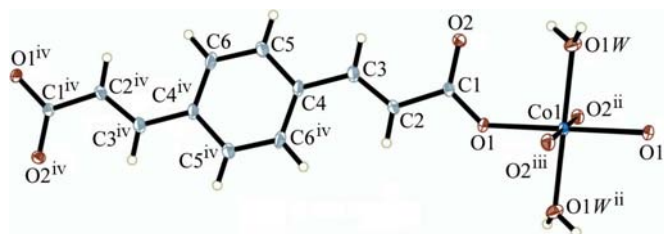


Figure 1

A view of the local coordination of the Co^{II} cations in (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. [Symmetry codes: (i) 2 - x, -y, 2 - z; (ii) 2 - x, y + $\frac{1}{2}$, $\frac{5}{2}$ - z; (iii) x, - $\frac{1}{2}$ - y, z - $\frac{1}{2}$; (iv) 1 - x, -1 - y, 3 - z.]

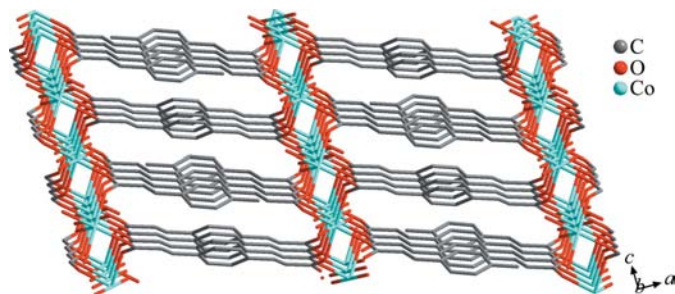


Figure 2
The three-dimensional framework structure of (I).

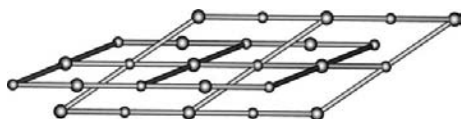


Figure 3
The shortest circuits of (I). Larger circles represent Co^{II} atoms and smaller circles represent L ligands. The two nodes are equivalent.

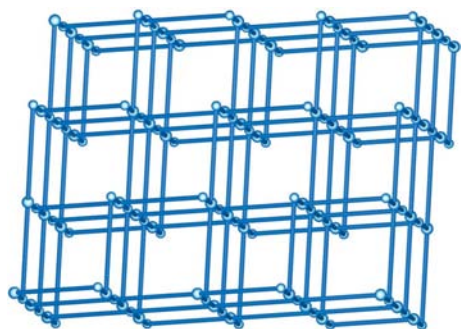


Figure 4
Schematic representation of the CdSO_4 -like net of (I).

be regarded as a square-planar 4-connected node (Fig. 3). The Co^{II} and L nodes are equivalent. According to the simplification principle, the resulting structure of (I) is a 4-connected three-dimensional net. The topology of a single framework can be rationalized by considering that the shortest circuits starting and ending at each Co^{II} cation and L ligand are hexagons and octagons, forming an overall $6^5.8$ CdSO_4 -like (cds) net (Wells, 1979).

So far, numerous fascinating archetypal topological structures, including NbO (nbo), Pt_3O_4 (pto), pyrite (pyr), quartz (qtz), rutile (rto), sodalite (sod), diamond (dia), SrSi_2 (10^3 -a) (srs), α - ThSi_2 (10^3 -b; ths) and PtS ($4^2.8^4$; pts), have provided experimental examples. 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 by 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 well documented (Wells, 1984; Hawkins *et al.*, 1993; Qi *et al.*, 2008; Long *et al.*, 2004; Fang *et al.*, 2008; Bhogala *et al.*, 2004; Carlucci *et al.*, 1998). So far, although CdSO_4 -like nets have been widely reported, those based on both a planar 4-connected organic ligand and a metal cation are relatively rare (Zhang *et al.*, 2006).

Experimental

A mixture of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (29.1 mg, 0.10 mmol), H_2L (21.8 mg, 0.10 mmol) and water (12 ml) was sealed in a Teflon reactor (15 ml), which was heated at 413 K for 3 d and then gradually cooled to room temperature. Purple crystals of (I) were isolated (yield 58% based on Co).

Crystal data

$[\text{Co}(\text{C}_{12}\text{H}_8\text{O}_4)(\text{H}_2\text{O})_2]$	$V = 610.94(3) \text{ \AA}^3$
$M_r = 311.15$	$Z = 2$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 12.9638(5) \text{ \AA}$	$\mu = 1.42 \text{ mm}^{-1}$
$b = 6.4039(2) \text{ \AA}$	$T = 293 \text{ K}$
$c = 7.3594(2) \text{ \AA}$	$0.21 \times 0.18 \times 0.12 \text{ mm}$
$\beta = 90.561(3)^\circ$	

Data collection

Bruker APEX diffractometer	2788 measured reflections
Absorption correction: multi-scan	1241 independent reflections
(<i>SADABS</i> ; Sheldrick, 1996)	989 reflections with $I > 2\sigma(I)$
$T_{\text{min}} = 0.733$, $T_{\text{max}} = 0.841$	$R_{\text{int}} = 0.025$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.026$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.060$	$\Delta\rho_{\text{max}} = 0.27 \text{ e \AA}^{-3}$
$S = 1.00$	$\Delta\rho_{\text{min}} = -0.31 \text{ e \AA}^{-3}$
1241 reflections	
96 parameters	

H atoms bonded to C atoms were positioned geometrically ($\text{C}-\text{H} = 0.93 \text{ \AA}$) and refined as riding, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. Water H atoms were located in a difference Fourier map and refined freely.

Data collection: *SMART* (Bruker, 1997); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1999); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics:

Table 1

Selected geometric parameters (\AA , $^\circ$).

$\text{Co1}-\text{O1}$	2.0754 (12)	$\text{Co1}-\text{O1W}^{\text{i}}$	2.0890 (15)
$\text{Co1}-\text{O1}^{\text{i}}$	2.0754 (12)	$\text{Co1}-\text{O2}^{\text{ii}}$	2.1072 (13)
$\text{O1W}-\text{Co1}$	2.0890 (15)	$\text{Co1}-\text{O2}^{\text{iii}}$	2.1072 (13)
$\text{O1}^{\text{i}}-\text{Co1}-\text{O1}$	180.0	$\text{O1W}^{\text{i}}-\text{Co1}-\text{O2}^{\text{ii}}$	92.27 (6)
$\text{O1}^{\text{i}}-\text{Co1}-\text{O1W}^{\text{i}}$	95.27 (6)	$\text{O1W}-\text{Co1}-\text{O2}^{\text{ii}}$	87.73 (6)
$\text{O1}-\text{Co1}-\text{O1W}^{\text{i}}$	84.73 (6)	$\text{O1}^{\text{i}}-\text{Co1}-\text{O2}^{\text{iii}}$	85.17 (5)
$\text{O1}^{\text{i}}-\text{Co1}-\text{O1W}$	84.73 (6)	$\text{O1}-\text{Co1}-\text{O2}^{\text{iii}}$	94.83 (5)
$\text{O1}-\text{Co1}-\text{O1W}$	95.27 (6)	$\text{O1W}^{\text{i}}-\text{Co1}-\text{O2}^{\text{iii}}$	87.73 (6)
$\text{O1W}^{\text{i}}-\text{Co1}-\text{O1W}$	180.0	$\text{O1W}-\text{Co1}-\text{O2}^{\text{iii}}$	92.27 (6)
$\text{O1}^{\text{i}}-\text{Co1}-\text{O2}^{\text{ii}}$	94.83 (5)	$\text{O2}^{\text{ii}}-\text{Co1}-\text{O2}^{\text{iii}}$	180.0
$\text{O1}-\text{Co1}-\text{O2}^{\text{ii}}$	85.17 (5)		

Symmetry codes: (i) $-x+2, -y, -z+2$; (ii) $-x+2, y+\frac{1}{2}, -z+\frac{5}{2}$; (iii) $x, -y-\frac{1}{2}, z-\frac{1}{2}$.

Table 2

Hydrogen-bond geometry (\AA , $^\circ$).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{O1W}-\text{HW11}\cdots\text{O2}^{\text{iv}}$	0.81 (3)	2.00 (3)	2.803 (2)	170 (2)
$\text{O1W}-\text{HW12}\cdots\text{O1}^{\text{v}}$	0.78 (3)	2.28 (3)	3.010 (2)	155 (3)

Symmetry codes: (iv) $-x+2, -y-1, -z+2$; (v) $-x+2, y-\frac{1}{2}, -z+\frac{5}{2}$.

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: EG3020). Services for accessing these data are described at the back of the journal.

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