

Poly[diaquacobalt(II)-di- μ_4 -benzene-1,2,4-tricarboxylato-bis[1,10-phenanthrolinecobalt(II)]]

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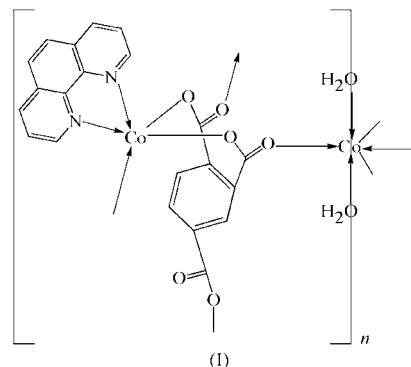
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In the polymeric title compound, $[\text{Co}_3(\text{btc})_2(\text{phen})_2(\text{H}_2\text{O})_2]_n$ [btc is the benzene-1,2,4-tricarboxylate trianion ($\text{C}_9\text{H}_3\text{O}_6$) and phen is 1,10-phenanthroline ($\text{C}_{12}\text{H}_8\text{N}_2$)], there are two different Co centres, Co1 and Co2. The Co1 centre has a deformed trigonal-bipyramidal geometry, while the Co2 centre lies on an inversion centre and has distorted octahedral geometry. Moreover, the 1,2-dicarboxylate groups of one btc ligand bridge the two adjacent Co2 centres, and each Co2 centre is coordinated by four carboxylate O atoms from four different btc ligands, forming a novel kind of intersecting double-chain structure, with a $\text{Co}\cdots\text{Co}$ separation of 7.755 Å, along the *a* axis. On the other hand, the two Co1 centres are bridged by two btc ligands and chelated by phen molecules, respectively, producing a binuclear unit with a $\text{Co}\cdots\text{Co}$ separation of 8.406 Å, and these binuclear units are linked by btc bridges and Co2 centres to extend hybrid chains of Co1 and Co2 along the [101] direction. Furthermore, each btc ligand acts as a pentadentate bridge, linking the Co2 double-chain structures and the hybrid chains of Co1 and Co2 to yield a two-dimensional network, and this leads to the formation of very different kinds of voids.

Comment

In recent years, versatile benzenepolycarboxylate ligands, such as benzene-1,3,5-tricarboxylic acid and benzene-1,2,4,5-tetracarboxylic acid, have been widely applied in the rational design and syntheses of metal-organic coordination polymers, owing to their high symmetry and the intriguing coordination modes of the carboxylate groups (Eddaoudi *et al.*, 2000; Hu *et al.*, 2003; Yaghi *et al.*, 1996). However, little attention has been paid so far to benzene-1,2,4-tricarboxylic acid (btc). It is of great interest to us that the carboxylate groups of benzenepolycarboxylate anions are capable of rotating in different directions with respect to the aromatic rings (Pisareva *et al.*, 2003), and the introduction of terminal ligands into the carboxylate system can result in the formation of low-

dimensional frameworks (Plater *et al.*, 1999). Thus, we have selected the phen-btc system (phen is 1,10-phenanthroline) in order to extend this research and we present here the crystal structure determination of the title compound, $[\text{Co}_3(\text{btc})_2(\text{phen})_2(\text{H}_2\text{O})_2]$, (I).

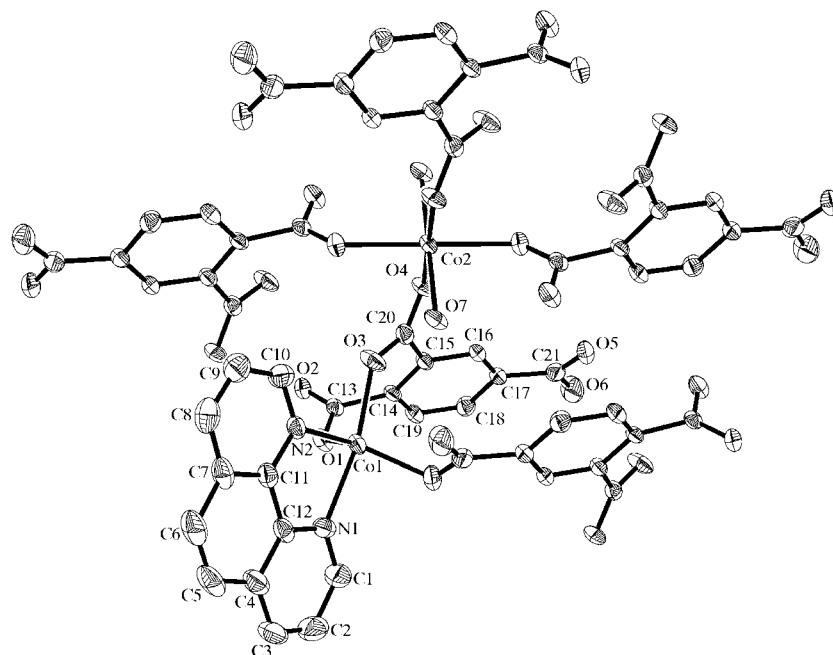


In the structure of (I) (Fig. 1), there are two different kinds of independent Co^{II} centres bridged by btc to form a novel two-dimensional network. The Co1 centre has a deformed trigonal-bipyramidal geometry completed by three carboxylate O atoms belonging to two btc ligands and two N atoms from a terminal phen molecule. The Co2 centre possesses a distorted octahedral geometry. The basal plane consists of two aqua O atoms and two carboxylate O atoms from two btc ligands. The two apical positions are filled by two carboxylate O atoms from two other btc ligands, the corresponding axial $\text{Co}-\text{O}$ bond distances [2.155 (3) Å] being longer than the equatorial $\text{Co}-\text{O}$ bond distances [2.073 (3)–2.077 (3) Å]. The separation of the independent Co centres (5.097 Å) is in agreement with that reported for a cobalt-2,2'-bipyridine-btc analogue (Plater *et al.*, 2001).

The neighbouring 1,2-dicarboxylate groups of one btc ligand bridge two adjacent Co2 centres, and each Co2 centre is coordinated by four carboxylate O atoms from four different btc ligands, forming a novel kind of intersecting double-chain structure, with a $\text{Co}\cdots\text{Co}$ separation of 7.7548 (12) Å along the *a* axis. This is comparable with what was found in $[\text{Co}_2(\text{C}_{10}\text{H}_2\text{O}_8)(\text{C}_{10}\text{H}_8\text{N}_2)_2(\text{H}_2\text{O})_2]_n$ (Xiao *et al.*, 2004), in which the Co centres are also bridged by neighbouring 1,2-dicarboxylate groups and 4,5-dicarboxylate groups.

On the other hand, pairs of Co1 centres are bridged by two btc ligands to produce a binuclear unit, with a $\text{Co}\cdots\text{Co}$ separation of 8.4064 (16) Å, and these binuclear units are linked by btc bridges and Co2 centres to extend hybrid chains of Co1 and Co2 along the [101] direction.

Thus, three carboxylate groups of each btc ligand connect two Co1 centres and Co2 centres, respectively, by two different coordination modes, *viz.* as a monodentate ligand with one Co centre and as a bidentate ligand with two Co centres. This is also comparable with what was found in an $\text{Fe}-\text{H}_2\text{O}$ -btc analogue (Riou-Cavellec *et al.*, 2003). In this way, each btc ligand acts as a pentadentate bridge, linking the Co2 double-chain structures and the hybrid chains of Co1 and Co2 to yield a two-dimensional network, and this leads to the formation of very different kinds of voids (Fig. 2).


Figure 1

The coordination environments of the two independent cations in (I), with the atom-numbering scheme, showing displacement ellipsoids at the 50% probability level.

Experimental

The title compound was synthesized by the hydrothermal method from a mixture of benzene-1,2,4-tricarboxylic acid (1 mmol, 0.21 g), $\text{CoCl}_2 \cdot 4\text{H}_2\text{O}$ (1 mmol, 0.20 g), 1,10-phenanthroline (4 mmol, 0.72 g) and water (20 ml) in a 30 ml Teflon-lined stainless steel reactor. The solution was heated to 438 K for 5 d. After slow cooling of the reaction system to room temperature, red prism-shaped crystals of (I) were collected and washed with distilled water.

Crystal data

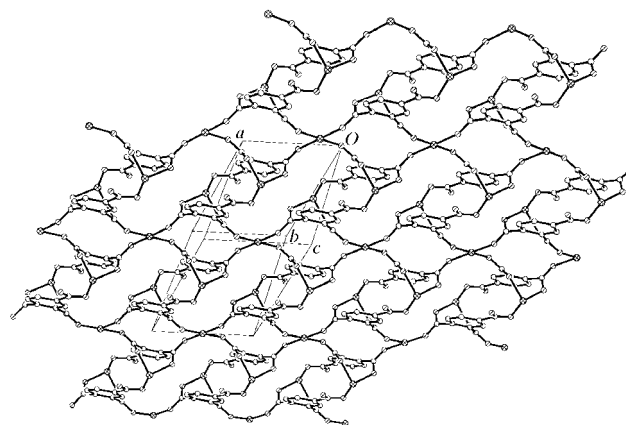
$[\text{Co}_3(\text{C}_9\text{H}_3\text{O}_6)_2(\text{C}_{12}\text{H}_8\text{N}_2)_2(\text{H}_2\text{O})_2]$	$Z = 1$
$M_r = 987.46$	$D_x = 1.795 \text{ Mg m}^{-3}$
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 7.7548 (12) \text{ \AA}$	Cell parameters from 824 reflections
$b = 10.5687 (16) \text{ \AA}$	$\theta = 2.3\text{--}21.4^\circ$
$c = 12.1678 (19) \text{ \AA}$	$\mu = 1.43 \text{ mm}^{-1}$
$\alpha = 88.238 (3)^\circ$	$T = 273 (2) \text{ K}$
$\beta = 77.760 (2)^\circ$	Prism, red
$\gamma = 69.813 (2)^\circ$	$0.20 \times 0.18 \times 0.10 \text{ mm}$
$V = 913.7 (2) \text{ \AA}^3$	

Data collection

Bruker APEX CCD area-detector diffractometer	3281 independent reflections
φ and ω scans	3089 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Bruker, 2002)	$R_{\text{int}} = 0.029$
$T_{\text{min}} = 0.763$, $T_{\text{max}} = 0.870$	$\theta_{\text{max}} = 25.2^\circ$
6767 measured reflections	$h = -9 \rightarrow 9$
	$k = -12 \rightarrow 12$
	$l = -14 \rightarrow 14$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0524P)^2 + 2.7427P]$
$R[F^2 > 2\sigma(F^2)] = 0.066$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.147$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.22$	$\Delta\rho_{\text{max}} = 0.95 \text{ e \AA}^{-3}$
3281 reflections	$\Delta\rho_{\text{min}} = -0.78 \text{ e \AA}^{-3}$
287 parameters	
H atoms treated by a mixture of independent and constrained refinement	


Figure 2

The two-dimensional network of (I). H atoms, water molecules and 1,10-phenanthroline molecules have been omitted for clarity.

The water H atoms were refined subject to the restraint $\text{O—H} = 0.82 (1) \text{ \AA}$. The other H atoms were positioned geometrically and allowed to ride on their parent atoms at C—H distances of 0.93 \AA , with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Data collection: *SMART* (Bruker, 2002); cell refinement: *SAINTE* (Bruker, 2002); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* (Bruker, 2002); software used to prepare material for publication: *SHELXL97*.

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Table 1

Selected geometric parameters (Å, °).

Co1—O1	2.024 (3)	Co1—N1	2.155 (4)
Co1—O3	2.044 (4)	Co2—O7	2.073 (3)
Co1—O5 ⁱ	2.053 (4)	Co2—O4	2.077 (3)
Co1—N2	2.093 (4)	Co2—O2 ⁱⁱ	2.155 (3)
O1—Co1—O3	88.42 (15)	O3—Co1—N1	166.54 (16)
O1—Co1—O5 ⁱ	98.79 (16)	O5 ⁱ —Co1—N1	90.65 (16)
O3—Co1—O5 ⁱ	102.01 (15)	N2—Co1—N1	77.67 (17)
O1—Co1—N2	110.90 (16)	O7—Co2—O4	93.96 (14)
O3—Co1—N2	89.05 (15)	O7—Co2—O2 ⁱⁱ	88.77 (13)
O5 ⁱ —Co1—N2	148.64 (17)	O4—Co2—O2 ⁱⁱ	88.54 (13)
O1—Co1—N1	94.23 (15)	O7—Co2—O2 ⁱⁱⁱ	91.23 (13)

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

Supplementary data for this paper are available from the IUCr electronic archives (Reference: DE1237). Services for accessing these data are described at the back of the journal.

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