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Polymeric aqua(μ_4-dihydrogen benzene-1,2,4,5-tetracarboxylato)-(1,10-phenanthroline)cobalt(II)

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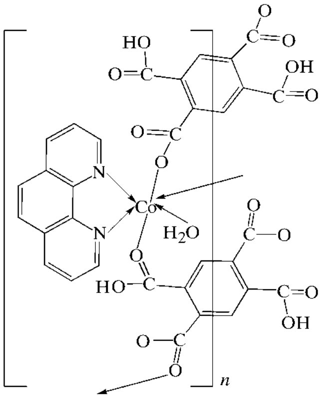
In the title compound, poly[[aqua(1,10-phenanthroline)-cobalt(II)]-μ_4-dihydrogen benzene-1,2,4,5-tetracarboxylato], $[Co(C_{10}H_4O_8)(C_{12}H_8N_2)(H_2O)]_n$, each cobalt(II) cation has an octahedral geometry completed by one aqua O atom, three carboxy O atoms belonging to three H_2TCB^{2-} anions (H_2TCB^{2-} is dihydrogen benzene-1,2,4,5-tetracarboxylate) and two N atoms from a 1,10-phenanthroline molecule. In the asymmetric unit, there are two half H_2TCB^{2-} anions lying about independent inversion centres. The bridging H_2TCB^{2-} anions have two coordination modes, *viz.* μ_2-H_2TCB^{2-} and μ_4-H_2TCB^{2-}, resulting in a two-dimensional coordination polymer. Furthermore, a three-dimensional network is formed by $O_{carboxy}\cdots O_{carboxy}$ hydrogen-bond interactions, with $H\cdots A$ distances in the range 1.69–1.82 Å, and $O_{carboxy}\cdots O_{water}$ interactions, with $H\cdots A$ distances in the range 1.91–1.94 Å.

Comment

Research on metal-directed coordination polymers has been proceeding rapidly owing to their interesting topologies and potential applications as functional materials (Kitagawa & Kondo, 1998; Yaghi *et al.*, 1998; Seo *et al.*, 2000). Bi- or multidentate ligands containing O- or N-donors are often used to coordinate to metal centers (Fujita & Ogura, 1996; Mori & Takamizawa, 2000). Accordingly, benzene-1,2,4,5-tetracarboxylic acid (H_4TCB) is a good bridging ligand that can sometimes be used to generate unexpected and interesting coordination polymers (Gutschke *et al.*, 2001), and small changes in experimental conditions (concentration, molecular ratio, solvent *etc.*) can lead to very different architectures. We report here the hydrothermal synthesis and crystal structure of a two-dimensional coordination polymer, *viz.* the title compound, (I).

In (I), each cobalt(II) cation has a six-coordinated environment, composed of one aqua O atom, three carboxy O atoms belonging to three H_2TCB^{2-} anions and two N atoms from a phen (phen is 1,10-phenanthroline) molecule (Fig. 1). The geometry around the cobalt(II) cation is octahedral, with the four equatorial positions occupied by the two phen N atoms, one carboxy O atom and the aqua O atom, and with all distances lying in the 2.0834 (13)–2.1266 (12) Å range (Table 1). The apical positions are filled by two carboxy O atoms from two different H_2TCB^{2-} anions, the axial bond lengths [2.1220 (12) and 2.1266 (12) Å] being longer than the equatorial bond lengths.



(I)

The μ-H_2TCB^{2-} ligands exhibit two coordination modes. In the first, four carboxylate groups, including two undeprotonated carboxylate groups, bond to four cobalt(II) cations; it should be noted that this coordination mode has been rarely reported (Livage *et al.*, 2001). In the second mode, only the two deprotonated carboxylate groups bind to two cobalt(II) cations (Fig. 2); this mode is similar to that reported for Cu(phen)(H_2TCB) (Hu *et al.*, 2003). The μ_2-H_2TCB^{2-} ligands are parallel to two neighboring phen molecules, but the dihedral angle between the μ_4-H_2TCB^{2-} ring and the neighboring phen ring is 65.35 (4)°. A two-dimensional network is thus formed by μ_4-H_2TCB^{2-} and μ_2-H_2TCB^{2-} ligands, central cobalt(II) cations, aqua molecules and terminal phen molecules. The μ_4-H_2TCB^{2-} and μ_2-H_2TCB^{2-} ligands and phen molecules are almost linear along [111]. Moreover, the

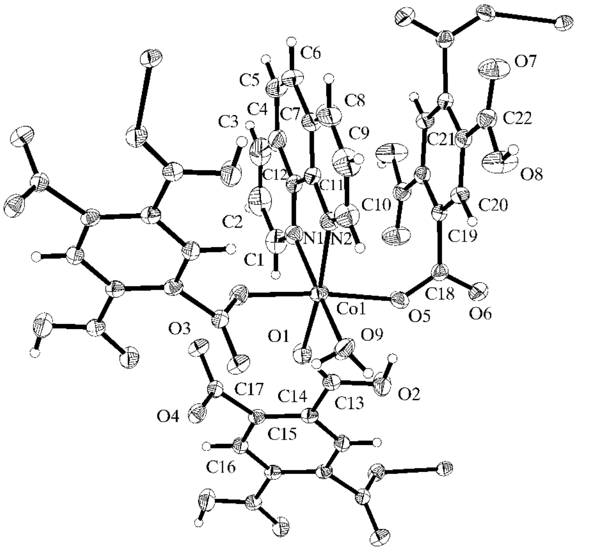


Figure 1
The coordination environment of the Co^{II} atom in (I), with the atom numbering, showing displacement ellipsoids at the 50% probability level.

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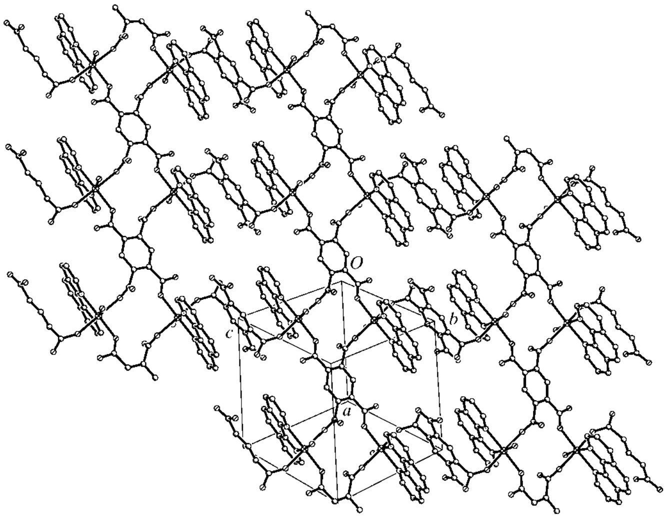

Figure 2
The two-dimensional network in (I).

$O_{carboxy}\cdots O_{carboxy}$ and $O_{carboxy}\cdots O_{water}$ hydrogen-bond interactions, with $H\cdots A$ distances in the 1.69–1.82 and 1.91–1.94 Å ranges, respectively (Table 2), connect the two-dimensional networks, resulting in a three-dimensional structure.

Experimental

The title compound was synthesized by a hydrothermal method from a mixture of benzene-1,2,4,5-tetracarboxylic acid (1 mmol, 0.257 g), $Co(SO_4)_2\cdot6H_2O$ (1 mmol, 0.281 g), 1,10-phenanthroline (0.05 mmol, 0.0991 g) and 2-aminopyrimidine (2 mmol, 0.192 g) in a 30 ml Teflon-lined stainless-steel reactor. The solution was heated at 403 K for 5 d and then cooled slowly to room temperature; red prism-shaped crystals of (I) were collected for X-ray analysis.

Crystal data

$[Co(C_{10}H_4O_8)(C_{12}H_8N_2)(H_2O)]$
$M_r = 509.28$
Triclinic, $P\overline{1}$
$a = 9.6876$ (9) Å
$b = 10.2079$ (10) Å
$c = 11.3561$ (11) Å
$\alpha = 86.808$ (1)°
$\beta = 72.141$ (1)°
$\gamma = 64.928$ (1)°
$V = 964.58$ (16) Å^3
$Z = 2$
$D_x = 1.753$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 248 reflections
$\theta = 2.4$–23.0°
$\mu = 0.95$ mm^{-1}
$T = 273$ (2) K
Prism, red
0.59 × 0.55 × 0.34 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)
$T_{min} = 0.571$, $T_{max} = 0.722$
6669 measured reflections
3371 independent reflections
3215 reflections with $I > 2\sigma(I)$
$R_{int} = 0.012$
$\theta_{max} = 25.1$°
$h = -11 \rightarrow 11$
$k = -12 \rightarrow 11$
$l = -13 \rightarrow 13$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.025$
$wR(F^2) = 0.066$
$S = 1.07$
3371 reflections
315 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0313P)^2 + 0.522P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.28$ e Å^{-3}
$\Delta\rho_{min} = -0.29$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0414 (17)

Table 1
Selected geometric parameters (Å, °).

Co1—O9	2.0834 (13)	Co1—O1	2.1131 (12)
Co1—N1	2.1028 (15)	Co1—O4^i	2.1220 (12)
Co1—N2	2.1103 (14)	Co1—O5	2.1266 (12)
O9—Co1—N1	173.81 (6)	N2—Co1—O4^i	84.46 (5)
O9—Co1—N2	94.98 (6)	O1—Co1—O4^i	93.95 (5)
N1—Co1—N2	79.21 (6)	O9—Co1—O5	85.42 (5)
O9—Co1—O1	94.40 (6)	N1—Co1—O5	97.40 (5)
N1—Co1—O1	91.33 (5)	N2—Co1—O5	97.47 (5)
N2—Co1—O1	170.41 (5)	O1—Co1—O5	85.23 (5)
O9—Co1—O4^i	87.74 (5)	O4^i—Co1—O5	173.03 (5)
N1—Co1—O4^i	89.54 (5)		

Symmetry code: (i) $-x, 1-y, 1-z$.

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

$D—H\cdots A$	$D—H$	$H\cdots A$	$D\cdots A$	$D—H\cdots A$
O2—H2···O5	0.82	1.69	2.494 (3)	166
C20—H20···O8	0.93	2.35	2.688 (2)	101
O8—H8···O3^{ii}	0.82	1.82	2.597 (2)	158
O9—H9*B*···O6^i	0.81 (3)	1.94 (2)	2.730 (2)	163 (2)
O9—H9···O3^{iii}	0.82	1.91	2.668 (2)	153
C8—H8*A*···O7^{iv}	0.93	2.56	3.297 (4)	137
C16—H16···O2^v	0.93	2.41	2.741 (2)	101

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

The O—H distance was refined subject to a distance restraint [O—H = 0.82 (1) Å]. The other H atoms were positioned geometrically and allowed to ride on their parent atoms at distances of 0.93 Å, with U_{iso}(H) values set at $1.2U_{eq}$(parent atom).

Data collection: *SMART* (Bruker, 2000); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 2000); program(s) used to solve structure: *SHELXTL* (Bruker, 2000); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1629). Services for accessing these data are described at the back of the journal.

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