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Triaqua(dihydrogen 1,2,4,5-benzenetetracarboxylato)(1,10-phenanthroline)cobalt(II) monohydrate

Ming-De Ye, Hong-Ping Xiao,* Ya-Qian Cheng and Mao-Lin Hu

Department of Chemistry and Materials Science,
Wenzhou Normal College, Wenzhou 325027,
People's Republic of China

Correspondence e-mail: hp_xiao@wznc.zj.cn

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Key indicators

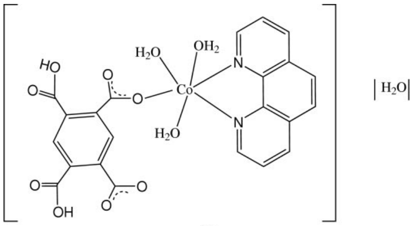
Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.004 Å
H-atom completeness 91%
Disorder in solvent or counterion
R factor = 0.052
wR factor = 0.122
Data-to-parameter ratio = 11.5

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

In the title compound, $[Co(C_{10}H_4O_8)(C_{12}H_8N_2)(H_2O)_3]\cdot H_2O$, the Co atom has an octahedral coordination geometry, involving three aqua O atoms, one carboxylate O atom and two N atoms from a 1,10-phenathroline (phen) molecule. O—H···O hydrogen bonds involving dihydrogen-1,2,4,5-benzenetetracarboxylate (H_2TCB) anions, aqua ligands and uncoordinated water molecules, along with π–π interactions between the phen and aromatic rings of symmetry-related H_2TCB anions, link the mononuclear units into a three-dimensional network structure.

Comment

In recent years, the design and construction of metal-organic complexes have been studied extensively because of their structural diversity and promising applications as functional materials (Stein *et al.*, 1993; Eddaoudi *et al.*, 2001; Chen *et al.*, 2003; Shi *et al.*, 2003). High-dimensional network structures are often formed *via* hydrogen bonds and π–π interactions (Shi *et al.*, 2001; Boldog *et al.*, 2002; Hu *et al.*, 2003; Liu *et al.*, 2003). The title compound, $[Co(phen)(H_2O)(H_2TCB)]\cdot H_2O$, (I) ($H_2TCB$ is dihydrogen-1,2,4,5-benzenetetracarboxylate), represents a good example, comprising a three-dimensional network structure built from mononuclear units.



(I)

In (I), the Co^{II} atom has a six-coordinate octahedral environment defined by one carboxylate O atom, three aqua O atoms and two N atoms from a phen molecule (Fig. 1). The two apical positions are occupied by atoms O11 and N1, the O11—Co1—N1 bond angle being 177.23 (10)°. The basal square plane is formed by atoms O1, O9, O10 and N2, and the bond angles O10—Co1—O1, O9—Co1—O1, O10—Co1—N2 and O9—Co1—N2 lie in the range 89.03 (10)–92.05 (10)°. The Co—O distances range from 2.030 (3) to 2.106 (2) Å, and the Co—N distances are 2.113 (2) and 2.137 (3) Å.

The coordination mode and deprotonation of the carboxy groups in the H_2TCB anion of (I) are significantly different from those in $[CuCl(phen)_2]_2(H_2TCB)_2\cdot H_2O$ (Xiao *et al.*, 2004), although they were obtained under the same reaction conditions. In $[CuCl(phen)_2]_2(H_2TCB)_2\cdot H_2O$, two *p*-carboxy groups are deprotoned to form free anions, while in (I), two

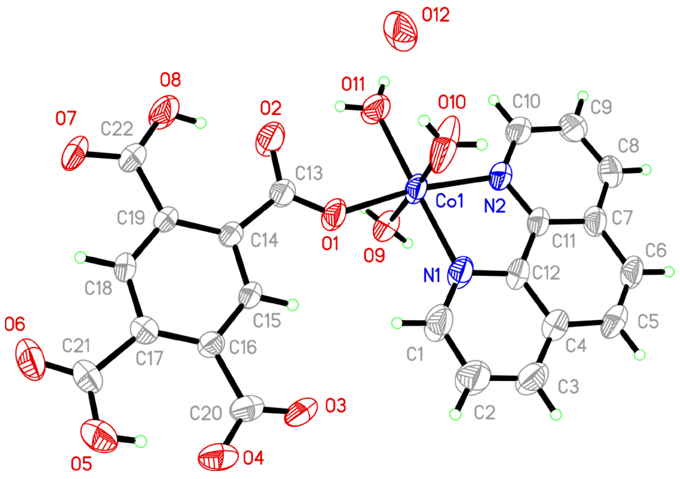


Figure 1
The structure of (I), showing 50% probability displacement ellipsoids and the atom-numbering scheme. Only the major component (85%) of the disordered water molecule (atom O12) is shown.

m-carboxy groups are deprotoned; only one binds to the Co^{II} ion in a monodendate manner and the other balances the charge.

In the H_2TCB anion, the carboxy H atoms are involved in intramolecular O—H···O hydrogen bonds with adjacent carboxylate O atoms (Table 2). In the crystal structure, the water molecules form O—H···O hydrogen bonds, with the carboxy and carboxylate O atoms as acceptors. Furthermore, weak π–π interactions are observed between the benzene ring of the phen moiety and the aromatic ring of the H_2TCB anion at ($x - \frac{1}{2}, \frac{1}{2} - y, z - \frac{1}{2}$), the ring centroids being separated by 3.894 (2) Å. These interactions link the mononulear units into a three-dimensional network structure (Fig. 2).

Experimental

A solution (10 ml) of dimethylformamide containing $CoCl_2{\cdot}6H_2O$ (0.5 mmol, 0.12 g) and H_4TCB (0.5 mmol, 0.13 g) was added slowly to a solution (10 ml) of dimethylformamide containing 1,10-phenanthroline (0.5 mmol, 0.10 g). The reaction mixture was stirred for a few minutes and left to stand at room temperature for three weeks, affording red prism-shaped crystals.

Crystal data

$[Co(C_{10}H_4O_8)(C_{12}H_8N_2)$-
$(H_2O)_3]{\cdot}H_2O$
$M_r = 563.33$
Monoclinic, $P2_1/n$
$a = 7.0862$ (7) Å
$b = 22.547$ (2) Å
$c = 14.8041$ (14) Å
$\beta = 97.875$ (2)°
$V = 2343.0$ (4) Å^3
$Z = 4$

$D_x = 1.597$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 812 reflections
$\theta = 2.4$–23.0°
$\mu = 0.80$ mm^{-1}
$T = 293$ (2) K
Prism, red
0.52 × 0.39 × 0.29 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)
$T_{\min} = 0.680$, $T_{\max} = 0.801$
17 167 measured reflections

4259 independent reflections
3955 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.024$
$\theta_{\max} = 25.3°$
$h = -8 \rightarrow 8$
$k = -27 \rightarrow 27$
$l = -17 \rightarrow 17$

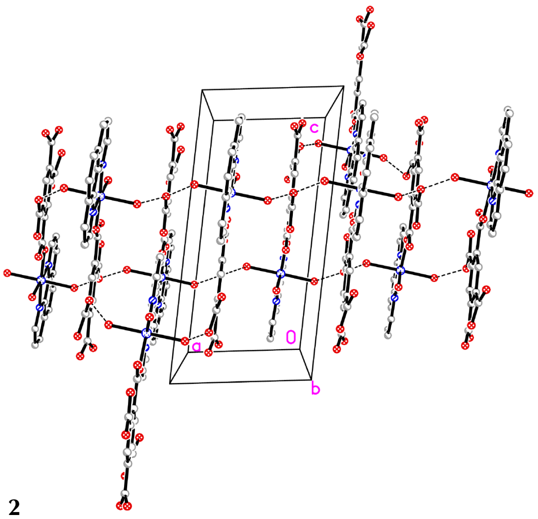


Figure 2
The three-dimensional network structure formed *via* O—H···O hydrogen bonds.

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.052$
$wR(F^2) = 0.122$
$S = 1.17$
4259 reflections
371 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0466P)^2 + 2.4736P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.40$ e Å^{-3}
$\Delta\rho_{\min} = -0.29$ e Å^{-3}
Extinction correction: *SHELXTL*
Extinction coefficient: 0.0032 (5)

Table 1
Selected geometric parameters (Å, °).

Co1—O10	2.030 (3)	Co1—O11	2.106 (2)
Co1—O9	2.055 (2)	Co1—N2	2.113 (2)
Co1—O1	2.097 (2)	Co1—N1	2.137 (3)
O10—Co1—O9	176.95 (11)	O1—Co1—N2	171.09 (9)
O10—Co1—O1	90.10 (12)	O11—Co1—N2	99.94 (10)
O9—Co1—O1	89.03 (10)	O10—Co1—N1	94.01 (13)
O10—Co1—O11	87.73 (14)	O9—Co1—N1	88.96 (10)
O9—Co1—O11	89.32 (11)	O1—Co1—N1	93.24 (9)
O1—Co1—O11	88.91 (9)	O11—Co1—N1	177.23 (10)
O10—Co1—N2	89.26 (12)	N2—Co1—N1	77.94 (9)
O9—Co1—N2	92.05 (10)		

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O5—H5*A*···O4	0.82	1.60	2.410 (4)	171
O8—H8*A*···O2	0.82	1.57	2.386 (4)	177
O9—H9*A*···O4$^{\rm i}$	0.82 (2)	2.04 (2)	2.827 (3)	162 (3)
O9—H9*B*···O7$^{\rm ii}$	0.82 (2)	1.95 (2)	2.770 (3)	177 (3)
O10—H10*A*···O3$^{\rm iii}$	0.82 (3)	1.84 (3)	2.656 (4)	171 (3)
O10—H10*B*···O7$^{\rm iv}$	0.82 (3)	1.92 (3)	2.731 (4)	170 (4)
O11—H11*A*···O12	0.82 (2)	1.92 (3)	2.723 (4)	169 (4)
O11—H11*B*···O2	0.82 (3)	2.00 (3)	2.731 (4)	147 (3)

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

H atoms of the coordinated water molecules were located in a difference map and were refined isotropically, with O—H and H···H distances restrained to 0.82 (1) and 1.32 (2) Å, respectively. The remaining H atoms were positioned geometrically (C—H = 0.93 Å and O—H = 0.82 Å) and allowed to ride on their parent atoms, with $U_{\rm iso}$(H) values equal to $1.2U_{\rm eq}$ or $1.5U_{\rm eq}$(O). Water atom O12 is disordered over two positions (O12 and O12′), with occupancies of 0.848 (7) and 0.152 (7), respectively. The H atoms attached to this disordered molecule were not located.

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*; software used to prepare material for publication: *SHELXTL*.

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