metal-organic papers

catena-Poly[piperazinium [diaquacobalt(II)-μ-benzene-1,3,5-tricaboxylato-tetraaquacobalt(II)-μ-benzene-1,3,5-tricaboxylato] dihydrate]

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The title polymer, $\{(C_4H_{12}N_2)[Co_2(C_9H_3O_6)_2(H_2O)_6]\cdot 2H_2O\}_n$, contains two independent Co^{II} atoms, both of which are located on inversion centres. The benzene-1,3,5-tricarboxylate ligand bridges the Co^{II} atoms in two coordination modes to form a one-dimensional polymeric zigzag chain structure. The zigzag chains are connected via O—H···O and N—H···O hydrogen bonds to form a three-dimensional network. This determination corrects a previous report which formulated this compound as $(C_4H_{10}N_2)_n[C_{18}H_{20}Co_2O_{18}]_n\cdot 2nH_2O$ [Chen & Liu (2004). *Chem. J. Chin. Univ.* **25**, 1189–1193].

Comment

Benzene-1,3,5-tricarboxylate (BTC) usually plays the role of a bridging ligand in metal complexes. We present here the crystal structure of the title Co^{II} complex, $[(C_{18}H_{18}Co_2O_{18})^{2-}]_n\cdot n[C_4H_{12}N_2]^{2+}\cdot 2nH_2O$, (I). This determination corrects a previous report which formulated this compound as $[C_{18}H_{20}Co_2O_{18}]_n\cdot n[C_4H_{10}N_2]\cdot 2nH_2O$, (II) (Chen & Liu, 2004). In compound (II), the C—O bond lengths [1.251 and 1.262 Å] of the uncoordinated carboxylate groups clearly indicate proton transfer from them to a piperazine ring, resulting in a $[C_4H_{12}N_2]^{2+}$ cation. However, in (II), the components were reported as neutral. In (I), the proton transfer is taken into account, and the protons are assigned to the piperazine ring.

(I)
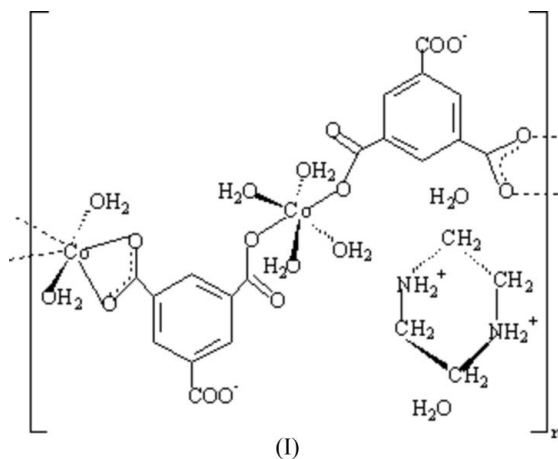
Compound (I) contains two independent Co^{II} atoms, which are located at the centres of different centrosymmetric CoO$_6$ octahedra (Fig. 1). Each BTC ligand bridges two Co^{II} atoms to form a polymeric zigzag chain, and these are further linked via O—H···O hydrogen bonds to form a three-dimensional network (Table 1). Two carboxylate groups of the BTC ligand coordinate to Co^{II} atoms, one in a monodentate fashion and the other in a bidentate chelating fashion. The third

carboxylate group is not coordinated to Co^{II}. The packing of the chains forms quadrilateral pores, which are occupied by $[C_4H_{12}N_2]^{2+}$ cations and uncoordinated water molecules (Fig. 2).

Experimental

An aqueous solution (10 ml) of benzene-1,3,5-tricarboxylic acid (0.210 g), terephthalic acid (0.166 g) and piperazine hexahydrate (0.132 g) was mixed with an aqueous solution (5 ml) of cobalt(III) nitrate hexahydrate (0.292 g) with continuous stirring. The mixture was sealed in a 40 ml Teflon-lined stainless steel vessel and heated at 453 K for 96 h under autogenous conditions. After cooling to room temperature, the resulting product was filtered off to obtain pale-red crystals of (I) (about 76.2% yield, based on the Co source). Spectroscopic analysis: IR (KBr, v, cm^{-1}): 3120, 2445, 2345, 1610, 1532, 1454, 1429, 1363, 1202, 1087, 754, 712, 542, 521, 459. Elemental analysis, calculated for $C_{11}H_{17}N$ Co O_{10}: C 34.54, H 4.48, N 3.66%; found: C 34.45, H 4.51, N 3.62%.

Crystal data

$(C_4H_{12}N_2)[Co_2(C_9H_3O_6)_2(H_2O)_6]$·$2H_2O$
$M_r = 764.38$
Triclinic, $P\bar{1}$
$a = 7.1443$ (11) Å
$b = 10.5308$ (16) Å
$c = 10.5385$ (16) Å
$\alpha = 110.753$ (2)°
$\beta = 102.521$ (2)°
$\gamma = 91.351$ (2)°
$V = 719.40$ (19) Å^3

$Z = 1$
$D_x = 1.764$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 1224
  reflections
$\theta = 2.1$–25.0°
$\mu = 1.25$ mm^{-1}
$T = 293$ (2) K
Block, pale red
$0.20 \times 0.12 \times 0.10$ mm

Data collection

Bruker SMART APEX2 CCD area-
  detector diffractometer
φ and ω scans
Absorption correction: multi-scan
  (SADABS; Sheldrick, 1996)
  $T_{min} = 0.638$, $T_{max} = 0.883$
3896 measured reflections

2503 independent reflections
1957 reflections with $I > 2\sigma(I)$
$R_{int} = 0.015$
$\theta_{max} = 25.1°$
$h = -8 \rightarrow 8$
$k = -12 \rightarrow 12$
$l = -8 \rightarrow 12$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.036$
$wR(F^2) = 0.098$
$S = 1.01$
2503 reflections
211 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0626P)^2]$
  where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.56$ e Å^{-3}
$\Delta\rho_{min} = -0.56$ e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N1—H1A$\cdots$O5^i	0.90	1.86	2.751 (4)	168
N1—H1B$\cdots$O9^{ii}	0.90	2.03	2.880 (4)	157
N1—H1B$\cdots$O8^{iii}	0.90	2.42	3.011 (4)	124
O7—H7A$\cdots$O4^{iv}	0.85	1.78	2.622 (3)	173
O7—H7B$\cdots$O11	0.85	1.93	2.733 (4)	157
O8—H8A$\cdots$O1^v	0.85	1.91	2.740 (3)	162
O8—H8B$\cdots$O6^{vi}	0.85	1.83	2.657 (3)	166
O9—H9A$\cdots$O6^v	0.85	1.87	2.703 (3)	165
O9—H9B$\cdots$O4	0.85	1.83	2.640 (3)	158
O11—H11A$\cdots$O5^{vi}	0.85	1.91	2.722 (4)	158
O11—H11B$\cdots$O7^{vii}	0.85	2.14	2.934 (4)	156

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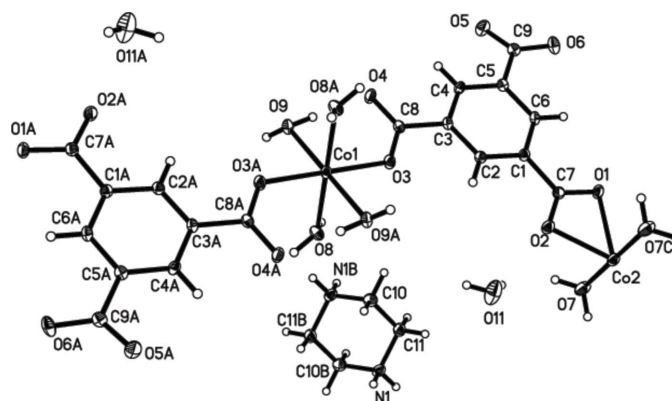

Figure 1
Part of the polymeric structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. Atoms labelled with the suffixes A, B and C are generated by the symmetry operations $(-x, 2 - y, -z)$, $(2 - x, 1 - y, -z)$ and $(-x, 1 - y, 1 - z)$, respectively.
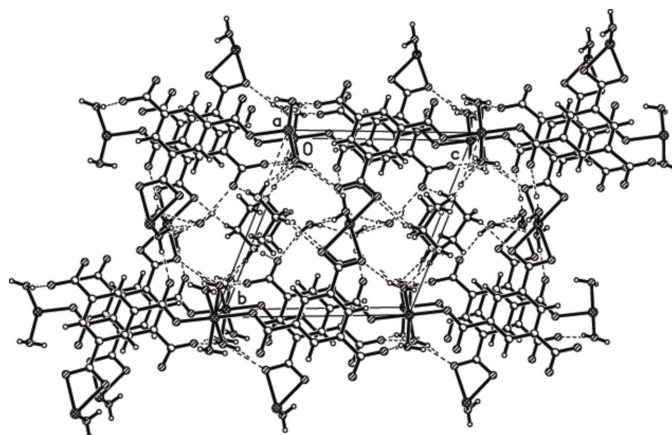

Figure 2
The crystal packing of (I), viewed along the a axis. Dashed lines indicate hydrogen bonds.

The water H atoms were located in a difference map; their bond lengths were set to ideal values [O—H = 0.85 and H$\cdots$H = 1.37 Å] and they were refined using a riding model [U_{iso}(H) = 1.5U_{eq}(O)]. The remaining H atoms were placed in idealized positions and constrained to ride on their parent atoms, with C—H = 0.93–0.97 Å and N—H = 0.90 Å, and with U_{iso}(H) = 1.2U_{eq}(C,N).

Data collection: APEX2 (Bruker, 1997); cell refinement: APEX2; data reduction: SAINT (Bruker, 1997); program(s) used to solve structure: SHELXS97 (Sheldrick, 1997a); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997a); molecular graphics: SHELXTL (Sheldrick, 1997b); software used to prepare material for publication: SHELXTL.

References

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