Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

A one-dimensional zigzag coordination polymer of diaqua(pyridine-2,3-dicarboxylato)cobalt(II)

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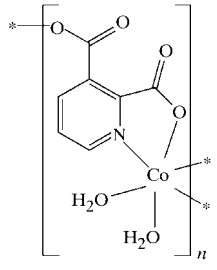
Received 2 June 2003
Accepted 6 June 2003
Online 12 July 2003

The asymmetric unit of the title one-dimensional coordination polymer, *catena*-poly[[μ-pyridine-2,3-dicarboxylato-1κO:2$\kappa^2 N$,O'-bis[diaquacobalt(II)]]-μ-pyridine-2,3-dicarboxylato-1$\kappa^2 N$,O:2$\kappa O'$:1′$\kappa O'$], $[Co(C_7H_3NO_4)(H_2O)_2]_n$, is composed of a cobalt(II) ion, a pyridine-2,3-dicarboxylate dianion and two water molecules. The polymer has a zigzag structure consisting of a chain of edge-fused rings, and the polymer chains are linked by O—H···O hydrogen bonds into a three-dimensional framework.

Comment

The design and synthesis of coordination polymers is one of the most stimulating research frontiers in contemporary chemistry, owing to the intriguing crystallographic structure and the functional properties of these compounds (Seo *et al.*, 2000; Eddaoudi *et al.*, 2001; Perles *et al.*, 2003). The 'node and spacer' approach which is based on the nature of the metal and the coordination behaviour of the ligand has been remarkably successful at producing predicatable coordination-polymer architectures (Batten & Robson, 1998). Many coordination



(I)

polymers can be generated by using metal ions as the 'node' and linking them *via* linear 'spacer' ligands, such as 1,4-benzenedicarboxylate, 4-pyridinecarboxylate and 4,4′-bipyridine (Hagrman *et al.*, 1999; Li *et al.*, 1999; Lu & Babb, 2001). We present here the structure of a one-dimensional zigzag-type coordination polymer, namely the title compound, (I).

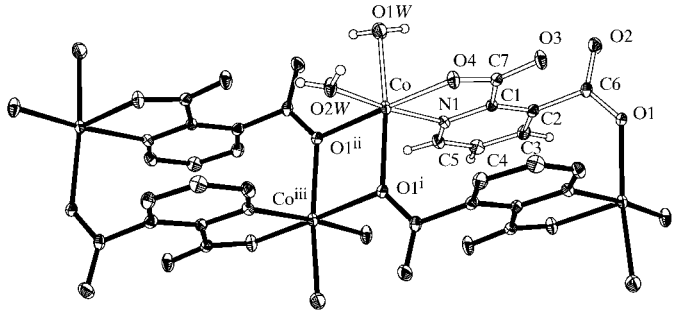


Figure 1
The molecular structure of (I), with displacement ellipsoids shown at the 30% probability level. H atoms unrelated to the asymmetric unit (open lines) have been omitted for clarity. [Symmetry codes: (i) $1-x, 1-y, 1-z$; (ii) $x, y, z-1$; (vi) $1-x, 1-y, -z$.]

The coordination motif of the Co^{II} atom is a distorted octahedron (Table 1 and Fig. 1) in which pyridyl atom N1, three carboxylate O atoms [O4, O1^{i} and O1^{ii}; symmetry codes: (i) $1-x, 1-y, 1-z$; (ii) $x, y, z-1$] and two water O atoms (O1*W* and O2*W*) occupy the vertices. Thus, one cobalt(II) ion is bound to three pyridine-2,3-dicarboxylate ligands. One of these ligands is joined to the Co^{II} atom *via* the pyridine N atom and one of the O atoms of the carboxylate group in the 2-position, thus generating a five-membered chelate ring (–C1—N1—Co—O4—C7–). The other carboxylate group (in the 3-position) lies almost perpendicular to the pyridine plane because of steric interaction between the two carboxylate groups. The dihedral angle between the pyridine ring and the O1/C6/O2 carboxylate group is 88.40 (13)°. One of the O atoms of this ligand acts as a bridge to connect two Co^{II} atoms in a μ_2 mode, thus forming a rhomboidal Co_2O_2 ring. The Co···Co^{i} distance is 3.4052 (8) Å, and the dihedral angle between the rhomboid ring and the five-membered chelate ring is 86.46 (7)°.

Along the *c* axis, two antiparallel ligands connect a pair of neighbouring Co^{II} atoms in a head-to-tail fashion, thus generating a chain of edge-fused rings; alternatively, the structure may be regarded as a pair of zigzag chains that are

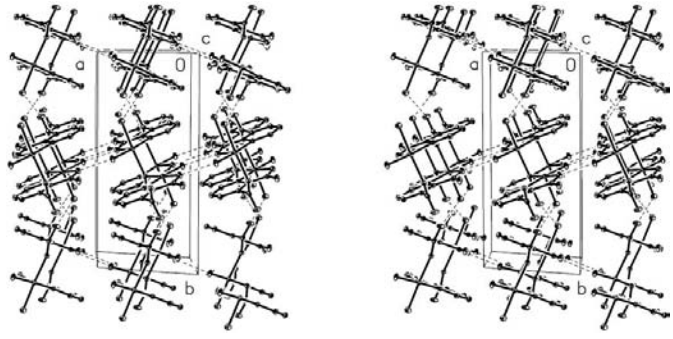


Figure 2
A stereoview of the structure of (I), viewed approximately along the *c* axis. H atoms have been omitted for clarity and dashed lines indicate O—H···O hydrogen bonds.

 DOI: 10.1107/S0108270103012551

joined together *via* the common Co_2O_2 rhomboid. The two parallel zigzag chains are related by inversion centres.

There are two intrachain hydrogen bonds, *viz*. O1*W*—H1*WA*···O2^{ii} and O2*W*—H2*WA*···O3^{ii} (Table 2), which may exert some influence on the overall conformation of the chain. The chains are arranged in a parallel fashion along the *a* axis and in a zigzag fashion along the *b* direction. As a result, along the *a* axis, the chains are connected by interchain O2*W*—H2*WB*···O4^{v} hydrogen bonds [symmetry code: (v) $-x, 1-y, -z$] to form a (010) sheet. Meanwhile, along the *b* axis, an interchain O1*W*—H1*WB*···O2^{iv} hydrogen bond [symmetry code: (iv) $x, \frac{3}{2}-y, z-\frac{1}{2}$], links the chains into puckered (100) sheets. The combination of the (100) and (010) sheets links all of the polymer chains into a three-dimensional hydrogen-bonded framework (Fig. 2).

Experimental

$Co(ClO_4)_2{\cdot}6H_2O$ (36.6 mg, 0.10 mmol), pyridine-2,3-dicarboxylic acid (16.7 mg, 0.10 mmol) and pyridine (0.4 ml) were dissolved in a mixture of water (3 ml) and ethanol (3 ml), and the mixture was placed in a Teflon-lined stainless-steel vessel (25 ml). The vessel was sealed and heated at 403 K for 3 d and then cooled to room temperature. Large red prismatic crystals were collected by filtration and washed with water and ethanol.

Crystal data

$[Co(C_7H_3NO_4)(H_2O)_2]$
$M_r = 260.07$
Monoclinic, $P2_1/c$
$a = 7.7200\ (15)$ Å
$b = 15.620\ (3)$ Å
$c = 7.8100\ (16)$ Å
$\beta = 113.95\ (3)^\circ$
$V = 860.7\ (4)$ Å^3
$Z = 4$
$D_x = 2.007$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 2.2$–13.9°
$\mu = 2.00$ mm^{-1}
$T = 298\ (2)$ K
Prism, red
0.37 × 0.24 × 0.20 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
ω scans
Absorption correction: ψ scan (*XCAD*4; Harms & Wocadlo, 1995)
$T_{min} = 0.470$, $T_{max} = 0.670$
1625 measured reflections
1509 independent reflections
1254 reflections with $I > 2\sigma(I)$
$R_{int} = 0.017$
$\theta_{max} = 25.0^\circ$
$h = 0 \rightarrow 9$
$k = 0 \rightarrow 18$
$l = -9 \rightarrow 8$
3 standard reflections
every 200 reflections
intensity decay: 1.1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.023$
$wR(F^2) = 0.062$
$S = 1.00$
1509 reflections
152 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0319P)^2 + 0.385P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.28$ e Å^{-3}
$\Delta\rho_{min} = -0.36$ e Å^{-3}

H atoms bonded to C atoms were treated as riding, with U_{iso}(H) values equal to $1.2U_{eq}$(C) and C—H distances of 0.93 Å. Water H atoms were located in difference maps and were refined subject to an O—H DFIX restraint of 0.82 (3) Å (eight restraints), with U_{iso}(H) values constrained to be $1.2U_{eq}$(O).

Table 1
Selected geometric parameters (Å, °) for (I).

Co—O2*W*	2.025 (2)	Co—O1^{i}	2.1821 (16)
Co—O4	2.0613 (17)	Co—O1^{ii}	2.1920 (17)
Co—N1	2.107 (2)	N1—C1	1.348 (3)
Co—O1*W*	2.133 (2)	O4—C7	1.271 (3)
O2*W*—Co—O4	95.81 (7)	N1—Co—O1^{i}	94.70 (7)
O2*W*—Co—N1	174.31 (8)	O2*W*—Co—O1^{ii}	83.37 (7)
O4—Co—N1	78.94 (7)	N1—Co—O1^{ii}	101.96 (7)
O2*W*—Co—O1*W*	89.93 (8)	O1^{i}—Co—O1^{ii}	77.75 (6)
O4—Co—O1*W*	86.84 (8)	C1—N1—Co	112.72 (15)
N1—Co—O1*W*	87.63 (8)	Co^{i}—O1—Co^{iii}	102.25 (6)
O2*W*—Co—O1^{i}	88.34 (7)	C7—O4—Co	116.81 (15)
C1—C2—C6—O2	−90.6 (3)	C1—C2—C6—O1	93.6 (3)

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

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*W*—H1*WB*···O2^{iv}	0.84 (3)	1.92 (3)	2.749 (3)	168 (4)
O1*W*—H1*WA*···O2^{ii}	0.81 (2)	1.83 (3)	2.604 (3)	160 (4)
O2*W*—H2*WA*···O3^{ii}	0.81 (2)	2.01 (2)	2.806 (3)	168 (3)
O2*W*—H2*WB*···O4^{v}	0.85 (3)	1.84 (3)	2.674 (3)	170 (4)

Symmetry codes: (ii) $x, y, z-1$; (iv) $x, \frac{3}{2}-y, z-\frac{1}{2}$; (v) $-x, 1-y, -z$.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *CAD*-4 *Software*; data reduction: *XCAD*4 (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 2000); software used to prepare material for publication: *SHELXTL*.

This work was funded by the NSFC (grant No. 90101028).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD1261). Services for accessing these data are described at the back of the journal.

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