

A novel one-dimensional coordination polymer, *catena*-poly[[diaqua-cobalt(II)]- μ -(2,2'-bipyridyl-3,3'-dicarboxylato- $\kappa^4 N, N': O, O'$)]

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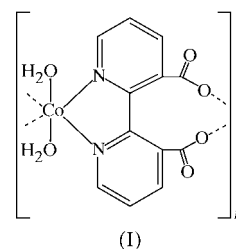
The title compound, $[\text{Co}(\text{C}_{12}\text{H}_6\text{N}_2\text{O}_4)(\text{H}_2\text{O})_2]_n$, has been hydrothermally synthesized and structurally characterized. It consists of polymeric chains of $[\text{Co}\{\mu\text{-(2,2'-bipyridyl-3,3'-dicarboxylato-}\kappa^4 N, N': O, O')\}(\text{H}_2\text{O})_2]$ units, in which each Co^{II} cation is octahedrally coordinated by two chelating pyridyl N atoms, two chelating carboxyl O atoms from different carboxylate groups of another bipyridyl ligand, and two water molecules as terminal ligands. A crystallographic twofold axis parallel to the chain axis, passes through the Co atom.

Comment

Transition metal coordination polymers of one-, two- and three-dimensional infinite frameworks have been an attractive research area because of their diverse structures and useful properties (Davis, 2002; Hagrman *et al.*, 1999). Polydentate ligands, which are used as bridges in the construction of coordination polymers, are quite important in the crystal engineering of supramolecular architectures organized by coordinate covalent or hydrogen bonding (Moulton & Zaworotko, 2001).

2,2'-Bipyridyl-3,3'-dicarboxylate (bpdc) is a potential bridging ligand in view of its functional groups. However, it usually acts as an N, N' -bidentate ligand, forming a chelate with one metal centre in the corresponding discrete complex molecules (Goddard *et al.*, 1990; Ravikumar *et al.*, 1997; Yoo *et al.*, 1997; Menon *et al.*, 1997). Only a few metal coordination polymers bridged by bpdc have been reported to date. For example, bpdc acts as an O, O' -bidentate μ_2 ligand, bridging two metal centres *via* one O atom of its two carboxylate groups in the polymer $[\text{Mn}(\text{bpdc})(\text{H}_2\text{O})_4]_n$ (Swamy *et al.*,

1998). The monoprotonated bpdc in $[\text{Ag}(\mu_3\text{-Hbpdc})(\text{H}_2\text{O})]_n$ (Tong *et al.*, 2000) coordinates as an N, N', O -tridentate μ_3 ligand, forming three bridges, *viz.* $\text{N}-\text{Ag}$, $\text{N}'-\text{Ag}$ and $\text{O}-\text{Ag}$. Furthermore, in $[\text{Cu}(\mu_2\text{-bpdc})(\text{H}_2\text{O})_2]_n$, bpdc also coordinates in an N, N', O -tridentate fashion, but as a μ_2 ligand, bridging two Cu^{II} ions through one $\text{N}-\text{Cu}-\text{N}'$ chelating system and one $\text{O}-\text{Cu}$ coordinate bond (Zhuang *et al.*, 1994; Ravikumar *et al.*, 1995). The title complex, $[\text{Co}(\mu_2\text{-bpdc})(\text{H}_2\text{O})_2]_n$, (I), is another one-dimensional coordination polymer, in which bpdc acts as a μ_2 ligand in an $N, N': O, O'$ -tetradentate fashion, forming two chelate bridges.



In complex (I), the bpdc ligand chelates one Co^{II} cation, which lies on a twofold axis, *via* its two pyridyl N atoms (N and N'), and another Co^{II} cation *via* its two carboxyl O atoms (O1 and O1'). Each Co^{II} cation is octahedrally coordinated, where the equatorial plane comprises the two N atoms of one bpdc ligand on one side and two carboxyl O atoms from different carboxylate groups of a second bpdc ligand on the other side. The apical positions are occupied by the O atoms of two coordinated water molecules (Fig. 1). This octahedron is distorted (Table 1).

The crystal structure of (I) consists of linear polymeric chains of $[\text{Co}(\mu_2\text{-bpdc})(\text{H}_2\text{O})_2]$ units. The chains incorporate a twofold axis along the chain direction, which is parallel to *b*. The chains are interconnected by hydrogen bonding involving atom H1 between adjacent chains, *via* the coordinated H_2O molecules of one chain and the non-coordinated carboxyl O atoms of the adjacent chain, forming a layer parallel to (001). There is one intra-chain hydrogen bond involving atom H2 (Fig. 2 and Table 2). These layers stack along the *c* axis to build up the whole crystal structure.

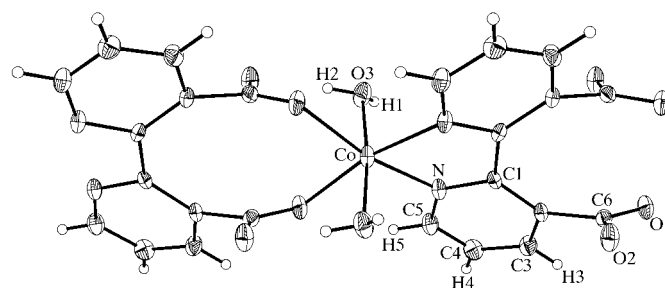


Figure 1

The coordination environment of Co^{II} in (I), with the atomic labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

metal-organic compounds

Complex (I) has the same chemical components as $[\text{Co}(\mu\text{-bpdc})(\text{H}_2\text{O})_2]_n$, but it has a totally different crystal structure to that reported for the latter. The different structures are a result of bpdc acting as a tetradentate ligand in the Co complex and as a tridentate ligand in the Cu complex.

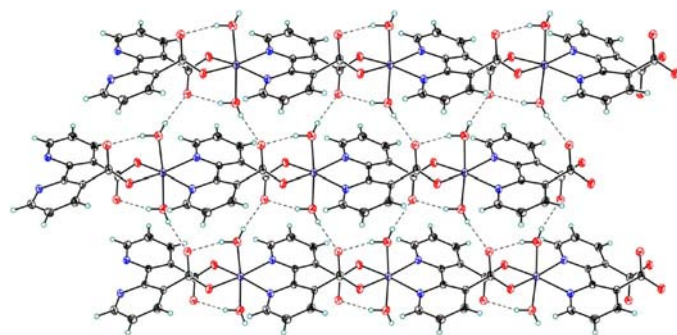


Figure 2
One layer of the structure of (I), showing the $[\text{Co}(\mu\text{-bpdc})(\text{H}_2\text{O})_2]_n$ chains lying parallel to *b*. Hydrogen bonds are shown as dashed lines. The *a* axis is approximately vertical in the diagram.

In order to explore the conductivity of (I), the Kubelka–Munk function, $F = (1 - R_{\text{inf}})^2/2R_{\text{inf}}$, was converted from the recorded diffuse reflectance data for (I), where R_{inf} is the relative diffuse reflectance of an infinitely thick layer (Kortum, 1969). The plot of the Kubelka–Munk function *versus* energy (eV) displayed a steep absorption edge in the UV–vis region, from which a band gap of about 2.7 eV was estimated (McCarthy *et al.*, 1993). This suggests that the crystal of (I) is a possible semiconductor.

Experimental

All chemicals and solvents were of reagent grade and were used without further purification. 2,2′-Bipyridyl-3,3′-dicarboxylic acid (2,2′-binicotinic acid, H_2bpdc) was prepared according to the literature method of Wimmer & Wimmer (1983). A mixture of CoCl_2 (0.1298 g, 1.0 mmol) and H_2bpdc (0.2560 g, 1.0 mmol) in a 1:1 molar ratio was sealed in a 25 ml Teflon-lined stainless steel Parr bomb containing methanol (11.2 ml) and water (2.8 ml), heated at 433 K for 3 d and then cooled to room temperature. Orange sheet-like crystals of (I) were isolated and washed, in turn, with water, ethanol and anhydrous ether. The reflectance spectrum of the compound was recorded on a UV-3100 recording spectrophotometer from 250 to 2500 nm.

Crystal data

$[\text{Co}(\text{C}_{12}\text{H}_6\text{N}_2\text{O}_4)(\text{H}_2\text{O})_2]$

$M_r = 337.15$

Monoclinic, $C2/c$

$a = 11.373$ (2) Å

$b = 7.8632$ (16) Å

$c = 13.162$ (3) Å

$\beta = 100.92$ (3)°

$V = 1155.8$ (4) Å³

$Z = 4$

$D_x = 1.938$ Mg m⁻³

Mo $K\alpha$ radiation

Cell parameters from 1437

reflections

$\theta = 3.2\text{--}31.2^\circ$

$\mu = 1.52$ mm⁻¹

$T = 293$ (2) K

Sheet, orange

$0.20 \times 0.10 \times 0.05$ mm

Data collection

Bruker SMART APEX-CCD area-detector diffractometer

φ and ω scans

Absorption correction: empirical (*SADABS*; Sheldrick, 1996)

$T_{\text{min}} = 0.764$, $T_{\text{max}} = 0.927$

5330 measured reflections

2133 independent reflections

1563 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.046$

$\theta_{\text{max}} = 33.5^\circ$

$h = -17 \rightarrow 17$

$k = -7 \rightarrow 11$

$l = -20 \rightarrow 19$

Refinement

Refinement on F^2

$R[F^2 > 2\sigma(F^2)] = 0.054$

$wR(F^2) = 0.132$

$S = 1.04$

2133 reflections

96 parameters

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0624P)^2 + 0.0074P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} < 0.001$

$\Delta\rho_{\text{max}} = 0.69$ e Å⁻³

$\Delta\rho_{\text{min}} = -0.40$ e Å⁻³

Table 1

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

Co–N	2.096 (2)	C1–C2	1.398 (3)
Co–O1 ⁱ	2.112 (2)	C1–C1 ⁱⁱ	1.504 (5)
Co–O3	2.116 (2)	C2–C3	1.395 (4)
O1–C6	1.258 (3)	C2–C6	1.505 (4)
O2–C6	1.249 (3)	C3–C4	1.382 (4)
N–C5	1.342 (3)	C4–C5	1.372 (4)
N–C1	1.343 (3)		
N ⁱⁱ –Co–N	76.35 (12)	N–Co–O3	84.75 (8)
N–Co–O1 ⁱ	99.38 (8)	O1 ⁱ –Co–O3	91.63 (8)
N–Co–O1 ⁱⁱⁱ	167.59 (8)	O1 ⁱⁱⁱ –Co–O3	84.49 (8)
O1 ⁱ –Co–O1 ⁱⁱⁱ	87.09 (11)	O3 ⁱⁱ –Co–O3	174.65 (12)
N–Co–O3 ⁱⁱ	99.49 (9)		

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

Table 2

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

$D\text{--}H\cdots A$	$D\text{--}H$	$H\cdots A$	$D\cdots A$	$D\text{--}H\cdots A$
O3–H1 ⁱ ⋯O2 ⁱ	0.80	1.97	2.748 (3)	166
O3–H2 ⁱ ⋯O2 ⁱⁱ	0.82	1.85	2.645 (3)	164

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

The water H atoms were included in the refinement in fixed positions, while the remaining H atoms were refined in riding mode, with C–H distances of 0.93 Å.

Data collection: *SMART* (Bruker, 1997–2000); cell refinement: *SMART*; data reduction: *SAINT* (Siemens, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* (Siemens, 1990); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1395). Services for accessing these data are described at the back of the journal.

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