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catena-Poly[[[tetraaquacobalt(II)]-μ-4,4′-bipyridine-κ^2N:N'] 3-carboxylatophenoxyacetate monohydrate]

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.004 Å
R factor = 0.045
wR factor = 0.101
Data-to-parameter ratio = 15.1

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

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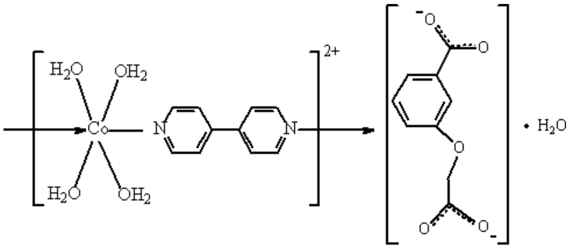
The asymmetric unit of the title one-dimensional coordination polymer, $\{[Co(C_{10}H_8N_2)(H_2O)_4](C_9H_6O_5)\cdot H_2O\}_n$, comprises two half-cations, $[Co(4,4'\text{-bipy})(H_2O)_4]_2^{2+}$ (4,4′-bipy is 4,4′-bipyridine), one 3-carboxylatophenoxyacetate (3-CPOA^{2-}) dianion and one non-coordinated water molecule. The Co^{II} ions, both of which are located on inversion centres, have approximately octahedral geometries, involving two N atoms of the centrosymmetric 4,4′-bipy ligand and four water molecules. Adjacent Co^{II} atoms are linked by 4,4′-bipy ligands into a chain, the shortest Co···Co separation within the polymeric chain being 11.456 (2) Å. The chains are further linked by hydrogen-bonding and π–π stacking interactions, generating a three-dimensional network.

Comment

Research on metal-directed supramolecular complexes has been expanding rapidly, due to their potential applications as functional materials. 4,4′-Bipyridine (4,4′-bipy) is a good example of a bridging ligand that can link metal centres into extended networks, and a number of one-, two- and three-dimensional metal–4,4′-bipy frameworks have been generated (Lu *et al.*, 1999; Zhou & Yu, 2001). In addition, the 3-carboxyphenoxyacetate dianion (3-CPOA^{2-}) can form hydrogen-bond arrays by functioning as both donor and acceptor, which could have a significant influence on the formation of supramolecular structures (Gu *et al.*, 2004). We have recently described the crystal structure of the analogous Zn^{II} complex, $[Zn(4,4'\text{-bipy})(H_2O)_4](3\text{-CPOA})\cdot H_2O$ (Zhao *et al.*, 2005). The title Co^{II} complex, (I), was synthesized under similar reaction conditions and is reported here. It is isostructural with its zinc congener.



(I)

As shown in Fig. 1, the asymmetric unit of (I) is composed of two half-cations, $[Co(4,4'\text{-bipy})(H_2O)_4]_2^{2+}$, one 3-carboxyphenoxyacetate dianion and one non-coordinated water molecule. The two Co^{II} ions are both located on inversion centres and both complete 4,4′-bipy molecules are generated from the half-molecules by inversion symmetry. Each Co^{II} ion

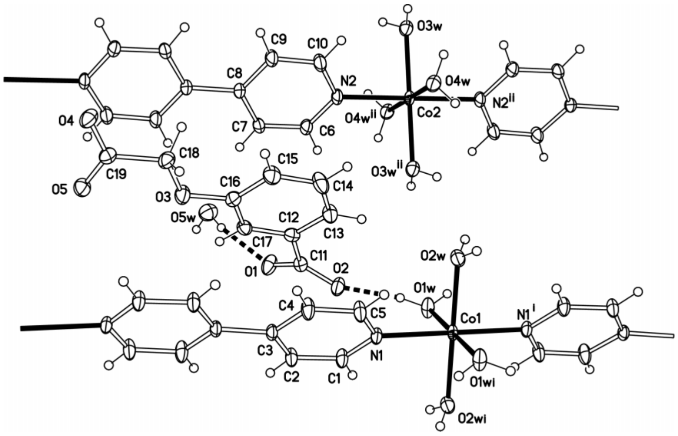


Figure 1
A view of (I), with displacement ellipsoids drawn at the 30% probability level and H atoms shown as arbitrary spheres. Hydrogen bonds are shown as dashed lines [symmetry codes: (i) $1 - x$, $-y$, $1 - z$; (ii) $-x$, $1 - y$, $1 - z$].

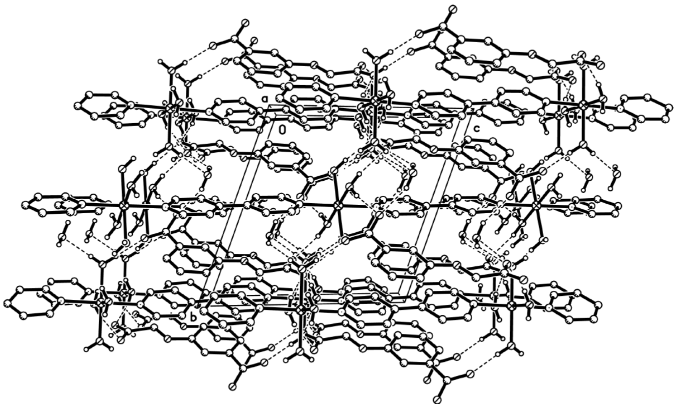


Figure 2
A packing diagram for (I). Hydrogen bonds are shown as dashed lines. H atoms attached to C atoms have been omitted for clarity.

is six-coordinated, by two N atoms of the 4,4′-bipy ligand and four water molecules, displaying an essentially regular octahedral geometry (Table 1).

The dihedral angles between the carboxyl groups and the benzene ring for the 3-CPOA^{2-} species are 29.5 (8)° (O1—C11—O2) and 14.6 (8)° (O4—C19—O5). The C12 benzene ring and the 4,4′-bipy ligands are almost parallel, with dihedral angles of 0.1 (8) and 12.3 (8)° for the N1/C1–C5 and N2/C6–C10 rings, respectively. The planes of the independent bipy rings (N1/C1–C5 and N2/C6–C10) are rotated by 12.3 (7)° with respect to each other.

The 4,4′-bipy ligands act in a bis-monodentate bridging mode to link two Co^{II} ions, giving rise to a one-dimensional chain running along the *c* axis of the unit cell, with a Co$\cdots$Co separation within the polymeric chain of 11.456 (2) Å. This value is slightly longer than the equivalent Zn$\cdots$Zn separation for the Zn^{II} analogue [11.425 (3) Å].

The polymeric chains are connected through extensive hydrogen bonds between the water molecules and the O atoms of the 3-carboxyphenoxyacetate anions, with O$\cdots$O distances in the range 2.657 (3)–3.440 (3) Å and O—H$\cdots$O angles in the range 141 (3)–179 (3)° (Table 2). There are also π–π stacking interactions between 4,4′-bipy molecules and 3-CPOA^{2-} benzene rings, with centroid–centroid distances of 3.777 (3) Å (N1 ring) and 3.704 (3) Å (N2 ring), leading to an extended network (Fig. 2).

Experimental

Cobalt diacetate trihydrate (2.38 g, 10 mmol), 4,4′-bipyridine (1.56 g, 10 mmol) and 3-CPOAH$_2$ (1.96 g, 10 mmol) were dissolved in water (20 ml), and the pH was adjusted to 7 with 0.1 *M* NaOH. The mixture was then sealed in a 25 ml Teflon-lined stainless steel bomb and held at 393 K for 5 d. The bomb was cooled to room temperature and pink prismatic crystals of (I) were obtained after several days. CHN analysis, calculated for $C_{38}H_{48}N_4O_{20}Co_2$: C 45.70, H 4.84, N 5.61%; found: C 45.87, H 4.79, N 5.65%.

Crystal data

$[Co(C_{10}H_8N_2)(H_2O)_4](C_9H_6O_5)\cdot H_2O$
$M_r = 499.33$
Triclinic, $P\overline{1}$
$a = 9.2704$ (19) Å
$b = 11.161$ (2) Å
$c = 11.456$ (2) Å
$\alpha = 108.72$ (3)°
$\beta = 106.56$ (3)°
$\gamma = 90.39$ (3)°
$V = 1069.7$ (5) Å^3
$Z = 1$
$D_x = 1.550$ Mg m^{-3}
Mo *K*α radiation
Cell parameters from 9892 reflections
$\theta = 3.2$–27.5°
$\mu = 0.86$ mm^{-1}
$T = 293$ (2) K
Prism, pink
0.35 × 0.26 × 0.17 mm

Data collection

Rigaku R-AXIS RAPID diffractometer
ω scans
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
$T_{min} = 0.752$, $T_{max} = 0.867$
10 238 measured reflections
4851 independent reflections
3354 reflections with $I > 2\sigma(I)$
$R_{int} = 0.036$
$\theta_{max} = 27.5°$
$h = -11 \rightarrow 12$
$k = -14 \rightarrow 14$
$l = -14 \rightarrow 13$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.045$
$wR(F^2) = 0.101$
$S = 1.02$
4851 reflections
322 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0528P)^2 + 0.1128P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.47$ e Å^{-3}
$\Delta\rho_{min} = -0.27$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Co1—N1	2.1644 (19)	Co1—O2*W*	2.1089 (19)
Co2—N2	2.161 (2)	Co2—O3*W*	2.0723 (19)
Co1—O1*W*	2.072 (2)	Co2—O4*W*	2.134 (2)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*W*—H1*W*1···O5*W*$^{\rm i}$	0.84 (3)	1.95 (3)	2.791 (3)	174 (3)
O1*W*—H1*W*2···O2	0.85 (3)	1.86 (3)	2.696 (3)	170 (3)
O2*W*—H2*W*1···O4$^{\rm iii}$	0.85 (3)	1.89 (3)	2.726 (3)	164 (3)
O2*W*—H2*W*2···O5$^{\rm iv}$	0.85 (3)	1.99 (3)	2.826 (3)	168 (3)
O3*W*—H3*W*1···O1$^{\rm v}$	0.85 (3)	1.83 (3)	2.657 (3)	164 (3)
O3*W*—H3*W*2···O5$^{\rm vi}$	0.85 (3)	1.91 (3)	2.756 (3)	170 (3)
O4*W*—H4*W*1···O2$^{\rm v}$	0.85 (3)	1.92 (3)	2.774 (3)	179 (3)
O4*W*—H4*W*2···O4$^{\rm iv}$	0.85 (3)	1.93 (3)	2.754 (3)	167 (2)
O5*W*—H5*W*1···O1	0.85 (2)	1.97 (3)	2.771 (3)	159 (3)
O5*W*—H5*W*2···O3$^{\rm vii}$	0.85 (3)	2.66 (3)	3.440 (3)	154 (3)
O5*W*—H5*W*2···O5$^{\rm vii}$	0.85 (3)	2.23 (2)	2.938 (3)	141 (3)

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

Water H atoms were located in a difference Fourier map and refined with O—H distance restraints of 0.85 (1) Å and constraints of $U_{\rm iso}$(H) = $1.5U_{\rm eq}$(O). H atoms on C atoms were placed in calculated positions, with C—H = 0.93 Å (aromatic) or 0.97 Å (aliphatic) and $U_{\rm iso}$(H) = $1.2U_{\rm eq}$(C), and were refined in the riding-model approximation.

Data collection: *RAPID-AUTO* (Rigaku, 1998); cell refinement: *RAPID-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC, 2002); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *SHELXL*97.

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