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Key indicators

Single-crystal X-ray study
 T = 293 K
 Mean $\sigma(C-C)$ = 0.003 Å
 R factor = 0.039
 wR factor = 0.105
 Data-to-parameter ratio = 14.9

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

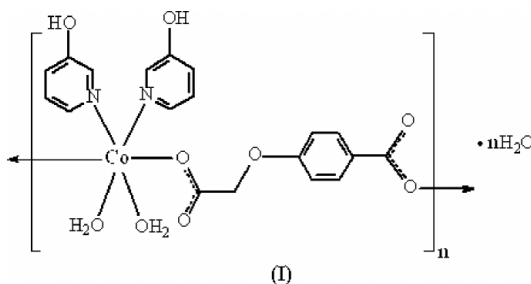
**catena-Poly[[[diaquabis(3-hydroxypyridine- κ N)-
 cobalt(II)]- μ -(4-carboxylatophenoxy)acetato- κ^2 O:O']
 monohydrate]**

In the title one-dimensional coordination polymer, $\{[Co(4-CPOA)(3-PyOH)_2(H_2O)_2] \cdot H_2O\}_n$ [4-CPOA²⁻ is the 4-carboxyphenoxyacetate dianion (C₉H₆O₅²⁻) and 3-PyOH is 3-hydroxypyridine (C₅H₅NO)], the Co^{II} atom has a distorted octahedral coordination geometry, defined by two carboxyl O-atom donors from two 4-CPOA²⁻ groups, two N-atom donors from two 3-PyOH co-ligands and two water molecules. The Co^{II} atoms are bridged by bis-monodentate carboxylate groups, forming a one-dimensional chain structure. The Co···Co separation within the polymer is 10.862 (3) Å. The chains are linked into a three-dimensional supramolecular network *via* O—H···O hydrogen bonds.

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Comment

Molecular self-assembly of supramolecular architectures has received much attention during recent decades (Tao *et al.*, 2000; Choi & Jeon, 2003). The structures and properties of such systems depend on the coordination and geometric preferences of both the central metal ions and the bridging building blocks, as well as on the influence of weaker non-covalent interactions, such as hydrogen bonds and π - π stacking interactions. As a building block, 4-carboxyphenoxyacetic acid (4-CPOAH₂) is a multidentate carboxylate ligand with both rigid and flexible parts, which not only has



multiple coordination possibilities but can also form regular hydrogen bonds by functioning as both a hydrogen-bond donor and acceptor. Hence, 4-CPOAH₂ is an excellent candidate for the construction of supramolecular complexes. However, there have been few reports to date on the coordination chemistry of 4-carboxyphenoxyacetic acid. Recently, we reported the structures of one mononuclear complex, [Mg(4-CPOAH)₂(H₂O)₄] (Gao *et al.*, 2004), and two one-dimensional polymers, [Mn(4-CPOA)(H₂O)₄]_n (Gu, Gao, Huo *et al.*, 2004) and [Ni(4-CPOA)(2,2'-bipyridine)(H₂O)]_n (Gu, Gao, Zhao *et al.*, 2004), in which the Mn^{II} and Ni^{II} atoms exhibit distorted pentagonal-bipyramidal and octahedral geometries, respectively. We have now isolated the title novel

one-dimensional Co^{II} complex, $\{[\text{Co}(4\text{-CPOA})(3\text{-PyOH})_2(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}\}_n$, (I), obtained by the reaction of 4-carboxyphenoxyacetic acid, 3-hydroxypyridine and cobalt diacetate trihydrate in an aqueous solution, and present its crystal structure here.

As illustrated in Fig. 1, the asymmetric unit of (I) consists of a single segment of a polymeric neutral Co^{II} complex, $[\text{Co}(4\text{-CPOA})(3\text{-PyOH})_2(\text{H}_2\text{O})_2]$, and one water molecule of crystallization. Each Co^{II} atom is coordinated by two O donors from different monodentate carboxyl groups, two N donors from two 3-PyOH co-ligands [mean $\text{Co}-\text{N}$ 2.151 (2) Å] and two water molecules, and displays a distorted octahedral coordination configuration. The equatorial plane is defined by the atoms O1W, O2W, N2 and O7ⁱ [symmetry code: (i) $x, y - 1, z$]; the r.m.s. deviation of this plane is 0.02 (3) Å and the deviation of the Co atom from the mean plane is 0.004 (2) Å. Atoms N1 and O3 occupy the apical sites, the N1–Co1–O3 angle being 177.53 (5)°.

The Co1–O3_{oxycarboxyl} distance [2.0974 (15) Å] is somewhat shorter than the Co1–O7_{carboxyl} distance [2.1266 (15) Å]. The two C–O bond distances of each carboxyl group are nearly identical (Table 1), suggesting delocalization of electrons throughout. The carboxyl group [O6–C19–O7] and benzene ring are almost coplanar, with a dihedral angle of 9.93 (5)°, while the phenoxyacetate group is twisted out of the benzene ring plane, the C13–O5–C12–C11 torsion angle being –81.1 (2)°. The dihedral angles between the benzene ring and 3-PyOH co-ligands are 70.9 (4) and 68.0 (4)°, and the dihedral angle between the 3-PyOH co-ligands is 50.7 (4)°.

Each 4-CPOA²⁻ group acts in a bis-monodentate mode to bridge two Co^{II} atoms, forming a one-dimensional chain structure (Fig. 2). The 3-PyOH molecules act as terminal co-ligands and lie on one side of the chain. These polymeric

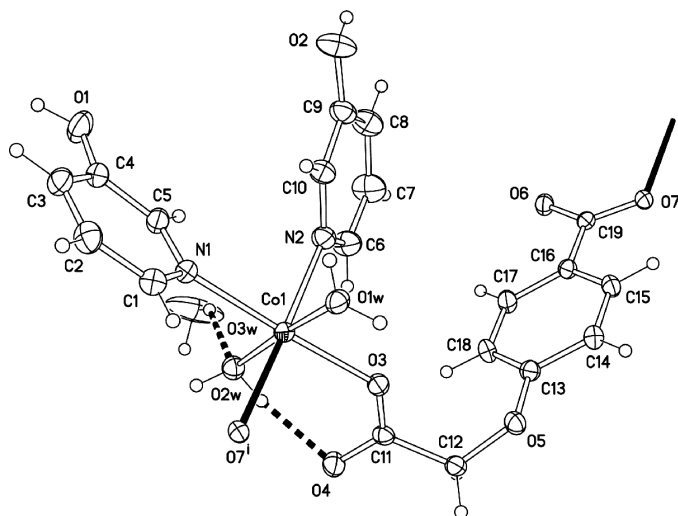


Figure 1

A view of the asymmetric unit of (I), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. Hydrogen bonds are shown as dashed lines.

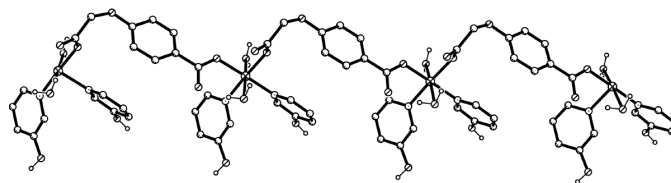


Figure 2

The one-dimensional chain structure of (I). C-bound H atoms and the O3W water molecule have been omitted for clarity.

chains run along the b axis of the unit cell and show a corrugated arrangement. Within the chain, the closest $\text{Co} \cdots \text{Co}$ distance is 10.862 (3) Å.

The chains are further connected through extensive O–H \cdots O hydrogen bonds involving water molecules, 3-PyOH molecules and 4-CPOA²⁻ groups, with the O \cdots O distances and O–H \cdots O angles varying from 2.600 (3) to 2.979 (4) Å and 145.4 to 177 (3)°, respectively, yielding a supramolecular hydrogen-bonded network (Table 2 and Fig. 3).

Experimental

The title complex was prepared by the addition of 3-hydroxypyridine (0.95 g, 10 mmol) and cobalt diacetate trihydrate (2.28 g, 10 mmol) to a hot aqueous solution of 4-carboxyphenoxyacetic acid (1.96 g, 10 mmol), and the pH was adjusted to 6 with 0.1 M sodium hydroxide. Pink crystals of (I) were separated from the filtered solution after several days. CHN analysis, calculated for $\text{C}_{19}\text{H}_{22}\text{N}_2\text{O}_{10}$: C 45.89, H 4.46, N 5.63%; found: C 46.01, H 4.40, N 5.68%.

Crystal data

$[\text{Co}(\text{C}_9\text{H}_6\text{O}_5)(\text{C}_5\text{H}_5\text{NO})_2(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$
 $M_r = 497.32$
 Triclinic, $P\bar{1}$
 $a = 7.5590$ (15) Å
 $b = 10.862$ (2) Å
 $c = 13.144$ (3) Å
 $\alpha = 72.12$ (3)°
 $\beta = 80.82$ (3)°
 $\gamma = 84.33$ (3)°
 $V = 1012.5$ (4) Å³

$Z = 2$
 $D_x = 1.631$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 8672 reflections
 $\theta = 3.2$ – 27.4 °
 $\mu = 0.91$ mm⁻¹
 $T = 293$ (2) K
 Prism, pink
 $0.36 \times 0.25 \times 0.18$ mm

Data collection

Rigaku R-Axis RAPID diffractometer
 ω scans
 Absorption correction: multi-scan (ABSCOR; Higashi, 1995)
 $T_{\min} = 0.735$, $T_{\max} = 0.853$
 9625 measured reflections

4570 independent reflections
 4127 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.023$
 $\theta_{\max} = 27.5$ °
 $h = -9 \rightarrow 9$
 $k = -14 \rightarrow 14$
 $l = -17 \rightarrow 17$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.039$
 $wR(F^2) = 0.105$
 $S = 1.03$
 4570 reflections
 307 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0647P)^2 + 0.5036P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.95$ e Å⁻³
 $\Delta\rho_{\min} = -0.65$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

Co1—N1	2.1621 (17)	Co1—O2W	2.1867 (17)
Co1—N2	2.1406 (19)	O3—C11	1.256 (2)
Co1—O3	2.0974 (15)	O4—C11	1.259 (2)
Co1—O7 ⁱ	2.1266 (15)	O6—C19	1.266 (2)
Co1—O1W	2.0695 (16)	O7—C19	1.272 (2)
N1—Co1—O2W	93.62 (6)	O7 ⁱ —Co1—N2	177.38 (6)
N2—Co1—N1	90.57 (7)	O7 ⁱ —Co1—O2W	85.75 (6)
N2—Co1—O2W	91.82 (7)	O1W—Co1—N1	87.73 (6)
O3—Co1—N1	177.53 (5)	O1W—Co1—N2	91.32 (7)
O3—Co1—N2	87.52 (7)	O1W—Co1—O3	90.74 (6)
O3—Co1—O7 ⁱ	93.38 (6)	O1W—Co1—O7 ⁱ	91.13 (7)
O3—Co1—O2W	88.01 (6)	O1W—Co1—O2W	176.56 (5)
O7 ⁱ —Co1—N1	88.59 (6)		

Symmetry code: (i) $x, y - 1, z$.

Table 2

Hydrogen-bonding geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1—H20 ^{iv} ···O6 ^{iv}	0.87 (3)	1.76 (3)	2.620 (2)	172 (4)
O2—H21 ^{iv} ···O3W ^{iv}	0.85 (3)	1.77 (3)	2.600 (3)	167 (4)
O1W—H1W2 ⁱⁱ ···O4 ⁱⁱ	0.84 (2)	1.96 (2)	2.798 (2)	177 (3)
O1W—H1W1 ⁱⁱⁱ ···O7 ⁱⁱⁱ	0.84 (2)	1.90 (2)	2.738 (2)	175 (3)
O2W—H2W2 ^{iv} ···O4	0.85 (2)	1.85 (2)	2.681 (2)	166 (3)
O2W—H2W1 ^{iv} ···O6 ⁱ	0.85 (2)	1.80 (2)	2.628 (2)	163 (3)
O3W—H3W2 ^v ···O1 ^v	0.85	2.24	2.979 (4)	145
O3W—H3W1 ^v ···O2W	0.85	2.01	2.752 (3)	146

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

H atoms bound to C atoms were placed in calculated positions, with $C-H = 0.93$ or 0.97 Å and $U_{iso}(H) = 1.2U_{eq}(C)$. The H atoms of the water molecules and hydroxy groups were located in a difference Fourier map and refined, with O—H distance restraints of 0.85 (1) Å and with $U_{iso}(H) = 1.5U_{eq}(O)$, except for the H atoms of the O3W water molecule, which were refined (AFIX AFX3-AFX0 command) in fixed positions, with $O-H = 0.85$ Å and $U_{iso}(H) = 1.5U_{eq}(O)$.

Data collection: *RAPID-AUTO* (Rigaku Corporation, 1998); cell refinement: *RAPID-AUTO*; data reduction: *CrystalStructure* (Rigaku/MS, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL97*.

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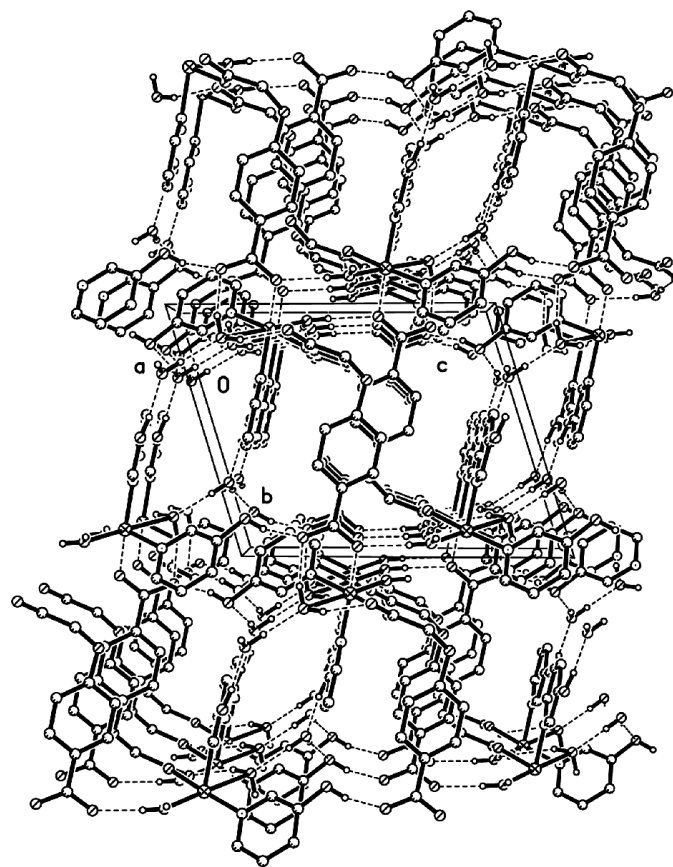


Figure 3

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

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