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Key indicators

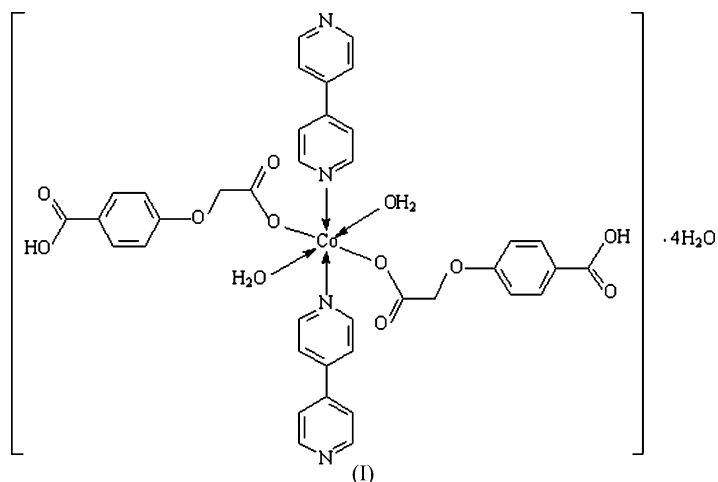
Single-crystal X-ray study
 $T = 295$ K
Mean $\sigma(\text{C}-\text{C}) = 0.004$ Å
 R factor = 0.042
 wR factor = 0.120
Data-to-parameter ratio = 15.0For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.Diaquabis(4,4'-bipyridine- κN)bis(4-carboxy-
phenoxyacetato- κO)cobalt(II) tetrahydrate

The crystal structure of the title complex, $[\text{Co}(\text{C}_9\text{H}_7\text{O}_5)_2(\text{C}_{10}\text{H}_8\text{N}_2)_2(\text{H}_2\text{O})_2] \cdot 4\text{H}_2\text{O}$ or $[\text{Co}(4\text{-CPOAH})_2(4,4'\text{-bipy})_2(\text{H}_2\text{O})_2] \cdot 4\text{H}_2\text{O}$ (4,4'-bipy is 4,4'-bipyridine and 4-CPOAH[−] is the 4-carboxyphenoxyacetate monoanion), consists of two independent mononuclear molecules that interact through the uncoordinated water molecules. The Co^{II} atoms lie on inversion centers and display an octahedral geometry defined by two oxyacetate O atoms of 4-CPOAH[−] groups, two N atoms of 4,4'-bipy ligands and two water molecules. A three-dimensional supramolecular network structure is formed through hydrogen-bonding interactions.

Received 31 October 2005
Accepted 3 November 2005
Online 10 November 2005

Comment

4-Carboxyphenoxyacetic acid (4-CPOAH₂) is a dicarboxylic acid with both rigid and flexible parts, and is an excellent candidate for the construction of supramolecular architectures. Recently, we have reported three one-dimensional Co^{II} polymers based on the 4-CPOA^{2−} ligand, namely $[\text{Co}(4\text{-CPOA})(3\text{-hydroxypyridine})_2(\text{H}_2\text{O})_2]_n$ (in which the 4-CPOA^{2−} group acts in a bis-monodentate mode; Gao *et al.*, 2004), $[\text{Co}(4\text{-CPOA})(1,10\text{-phenanthroline})(\text{H}_2\text{O})]_n$ and $[\text{Co}(4\text{-CPOA})(2,2'\text{-bipyridine})(\text{H}_2\text{O})]_n$ (in which the 4-CPOA^{2−} groups act in a tridentate mode; Gao, Huo, Gu, Liu *et al.*, 2005; Gao, Huo, Gu, Zhao *et al.*, 2005). In order to gain further insight into the Co^{II} binding modes of the 4-CPOAH₂ ligand, we have now isolated the title mononuclear Co^{II} complex, $[\text{Co}(4\text{-CPOAH})_2(4,4'\text{-bipy})_2(\text{H}_2\text{O})_2] \cdot 4\text{H}_2\text{O}$, (I), obtained by the reaction of 4-carboxyphenoxyacetic acid, 4,4'-bipyridine and cobalt diacetate trihydrate in an aqueous solution.



As illustrated in Fig. 1, the crystal structure consists of two independent neutral mononuclear Co^{II} molecules and eight

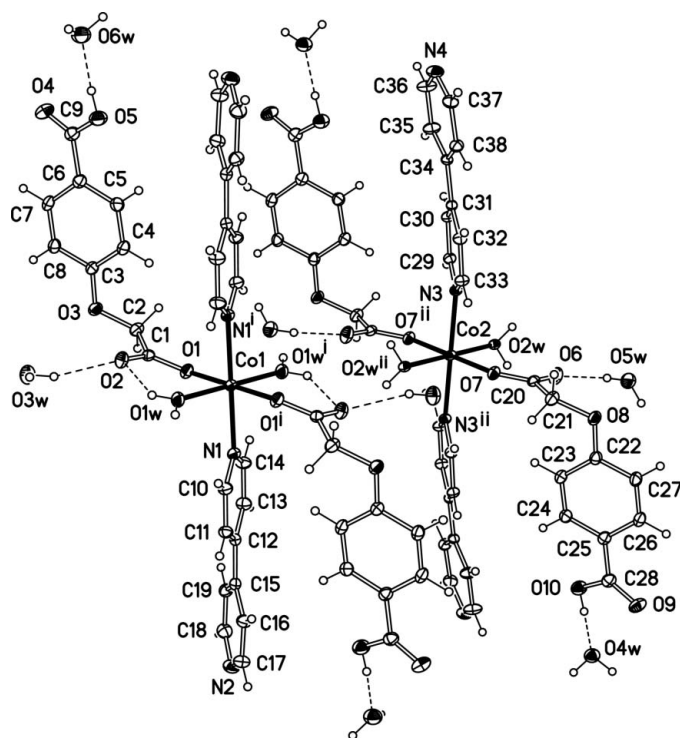


Figure 1
ORTEP plot (Johnson, 1976) of the title complex, with displacement ellipsoids drawn at the 30% probability level. Hydrogen bonds are indicated by dashed lines. [Symmetry codes: (i) $-x, 1-y, -z$; (ii) $1-x, 1-y, 1-z$.]

uncoordinated water molecules. The Co^{II} atoms are located on inversion centers and the 4-CPOAH⁻ ligands is mono-deprotonated. The Co^{II} atoms of the two molecules both display octahedral coordination, defined by two O atoms of 4-CPOAH⁻ groups, two N atoms of 4,4'-bipy ligands and two water molecules. Similar bond distances and angles are observed in the molecules, except that the $\text{Co1}-\text{O1w}$ bond is somewhat shorter than the $\text{Co2}-\text{O2w}$ bond (Table 1). The $\text{Co}-\text{N}$ and $\text{Co}-\text{O}$ bond distances are within the normal range in the reported Co^{II} complexes containing the 4-CPOA²⁻ ligand (Gao *et al.*, 2004; Gao, Huo, Gu, Liu *et al.*, 2005; Gao, Huo, Gu, Zhao *et al.*, 2005). The oxyacetate group is twisted out of the benzene plane and the $\text{C3}-\text{O3}-\text{C2}-\text{C1}$ and $\text{C22}-\text{O8}-\text{C21}-\text{C20}$ torsion angles are $88.3(3)$ and $-75.4(3)^\circ$, respectively. A three-dimensional supramolecular network structure is formed through the extended hydrogen-bonding interactions between water molecules, carboxylic acid OH groups and carboxylate O atoms (Table 2).

Experimental

The title complex was prepared by the addition of cobalt diacetate trihydrate (2.31 g, 10 mmol) and 4,4'-bipyridine (1.56 g, 10 mmol) to a hot aqueous solution of 4-carboxyphenoxyacetic acid (1.96 g, 10 mmol); the pH was adjusted to 6 with 0.1 M sodium hydroxide. The solution was allowed to evaporate at room temperature. Pink prismatic crystals separated from the filtered solution after several days. Analysis calculated for $\text{C}_{38}\text{H}_{42}\text{CoN}_4\text{O}_{16}$: C 52.48, H 4.87, N 6.44%; found: C 52.45, H 4.84, N 6.46%.

Crystal data

$[\text{Co}(\text{C}_9\text{H}_7\text{O}_5)_2(\text{C}_{10}\text{H}_8\text{N}_2)_2 \cdot (\text{H}_2\text{O})_2] \cdot 4\text{H}_2\text{O}$
 $M_r = 869.69$
 Triclinic, $P\bar{1}$
 $a = 10.807(2) \text{ \AA}$
 $b = 12.614(3) \text{ \AA}$
 $c = 16.055(3) \text{ \AA}$
 $\alpha = 103.89(3)^\circ$
 $\beta = 108.77(3)^\circ$
 $\gamma = 103.69(3)^\circ$
 $V = 1890.7(10) \text{ \AA}^3$

$Z = 2$
 $D_x = 1.528 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation
 Cell parameters from 13808 reflections
 $\theta = 3.2-27.5^\circ$
 $\mu = 0.54 \text{ mm}^{-1}$
 $T = 295(2) \text{ K}$
 Prism, pink
 $0.36 \times 0.26 \times 0.21 \text{ mm}$

Data collection

Rigaku R-Axis RAPID diffractometer
 ω scans
 Absorption correction: multi-scan (ABSCOR; Higashi, 1995)
 $T_{\text{min}} = 0.830, T_{\text{max}} = 0.895$
 18606 measured reflections

8539 independent reflections
 5898 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.026$
 $\theta_{\text{max}} = 27.5^\circ$
 $h = -13 \rightarrow 14$
 $k = -14 \rightarrow 16$
 $l = -20 \rightarrow 20$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.042$
 $wR(F^2) = 0.121$
 $S = 1.02$
 8539 reflections
 571 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0687P)^2 + 0.0415P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.58 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.27 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters ($\text{\AA}, ^\circ$).

$\text{Co1}-\text{O1w}$	2.0869 (18)	$\text{Co2}-\text{O7}$	2.0383 (15)
$\text{Co1}-\text{O1}$	2.0934 (17)	$\text{Co2}-\text{N3}$	2.1698 (17)
$\text{Co1}-\text{N1}$	2.1739 (18)	$\text{Co2}-\text{O2w}$	2.1718 (17)
$\text{O1w}-\text{Co1}-\text{O1w}^{\text{i}}$	180.0	$\text{O2w}^{\text{ii}}-\text{Co2}-\text{O2w}$	180.0
$\text{O1w}-\text{Co1}-\text{O1}$	91.61 (7)	$\text{O7}-\text{Co2}-\text{O2w}$	96.64 (6)
$\text{O1w}-\text{Co1}-\text{O1}^{\text{i}}$	88.39 (7)	$\text{O7}-\text{Co2}-\text{O2w}^{\text{ii}}$	83.36 (6)
$\text{O1w}-\text{Co1}-\text{N1}$	91.27 (8)	$\text{O7}^{\text{ii}}-\text{Co2}-\text{O7}$	180.0
$\text{O1w}-\text{Co1}-\text{N1}^{\text{i}}$	88.73 (8)	$\text{O7}-\text{Co2}-\text{N3}$	89.48 (7)
$\text{O1}-\text{Co1}-\text{O1}^{\text{i}}$	180.0	$\text{O7}-\text{Co2}-\text{N3}^{\text{ii}}$	90.52 (7)
$\text{O1}-\text{Co1}-\text{N1}^{\text{i}}$	89.34 (7)	$\text{N3}-\text{Co2}-\text{O2w}$	91.14 (7)
$\text{O1}-\text{Co1}-\text{N1}$	90.66 (7)	$\text{N3}-\text{Co2}-\text{O2w}^{\text{ii}}$	88.86 (7)
$\text{N1}^{\text{i}}-\text{Co1}-\text{N1}$	180.0	$\text{N3}-\text{Co2}-\text{N3}^{\text{ii}}$	180.0

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

Table 2

Hydrogen-bond geometry ($\text{\AA}, ^\circ$).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{O1w}-\text{H1w1}\cdots\text{O2}$	0.84 (2)	2.06 (2)	2.765 (3)	141 (2)
$\text{O1w}-\text{H1w2}\cdots\text{O5w}^{\text{iii}}$	0.85 (1)	2.01 (1)	2.835 (3)	165 (2)
$\text{O2w}-\text{H2w1}\cdots\text{N4}^{\text{iv}}$	0.85 (1)	2.05 (1)	2.884 (2)	167 (2)
$\text{O2w}-\text{H2w2}\cdots\text{N2}^{\text{v}}$	0.85 (2)	1.98 (1)	2.801 (3)	161 (2)
$\text{O3w}-\text{H3w1}\cdots\text{O2w}^{\text{iii}}$	0.85	2.05	2.867 (2)	160
$\text{O3w}-\text{H3w2}\cdots\text{O2}$	0.85	2.09	2.843 (2)	147
$\text{O4w}-\text{H4w1}\cdots\text{O3w}^{\text{vi}}$	0.87 (1)	1.96 (1)	2.828 (3)	176 (3)
$\text{O4w}-\text{H4w2}\cdots\text{O3w}^{\text{vii}}$	0.88 (3)	1.94 (3)	2.808 (3)	173 (3)
$\text{O5w}-\text{H5w1}\cdots\text{O4w}^{\text{vii}}$	0.86 (3)	2.14 (2)	2.869 (3)	143 (3)
$\text{O5w}-\text{H5w2}\cdots\text{O6}$	0.86 (3)	1.79 (3)	2.638 (3)	168 (4)
$\text{O6w}-\text{H6w1}\cdots\text{O5w}^{\text{viii}}$	0.85 (1)	1.97 (2)	2.734 (3)	150 (3)
$\text{O6w}-\text{H6w2}\cdots\text{O1}^{\text{ix}}$	0.84 (3)	2.17 (3)	2.995 (3)	165 (3)
$\text{O5}-\text{H12}\cdots\text{O6w}$	0.86 (1)	1.77 (1)	2.614 (3)	170 (4)
$\text{O10}-\text{H9}\cdots\text{O4w}$	0.85 (1)	1.71 (1)	2.561 (2)	174 (3)

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

C-bound H atoms were placed in calculated positions, with C—H = 0.93 or 0.97 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$, and were refined in the riding-model approximation. H atoms of the O3w water molecule were added using the *HYDROGEN* program (Nardelli, 1999), and refined with O—H = 0.85 Å and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O3w})$. The other H atoms of the water molecules and hydroxy groups were located in a difference map and refined with O—H restraints of 0.85 (1) Å, and with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$.

Data collection: *RAPID-AUTO* (Rigaku, 1998); cell refinement: *RAPID-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC, 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*.

The authors thank the National Natural Science Foundation of China (No. 20101003), the Scientific Fund of Remarkable

Teachers of Heilongjiang Province (No. 1054 G036), and Heilongjiang University for supporting this study.

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