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Aqua(benzene-1,4-dioxyacetate)bis(2,2-bipyridine)-cobalt(II) tetrahydrate

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Key indicators

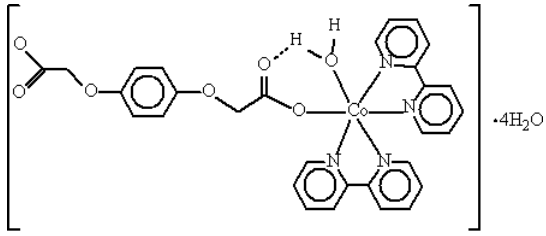
Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.004 Å
R factor = 0.051
wR factor = 0.097
Data-to-parameter ratio = 15.9

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

The title complex, $[Co(C_{10}H_8O_6)(C_{10}H_8N_2)_2(H_2O)]\cdot 4H_2O$, comprises a neutral Co^{II} complex and four solvent water molecules. The Co^{II} ion exhibits a slightly distorted octahedral configuration, defined by one O atom of the diacetate ligand, four N atoms of the 2,2-bipyridine ligands and one water molecule. The presence of hydrogen bonding and π–π stacking interactions leads to a supramolecular network structure.

Comment

Benzene-1,4-dioxyacetic acid (1,4-$BDOAH_2$), which has versatile binding ability, is a good candidate for the construction of supramolecular architectures. However, there is, as yet, limited structural information on complexes derived from the 1,4-$BDOAH_2$ ligand. Recently, we have reported some mononuclear structures containing the 1,4-BDOA dianion, namely $[MnCl(1,10\text{-phenanthroline})_2(H_2O)]_2(1,4\text{-BDOA})\cdot 2H_2O$ (Gao, Liu, Huo, Zhao & Zhao, 2004), $[Mn(H_2O)_6](1,4\text{-BDOA})$ (Liu, Huo *et al.*, 2004), $[Co(H_2O)_6](1,4\text{-BDOA})$ (Liu, Gao *et al.*, 2004), and $[Co(\text{triethanolamine})_2](1,4\text{-BDOA})$ (Gao, Liu, Huo & Ng, 2004), in which the carboxylate ligands do not coordinate to metal ions but rather function as counter-ions. In order to explore further the coordination behavior of metal ions with 1,4-$BDOAH_2$, we isolated a new Co^{II} complex, $[Co(1,4\text{-BDOA})(2,2'\text{-bipy})_2(H_2O)]\cdot 4H_2O$, (I), the crystal structure of which is reported here.



(I)

As shown in Fig. 1, the crystal structure of (I) consists of a neutral cobalt complex and four solvent water molecules. The Co atom is six-coordinate within a distorted octahedral N_4O_2 environment, defined by four N atoms of two 2,2′-bipy molecules, one O atom of a monodentate carboxylate ligand and one aqua ligand. The chelation of the 2,2′-bipy molecules is unsymmetrical, with the Co—N bond distances varying from 2.081 (2) to 2.104 (2) Å. The distance of Co—O(carboxylate) [2.106 (2) Å] is slightly shorter than that of Co—O(water) [2.125 (2) Å]. Around the Co atom, the *cis* angles vary from 78.59 (8) to 95.58 (8)°, and the *trans* angles from 170.42 (7) to

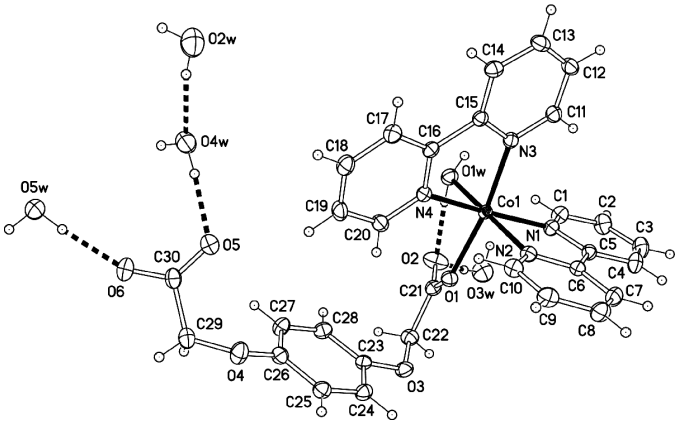


Figure 1
*ORTEP*II plot (Johnson, 1976) of (I), with displacement ellipsoids drawn at the 30% probability level, showing the hydrogen-bonding interactions as broken lines.

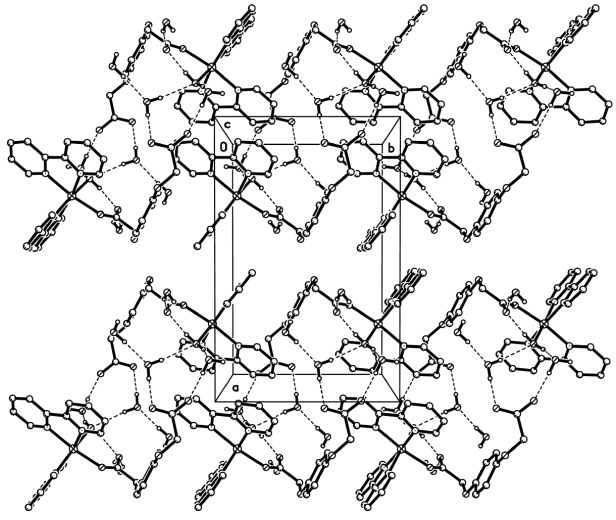


Figure 2
Packing diagram for (I). Dashed lines indicate hydrogen bonds.

173.55 (7)°. The 2,2′-bipy ligands are nearly perpendicular to each other [dihedral angle = 85.6 (3)°]. Extensive hydrogen bonding exists between the uncoordinated carboxylate O atoms and solvent water molecules, as well as the intramolecular interaction shown in Fig. 1; geometric parameters are given in Table 2. There are also π–π stacking interactions in the crystal structure, with the closest of these involving centrosymmetrically related 2,2′-bipy ligands; the shortest *Cg*···*Cg* (*Cg* is the centroid of the pyridine ring) contact of 3.8582 (12) Å occurs between rings containing atoms N3 and N4^{i} [symmetry code: (i) $1-x, 2-y, 1-z$]. In this way, a supramolecular three-dimensional network structure is constructed, as illustrated in Fig. 2.

Experimental

Benzene-1,4-dioxyacetic acid was prepared according to the method described for the synthesis of benzene-1,2-dioxyacetic acid by Mirci (1990). The title complex was prepared by the addition of a stoichiometric amount of $Co(OAc)_2{\cdot}6H_2O$ (20 mmol), NaOH (40 mmol) and 2,2′-bipy (20 mmol) to a hot aqueous solution of 1,4-$BDOAH_2$ (20 mmol), with subsequent filtration. Pink crystals were obtained at room temperature over several days. Analysis calculated for $C_{30}H_{34}CoN_4O_{11}$: C 52.56, H 5.00, N 8.17%; found: C 52.81, H 4.94, N 8.26%.

Crystal data

$[Co(C_{10}H_8O_6)(C_{10}H_8N_2)_2(H_2O)]\cdot 4H_2O$
$M_r = 685.54$
Monoclinic, $P2_1/n$
$a = 15.639$ (3) Å
$b = 10.152$ (2) Å
$c = 19.996$ (4) Å
$\beta = 92.23$ (3)°
$V = 3172.3$ (11) Å^3
$Z = 4$
$D_x = 1.435$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 23 569 reflections
$\theta = 3.1$–27.5°
$\mu = 0.61$ mm^{-1}
$T = 293$ (2) K
Prism, pink
0.36 × 0.24 × 0.18 mm

Data collection

Rigaku R-AXIS RAPID diffractometer
ω scans
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
$T_{min} = 0.811$, $T_{max} = 0.899$
28 373 measured reflections
7075 independent reflections
4616 reflections with $I > 2\sigma(I)$
$R_{int} = 0.067$
$\theta_{max} = 27.4°$
$h = -20 \rightarrow 20$
$k = -11 \rightarrow 13$
$l = -25 \rightarrow 25$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.051$
$wR(F^2) = 0.097$
$S = 1.01$
7075 reflections
445 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0409P)^2 + 0.6545P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.37$ e Å^{-3}
$\Delta\rho_{min} = -0.24$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Co1—O1	2.106 (2)	Co1—N2	2.103 (2)
Co1—O1*W*	2.125 (2)	Co1—N3	2.104 (2)
Co1—N1	2.090 (2)	Co1—N4	2.081 (2)
O1—Co1—O1*W*	87.40 (8)	O1*W*—Co1—N4	91.85 (8)
O1—Co1—N1	94.00 (7)	N1—Co1—N2	78.59 (8)
O1—Co1—N2	90.24 (8)	N1—Co1—N3	95.58 (8)
O1—Co1—N3	170.42 (7)	N1—Co1—N4	171.03 (8)
O1—Co1—N4	91.35 (7)	N2—Co1—N3	91.97 (8)
O1*W*—Co1—N1	95.58 (8)	N2—Co1—N4	94.21 (8)
O1*W*—Co1—N2	173.55 (7)	N3—Co1—N4	79.19 (8)
O1*W*—Co1—N3	91.34 (8)		

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*W*—H1*W*1···O2	0.85 (2)	1.79 (3)	2.626 (3)	165 (3)
O1*W*—H1*W*2···O5*W*^{i}	0.86 (3)	1.92 (4)	2.735 (3)	159 (3)
O2*W*—H2*W*1···O4*W*	0.85 (3)	2.09 (4)	2.924 (4)	165 (5)
O2*W*—H2*W*2···O5*W*^{ii}	0.84 (3)	2.31 (4)	3.138 (4)	166 (4)
O3*W*—H3*W*1···O2*W*^{iii}	0.85 (3)	2.01 (4)	2.846 (4)	168 (5)
O3*W*—H3*W*2···O2	0.85 (3)	1.99 (4)	2.813 (3)	163 (4)
O4*W*—H4*W*1···O5	0.86 (3)	1.86 (3)	2.722 (3)	176 (4)
O4*W*—H4*W*2···O1*W*^{i}	0.85 (3)	2.32 (4)	3.170 (3)	172 (4)
O5*W*—H5*W*1···O6	0.85 (3)	1.87 (3)	2.728 (3)	175 (4)
O5*W*—H5*W*2···O3*W*^{iv}	0.86 (2)	1.93 (3)	2.779 (4)	168 (3)

Symmetry codes: (i) $2-x, 1-y, 1-z$; (ii) $\frac{5}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$; (iii) $x-\frac{1}{2}, \frac{3}{2}-y, \frac{1}{2}+z$; (iv) $\frac{1}{2}+x, \frac{1}{2}-y, z-\frac{1}{2}$.

C-bound H atoms were placed in calculated positions [C—H = 0.93 (aromatic) or 0.97 Å (aliphatic) and $U_{iso}(H) = 1.2U_{eq}(C)$] in the riding-model approximation. Water H atoms were located in a difference map and refined with O—H and H···H distance restraints of 0.85 (1) and 1.39 (1) Å, respectively, and $U_{iso}(H) = 1.5U_{eq}(O)$.

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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