

Bis(acetato-*O*)diaqua(2,2'-bipyridyl-*N,N'*)cobalt(II) (OC-13): a two-dimensional material

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Key indicators

Single-crystal X-ray study

$T = 293\text{ K}$

Mean $\sigma(\text{C}-\text{C}) = 0.003\text{ \AA}$

R factor = 0.032

wR factor = 0.084

Data-to-parameter ratio = 17.0

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

The structure of the title compound, $[\text{Co}(\text{AcO})_2(2,2'\text{-bipy})(\text{H}_2\text{O})_2]$ or $[\text{Co}(\text{C}_2\text{H}_3\text{O}_2)_2(\text{C}_{10}\text{H}_8\text{N}_2)(\text{H}_2\text{O})_2]$, consists of mononuclear molecules with crystallographic twofold rotation symmetry. The Co atom displays a distorted tetragonally compressed octahedral environment, with a unique Co–N distance of 2.1227 (14) Å and Co–O distances in the range 2.0976 (13)–2.1256 (14) Å. The molecules are self-assembled *via* hydrogen bonds to form an one-dimensional chain and *via* aromatic–aromatic interactions giving a two-dimensional structure.

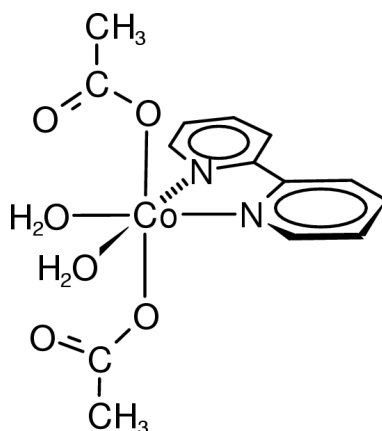
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Comment

The construction of coordination polymers with one-, two- and three-dimensional frameworks using directional interactions such as hydrogen-bonding and dative coordinate bonding has attracted much attention. In this sense, the utilization of hydrogen bonding is a well known design principle in the construction of a supramolecular architecture (Lehn, 1995). The introduction of hydrogen bonds can be achieved by the use of coordinating water molecules which tend to form hydrogen bonds with neighbouring nitrogen- and oxygen-containing organic units in order to link the network structures. As part of a study of the supramolecular organization of cobalt(II) carboxylate complexes (Carballo *et al.*, 2001), we report here the two-dimensional structure of the mononuclear mixed-ligand compound $[\text{Co}(\text{AcO})_2(2,2'\text{-bipy})(\text{H}_2\text{O})_2]$, (I).



(I)

Compound (I) is isostructural with the nickel(II) complex $[\text{Ni}(\text{AcO})_2(2,2'\text{-bipy})(\text{H}_2\text{O})_2]$ (Ye *et al.*, 1998), which has a two-dimensional structure generated *via* hydrogen bonding between the hydrophilic groups and *via* π - π interactions

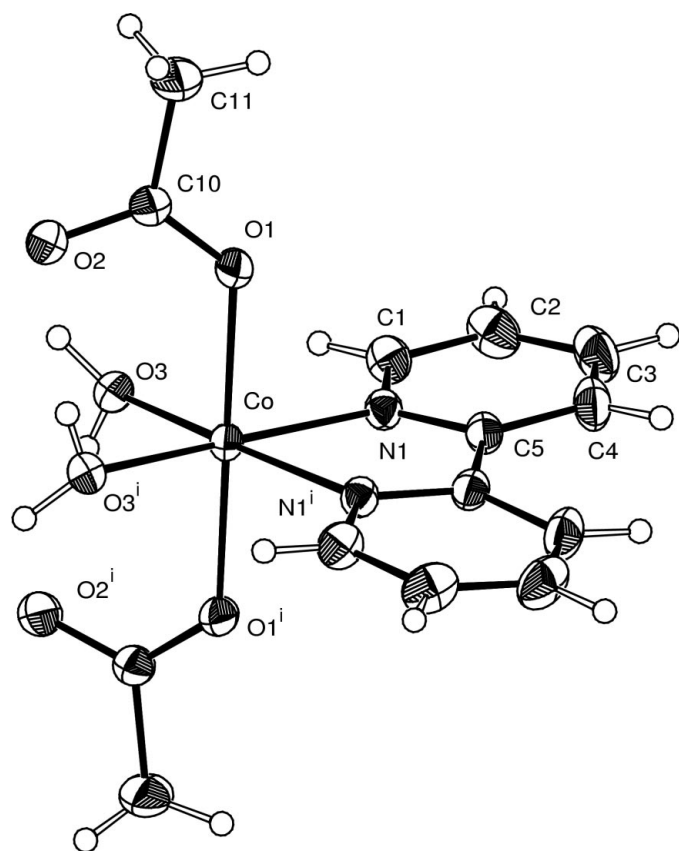


Figure 1
ZORTEP (Zsolnai & Huttner, 1994) diagram of $[\text{Co}(\text{AcO})_2(2,2'\text{-bipy})(\text{H}_2\text{O})_2]$ showing the atom-numbering system. Non-H atoms are represented as ellipsoids drawn at the 30% probability level.

between the hydrophobic groups. In (I), the cobalt(II) atom lies on a twofold axis (*e* position in the Wyckoff notation) and is six-coordinate, bound in equatorial positions to the nitrogen atoms of one 2,2'-bipyridyl molecule and two aqua ligands, and in apical positions to two unidentate acetates. The bond lengths between cobalt and its surrounding atoms (Table 1) are similar, but not exactly equal, to those found in the nickel compound. The $\text{Co}-\text{O}_{\text{acetate}}$ bond is only slightly longer than $\text{Ni}-\text{O}_{\text{acetate}}$ [2.079 (2) Å], but more significant is the lengthening of the $\text{Co}-\text{N}$ bond [2.1229 (14) Å] compared with $\text{Ni}-\text{N}$ (2.069(2) Å). However, the two mutually *trans* $\text{Co}-\text{O}_{\text{acetate}}$ distances are shorter than the remaining four bond distances in (I), denoting a kind of distortion in the octahedral coordination geometry around Co^{II} absent in the Ni^{II} analogue. The Co^{II} ion with a high-spin d^7 electron configuration is subject to a Jahn–Teller effect and, as a result, a tetragonally compressed octahedral geometry is present in (I). There are no significant differences in the C–O distances in the acetate group [1.257 (2) and 1.253 (2) Å], due to the involvement of the uncoordinated O2 in two strong hydrogen bonds, giving rise to a pseudo-bridging behaviour of the carboxylate group (Deacon & Phillips, 1980). The individual pyridine rings of the 2,2'-bipyridyl ligand are planar, but the dihedral angle between the two pyridyl rings is 8.2 (1)°.

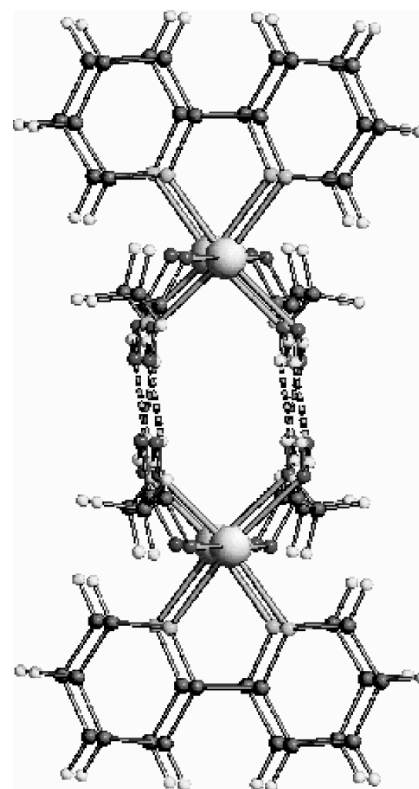


Figure 2
SCHAKAL (Keller, 1988) diagram showing the packing due to $\pi-\pi$ interactions.

There are intra- and intermolecular hydrogen-bonding interactions between the water molecules and the uncoordinated $\text{O}_{\text{carboxylate}}$ O2 (Table 2). Each water molecule, as donor, and each O2 atom, as acceptor, participate in two hydrogen bonds, one intra- ($\text{O}3-\text{H}3\text{A}\cdots\text{O}2^{\text{i}}$; symmetry code as in Table 2) and another intermolecular ($\text{O}3-\text{H}3\text{B}\cdots\text{O}2^{\text{ii}}$; symmetry code as in Table 2). The intermolecular hydrogen bond involves two O2 atoms of two neighbouring molecules, giving a one-dimensional zigzag chain extending along the *c* axis, thus forming channels as shown in Fig. 2. The separation between the planes of each pair of adjacent pyridyl rings in this chain is 8.15 Å. The intercalation of bipyridyl groups on one side of a chain with those on the next chain expands the structure into a two-dimensional network (Fig. 3). As result of the intercalation, the aromatic ring planes overlap in an offset or displaced geometry with a significant ring slippage, to the extent that only some atom–atom contacts have distance values accepted for a $\pi-\pi$ interaction (Janiak, 2000), the shortest distance being 3.698 Å for $\text{C}4\cdots\text{C}5^{\text{iii}}$ [symmetry code: (iii) $x, -y, 1/2+z$].

Experimental

Compound (I) was obtained as a by-product from the mother liquor resulting from the synthesis of $[\text{Co}(\text{HBENO})_2(2,2'\text{-bipy})_2]$ (Carballo *et al.*, unpublished) from cobalt(II) acetate, benzoic acid (=

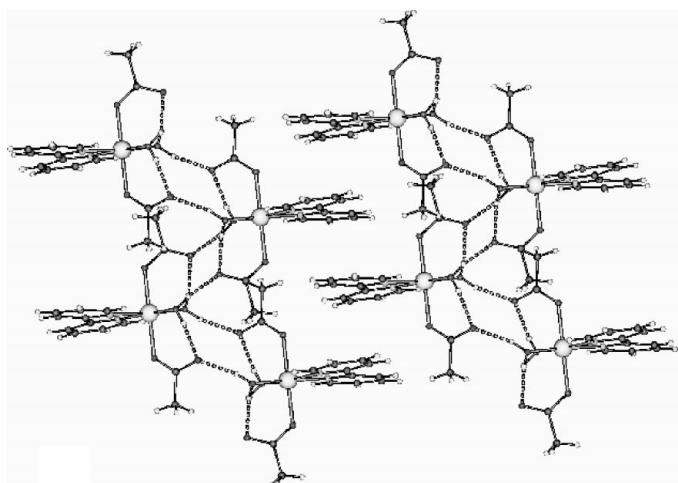


Figure 3
SCHAKAL (Keller, 1988) diagram showing the one-dimensional zigzag chains.

H₂BENO) and 2,2'-bipyridyl in isopropyl alcohol; m.p. >523 K. Analysis found: C 45.5, H 5.2, N 7.6%; C₁₄H₁₈N₂O₆Co requires: C 45.5, H 4.9, N 7.6%. IR (KBr, cm⁻¹): 3284 (vs, br) ν(OH), 1557 (vs) ν_{asym}(COO), 1417 (vs) ν_{sym}(COO) [$\Delta\nu = \nu_{asym}(\text{COO}) - \nu_{sym}(\text{COO}) = 140$]; 1471 (m), 1340 (m), 1162 (m), 1050 (m), 1020 (m), 773 (s), 739 (m), 657 (s) bands due to 2,2'-bipyridyl.

Crystal data

[Co(C ₂ H ₃ O ₂) ₂ (C ₁₀ H ₈ N ₂)(H ₂ O) ₂]	$D_x = 1.514 \text{ Mg m}^{-3}$
$M_r = 369.23$	Mo $K\alpha$ radiation
Monoclinic, C2/c	Cell parameters from 2454 reflections
$a = 15.4398 (17) \text{ \AA}$	$\theta = 2.6\text{--}28.0^\circ$
$b = 12.8818 (14) \text{ \AA}$	$\mu = 1.09 \text{ mm}^{-1}$
$c = 8.1537 (9) \text{ \AA}$	$T = 293 (2) \text{ K}$
$\beta = 92.890 (2)^\circ$	Prism, orange
$V = 1619.6 (3) \text{ \AA}^3$	$0.24 \times 0.14 \times 0.12 \text{ mm}$
$Z = 4$	

Data collection

Bruker SMART CCD area-detector diffractometer	1907 independent reflections
φ and ω scans	1623 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	$R_{\text{int}} = 0.029$
$T_{\text{min}} = 0.783$, $T_{\text{max}} = 0.877$	$\theta_{\text{max}} = 28.0^\circ$
5035 measured reflections	$h = -19 \rightarrow 20$
	$k = -17 \rightarrow 12$
	$l = -10 \rightarrow 10$

Refinement

Refinement on F^2	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)] = 0.032$	$w = 1/[\sigma^2(F_o^2) + (0.0486P)^2]$
$wR(F^2) = 0.084$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.03$	$(\Delta/\sigma)_{\text{max}} = 0.001$
1907 reflections	$\Delta\rho_{\text{max}} = 0.33 \text{ e \AA}^{-3}$
112 parameters	$\Delta\rho_{\text{min}} = -0.34 \text{ e \AA}^{-3}$

Table 1

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

Co—O1	2.0974 (13)	O2—C10	1.253 (2)
Co—N1	2.1229 (14)	C10—C11	1.511 (3)
Co—O3	2.1258 (13)	N1—C5	1.343 (2)
O1—C10	1.257 (2)	N1—C1	1.343 (2)
O1 ⁱ —Co—O1	179.96 (7)	N1—Co—O3 ⁱ	170.59 (5)
O1—Co—N1 ⁱ	90.83 (5)	O1—Co—O3	92.71 (5)
O1—Co—N1	89.14 (5)	N1—Co—O3	94.72 (6)
N1 ⁱ —Co—N1	76.62 (8)	O3 ⁱ —Co—O3	94.15 (8)
O1—Co—O3 ⁱ	87.32 (5)		

Symmetry code: (i) $-x, y, \frac{3}{2} - z$.

Table 2

Hydrogen-bonding geometry (\AA , $^\circ$).

$D\text{--}H\cdots A$	$D\text{--}H$	$H\cdots A$	$D\cdots A$	$D\text{--}H\cdots A$
O3—H3A ⁱ ⋯O2 ⁱ	0.768 (16)	1.887 (17)	2.635 (2)	164 (3)
O3—H3B ⁱ ⋯O2 ⁱⁱ	0.86 (2)	1.92 (2)	2.7663 (19)	165 (2)

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

The H atoms bound to O3 (aqua ligand) were refined with a common isotropic displacement parameter. All other H atoms were included with a riding model.

Data collection: SMART (Bruker, 1998); cell refinement: SAINT (Bruker, 1998); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1990); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: ZORTEP (Zsolnai & Huttner, 1994) and SCHAKAL (Keller, 1988); software used to prepare material for publication: SHELXL97.

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