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μ-Acetato-di-μ-hydroxo-bis{acetato[bis(2-pyridyl)amine]cobalt(III)} acetate tetrahydrate: a novel mixed-bridged dinuclear Co^{III} complex with bis(2-pyridyl)amine as terminal ligands

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Key indicators

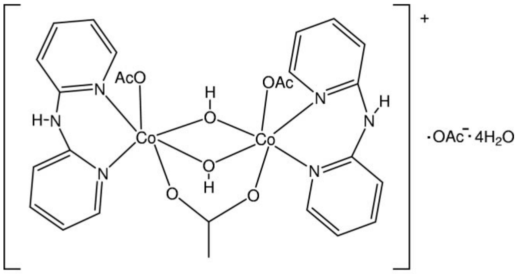
Single-crystal X-ray study
T = 298 K
Mean σ(C–C) = 0.008 Å
H-atom completeness 81%
R factor = 0.048
wR factor = 0.142
Data-to-parameter ratio = 14.5

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

The complex cation of the title compound, $[Co_2(C_2H_3O_2)_3(OH)_2(C_{10}H_9N_3)_2](C_2H_3O_2)\cdot 4H_2O$, has a $[Co_2(\mu\text{-}OH)_2(\mu\text{-}OAc)(OAc)_2(bpa)_2]^+$ dimeric core [bpa is bis(2-pyridyl)amine and OAc is acetate], in which two Co^{III} centers are linked by two OH$^-$ and one OAc$^-$ bridges with a Co$\cdots$Co separation of 2.8276 (10) Å. Each Co^{III} ion has an approximate octahedral geometry, coordinated by two pyridyl N atoms of the terminal bpa ligand, and four O-atom donors derived from two OH$^-$ bridges, one OAc$^-$ bridge and a monodentate coordinated OAc$^-$ anion. Intramolecular and intermolecular hydrogen-bonding interactions stabilize this structure.

Comment

The bis(2-pyridyl)amine molecule (bpa) represents an important class of chelating ligand, and has attracted considerable interest for a long period (Du *et al.*, 2003, and references therein). The reaction of bis(2-pyridyl)amine with Co^{II} perchlorate in the presence of azide anions affords the mononuclear complex diazido[bis(2-pyridyl)amine-κ^2N,N']cobalt(III) perchlorate (Du *et al.*, 2001). We report here the molecular structure of a novel triply bridged dinuclear Co^{III} complex, $[Co_2(\mu\text{-}OH)_2(\mu\text{-}OAc)(OAc)_2(bpa)_2](OAc)\cdot 4H_2O$, (I).



(I)

The crystal structure of (I) consists of a $[Co_2(\mu\text{-}OH)_2(\mu\text{-}OAc)(OAc)_2(bpa)_2]^+$ cation, one OAc$^-$ ion and four uncoordinated water molecules. In the dinuclear complex cation (Fig. 1), two crystallographically independent Co^{III} ions are bridged by two OH$^-$ ions and one OAc$^-$ group (in *syn–syn* mode), with a Co$\cdots$Co separation of 2.8276 (10) Å. Each Co^{III} center is coordinated by two pyridyl N atoms of the terminal bpa ligand (in *trans–trans* mode), and four O-atom donors derived from two OH$^-$ bridges, one OAc$^-$ bridge and a monodentate coordinated OAc$^-$ ion, forming an approximate octahedral geometry. Selected bond lengths and angles are listed in Table 1. The two Co—O$_{OH}$—Co bridging angles are

96.94 (12) and 96.58 (12)°. The Co—O_{OH} distances are in the range 1.883 (3)–1.894 (3) Å, with a mean value of 1.891 (3) Å, agreeing well with the structural parameters of related compounds (Okamoto *et al.*, 1991; Chen *et al.*, 1995). Two terminal bidentate bis(2-pyridyl)amine molecules coordinate to the Co^{III} ions to form two six-membered chelate rings, each with a flattened boat conformation. The dihedral angles between the pyridyl rings within each bpa ligand are 27.1 (3) and 28.0 (3)°.

An analysis of the crystal packing shows the existence of intramolecular and intermolecular hydrogen bonds, which stabilize this structure. Each bridging O—H group forms an intramolecular hydrogen bond with the adjacent monodentate OAc^- ion (Fig. 1 and Table 2). Two N—H groups of the bpa ligands form a pair of N—H···O hydrogen bonds with the uncoordinated OAc^- ion and one uncoordinated water molecule; the geometry is typical of normal hydrogen bonds (Desiraju & Steiner, 1999). Examination of this structure with *PLATON* (Spek, 2003) indicates that there are no solvent-accessible voids in the crystal structure.

Experimental

A mixture of $Co(OAc)_2·H_2O$ (39 mg, 0.2 mmol) and bis(2-pyridyl)amine (34 mg, 0.2 mmol) was dissolved in methanol/water (25 ml) with stirring and heating. The resultant red solution was filtered and left to stand at room temperature. Well defined block-shaped single crystals of the title complex were obtained by slow evaporation of the solvent over a period of two weeks (yield: 36 mg, 45%). IR (KBr pellet, cm^{-1}): 3423 (*b*), 1641 (*s*), 1590 s (*s*), 1535 (*s*), 1479 (*vs*), 1421 (*s*), 1338 (*m*), 1270 (*w*), 1237 (*m*), 1160 (*m*), 1025 (*m*), 772 (*m*). Analysis calculated for the title compound: C 41.91, H 5.02, N 10.47%; found: C 41.80, H 4.68, N 10.56%.

Crystal data

$[Co_2(C_2H_3O_2)_3(OH)_2(C_{10}H_9N_3)_2](C_2H_3O_2)·4H_2O$
$M_r = 802.52$
Triclinic, $P\bar{1}$
$a = 11.285 (3)$ Å
$b = 11.862 (3)$ Å
$c = 16.449 (4)$ Å
$\alpha = 80.970 (4)°$
$\beta = 71.818 (4)°$
$\gamma = 62.518 (4)°$
$V = 1855.7 (8)$ Å^3
$Z = 2$
$D_x = 1.436$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 957 reflections
$\theta = 1.6–22.4°$
$\mu = 0.96$ mm^{-1}
$T = 298 (2)$ K
Block, red
0.38 × 0.30 × 0.24 mm

Data collection

Bruker SMART 1000 diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1997)
$T_{min} = 0.711$, $T_{max} = 0.802$
7796 measured reflections
6534 independent reflections
4413 reflections with $I > 2\sigma(I)$
$R_{int} = 0.028$
$\theta_{max} = 25.0°$
$h = -7 \rightarrow 13$
$k = -13 \rightarrow 14$
$l = -17 \rightarrow 19$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.048$
$wR(F^2) = 0.142$
$S = 1.00$
6534 reflections
451 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0765P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.65$ e Å^{-3}
$\Delta\rho_{min} = -0.32$ e Å^{-3}

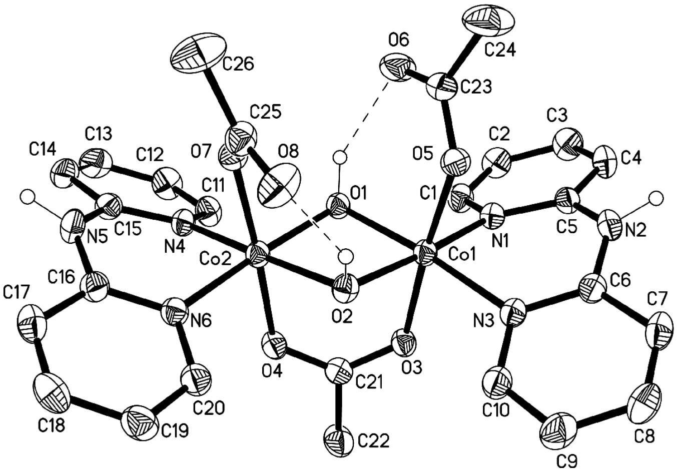


Figure 1
The molecular structure of the cation of (I), showing the intramolecular hydrogen-bonding interactions (indicated by dashed lines), with displacement ellipsoids drawn at the 30% probability level. The uncoordinated water molecules and uncoordinated OAc^- ion have been omitted for clarity.

Table 1
Selected geometric parameters (Å, °).

Co1—O2	1.894 (3)	Co2—O1	1.883 (3)
Co1—O1	1.894 (3)	Co2—O2	1.894 (3)
Co1—O5	1.898 (3)	Co2—O7	1.907 (3)
Co1—O3	1.907 (3)	Co2—O4	1.913 (3)
Co1—N3	1.934 (3)	Co2—N6	1.925 (3)
Co1—N1	1.937 (3)	Co2—N4	1.926 (3)
Co1—Co2	2.8276 (10)		
O2—Co1—O1	82.21 (11)	O1—Co2—O7	91.51 (12)
O2—Co1—O5	91.74 (12)	O2—Co2—O7	96.08 (12)
O1—Co1—O5	96.43 (11)	O1—Co2—O4	89.55 (12)
O2—Co1—O3	88.09 (12)	O2—Co2—O4	88.18 (12)
O1—Co1—O3	88.78 (11)	O7—Co2—O4	175.71 (12)
O5—Co1—O3	174.72 (12)	O1—Co2—N6	176.31 (12)
O2—Co1—N3	93.70 (13)	O2—Co2—N6	93.92 (13)
O1—Co1—N3	174.61 (12)	O7—Co2—N6	89.77 (13)
O5—Co1—N3	87.18 (13)	O4—Co2—N6	89.43 (13)
O3—Co1—N3	87.56 (13)	O1—Co2—N4	92.29 (13)
O2—Co1—N1	174.86 (12)	O2—Co2—N4	173.92 (13)
O1—Co1—N1	92.68 (13)	O7—Co2—N4	87.16 (13)
O5—Co1—N1	89.44 (13)	O4—Co2—N4	88.65 (13)
O3—Co1—N1	91.19 (13)	N6—Co2—N4	91.23 (14)
N3—Co1—N1	91.35 (14)	O1—Co2—Co1	41.67 (8)
O2—Co1—Co2	41.71 (8)	O2—Co2—Co1	41.71 (8)
O1—Co1—Co2	41.38 (8)	O7—Co2—Co1	101.72 (8)
O5—Co1—Co2	102.07 (9)	O4—Co2—Co1	81.81 (8)
O3—Co1—Co2	81.27 (8)	N6—Co2—Co1	134.65 (10)
N3—Co1—Co2	133.92 (10)	N4—Co2—Co1	132.58 (10)
N1—Co1—Co2	133.15 (10)	Co2—O1—Co1	96.94 (12)
O1—Co2—O2	82.50 (11)	Co1—O2—Co2	96.58 (12)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2*B*···O9^i	0.86	1.998	2.789 (5)	153
N5—H5*A*···O11	0.86	2.036	2.814 (6)	150
O1—H1···O6	0.84	1.940	2.657 (6)	142
O2—H2···O8	0.85	1.925	2.683 (6)	148

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

With the exception of the H atoms of the water molecules, which could not be located, all the H atoms were placed in geometrically calculated positions after checking their presence in a difference map, and included in the final refinement in the riding-model approximation: N—H = 0.86 Å, O—H = 0.84 Å, C—H = 0.93–0.96 Å, and $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C,N) for aromatic C and N atoms, and 1.5$U_{\rm eq}$(O,C) for hydroxy O and acetate C atoms.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1998); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL* (Bruker, 1998); software used to prepare material for publication: *SHELXL*97.

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