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Key indicators

Single-crystal X-ray study
 T = 295 K
 Mean $\sigma(\text{C}-\text{C}) = 0.003 \text{ \AA}$
 H-atom completeness 98%
 Disorder in solvent or counterion
 R factor = 0.032
 wR factor = 0.078
 Data-to-parameter ratio = 13.2

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

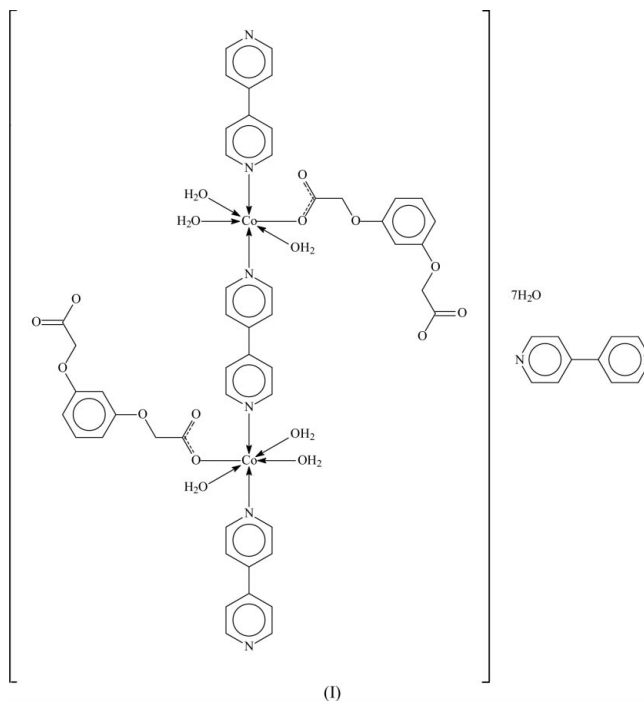
μ -4,4'-Bipyridine- $\kappa^2\text{N}:\text{N}'$ -bis[triaqua(4,4'-bipyridine- $\kappa^2\text{N},\text{N}'$)[1,3-phenylenedi(oxyacetato)- κO]cobalt(II)] 4,4'-bipyridine heptahydrate

The reaction of cobalt(II) diacetate, disodium 1,3-phenyldi(oxyacetate) and 4,4'-bipyridine in water at neutral pH affords the title compound, $[\text{Co}_2(\text{C}_{10}\text{H}_8\text{O}_6)_2(\text{C}_{10}\text{H}_8\text{N}_2)_3(\text{H}_2\text{O})_6] \cdot \text{C}_{10}\text{H}_8\text{N}_2 \cdot 7\text{H}_2\text{O}$. The dinuclear complex is generated from a unique half-molecule by twofold symmetry; it contains a bridging 4,4'-bipyridine molecule connected to two cobalt(II) atoms, each of which is covalently bonded to a carboxylate unit, another 4,4'-bipyridine molecule and three water molecules in octahedral geometry. The non-coordinated 4,4'-bipyridine molecule is stacked over the bridging 4,4'-bipyridine molecule at a separation of about 3.5 Å, and accepts hydrogen bonds at each N atom from coordinated water molecules.

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Comment

The cobalt(II) derivative of 1,3-phenyldi(oxyacetic acid) exists as a tetraaqua tetrahydrate complex in which the metal atom is linked to four water molecules and two hydrogen 1,3-phenyldi(oxyacetate) monoanions (Liu, Huo, Gao, Zhao & Zhao, 2004b). The introduction of the 4,4'-bipyridine spacer ligand was expected to neutralize the carboxylic acid $-\text{CO}_2\text{H}$ groups, but this reaction did not occur. Instead, the title



compound (I) (Fig. 1) arose, in which the ligand functions as a spacer between two cobalt centers, each of which is also coordinated by three water molecules and the carboxyl $-\text{CO}_2$

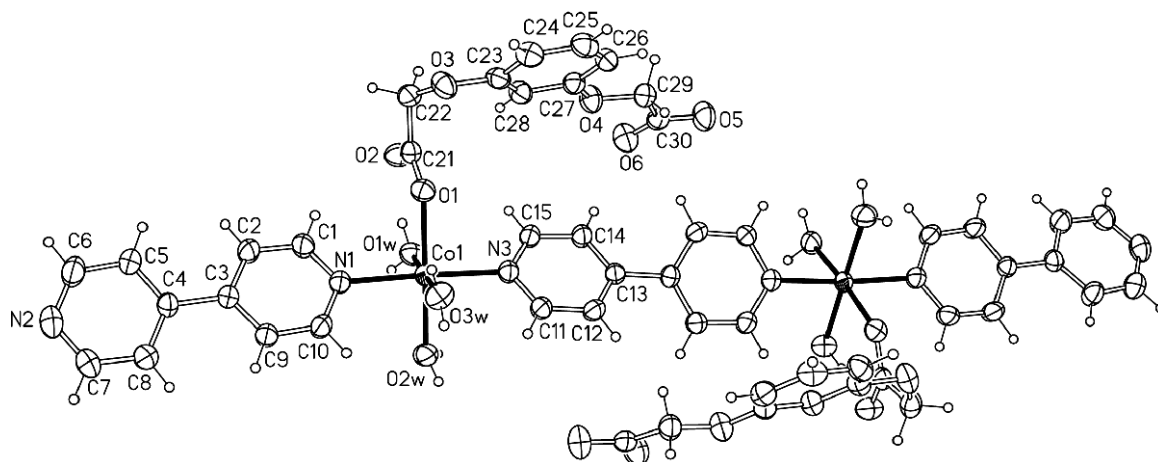


Figure 1
View of the $[(C_{10}H_8N_2)_3(C_{10}H_8O_6)_2(H_2O)_6Co_2]$ molecule in (I) with displacement ellipsoids drawn at the 50% probability level and H atoms shown as spheres of arbitrary radii. The dinuclear molecule lies on a twofold rotation axis that passes mid-way between the pyridyl rings of the bridging 4,4'-bipyridine ligand.

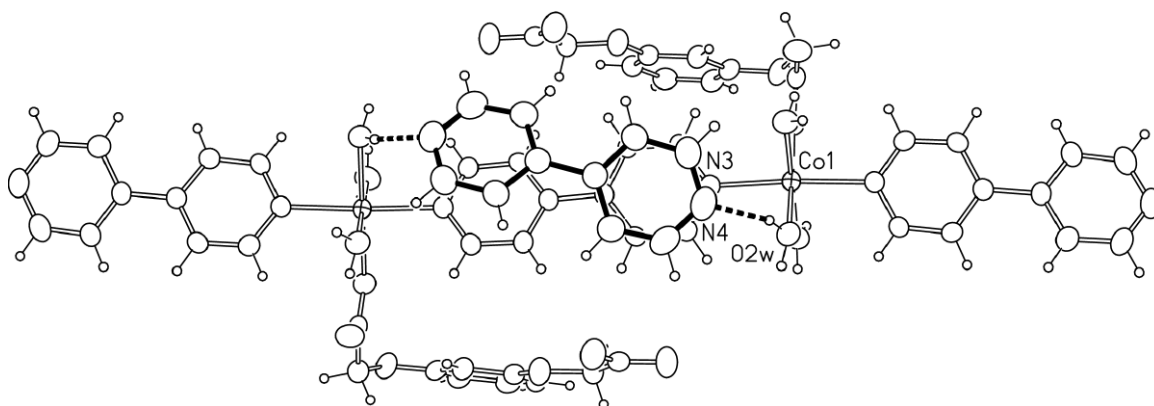


Figure 2
Detail of (I), showing the stacking of the non-coordinated 4,4'-bipyridine over the bridging 4,4'-bipyridine unit of the $[(C_{10}H_8N_2)_3(C_{10}H_8O_6)_2(H_2O)_6Co_2]$ molecule. Displacement ellipsoids are drawn at the 50% probability level. H atoms are shown as spheres of arbitrary radii. Hydrogen bonds are shown as dashed lines.

end of a doubly deprotonated 1,3-phenyldi(oxyacetate) dianion. A second 4,4'-bipyridine molecule uses only one N atom to coordinate, the other accepting hydrogen bond interactions. Overall, the dinuclear complex is generated by twofold symmetry from the unique atoms. The dihedral angle between the two central pyridine rings containing C13 and C13ⁱ ($i = -x, y, 1 - z$) is 31.4 (1)°. Seven non-coordinated water molecules are present in (I) and help to consolidate the unit cell packing through hydrogen bonds (Table 2). A non-coordinated 4,4'-bipyridine molecule is stacked over the bridging spacer ligand, and is held in place at both ends of the molecule by O—H...N hydrogen bonds from coordinated water molecules (Fig. 2). The dihedral angle between the two pyridine rings containing C18 and C18ⁱ is 14.3 (1)°.

Experimental

An aqueous solution (10 ml) of cobalt(II) diacetate tetrahydrate (4.76 g, 20 mmol) and 4,4'-bipyridine (3.12 g, 20 mmol) was added to an aqueous solution (20 ml) of 1,3-phenyldi(oxyacetic acid) (4.52 g, 20 mmol). The pH of the solution was adjusted to approximately 7 by

the addition of 0.1 M sodium hydroxide. The clear solution was filtered; pink crystals of (I) deposited from solution after several days. C, H & N analysis. Calc. for $C_{60}H_{74}N_8O_{25}Co_2$ (found, %): C 50.64 (50.56), H 5.10 (5.23) N 7.88 (7.86).

Crystal data

$[Co_2(C_{10}H_8O_6)_2(C_{10}H_8N_2)_3 \cdot (H_2O)_6] \cdot C_{10}H_8N_2 \cdot 7H_2O$
 $M_r = 1425.13$
 Monoclinic, $C2$
 $a = 34.738$ (4) Å
 $b = 7.450$ (2) Å
 $c = 12.929$ (4) Å
 $\beta = 106.23$ (2)°
 $V = 3213$ (1) Å³
 $Z = 2$

$D_x = 1.473$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 13866 reflections
 $\theta = 3.2$ – 28.0 °
 $\mu = 0.61$ mm⁻¹
 $T = 295$ (2) K
 Prism, pink
 $0.38 \times 0.24 \times 0.19$ mm

Data collection

Rigaku RAXIS RAPID diffractometer
 ω scans
 Absorption correction: multi-scan *ABSCOR* (Higashi, 1995)
 $T_{min} = 0.607$, $T_{max} = 0.894$
 14697 measured reflections

6280 independent reflections
 5750 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.023$
 $\theta_{max} = 27.5$ °
 $h = -44 \rightarrow 44$
 $k = -9 \rightarrow 8$
 $l = -16 \rightarrow 16$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0496P)^2 + 0.6741P]$
$R[F^2 > 2\sigma(F^2)] = 0.032$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.078$	$(\Delta/\sigma)_{\max} = 0.001$
$S = 1.02$	$\Delta\rho_{\max} = 0.56 \text{ e } \text{\AA}^{-3}$
6280 reflections	$\Delta\rho_{\min} = -0.19 \text{ e } \text{\AA}^{-3}$
475 parameters	Absolute structure: Flack (1983)
H atoms treated by a mixture of independent and constrained refinement	parameter; 2337 Friedel pairs
	Flack parameter = 0.02 (1)

Table 1
Selected bond lengths (Å).

Co1—O1	2.180 (2)	Co1—O3w	2.097 (2)
Co1—O1w	2.053 (2)	Co1—N1	2.167 (2)
Co1—O2w	2.146 (2)	Co1—N3	2.145 (2)

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

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O1w—H1w1...O2	0.85 (1)	1.80 (1)	2.625 (2)	163 (2)
O1w—H1w2...O4w	0.85 (1)	1.79 (1)	2.642 (3)	175 (2)
O2w—H2w1...O6w	0.85 (1)	1.80 (1)	2.632 (4)	169 (4)
O2w—H2w2...N4	0.85 (1)	2.04 (1)	2.850 (3)	159 (4)
O3w—H3w2...O4w ⁱⁱ	0.85 (1)	1.91 (1)	2.730 (3)	161 (3)
O3w—H3w1...O7w ⁱⁱ	0.85 (1)	1.92 (1)	2.762 (3)	170 (3)
O4w—H4w2...O1 ⁱⁱⁱ	0.85 (1)	2.02 (3)	2.745 (3)	143 (4)
O4w—H4w1...N2 ^{iv}	0.85 (1)	1.91 (1)	2.755 (2)	172 (4)
O5w—H5w2...O6 ^v	0.85 (1)	2.02 (1)	2.851 (3)	166 (4)
O5w—H5w1...O7w	0.85 (1)	2.06 (2)	2.817 (3)	147 (4)
O6w—H6w1...O5 ⁱ	0.86 (1)	2.01 (2)	2.801 (5)	152 (3)
O7w—H7w1...O5 ^{vi}	0.85 (1)	1.85 (2)	2.680 (3)	164 (4)

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

The carbon-bound H atoms were placed in calculated positions [C—H_{aromatic} 0.93 Å and C—H_{aliphatic} 0.96 Å; $U(H) = 1.2U_{eq}(C)$], and they were included in the refinement in the riding model approximation. For the water molecules occupying general positions, their H atoms were located in difference maps and refined with distance restraints of O—H 0.85 (1) and H...H 1.39 (1) Å; $U(H) = 1.2U_{eq}(O)$. One water molecule O atom (O6w) is disordered over two positions about the twofold axis [$d(O\cdots O) = 1.07 \text{ \AA}$] and its occupation factor was fixed at 0.5 for each site.

The atom O7w was refined as a water molecule O atom so that overall charge balance would confer a +2 oxidation state for the

cobalt atoms. However, when this atom was refined with two H atoms (with distance restraints), one of them was 2 Å from the symmetry-related atom. Consequently, O7w was refined with only one H atom as the other could neither be located nor be placed at any chemically sensible position. The O7w water molecule could conceivably be part of a hydroxide ion; however, as two other syntheses with the related 1,4-phenyldi(oxyacetic acid) (Gao *et al.*, 2004; Liu, Huo, Gao & Ng, 2004) did not lead to oxidation of the cobalt(II) reagent, it is not likely that the oxidation state of the metal atom is +3 in the pink title complex. The structural literature on cobalt complexes occasionally mentions the formation of cobalt(III) hydroxides through oxidation of the starting cobalt(II) reagent, *e.g.*, bis(2,2'-bipyridine)-nitratocobalt(III) nitrate hydroxide, but the product is a deep red compound (Reimann *et al.*, 1971).

Data collection: *RAPID-AUTO* (Rigaku Corporation, 1998); cell refinement: *RAPID-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSK and Rigaku Corporation, 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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