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Hexaaquacobalt(**II**) *trans*-bis(η^3-pyridine-2,6-dicarboxylato-κ^3O,N,O')cobaltate(**II**) dihydrate

Kom-Bei Shiu,[a]* Chia-Hung Yen,[a] Fen-Ling Liao[b] and Sue-Lein Wang[b]

[a]Department of Chemistry, National Cheng Kung University, 701 Tainan City, Taiwan, and [b]Instrument Center, National Tsing Hua University, 300 Hsinchu, Taiwan

Correspondence e-mail:
kbshiu@mail.ncku.edu.tw

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The title compound, $[Co(H_2O)_6][Co(C_7H_3NO_4)_2]\cdot 2H_2O$, was obtained by a hydrothermal reaction of cobalt chloride hexahydrate, 2,6-pyridinedicarboxylic acid, and Et_3N (molar ratio 1:1:7). The compound contains six-coordinated Co^{II} ions, with six O atoms of water molecules attached to the Co atoms in the two independent centrosymmetric cations and four O and two N atoms of two *trans* 2,6-pyridinedicarboxylate groups bonded to the Co atom in the anion. Intermolecular hydrogen-bonding interactions are present, linking the cobalt complex cations, anions and uncoordinated water molecules in the crystal structure.

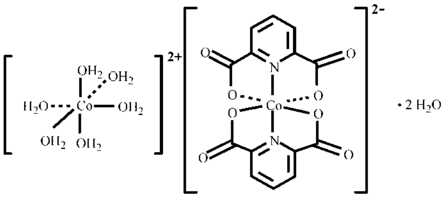
Key indicators

Single-crystal X-ray study
T = 295 K
Mean σ(C–C) = 0.012 Å
R factor = 0.094
wR factor = 0.228
Data-to-parameter ratio = 17.1

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

Comment

The complexation of metal ions using the deprotonated conjugate base of 2,6-pyridinedicarboxylic acid as a ligand has been reported extensively (Cousson *et al.*, 1992; Laine *et al.*, 1995*a*,*b*). Owing to the unique ability of the ligand to form stable chelates with various coordination modes and its biological activity, many crystal structures have been determined. We report here the synthesis and crystal structure of the title cobalt complex, (I).



(I)

The asymmetric unit of the title compound, (I), consists of two halves of centrosymmetric hexaaquacobalt(II) cations, one whole *trans*-bis(η^3-pyridine-2,6-dicarboxylato-*N*,*O*,*O*′)-cobaltate(II) anion, and two uncoordinated water molecules. All three cobalt atoms are octahedrally coordinated, with Co1 surrounded by two N atoms, N1 and N2, and four O atoms, O1, O3, O5, and O7 of two *trans* 2,6-pyridinedicarboxylate groups, and with atoms Co2 and Co3 each ligated by six O atoms of water molecules, (O9, O10, O11, O9′, O10′, and O11′) and (O12, O13, O14, O12′, O13′, and O14′), respectively (Fig. 1). For the four symmetry-unrelated Co1—O bond lengths, we might expect to observe four similar values; the Co1—O3 bond length is found to be significantly shorter than those for Co1—O1, Co1—O5, and Co1—O7 (Table 1). The difference is apparently and dominantly caused by many intermolecular hydrogen-bonding interactions between H atoms of the coordinated and uncoordinated water molecules (Fig. 2).

The hydrogen-bonding interactions are normal (Steed & Atwood, 2000), based on H⋯A distances of 1.71–2.49 Å,

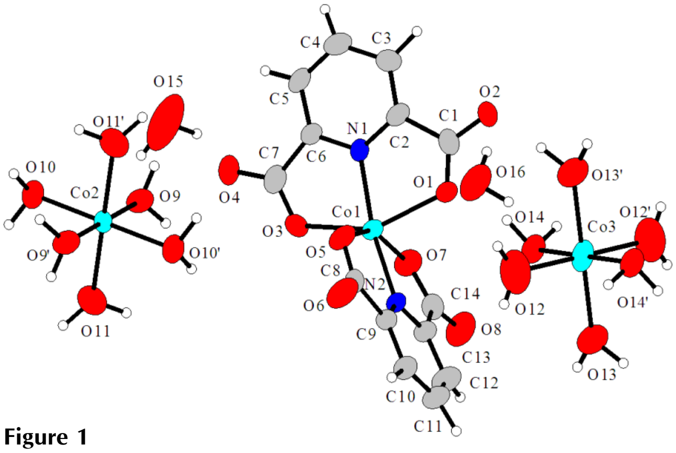


Figure 1
The molecular structure of (I), showing the atom-numbering scheme and displacement ellipsoids at the 50% probability level.

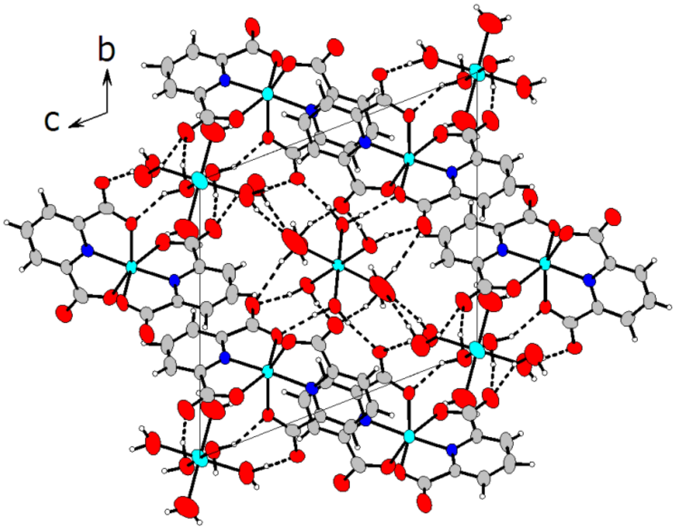


Figure 2
A crystal packing diagram of (I), viewed along the *a* axis, with hydrogen bonds shown as dashed lines. The Co3 and Co2 hexaaqua complexes are located at the central and corner positions, respectively.

$D\cdots A$ distances of 2.69 (3)–3.39 (2) Å and bond angles of 147–176° (Table 2). There are π–π stacking interactions between neighboring complexes in the structure (Fig. 2). The pyridine ring containing N1 is sandwiched between those related by a center of symmetry (symmetry codes: $1 - x$, $2 - y$, $1 - z$; $-x$, $2 - y$, $1 - z$). The distances between the neighboring two ring centers are 4.55 Å and 3.77 Å, respectively. The pyridine ring containing N2 is also stacked with that related by a center of symmetry (symmetry code: $-x$, $1 - y$, $-z$), the distance between the two ring centers being 3.59 Å.

Experimental

The title compound (I) was synthesized by heating a mixture of 2,6-pyridinedicarboxylic acid (0.0862 g, 0.505 mmol), cobalt chloride hexahydrate (0.119 g, 4.96 mmol), Et_3N (0.5 ml, *ca.* 3.6 mmol), and 9.5 ml of PhCN at 423 K for 72 h. The solid product was washed with distilled water and crystals were isolated by suction filtration (yield 30%).

Crystal data

$[Co(H_2O)_6][Co(C_7H_3NO_4)_2]\cdot 2H_2O$
$M_r = 592.20$
Triclinic, $P\overline{1}$
$a = 8.258$ (6) Å
$b = 11.615$ (8) Å
$c = 12.873$ (9) Å
$\alpha = 108.694$ (11)°
$\beta = 99.900$ (12)°
$\gamma = 98.089$ (13)°
$V = 1126.6$ (13) Å^3

$Z = 2$
$D_x = 1.746$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2061 reflections
$\theta = 2.5$–25°
$\mu = 1.55$ mm^{-1}
$T = 295$ (2) K
Column, red
0.30 × 0.10 × 0.10 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1995)
$T_{min} = 0.678$, $T_{max} = 0.856$
11 729 measured reflections

5293 independent reflections
2686 reflections with $I > 2\sigma(I)$
$R_{int} = 0.083$
$\theta_{max} = 28.4°$
$h = -11 \rightarrow 10$
$k = -14 \rightarrow 15$
$l = -17 \rightarrow 17$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.094$
$wR(F^2) = 0.228$
$S = 1.06$
5293 reflections
310 parameters

H-atom parameters not refined
$w = 1/[\sigma^2(F_o^2) + (0.1003P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 1.02$ e Å^{-3}
$\Delta\rho_{min} = -0.84$ e Å^{-3}

Table 1
Selected geometric parameters (Å).

Co1—N2	2.012 (6)	Co2—O10	2.107 (5)
Co1—N1	2.017 (6)	Co2—O9	2.118 (6)
Co1—O3	2.106 (5)	Co2—O11	2.148 (6)
Co1—O1	2.181 (5)	Co3—O14	2.092 (6)
Co1—O5	2.193 (5)	Co3—O13	2.136 (6)
Co1—O7	2.200 (6)	Co3—O12	2.150 (8)

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

$D—H\cdots A$	$D—H$	$H\cdots A$	$D\cdots A$	$D—H\cdots A$
O14—H14*B*···O1	0.98	1.91	2.77 (1)	147
O13—H13*A*···O2^{i}	1.05	1.81	2.85 (2)	169
O9—H9*B*···O2^{ii}	0.94	1.86	2.79 (3)	172
O10—H10*B*···O4^{iii}	1.01	1.71	2.69 (3)	163
O15—H15*B*···O4	1.05	1.87	2.84 (2)	154
O9—H9*A*···O5^{iv}	0.92	1.85	2.76 (1)	176
O10—H10*A*···O6^{v}	0.94	1.83	2.76 (2)	168
O11—H11*B*···O6^{iv}	0.99	2.49	3.39 (2)	153
O14—H14*A*···O8^{vi}	1.01	1.83	2.75 (2)	152
O16—H16*A*···O8^{vi}	0.99	1.98	2.92 (2)	156
O13—H13*B*···O15^{vii}	0.80	2.38	3.16 (4)	165
O16—H16*B*···O15^{ii}	0.98	2.32	3.28 (3)	166
C5—H5*A*···O16^{ii}	0.93	2.34	3.25 (2)	166

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

H atoms were located from difference Fourier maps but not refined; their U_{iso} values were set to 0.05 Å^2. The C—H and O—H bond lengths are 0.93–1.04 Å and 0.80–1.05 Å, respectively. The highest residual peak is 0.989 Å from Co1.

Data collection: *SMART* (Bruker, 1997); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1997); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics:

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SHELXTL (Bruker, 1998); software used to prepare material for publication: *SHELXTL*.

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