Tetraaqua(4-hydroxypyridine-2,6-dicarboxylato)-cobalt(II)

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The title compound, $[Co(C_7H_4NO_4)_2(H_2O)_4]$, consists of one cobalt cation, two 4-hydroxypyridine-2,6-dicarboxylate ligands, and four coordinated water molecules. The geometry around the cobalt(II) cation, which is located on a centre of inversion, is distorted octahedral. The four coordinated water molecules and the hydroxyl atoms from the ligand form intermolecular hydrogen bonds, resulting in a three-dimensional supramolecular network.

Comment

The formation of metal–organic framework (MOF) structures is an active area of research as these compounds have potential uses in gas storage, molecular sieves, magnetism, opto-electronic devices and so on (Davis, 2002; Leadbeater & Marco, 2002; Moulton & Zaworotko, 2001). Carboxylate ligands play an important role in the construction of novel MOFs in coordination chemistry. 4-Hydroxypyridine-2,6-dicarboxylic acid (H_2chedam) is a very important carboxylate derivative. Systematic studies of $3d$, $4f$ and $3d$–$4f$ complexes based on H_2chedam have been reported in our previous work (Gao *et al.*, 2006; Zhao *et al.*, 2006).

(I)
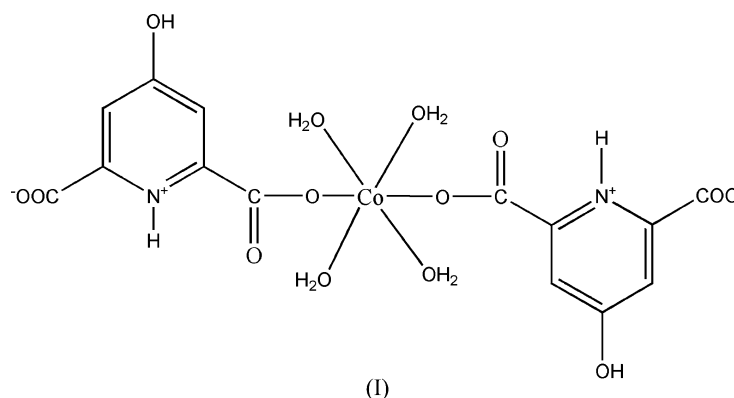
A new compound, $[Co(Hchedam)_2(H_2O)_4]$, (I) was isolated under hydrothermal conditions and characterized by elemental analysis, IR spectroscopy and single-crystal X-ray diffraction. The molecular structure of (I) is composed of one cobalt(II) cation, two chedam ligands and four aqua ligands (Fig. 1). The cobalt(II) cation, which is located on a centre of inversion, is six-coordinate and the geometry around the cobalt ion is slightly distorted octahedral. The equatorial sites are occupied by four O atoms from four aqua ligands. The axial sites are occupied by two O atoms from two ligands. It was observed that the H atoms linked to O4 and O4*A* have moved to N1 and N1*A*, respectively, forming an inner salt. The four coordinated water molecules and the hydroxyl atoms

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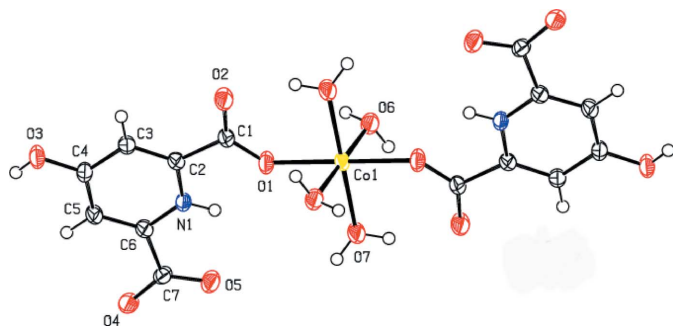
Figure 1
The molecular structure and atom-labelling scheme of (I). Displacement ellipsoids are drawn at the 50% probability level. Unlabelled atoms are related to labelled atoms by the symmetry operator $(-x, -y, -z)$.
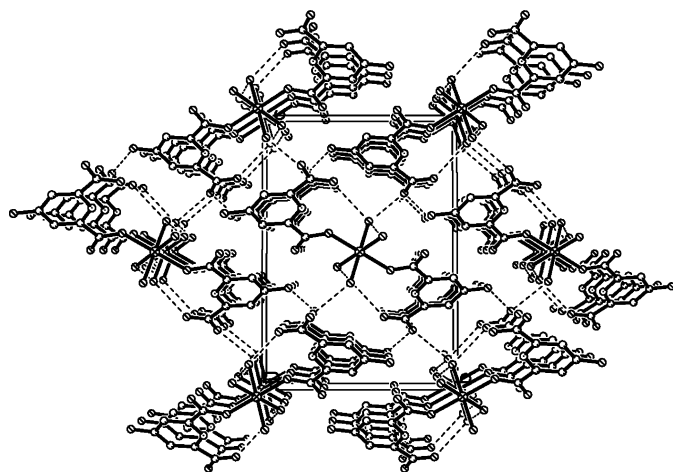
Figure 2
The three-dimensional supramolecular structure of (I). Dashed lines indicate hydrogen bonds. H atoms have been omitted.

from the ligand form intermolecular hydrogen bonds, resulting in a three-dimensional supramolecular network (Fig. 2 and Table 2).

Experimental

[Co(Hchedam)(H$_2$O)$_4$] was synthesized from a reaction mixture of [Co(SO$_4$)$_2$]·6H$_2$O (0.2 mmol, 0.0483 g), H$_2$chedam (0.4 mmol, 0.0804 g), H$_2$O (10 ml) and C$_2$H$_5$OH (2 ml) in a 25 ml Teflon reactor, under autogenous pressure at 453 K for 3 d, and then cooled to room temperature at a rate of 10 K h^{-1}. Red crystals of (I) were obtained (yield 61%, based on Co) and were washed with ethanol. The complex decomposes at 455 K. Analysis calculated for C$_{14}$H$_{16}$CoN$_2$O$_{14}$: C 39.95%, H 3.26%, N 2.66%; found: C 39.91%, H 3.23%, N 2.68%.

Crystal data

[Co(C$_7$H$_4$NO$_4$)$_2$(H$_2$O)$_4$]	$Z = 2$
$M_r = 495.22$	$D_x = 1.838$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 5.3747$ (8) Å	$\mu = 1.05$ mm^{-1}
$b = 10.8834$ (16) Å	$T = 294$ (2) K
$c = 15.342$ (2) Å	Block, red
$\beta = 94.496$ (2)°	0.18 × 0.10 × 0.06 mm
$V = 894.7$ (2) Å^3	

Data collection

Bruker SMART CCD area-detector diffractometer	4447 measured reflections
	1578 independent reflections
φ and ω scans	1434 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)	$R_{int} = 0.023$
$T_{min} = 0.834$, $T_{max} = 0.940$	$\theta_{max} = 25.0°$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0351P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.025$	$+ 0.3708P]$
$wR(F^2) = 0.069$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.10$	$(\Delta/\sigma)_{max} = 0.003$
1578 reflections	$\Delta\rho_{max} = 0.25$ e Å^{-3}
145 parameters	$\Delta\rho_{min} = -0.29$ e Å^{-3}
H atoms treated by a mixture of independent and constrained refinement	

Table 1
Selected geometric parameters (Å, °).

Co1—O1	2.0653 (12)	Co1—O6	2.1266 (13)
Co1—O7	2.0764 (13)		
O1—Co1—O1^i	180	O7—Co1—O6^i	90.61 (6)
O1—Co1—O7^i	89.58 (5)	O1—Co1—O6	92.44 (5)
O1—Co1—O7	90.42 (5)	O7—Co1—O6	89.39 (6)
O7^i—Co1—O7	180	O6^i—Co1—O6	180
O1—Co1—O6^i	87.56 (5)		

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

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N1—H1$\cdots$O1	0.85 (2)	2.14 (2)	2.560 (2)	110.1 (17)
N1—H1$\cdots$O5	0.85 (2)	2.25 (2)	2.602 (2)	105.5 (17)
O3—H3$\cdots$O4^{ii}	0.81	1.83	2.6049 (19)	159
O6—H6$A\cdots$O5^{iii}	0.83	1.85	2.6778 (19)	174
O6—H6$B\cdots$O4^{iv}	0.88	1.84	2.6878 (19)	159
O7—H7$A\cdots$O2^i	0.85	1.93	2.727 (2)	156
O7—H7$B\cdots$O6^v	0.85	2.00	2.845 (2)	172
C3—H3$A\cdots$O2^{vi}	0.93	2.35	3.239 (2)	161
C5—H5$\cdots$O5^{ii}	0.93	2.37	3.265 (2)	162

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

Atom H1 (bound to N1) was found in a Fourier map and refined freely. All other H atoms were positioned geometrically and treated as riding atoms, with C—H = 0.93 Å, O—H = 0.82–0.88 Å and U_{iso}(H) = $1.2U_{eq}$(C,O).

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINT* (Bruker, 1997); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1997); software used to prepare material for publication: *SHELXTL*.

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