metal-organic papers

Poly[diaquabis[μ-1-(carboxylatomethyl)-pyridinium-4-carboxylato-$\kappa^2 O^1$:O^3]-cobalt(II)]

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Key indicators

Single-crystal X-ray study
T = 296 K
Mean σ(C–C) = 0.003 Å
R factor = 0.031
wR factor = 0.072
Data-to-parameter ratio = 13.5

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

In the title compound, $[Co(C_8H_6NO_4)_2(H_2O)_2]_n$, the Co^{II} ion (site symmetry $\bar{1}$) adopts a distorted octahedral coordination geometry. Neighboring metal ions are bridged by 1-(carboxylatomethyl)pyridinium-3-carboxylate ligands, forming a two-dimensional coordination network which is stabilized by O—H···O hydrogen bonds.

Comment

The synthesis and characterization of coordination polymers using di- and polycarboxylate O-donor ligands such as benzene-1,4-dicarboxylate, benzene-1,2-dicarboxylate, benzene-1,3,5-tricarboxylate, and benzene-1,2,4,5-tetracarboxylate has attracted the attention of many laboratories (Zheng & Sun, 2003).

(I)
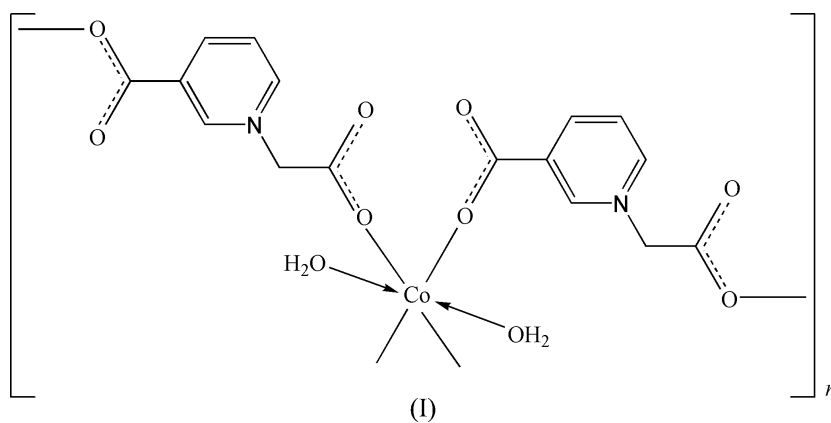
In the present work, a pyridinium dicarboxylate anion, namely 1-(carboxylatomethyl)pyridinium-3-carboxylate (L), was used as a ligand to generate the title compound, (I). The L molecule comprises a betaine grouping (containing a positively charged N atom and a negatively charged carboxylate group in the same molecule) (Szafran *et al.*, 2003; Zhang *et al.*, 2003), which endows this ligand with zwitterionic properties as well as flexibility and conformational freedom in the molecular assembly process.

As depicted in Fig. 1, the Co^{II} ions in (I) are each located on an inversion center. Each Co^{II} ion is six-coordinated in a distorted octahedral geometry, surrounded by six O atoms from four different L ligands and two water molecules. The Co—O(carboxylate) bond lengths are in the range 2.103 (1)–2.110 (1) Å, comparable with those found in monodentate carboxylate groups of other cobalt(II) dicarboxylate complexes (Choi *et al.*, 2006; Zheng *et al.*, 2004; Su *et al.*, 2004). The range of *cis* bond angles about Co [83.77 (6)–96.23 (6)°] reflects the degree of distortion from an ideal octahedral
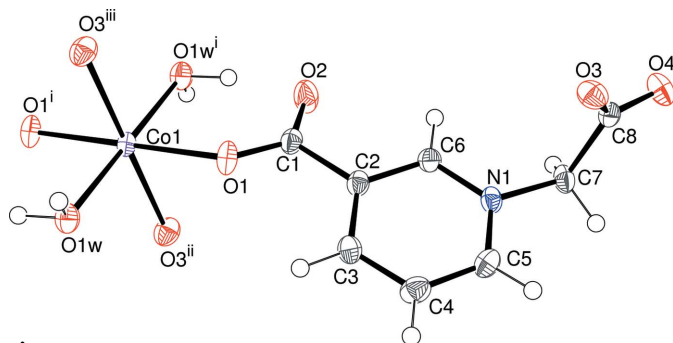
Figure 1

The asymmetric unit of (I), expanded to show the Co coordination environment (50% displacement ellipsoids and arbitrary spheres for the H atoms). [Symmetry codes: (i) $1 - x, 1 - y, 1 - z$; (ii) $x, \frac{1}{2} - y, z - \frac{1}{2}$; (iii) $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$.]
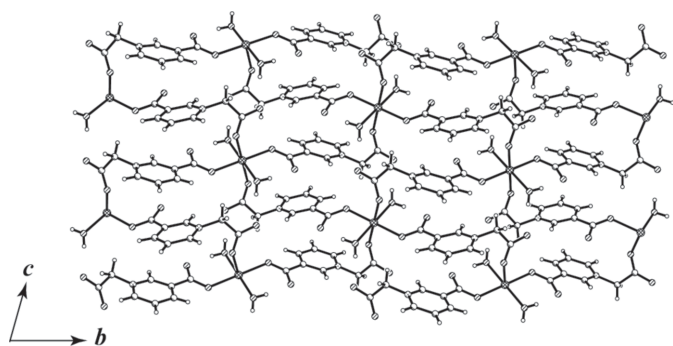

Figure 2

The two-dimensional structure of (I), viewed along the a axis.

geometry. The carboxylate C—O bond lengths indicate delocalization of the negative charges in these groups.

The Co^{II} ions are linked by bridging L ligands with the *syn–syn* monodentate coordination mode of both carboxylate groups, generating two one-dimensional chains extending along the [011] and [0$\bar{1}$1] directions. These one-dimensional chains are further crosslinked into two-dimensional layers lying in the (100) family of planes. Finally, O—H$\cdots$O hydrogen bonds linking water molecules to uncoordinated carboxylate O atoms complete the structure (Table 2).

Experimental

4-Carboxy-1-carboxymethylpyridinium hydroxide was synthesized according to the literature procedure of Wang *et al.* (2003). The sodium salt NaL was obtained by dissolving 4-carboxy-1-carboxymethylpyridinium hydroxide in aqueous sodium bicarbonate, and methanol was added to precipitate out the product. Compound (I) was prepared by reaction of NaL (0.204 g, 1 mmol) and Co(ClO$_4$)$_2\cdot$6H$_2$O (0.366 g, 1 mmol) in 8 ml distilled water. The resulting mixture was stirred at about 296 K for 15 min and then filtered. The filtrate was left to stand in air at room temperature for several days and pink block- and plate-shaped crystals of (I) were obtained in 85% yield. Analysis calculated for C$_{16}$H$_{16}$CoN$_2$O$_{10}$: C 42.21, H 3.54, N 6.15%; found: C 42.67, H 3.55, N 5.91%. IF–IR (KBr, cm^{-1}): ν(CO) 1601 (*vs*), 1377 (*vs*).

Crystal data

[Co(C$_8$H$_6$NO$_4$)$_2$(H$_2$O)$_2$]	$Z = 2$
$M_r = 455.24$	$D_x = 1.823$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 7.5954$ (5) Å	$\mu = 1.10$ mm^{-1}
$b = 16.901$ (4) Å	$T = 296$ (2) K
$c = 7.2755$ (5) Å	Block, pink
$\beta = 117.378$ (5)°	$0.22 \times 0.22 \times 0.18$ mm
$V = 829.32$ (19) Å^3	

Data collection

Siemens P4 diffractometer	1550 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.018$
Absorption correction: ψ scan	$\theta_{max} = 27.0°$
(North *et al.*, 1968)	3 standard reflections
$T_{min} = 0.794$, $T_{max} = 0.826$	every 120 reflections
2090 measured reflections	intensity decay: 3.3%
1815 independent reflections	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.03P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.031$	$+ 0.536P]$
$wR(F^2) = 0.072$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.09$	$(\Delta/\sigma)_{max} < 0.001$
1815 reflections	$\Delta\rho_{max} = 0.36$ e Å^{-3}
134 parameters	$\Delta\rho_{min} = -0.36$ e Å^{-3}
H-atom parameters constrained	Extinction correction: *SHELXL97*
	Extinction coefficient: 0.0153 (17)

Table 1
Selected bond lengths (Å).

Co1—O1	2.1025 (14)	C1—O2	1.249 (3)
Co1—O3^i	2.1101 (15)	C8—O4	1.244 (2)
Co1—O1W	2.1573 (14)	C8—O3	1.257 (2)
C1—O1	1.258 (2)		

Symmetry code: (i) $x, -y + \frac{1}{2}, z - \frac{1}{2}$.

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O1W—H1$WA\cdots$O2^{ii}	0.95	1.68	2.612 (2)	167
O1W—H1$WB\cdots$O4^{iii}	0.95	1.84	2.788 (2)	176

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

All H atoms other than those of water molecules were positioned geometrically (C—H = 0.93–0.97 Å) and refined as riding, with U_{iso}(H) = 1.2U_{eq}(C). The H atoms of water molecules were located in a difference map and refined as riding in their as-found relative positions, with U_{iso}(H) = 1.5U_{eq}(O).

Data collection: *XSCANS* (Siemens, 1994); cell refinement: *XSCANS*; data reduction: *XSCANS*; 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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References

Bruker (1997). *SHELXTL*. Version 5.10. Bruker AXS Inc., Madison, Wisconsin, USA.

Choi, D. H., Yoon, J. H., Lim, J. H., Kim, H. C. & Hong, C. S. (2006). *Inorg. Chem.* **45**, 5947–5952.

North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.

Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.

Siemens (1994). *XSCANS*. Version 2.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Su, J.-R., Liu, Y. & Xu, D.-J. (2004). *Acta Cryst.* E**60**, m1298–m1300.

Szafran, M., Kowalczyk, I., Katrusiak, A. & Dega-Szafran, Z. (2003). *J. Mol. Struct.* **651–653**, 621–634.

Wang, X.-B., Dacres, J. E., Yang, X., Broadus, K. M., Lis, L., Wang, L.-S. & Kass, S. R. (2003). *J. Am. Chem. Soc.* **125**, 296–304.

Zhang, L.-P., Song, H.-B., Wang, Q.-M. & Mak, T. C. W. (2003). *Polyhedron*, **22**, 811–818.

Zheng, Y.-Q. & Sun, J. (2003). *J. Solid State Chem.* **172**, 288–295.

Zheng, Y.-Q. & Xie, H.-Z. (2004). *J. Solid State Chem.* **177**, 1352–1358.