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catena-Poly[[[triaquacobalt(II)]-μ-2,6-dioxo-1,2,3,6-tetrahydropyrimidine-4-carboxylato(2–)] 1.72-hydrate]

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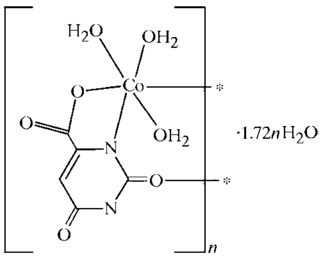
The Co^{II} ion in the title complex {[Co(C$_5$H$_2$N$_2$O$_4$)(H$_2$O)$_3$]·1.72H$_2$O}$_n$, has a distorted octahedral coordination geometry comprised of three water ligands, one deprotonated pyrimidine N atom and an adjacent carboxylate O atom of one orotate ligand. The sixth coordination site is occupied by an exocyclic O atom from a neighbouring orotate moiety, and through this interaction a helicoidal chain is formed. The molecules are linked by intramolecular O$_{\rm water}$—H···O and intermolecular N—H···O and O$_{\rm water}$—H···O hydrogen bonds, forming a three-dimensional network.

Comment

Orotic acid (vitamin B$_{13}$, H$_3$Or) continues to attract attention because of its multidentate functionality and its great significance in living organisms as a precursor of pyrimidine nucleosides (Genchev, 1970; Rawn, 1989; Lalioti *et al.*, 1998). Metal orotates have potential applications in medicine and some orotate complexes have already been screened as therapeutic agents for cancer treatment (Castan *et al.*, 1990; Kumberger *et al.*, 1993). Orotic acid and its anions, *viz*. H$_2$Or$^-$, HOr^{2-} and Or^{3-}, are also interesting multidentate ligands, especially above the deprotonation pH values. The coordination around the metal ions is formed by an N atom, the two carbonyl O atoms and a carboxylate O atom. H$_3$Or can act as a dibasic acid, depending on the pH range. In the pH range 3–9, orotic acid exists mainly as the readily coordinating mono-deprotonated HOr^{2-} anion (the carboxylic acid group has a pK_a value of 2.07; Lutz, 2001). In basic solutions (pH 9), both the carboxyl group and a heterocylic N atom are deprotonated, so the anion acts as a bidentate ligand. Existing studies of its coordination complexes demonstrate that it occurs as a dianion, often coordinating *via* the N atom and carboxylic acid group, so forming a five-membered chelate ring (Maistralis *et al.*, 2000; Wysokinski *et al.*, 2002; Icbudak *et al.*, 2003; Ölmez *et al.*, 2004). In polymeric orotic acid complexes, the orotate anion bridges the metal ions through the carboxylate group and N and O atoms, forming one-dimensional polymeric chains (Castan *et al.*, 1990; Sun *et al.*, 2002). We present here the crystal structure of the title Co complex of H$_3$Or, (I).



(I)

A view of the molecule of (I) is presented in Fig. 1. The Co^{II} ion has a distorted octahedral coordination geometry, comprised of atoms N1 and O4 from a doubly deprotonated bidentate orotate ligand, three water molecules (O1*W*, O2*W* and O3*W*) and an exocyclic O atom (O5$^{\rm i}$; see Table 1 for symmetry code) from a neighbouring orotate moiety. Atoms N1 and O4 are bonded to Co1 to form a five-membered chelate ring (C4/N1/Co1/O4/C5) and, in conjunction with O3*W* and O5$^{\rm i}$, they define the approximately planar equatorial plane, with an r.m.s. deviation of 0.0179 Å and a largest deviation from the mean plane of 0.026 (3) Å for atom C5. This is apparently due to the strong intermolecular hydrogen-bonding interaction between atom H2 of the pyrimidine ring and carboxylate atom O4$^{\rm i}$. Finally, the apical positions of the Co^{II} coordination octahedron are occupied by O1*W* and O2*W*.

All N—Co—O and O—Co—O bond angles of (I) deviate significantly from 90 or 180°, presumably as a result of the steric constraints arising from the shape of the ligand. The angle subtended at the Co atom by the orotate ligand is 77.69 (13)°, which is in agreement with the values reported previously for other Co^{II} complexes (Zhang & You, 2003).

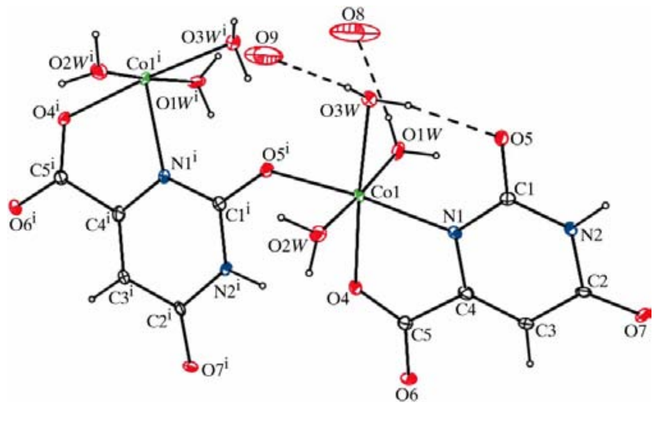


Figure 1
A view of the molecule of (I), showing the atom-numbering scheme. The hydrogen bonding is indicated by dashed lines. Displacement ellipsoids are drawn at the 30% probability level. [Symmetry code: (i) $y, 1 - x + y, z - \frac{1}{6}$.]

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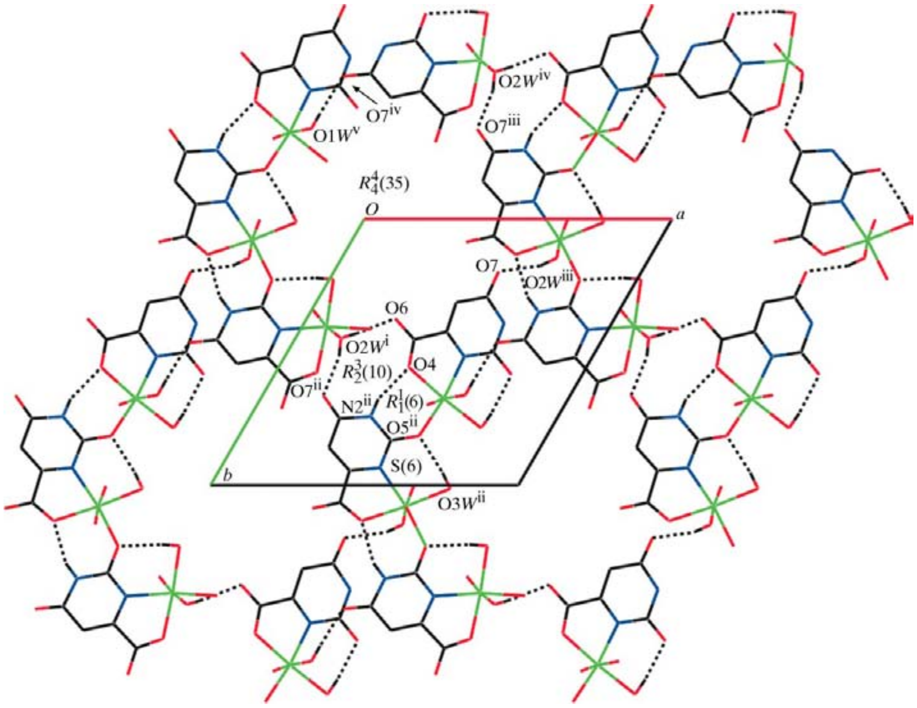

Figure 2
A perspective view of the molecular packing of compound (I). Dashed lines indicate hydrogen bonds. H atoms not involved in hydrogen bonds have been omitted for clarity. [Symmetry codes: (i) $-x + y, 1 - x, z - \frac{1}{3}$; (ii) $y, 1 - x + y, z - \frac{1}{6}$; (iii) $y, -x + y, z - \frac{1}{6}$; (iv) $-x + y, -x, z - \frac{1}{3}$; (v) $-1 + x, -1 + y, -z$.]

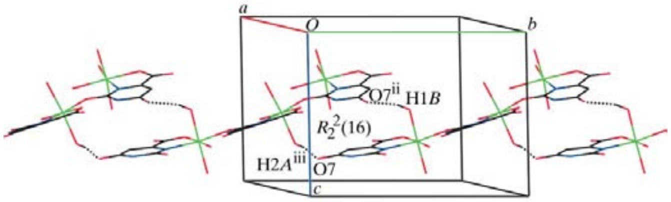

Figure 3
The molecular structure of (I), viewed along the *a* axis. Dashed lines indicate hydrogen bonds. H atoms not involved in hydrogen bonds have been omitted for clarity. [Symmetry codes: (ii) $1 - x + y, 1 - x, z - \frac{1}{3}$; (iii) $y, -x + y, z - \frac{1}{6}$.]

The orotate group of (I) is essentially planar (r.m.s. deviation = 0.0142 Å), with a slight deviation from planarity arising from the non-zero torsion angle between the carboxylate group and the ring. Of all the N—C bonds in the uracylic ring, N1—C1 and N1—C4 are the shortest. This indicates that there is considerable π-electron delocalization within the C3/C4/N1/C1 skeleton. The dihedral angle between the pyrimidine ring and the five-membered chelate ring is 4.82 (2)°, while that between the pyrimidine ring and the O4/C5/O6 carboxylate group is 6.07 (3)°. The C═O bond lengths for exocyclic atoms O5 and O7 clearly indicate their double-bond character (Table 1).

Crystal packing in (I) is achieved *via* intermolecular hydrogen bonding (Fig. 2 and Table 2). Graph-set notation (Bernstein *et al.*, 1995) is used to describe these hydrogen-bonding patterns. Thus, the intramolecular O—H⋯O hydrogen bond can be described as an *S*(6) motif. Fig. 2 shows the way in which the three water ligands and carboxylate O6 and carbonyl O7 atoms enter into inter- and intramolecular hydrogen-bonding interactions. As a result, zigzag tapes are formed through $O2W^{i}—H2A^{i}\cdots O7^{ii}$, $N2^{ii}—H2^{ii}\cdots O4$ and $O2W^{i}—H2B^{i}\cdots O6$ interactions [symmetry codes: (i) $-x + y, 1 - x, z - \frac{1}{3}$; (ii) $y, 1 - x + y, z - \frac{1}{6}$], which define $R_2^3(10)$ and $R_1^1(6)$ ring patterns. Furthermore, an $R_4^4(35)$ motif appears *via* the $O1W^{v}—H1B^{v}\cdots O7^{iv}$, $O2W^{iv}—H2A^{iv}\cdots O7^{iii}$ and $O2W^{iii}—H2A^{iii}\cdots O7$ interactions [symmetry codes: (iii) $y, -x + y, z - \frac{1}{6}$; (iv) $-x + y, -x, z - \frac{1}{3}$; (v) $-1 + x, -1 + y, -z$]. These helicoidal chains zigzagging along the *a* axis are interlinked through $O1W—H1B\cdots O7^{vi}$ and $O2W^{iii}—H2A^{iii}\cdots O7$ interactions [symmetry code: (vi) $1 - x + y, 1 - x, z - \frac{1}{3}$], which in turn define an $R_2^2(16)$ ring pattern (Fig. 3).

Experimental

A solution of $Co(CH_3COO)_2 \cdot H_2O$ (1 mmol) in water (300 ml) was added to a solution of orotic acid (2 mmol) in water (100 ml). The solution was heated at 338 K and stirred for 1 d to remove CH_3COOH. The mixture was then left for crystallization. After two weeks, the product obtained was filtered off and dried in air. Analysis calculated for $C_5H_{10}CoN_2O_9$: C 21.0, H 3.50, N 9.8%; found: C 20.32, H 4.09, N 9.12%. IR (KBr, ν, cm^{-1}): 3390–3100 (*b*), 1652 (*vs*), 1605 (*sh*), 1376 (*m*), 1480 (*w*), 1021 (*m*).

Crystal data

$[Co(C_5H_2N_2O_4)(H_2O)_3] \cdot 1.72H_2O$
$M_r = 294.6$
Hexagonal, $P6_1$
$a = 13.4646 (12)$ Å
$c = 9.8777 (7)$ Å
$V = 1550.9 (2)$ Å^3
$Z = 6$
$D_x = 1.893$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 1.70$ mm^{-1}
$T = 100$ K
Rod, brown
0.50 × 0.30 × 0.10 mm

Data collection

Stoe IPDS-II diffractometer
ω scans
Absorption correction: integration (*X-RED32*; Stoe & Cie, 2002)
$T_{\min} = 0.672$, $T_{\max} = 0.875$
5840 measured reflections
1993 independent reflections
1810 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.036$
$\theta_{\max} = 26.0°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.038$
$wR(F^2) = 0.087$
$S = 1.06$
1993 reflections
173 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0318P)^2 + 3.8738P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.003$
$\Delta\rho_{\max} = 0.92$ e Å^{-3}
$\Delta\rho_{\min} = -0.94$ e Å^{-3}
Absolute structure: Flack (1983), with 909 Friedel pairs
Flack parameter: −0.03 (3)

Table 1
Selected geometric parameters (Å, °).

Co1—O2*W*	2.054 (4)	Co1—O3*W*	2.148 (3)
Co1—O5^{i}	2.074 (3)	C1—O5	1.272 (5)
Co1—O1*W*	2.072 (4)	C1—N1	1.328 (6)
Co1—O4	2.089 (3)	C2—O7	1.249 (6)
Co1—N1	2.091 (4)	C4—N1	1.353 (6)
O4—Co1—N1	77.69 (13)		
C3—C4—C5—O6	8.1 (7)	N1—C4—C5—O4	5.4 (6)

Symmetry code: (i) $y, -x+y+1, z-\frac{1}{6}$.

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

D—H$\cdots$*A*	*D*—H	H$\cdots$*A*	*D*$\cdots$*A*	*D*—H$\cdots$*A*
N2—H2$\cdots$O4^{ii}	0.86	1.93	2.736 (5)	155
O1*W*—H1*A*$\cdots$O8	0.83 (3)	2.01 (3)	2.819 (7)	164 (6)
O1*W*—H1*B*$\cdots$O7^{iii}	0.83 (3)	1.89 (3)	2.719 (4)	173 (5)
O2*W*—H2*A*$\cdots$O7^{iv}	0.81 (3)	1.95 (3)	2.717 (5)	157 (5)
O2*W*—H2*B*$\cdots$O6^{v}	0.86 (3)	1.90 (3)	2.750 (5)	174 (5)
O3*W*—H3*A*$\cdots$O9	0.82 (3)	1.92 (3)	2.676 (9)	153 (5)
O3*W*—H3*B*$\cdots$O5	0.82 (3)	1.92 (3)	2.722 (5)	164 (5)

Symmetry codes: (ii) $x-y+1, x, z+\frac{1}{6}$; (iii) $-x+y+1, -x+1, z-\frac{1}{3}$; (iv) $x-y, x, z+\frac{1}{6}$; (v) $-y+1, x-y+1, z+\frac{1}{3}$.

H atoms bonded to C and N atoms were included in their expected positions and allowed to ride, with C—H and N—H distances restrained to 0.93 and 0.86 Å, respectively. Water H atoms were located in difference maps and refined subject to a DFIX restraint of O—H = 0.83 (3) Å. In all cases, H atoms were assigned a $U_{\rm iso}$(H) value of $1.2U_{\rm eq}$ of the parent atom. Attempts to refine O9 resulted in a partial occupancy of 0.716, which was later fixed at 0.72. The H atoms attached to non-coordinated water molecules O8 and O9 could not be located, though they appeared to be involved in strong hydrogen bonding to a neighbouring O atom.

Data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-AREA*; data reduction: *X-RED* (Stoe & Cie, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BG3013). Services for accessing these data are described at the back of the journal.

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