

*mer*-Diaquabis(1*H*-imidazole- $\kappa$ N<sup>3</sup>)-  
[orotato(2-)]cobalt(II)

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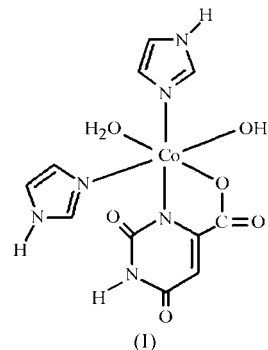
In the title complex, *mer*-diaqua[2,6-dioxo-1,2,3,6-tetrahydropyrimidine-4-carboxylato(2-)]bis(1*H*-imidazole- $\kappa$ N<sup>3</sup>)cobalt(II), [Co(C<sub>5</sub>H<sub>2</sub>N<sub>2</sub>O<sub>4</sub>)(C<sub>3</sub>H<sub>4</sub>N<sub>2</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>], the Co<sup>II</sup> ion is coordinated by a deprotonated N atom and the carboxylate O atom of the orotate ligand, two imidazole N atoms and two aqua ligands in a distorted octahedral geometry. The title complex exists as discrete doubly hydrogen-bonded dimers, and a three-dimensional network of O—H···O and N—H···O hydrogen bonds and weak  $\pi$ – $\pi$  interactions is responsible for crystal stabilization.

Comment

Orotic acid (vitamin B13, H<sub>3</sub>Or) is an interesting ligand due to its potential multidentate nature, especially above the deprotonation pH values. It coordinates to metal ions as a bidentate ligand through both the N atom of the pyrimidine ring and the O atom of the carboxyl group. Examples are found in the crystal structures of Co<sup>II</sup>–orotate complexes with water, ethylenediamine (Içbudak *et al.*, 2003), nicotinamide (Yeşilel *et al.*, 2005) or di-2-pyridylamine (Plater *et al.*, 2002). The orotate ligand acts as a bridging bidentate ligand in the polymeric complex [Co(HOr)(H<sub>2</sub>O)<sub>3</sub>]<sub>n</sub> (Şahin *et al.*, 2006; Plater *et al.*, 2002; Sun *et al.*, 2002), and in [Co(H<sub>2</sub>Or)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>]·H<sub>2</sub>O, orotate acts as a monodentate ligand through the carboxylate O atom (Kose *et al.*, 2006). In the [Co(H<sub>2</sub>O)<sub>2</sub>(phen)<sub>2</sub>](H<sub>2</sub>Or)<sub>2</sub> complex (phen is 1,10-phenanthroline), orotic acid acts as a counter-ion (Bulut *et al.*, 2003). In this study, we report the structural characterization of the title *mer*-[Co(HOr)(H<sub>2</sub>O)<sub>2</sub>(im)<sub>2</sub>] complex (im is imidazole), (I). The molecular structure of (I) is shown in Fig. 1 and selected geometric parameters are given in Table 1.

The Co<sup>II</sup> ion of (I) has a distorted octahedral coordination geometry comprised of a pyrimidine N atom and a carboxylate O atom from a dideprotonated bidentate orotate ligand [Co1–N1 = 2.117 (2) Å and Co1–O1 = 2.085 (2) Å], two water O atoms [Co1–O5 = 2.094 (2) Å and Co1–O6 = 2.185 (2) Å] and two N atoms from two imidazole ligands

[Co1–N3 = 2.120 (2) Å and Co1–N5 = 2.123 (2) Å]. The orotate ligand is essentially planar [r.m.s. deviation = 0.024 (2) Å], with a slight deviation from planarity arising from the non-zero torsion angle between the carboxylate group and the ring [N1–C2–C1–O1 = 1.8 (3)°]. This torsion angle indicates distortion of the orotate ligand caused by coordination to the Co<sup>II</sup> ion.

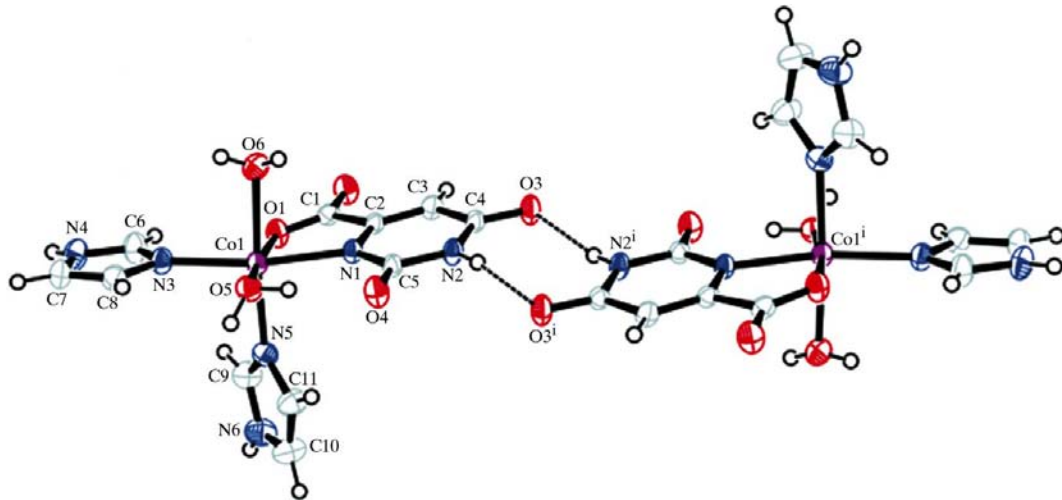


The carboxylate O atoms have different environments. Atom O1 coordinates to the Co<sup>II</sup> ion, while atom O2 acts as an acceptor for two linear hydrogen bonds. However, the C–O distances [C1–O1 = 1.251 (3) Å and C1–O2 = 1.254 (3) Å] are practically equal. These bond distances are comparable with those in similar complexes (Uçar *et al.*, 2004; Içbudak *et al.*, 2003; Lutz, 2001).

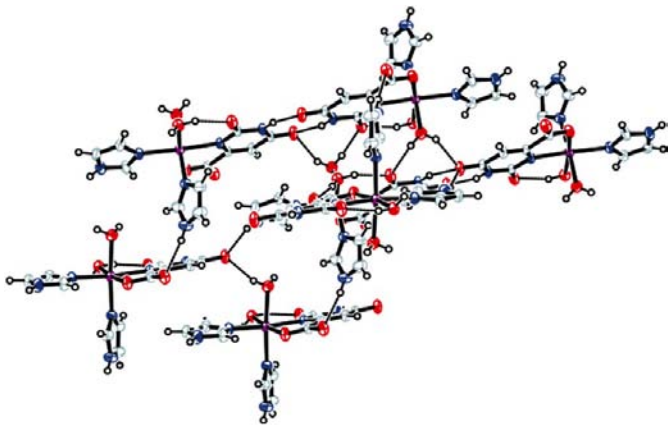
The two imidazole rings are individually planar and the maximum deviations from these planes are 0.002 (3) Å for atom N4 and 0.003 (3) Å for atom C9. These planes are approximately perpendicular, with a dihedral angle of 88.35 (17)°, in agreement with the value previously reported for the diaquabis(imidazole)(orotato)nickel(II) complex (Uçar *et al.*, 2004).

The crystal packing of (I) is formed *via* intermolecular hydrogen bonds, and weak  $\pi$ – $\pi$  and C–H··· $\pi$  interactions. Two orotate ligands are joined by two N2–H2···O3 hydrogen bonds, which leads to the formation of a centrosymmetric dimer of (I) (Fig. 1). Two aqua ligands and imidazole atoms N4 and N6 also form intermolecular hydrogen-bonding interactions with the orotate ligand, through carboxylate atom O2 [N6–H6···O2 = 2.891 (3) Å and O5–H5B···O2 = 2.687 (3) Å] and carbonyl atoms O3 [N4–H4···O3 = 2.879 (3) Å and O6–H6B···O3 = 2.783 (3) Å] and O4 [O5–H5A···O4 = 2.729 (3) Å and O6–H6A···O4 = 2.816 (3) Å] (Fig. 2).

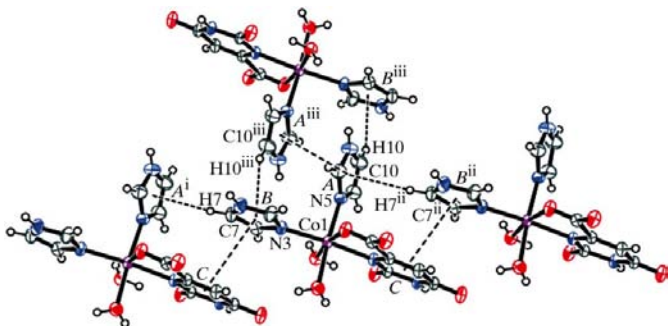
In the extended structure of (I), there are also weak  $\pi$ – $\pi$  and C–H··· $\pi$  interactions (Fig. 3). Two intermolecular  $\pi$ – $\pi$  interactions occur between two symmetry-related imidazole rings (N5/N6/C9–C11, ring A) of neighbouring molecules. Ring A is oriented in such a way that the perpendicular distances from A to A<sup>iii</sup> is 3.354 Å, the closest interatomic distance being C10···C9<sup>iii</sup> [3.435 (3) Å; symmetry code: (iii)  $-x, 1 - y, 2 - z$ ]. The distance between the ring centroids is 3.646 (2) Å. Also,  $\pi$ – $\pi$  interactions occur between the other imidazole ring (N3/N4/C6–C8, ring B) and the pyrimidine ring of the orotate ligand (N1/N2/C2–C5, ring C). Rings B and C are oriented in such a way that the perpendicular distance

**Figure 1**

The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. The *AD-DA* dimer pairs are shown (dashed lines). [Symmetry code (i) and symmetry code used to generate unlabelled atoms:  $1 - x, 1 - y, 1 - z$ .]

**Figure 2**

The hydrogen-bonding interactions of (I), shown as dashed lines.

**Figure 3**

The  $\pi$ - $\pi$  and C-H $\cdots$  $\pi$  interactions of (I), shown as dashed lines. [Symmetry codes: (i)  $x - 1, y, z$ ; (ii)  $-x, -y, -z + 1$ ; (iii)  $x + 1, y, z$ .]

from *B* to *C* is 3.575 Å, the closest interatomic distance is  $C7 \cdots C2^i$  [3.430 (3) Å; symmetry code: (i)  $-1 + x, y, z$ ] and the distance between the ring centroids is 3.950 (2) Å. The dihedral angle between the planes of rings *B* and *C* is 10.51 (14)°. Rings *A* and *B* are also involved in intermolecular C-H $\cdots$  $\pi$  interactions with atoms *C7* and *C10*. For the  $C7-H7 \cdots \pi$  and  $C10-H10 \cdots \pi$  contacts, the distance between atom *H7* and

the centroid of ring *A* (*CgA*) is 2.97 (3) Å and the  $C7-H7 \cdots CgA$  angle is 171 (2)°, while the distance between atom *H10* and the centroid of ring *B* (*CgB*) is 2.81 (4) Å and the  $C10-H10 \cdots CgB$  angle is 149 (3)°.

## Experimental

The title complex was prepared according to the method of Yeşilel *et al.* (2007), and was recrystallized from water.

### Crystal data

$[\text{Co}(\text{C}_5\text{H}_2\text{N}_2\text{O}_4)(\text{C}_3\text{H}_4\text{N}_2)_2(\text{H}_2\text{O})_2]$	$V = 1572.9 (2) \text{ \AA}^3$
$M_r = 385.21$	$Z = 4$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 8.6280 (10) \text{ \AA}$	$\mu = 1.13 \text{ mm}^{-1}$
$b = 13.5160 (10) \text{ \AA}$	$T = 296 (2) \text{ K}$
$c = 13.6950 (10) \text{ \AA}$	$0.35 \times 0.30 \times 0.16 \text{ mm}$
$\beta = 99.978 (6)^\circ$	

### Data collection

Enraf-Nonius CAD-4 diffractometer	3009 measured reflections
Absorption correction: integration ( <i>CAD-4 EXPRESS</i> ; Enraf-Nonius, 1993)	2815 independent reflections
$T_{\min} = 0.679, T_{\max} = 0.745$	2552 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.038$

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.038$	5 restraints
$wR(F^2) = 0.105$	All H-atom parameters refined
$S = 1.11$	$\Delta\rho_{\max} = 0.89 \text{ e \AA}^{-3}$
2815 reflections	$\Delta\rho_{\min} = -0.80 \text{ e \AA}^{-3}$
274 parameters	

All H atoms were refined freely; the  $C6-H6$ ,  $C7-H7$  and  $C4-H11$  bond lengths were fixed at 1.00 (2) Å, and the  $\text{Co1}-\text{O5}$  and  $\text{C2}-\text{C1}$  bond lengths were fixed at 2.00 (2) and 1.40 (2) Å, respectively.

Data collection: *CAD-4 EXPRESS* (Enraf-Nonius, 1993); cell refinement: *CAD-4 EXPRESS*; data reduction: *CAD-4 EXPRESS*; 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).

**Table 1**

Selected geometric parameters (Å, °).

N1—Co1	2.117 (2)	O1—Co1	2.0846 (17)
N3—Co1	2.119 (2)	O5—Co1	2.0941 (17)
N5—Co1	2.123 (2)	O6—Co1	2.1845 (18)
O1—Co1—N1	78.85 (7)	N1—Co1—N5	93.07 (8)
O5—Co1—N1	92.87 (8)	N3—Co1—N5	93.83 (8)
O1—Co1—N3	95.22 (7)	O1—Co1—O6	87.34 (7)
O5—Co1—N3	92.63 (8)	O5—Co1—O6	88.64 (7)
N1—Co1—N3	170.95 (8)	N1—Co1—O6	82.93 (8)
O1—Co1—N5	90.65 (8)	N3—Co1—O6	90.02 (8)
O5—Co1—N5	92.83 (8)	N5—Co1—O6	175.80 (8)

**Table 2**

Hydrogen-bond 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>
N2—H2...O3 <sup>i</sup>	0.83 (3)	2.06 (3)	2.874 (3)	165 (3)
N4—H4...O3 <sup>ii</sup>	0.82 (4)	2.08 (4)	2.879 (3)	166 (3)
N6—H6N...O2 <sup>iii</sup>	0.79 (4)	2.11 (4)	2.891 (3)	169 (3)
O5—H5A...O4	0.89 (4)	1.88 (4)	2.729 (3)	160 (3)
O5—H5B...O2 <sup>iv</sup>	0.84 (4)	1.85 (4)	2.687 (3)	170 (3)
O6—H6A...O4 <sup>v</sup>	0.84 (4)	1.98 (4)	2.816 (3)	173 (3)
O6—H6B...O3 <sup>vi</sup>	0.82 (4)	2.05 (4)	2.783 (3)	150 (4)

 Symmetry codes: (i)  $-x + 1, -y + 1, -z + 1$ ; (ii)  $x - 1, -y + \frac{1}{2}, z + \frac{1}{2}$ ; (iii)  $x, -y + \frac{1}{2}, z + \frac{1}{2}$ ; (iv)  $-x, y + \frac{1}{2}, -z + \frac{3}{2}$ ; (v)  $-x, -y + 1, -z + 1$ ; (vi)  $x - 1, y, z$ .

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SF3031). Services for accessing these data are described at the back of the journal.

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