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Diaquabis(1,10-phenanthroline)cobalt(II) diorotate 2.25-hydrate

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.003 Å
H-atom completeness 99%
Disorder in solvent or counterion
R factor = 0.037
wR factor = 0.100
Data-to-parameter ratio = 17.3

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

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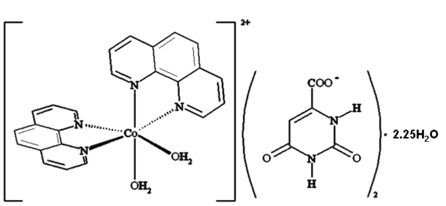
In the title compound, $[Co(C_{12}H_8N_2)_2(H_2O)_2](C_5H_3N_2O_4)_2\cdot 2.25H_2O$, the cobalt cation, located on a twofold axis, is coordinated by two symmetry-related aqua ligands together with a pair of symmetry-related bidentate phenanthroline (phen) molecules, and exhibits a distorted octahedral coordination. The unique orotate anion in the asymmetric unit has a single negative charge. The coordinated water molecules link the orotate ions to the metal complex *via* O—H···O hydrogen bonds. Each uncoordinated water molecule is hydrogen bonded to orotate ions through O—H···O hydrogen bonds.

Comment

Orotic acid (uracil-6-carboxylic acid, vitamin B13) and its metal-ion complexes play a crucial role in the metabolism of pyridine nucleotides and in many living organisms (Lalioti *et al.*, 1998). Its metal-ion complexes are of special interest in curing illnesses associated with a deficiency of various metal ions (Kumberger *et al.*, 1993). Thus, the coordination chemistry of orotic acid has been the subject of many studies (Sabat *et al.*, 1980; Karipides & Thomas, 1986; Castan *et al.*, 1990). Furthermore, DNA interaction of mixed-ligand metal complexes with phenanthroline (phen) has also been investigated (Sastri *et al.*, 2003). To study further the effects of metal ions on the complexation of orotic acid and its possible use in pharmocology, we have prepared the title compound, (I), and determined its structure.



(I)

Fig. 1 shows an *ORTEP*-3 (Farrugia, 1997) plot of (I). The Co^{II} atom, located on a twofold axis, is octahedrally coordinated by a pair of bidentate phen molecules together with two water molecules. The mean planes through the bidentate phen ligands form a dihedral angle of 75.33 (2)°. The Co—O distance is 2.1089 (13) Å and Co—N distances lie in the range 2.1216 (15)–2.1300 (14) Å (Table 1). The geometry of the phen ligand is comparable to that observed in a phen-containing cobalt complex (Hökelek & Necefoğlu, 1997). The unique orotate anion in the asymmetric unit carries a single negative charge and is not coordinated to Co. The orotate moieties are

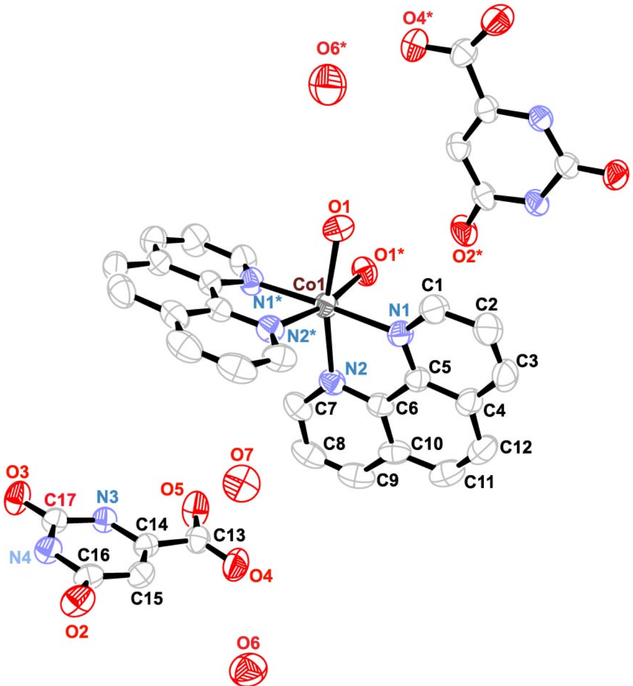


Figure 1
An *ORTEP*-3 (Farrugia, 1997) drawing of the title compound, showing the atom-numbering scheme and 50% probability displacement ellipsoids. H atoms have been omitted for clarity. Atoms with an asterisk are at the symmetry position ($1 - x, y, \frac{1}{2} - z$). Water oxygen O7 is disordered, with an occupancy of 0.25 at each site.

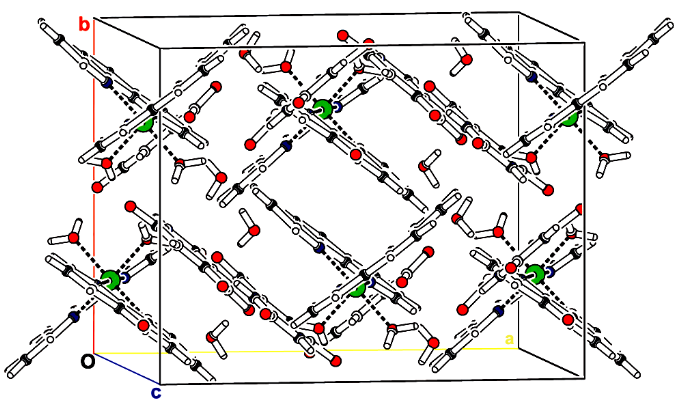


Figure 2
The crystal structure of (I).

almost planar. Nevertheless, there is a slight deviation from planarity, the torsion angle N3—C14—C13—O5 being 5.0 (2)°. The mean plane through the orotate anion in the asymmetric unit is almost parallel [dihedral angle 2.74 (5)°] to that through the phen moiety.

The crystal structure of (I) is shown in Fig. 2. The coordinated water molecules link the orotate ions to the metal complex *via* O1—H1*A*···O2^{i} and O1—H1*B*···O5^{ii} hydrogen bonds (symmetry codes as in Table 2). Each uncoordinated water molecule (O6) is hydrogen bonded to orotate ions through O6—H6*B*···O4 and O6—H6*A*···O3^{v} hydrogen bonds. Furthermore, the symmetry-related orotate ions are linked by N3—H3···O3^{iii} and N4—H4···O2^{iv} hydrogen bonds to form chains (see Table 2 for symmetry codes).

Experimental

The [Co(HOra)$(H_2O)_4$]·H_2O (Ora = orotate) precursor was prepared as previously described by İçbudak *et al.* (2003). A solution of phenanthroline (0.748 g, 4 mmol) in ethanol (15 ml) was added dropwise to a stirred solution of [Co(HOra)$(H_2O)_4$]·H_2O (0.61 g, 2 mmol) in water (50 ml). The resulting solution was heated to 333 K in a temperature-controlled bath and then refluxed and stirred for 12 h at 333 K. The orange crystals of the title compound, that formed after cooling to room temperature, were filtered off and washed with 10 ml portions of cold distilled water and acetone and dried *in vacuo*. Yield: 0.92 g (79.3%). Found: C 50.79, H 4.01, N 13.56%; calculated for $C_{34}H_{30.5}CoN_8O_{12.25}$: C 50.66, H 3.81, N 13.90%.

Crystal data

[Co$(C_{12}H_8N_2)_2(H_2O)_2$]-
$(C_5H_3N_2O_4)_2$·2.25H_2O
M_r = 806.09
Monoclinic, $C2/c$
a = 16.1401 (11) Å
b = 12.5692 (10) Å
c = 16.5650 (11) Å
β = 92.435 (5)°
V = 3357.5 (4) Å^3
Z = 4
D_x = 1.595 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 4607 reflections
θ = 2.1–29.7°
μ = 0.59 mm^{-1}
T = 293 (2) K
Prism, orange
0.35 × 0.23 × 0.15 mm

Data collection

Stoe IPDS-2 diffractometer
φ scans
Absorption correction: none
4607 measured reflections
4607 independent reflections
3086 reflections with $I > 2\sigma(I)$
θ_{max} = 29.4°
$h = -22 \rightarrow 22$
$k = 0 \rightarrow 17$
$l = 0 \rightarrow 22$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.037
$wR(F^2)$ = 0.100
S = 0.91
4607 reflections
267 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0648P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ < 0.001
$\Delta\rho_{max}$ = 0.26 e Å^{-3}
$\Delta\rho_{min}$ = −0.51 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Co1—O1	2.1089 (13)	N1—C5	1.352 (2)
Co1—N2	2.1216 (15)	N2—C7	1.327 (2)
Co1—N1	2.1300 (14)	N2—C6	1.358 (2)
O2—C16	1.241 (2)	N3—C17	1.355 (2)
O3—C17	1.225 (2)	N3—C14	1.363 (2)
O4—C13	1.234 (2)	N4—C17	1.371 (2)
O5—C13	1.242 (2)	N4—C16	1.373 (2)
N1—C1	1.325 (2)		
O1—Co1—O1^{i}	84.08 (8)	C7—N2—Co1	128.95 (14)
O1—Co1—N2	167.01 (5)	C6—N2—Co1	113.15 (11)
O1^{i}—Co1—N2	91.50 (6)	C17—N4—C16	126.05 (15)
O1—Co1—N2^{i}	91.50 (6)	O4—C13—O5	128.15 (18)
N2—Co1—N2^{i}	95.31 (8)	O4—C13—C14	116.55 (16)
O1—Co1—N1^{i}	92.20 (6)	O5—C13—C14	115.30 (16)
N2—Co1—N1^{i}	100.01 (6)	C15—C14—C13	124.09 (16)
O1—Co1—N1	89.88 (5)	N3—C14—C13	115.10 (14)
N2—Co1—N1	78.06 (5)	O2—C16—N4	118.86 (17)
N2^{i}—Co1—N1	100.01 (6)	O2—C16—C15	125.97 (16)
N1^{i}—Co1—N1	177.19 (8)	N4—C16—C15	115.17 (14)
C1—N1—C5	118.12 (16)	O3—C17—N3	123.81 (15)
C1—N1—Co1	128.71 (13)	O3—C17—N4	121.04 (16)
C5—N1—Co1	112.72 (11)	N3—C17—N4	115.15 (14)
C7—N2—C6	117.77 (17)		

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

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

D—H···A	D—H	H···A	D···A	D—H···A
N3—H3···O5	0.86	2.27	2.639 (2)	106
O6—H6B···O4	0.88 (4)	1.95 (4)	2.790 (3)	160 (3)
O1—H1A···O2^{vi}	0.85 (3)	1.96 (3)	2.798 (2)	173 (2)
O1—H1B···O5^{ii}	0.85 (3)	1.94 (4)	2.735 (2)	156 (3)
N3—H3···O3^{iii}	0.86	2.03	2.876 (2)	167
N4—H4···O2^{iv}	0.86	2.02	2.868 (2)	170
O6—H6A···O3^{v}	0.82 (5)	2.41 (5)	3.103 (3)	143 (4)

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

H atoms attached to the water atoms O1 and O6 were located in a difference Fourier map and their coordinates and U_{iso} parameters were refined [O—H = 0.82 (5)–0.88 (4) Å]. The remaining H atoms were placed geometrically and allowed to ride on their parent atoms, with C—H = 0.93 Å, N—H = 0.86 Å and U_{iso}(H) = 1.2U_{eq}(C or N). At this stage, the maximum difference density of 1.61 e Å^{-3} (the ratio of maximum/minimum residual density is 3.22) indicated the presence of a possible atom site. A check for the solvent-accessible volume using *PLATON* (Spek, 1997) showed a total potential solvent area volume of 74 Å^3. Attempts to refine this peak as a water O atom (O7) resulted in a partial occupancy of 0.262 (10). The occupancy was later fixed at 0.25 to result in one water (O7) per unit cell. H atoms attached to O7 were not located.

Data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-AREA*; data reduction: *X-RED* (Stoe & Cie, 2002); program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 (Farrugia, 1997) and *PLATON* (Spek, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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