Tetraaquaorotatonickel(II) Monohydrate

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Abstract. $[Ni(C_5H_2N_2O_4)(H_2O)_4].H_2O$, C_5H_{10}-$N_2NiO_8.H_2O$, triclinic, $P\bar{1}$, $a = 7.235$ (1), $b = 8.295$ (1), $c = 10.060$ (1) Å, $\alpha = 80.18$ (1), $\beta = 109.55$ (1), $\gamma = 114.36$ (1)°, $V = 517.9$ Å^3, $Z = 2$, $D_m = 1.93$, $D_c = 1.94$ Mg m^{-3}. The structure has been determined from 1229 diffractometer-measured intensities (Cu $K\alpha$ radiation, $\lambda = 1.5418$ Å) and refined to $R = 0.040$. The orotate ligand is bonded to Ni through the carboxylic O atom [Ni–O(1) 2.023 (3) Å] and N(1) from the pyrimidine ring [Ni–N(1) 2.049 (3) Å].

Introduction. Green crystals of the compound were obtained from an aqueous solution containing $NiCl_2$ and orotic acid in the molar ratio 1:1. All measurements for a crystal $0.15 \times 0.15 \times 0.20$ mm were made on a Syntex $P2_1$ four-circle diffractometer with graphite-monochromated Cu $K\alpha$ radiation. Of the 1294 reflections measured up to $2\theta = 110°$ by the θ–2θ scan technique, 1229 with $I > 1.96\sigma(I)$ were used in the subsequent calculations. The scan rate varied from 3.0 to 20.0° min^{-1}, depending on the intensity of reflection. The intensities were corrected for Lorentz and polarization factors, but not for absorption.

The structure was solved by Patterson and Fourier syntheses and refined by full-matrix least squares to $R = 0.040$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} = 0.050$.* The function minimized was $\sum w(|F_o| - |F_c|)^2$ with $w^{-1} = \sigma^2(F_o) + (0.01F_o)^2$. The H atoms were located from a difference map and included in the refinement with isotropic thermal parameters. Scattering factors were taken from Cromer & Waber (1974) with anomalous-dispersion corrections for Ni according to Templeton (1962).

All calculations were performed on a Nova 1200 computer with programs from the Syntex *XTL* structure determination system. Final positional parameters are given in Table 1.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34922 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Fractional atomic coordinates* ($\times 10^5$ *for* Ni, $\times 10^3$ *for* H, $\times 10^4$ *for others*)

	x	y	z
Ni	25222 (8)	34461 (7)	18399 (6)
O(1)	2315 (4)	1247 (3)	1087 (3)
O(2)	2547 (4)	3590 (3)	5147 (3)
O(3)	2017 (5)	−1528 (3)	1612 (3)
O(4)	2687 (4)	−1769 (3)	6886 (2)
O(W5)	2739 (5)	5523 (4)	2769 (4)
O(W6)	−780 (4)	2685 (4)	1010 (3)
O(W7)	5865 (4)	4429 (4)	2488 (3)
O(W8)	2705 (5)	4893 (4)	−17 (3)
O(W9)	3485 (8)	1587 (7)	−1260 (4)
N(1)	2375 (4)	1786 (4)	3594 (3)
N(3)	2593 (5)	898 (4)	5956 (3)
C(2)	2515 (5)	2164 (5)	4895 (4)
C(4)	2545 (5)	−746 (5)	5829 (4)
C(5)	2335 (6)	−1102 (5)	4431 (4)
C(6)	2296 (5)	171 (5)	3417 (4)
C(7)	2193 (6)	−77 (5)	1925 (4)
H(3)	266 (7)	107 (6)	689 (5)
H(5)	218 (7)	−212 (5)	426 (4)
H(5A)	259 (9)	530 (8)	348 (7)
H(5B)	238 (7)	631 (7)	252 (5)
H(6A)	−123 (8)	201 (7)	23 (6)
H(6B)	−145 (8)	215 (6)	153 (5)
H(7A)	640 (8)	517 (7)	314 (6)
H(7B)	626 (8)	353 (7)	282 (5)
H(8A)	202 (7)	549 (6)	−39 (5)
H(8B)	295 (9)	467 (8)	−58 (7)
H(9A)	312 (10)	135 (9)	−59 (8)
H(9B)	450 (10)	225 (9)	−102 (7)

Table 2. *Bond angles* (°)

O(1)–Ni–N(1)	80.0 (1)	Ni–N(1)–C(6)	113.6 (2)
O(1)–Ni–O(W5)	174.7 (1)	C(2)–N(1)–C(6)	118.3 (3)
O(1)–Ni–O(W6)	90.0 (1)	N(1)–C(2)–O(2)	122.8 (3)
O(1)–Ni–O(W7)	91.8 (1)	N(1)–C(2)–N(3)	117.9 (3)
O(1)–Ni–O(W8)	93.5 (1)	N(3)–C(2)–O(2)	119.3 (3)
O(W5)–Ni–O(W6)	90.8 (1)	C(2)–N(3)–C(4)	125.8 (3)
O(W5)–Ni–O(W7)	88.0 (1)	N(3)–C(4)–O(4)	119.8 (3)
O(W5)–Ni–O(W8)	91.8 (2)	N(3)–C(4)–C(5)	114.2 (3)
O(W6)–Ni–O(W7)	173.6 (1)	C(5)–C(4)–O(4)	126.0 (4)
O(W6)–Ni–O(W8)	86.3 (1)	C(4)–C(5)–C(6)	118.7 (4)
O(W7)–Ni–O(W8)	87.4 (1)	N(1)–C(6)–C(5)	125.0 (4)
N(1)–Ni–O(W5)	94.7 (1)	N(1)–C(6)–C(7)	113.3 (3)
N(1)–Ni–O(W6)	94.6 (1)	C(5)–C(6)–C(7)	121.7 (4)
N(1)–Ni–O(W7)	91.8 (1)	O(1)–C(7)–O(3)	124.3 (4)
N(1)–Ni–O(W8)	173.5 (1)	C(6)–C(7)–O(1)	116.3 (3)
Ni–O(1)–C(7)	116.7 (3)	C(6)–C(7)–O(3)	119.4 (3)
Ni–N(1)–C(2)	127.9 (3)		

Discussion. The molecular structure and bond lengths are shown in Fig. 1. Valence angles are summarized in Table 2. The orotate ligand is coordinated to Ni through the carboxylic O(1), and N(1) from the pyrimidine ring with Ni—O(1) = 2·023 (3) and Ni—N(1) = 2·049 (3) Å. The octahedral coordination around Ni is completed by four water O atoms. The Ni—O(W) distances range from 2·024 (4) to 2·107 (3) Å. The mode of chelation found is consistent with that postulated from potentiometric and ion-exchange studies (Doody, Tucci, Scruggs & Li, 1966).

Structural features of the five-membered chelate ring formed by Ni, N(1), C(6), C(7) and O(1) are close to those of a similar system found in diaquabis(pico-linato)nickel(II) (Loiseleur, 1972), although the Ni—O and Ni—N distances of the orotate are slightly shorter than the analogous distances, 2·053 and 2·068 Å respectively, in the picolinate. However, other inter-atomic distances and valence angles of the ring have almost identical values in both compounds. The structure of the uracil fragment of the complex undergoes no appreciable changes compared with that of the free orotic acid (Takusagawa & Shimada, 1973) or with that of uracil itself (Stewart & Jensen, 1967).

Like the molecule in the crystal of free orotic acid, the orotate ligand in the Ni complex occurs in the keto form. The most noticeable difference appears in the C(2)—N(1)—C(6) angle whose value of 118·3° in the Ni complex is smaller than that found in orotic acid, 122·7°. On the other hand, the N(1)—C(6)—C(5) (125·0°) and N(1)—C(2)—N(3) (117·9°) angles are
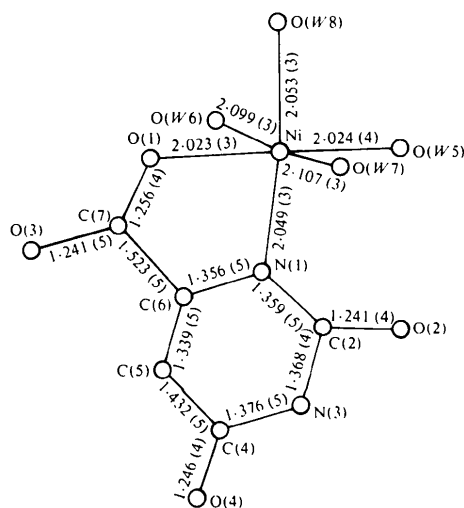
slightly increased compared with those in orotic acid, 121·7 and 114·7° respectively. One can also observe an elongation of the C(2)—O(2) and C(4)—O(4) lengths with respect to the analogous bonds in orotic acid.

The largest deviation from the least-squares plane through the pyrimidine ring (equation: $0·8979X + 0·3762Y + 0·2290Z = 1·2391$) for the atoms defining that plane are 0·012 (4) and −0·015 (5) Å for C(4) and C(5) respectively. The angle between this plane and the plane through the chelate ring is 4·7°.

Of the four coordinated water molecules, three form quite strong hydrogen bonds with the exocyclic O atoms and carboxylic groups of adjacent molecules (Table 3), with W(5) also included in the intra-molecular hydrogen bond with O(2). Apart from the hydrogen bonds in which the coordinated water molecules are involved, we also find N—H···O bonds in which N(3) from the pyrimidine ring is a donor and O(W9) from the lattice water molecule an acceptor. The latter molecule is also involved in the formation of an O(W9)—H···O(1) hydrogen bond with the carboxylic O atom from the coordination sphere. The values of the D—H···A angles indicate that the geometry of the hydrogen bonds does not differ significantly from linearity.

Table 3. *Hydrogen-bond distances* (Å) *and angles* (°)

D-H···A	D···A	D—H	H···A	∠D—H···A
O(W5) H(5A)···O(2)^i	2·654 (4)	0·74 (6)	2·01 (6)	147 (7)
O(W5)-H(5B)···O(3)^{ii}	2·699 (5)	0·77 (6)	1·95 (5)	165 (6)
O(W6)-H(6A)···O(3)^{iii}	2·694 (4)	0·93 (6)	1·81 (6)	158 (6)
O(W6) H(6B)···O(4)^{iv}	2·739 (4)	0·79 (6)	1·99 (6)	157 (5)
O(W7)-H(7A)···O(2)^v	2·763 (4)	0·86 (5)	1·92 (5)	168 (5)
O(W7)-H(7B)···O(4)^{vi}	2·711 (4)	0·88 (6)	1·85 (6)	166 (6)
O(W9) -H(9A)···O(1)^i	2·698 (6)	0·77 (6)	1·94 (8)	168 (8)
N(3) H(3)···O(W9)	2·761 (5)	0·96 (5)	1·82 (5)	166 (5)

Symmetry code: (i) x,y,z; (ii) x, 1 + y, z; (iii) − x, −y, −z; (iv) −x, −y, 1 − z; (v) 1 − x, 1 − y, 1 − z; (vi) 1 x, −y, 1 − z.

Fig. 1. Atom numbering and bond lengths (Å) with e.s.d.'s in parentheses.

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