S1—O12	1.434 (5)	S3—O32	1.431 (6)
S1—O11	1.439 (5)	S3—C37	1.746 (8)
S1—C17	1.753 (10)	S3—C34	1.786 (7)
S1—C14	1.762 (8)		
C11—Sn—C21	123.0 (3)	C31—Sn—Cl	101.9 (2)
C11—Sn—C31	115.8 (3)	C11—Sn—O11^i	69.9 (2)
C21—Sn—C31	109.2 (3)	C21—Sn—O11^i	80.3 (2)
C11—Sn—Cl	102.5 (2)	C31—Sn—O11^i	86.2 (2)
C21—Sn—Cl	100.6 (2)	Cl—Sn—O11^i	170.92 (11)

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

Data collection: *TEXSAN* (Molecular Structure Corporation, 1985). Cell refinement: *TEXSAN*. Data reduction: *DATRD2* in *NRCVAX* (Gabe, Le Page, Charland, Lee & White, 1989). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ORTEPII* (Johnson, 1976) in *NRCVAX*.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and torsion angles have been deposited with the IUCr (Reference: FG1190). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Triclinic Form of Tetraaqua(orotato-N,O)-magnesium(II) Hydrate at 153 K

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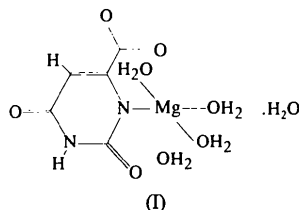
Abstract

In the title complex, [Mg(C₅H₂N₂O₄)(H₂O)₄].H₂O, orotic acid (uracil-6-carboxylic acid or 1,2,3,6-tetrahydro-2,6-dioxo-4-pyrimidinecarboxylic acid) coordinates to Mg through the deprotonated heterocyclic N1 atom and the O atom of the adjacent carboxylate group. The coordination sphere of the Mg atom is octahedral with water molecules occupying the four remaining coordination positions. The bond lengths in the coordination sphere are in the range 2.0128 (13) to 2.1295 (13) Å for the Mg—O bonds and 2.1663 (14) Å for the Mg—N bond. The C=O bond lengths for the exocyclic O2 and O4 atoms of the orotato ligand are 1.247 (2) and 1.249 (2) Å, respectively.

Comment

Orotic acid (uracil-6-carboxylic acid, vitamin B₁₃) occupies a unique position biologically by being the only effective precursor in the biosynthesis of the pyrimidine bases of nucleic acids. It has been established that during these processes the presence of metal ions, especially magnesium, is necessary, particularly during the phosphoribosylation of orotic acid (Victor, Greenberg & Sloan, 1979). Besides the biological interest, orotic acid is also interesting as a ligand because the tautomerism between the ketonic and enolic forms makes multifaceted coordination possible. Orotic acid is potentially a polydentate ligand, since, especially above

the deprotonation pH values, coordination may occur through the heterocyclic N atoms, the carboxyl group and the exocyclic carbonyl O atoms. The coordination sites with the greatest potential above the deprotonation pH are the ring N atoms, but once they are deprotonated or coordinated to a metal ion, complexation of the carbonyl O atoms is greatly enhanced.

In polymeric Co[III] and Ni[II] complexes, orotic acid coordinates to metal ions through the N1 ring atom and the adjacent carboxylate O atom, and through the exocyclic O4 atom, which is the more basic of the two exocyclic O atoms, to another metal ion (Mutikainen & Lumme, 1980). The orotato anion is thus a tridentate ligand in these complexes and acts as a bridge between metal ions. In Cu[II] (Arrizabalaga, Castan & Dahan, 1983), Ni[II] (Sabat, Zglinska & Jezowska-Trzebiatowska, 1980) and Zn[II] (Mutikainen, 1989; Kumberger, Riede & Schmidbaur, 1991) complexes, the interaction of the O4 atom with metal ions is small or absent altogether. In the Ca[II]–orotato complex, one orotato ligand binds three Ca^{2+} ions and the O4 atom does not participate in coordination at all (Kumberger *et al.*, 1991). As an extension of these studies, the structure of tetra-aqua(orotato-*N,O*)magnesium(II) hydrate, (I), has been determined and is presented here.

(I)

The deprotonated orotato ligand in (I) coordinates to the Mg atom through both the heterocyclic N1 atom and the O atom of the adjacent carboxylate group (Fig. 1). The Mg coordination sphere is octahedral, with bond
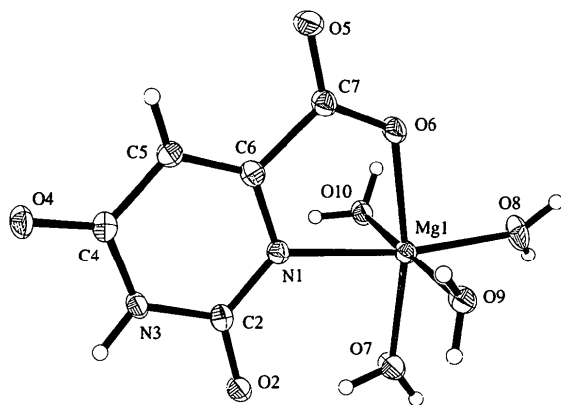
lengths in the range 2.0128 (13) to 2.1295 (13) Å for the Mg—O bonds and 2.1663 (14) Å for the Mg—N bond. The C=O bond lengths for the exocyclic O2 and O4 atoms of the orotato ligand are 1.247 (2) and 1.249 (2) Å, respectively. These values are typical for orotato complexes. One of the carbonyl O atoms forms an intramolecular hydrogen bond with a coordinated water molecule (O7), where the distance from O2 to O7 is 2.682 (2) Å and the O7—H7*A*···O2 angle is 155 (2)°. The water of crystallization is engaged only in hydrogen bonding and the magnesium–orotato molecules are held together *via* an extended three-dimensional hydrogen-bond network.

Experimental

The title compound was prepared by mixing equimolar amounts of MgO and orotic acid in water solution with gentle warming. The reaction mixture was then filtered and placed in a closed vessel in an oven. Small needle-shaped crystals were obtained at 310 K after 24 h. These crystals were the orthorhombic form of the magnesium–orotato complex with 2.5 waters of crystallization (Mutikainen, 1996). When the crystals were stored in their mother solution, they dissolved and large prismatic crystals were formed over a period of six months. A suitable crystal was selected for the X-ray measurements and it was mounted on a glass fibre using the oil-drop method (Kottke & Stalke, 1993). Data were collected at 153 K. The density D_m was measured by flotation.

Crystal data

[Mg(C$_5$H$_2$N$_2$O$_4$)(H$_2$O)$_4$].-H$_2$O	Mo $K\alpha$ radiation
$M_r = 268.48$	$\lambda = 0.71073$ Å
Triclinic	Cell parameters from 25
$P\bar{1}$	reflections
$a = 7.135 (1)$ Å	$\theta = 3.5–6.0°$
$b = 8.338 (2)$ Å	$\mu = 0.214$ mm^{-1}
$c = 10.089 (2)$ Å	$T = 293 (2)$ K
$\alpha = 80.53 (3)°$	Prismatic
$\beta = 71.16 (3)°$	$0.35 \times 0.30 \times 0.25$ mm
$\gamma = 67.56 (3)°$	Colourless
$V = 524.5 (2)$ Å^3	
$Z = 2$	
$D_x = 1.700$ Mg m^{-3}	
$D_m = 1.70 (1)$ Mg m^{-3}	

Data collection

Rigaku AFC-7S diffractometer	2088 observed reflections [$F^2 > 2\sigma(F^2)$]
$\omega/2\theta$ scans	$\theta_{max} = 26.50°$
Absorption correction:	$h = -8 \rightarrow 7$
ψ-scan (North, Phillips & Mathews, 1968)	$k = -10 \rightarrow 0$
	$l = -12 \rightarrow 12$
$T_{min} = 0.964$, $T_{max} = 1.000$	3 standard reflections monitored every 200
2143 measured reflections	reflections
2143 independent reflections	intensity decay: 0.3%

Fig. 1. A view of the title magnesium–orotato complex with ellipsoids drawn at the 50% probability level. The water of crystallization has been omitted.

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0328$
$wR(F^2) = 0.0859$
$S = 1.060$
2143 reflections
203 parameters
H atoms refined freely with isotropic displacement parameters
$w = 1/[\sigma^2(F_o^2) + (0.0434P)^2 + 0.2995P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.009$

$\Delta\rho_{max} = 0.388$ e Å⁻³
$\Delta\rho_{min} = -0.245$ e Å⁻³
Extinction correction:
SHELXL93 (Sheldrick, 1993)
Extinction coefficient: 0.121 (8)
Atomic scattering factors from International Tables for Crystallography (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Mg1	0.24658 (7)	0.35082 (6)	0.67661 (5)	0.0154 (2)
N1	0.2577 (2)	0.17876 (15)	0.86213 (12)	0.0150 (3)
C2	0.2485 (2)	0.2131 (2)	0.99113 (14)	0.0149 (3)
O2	0.2426 (2)	0.35557 (13)	1.01891 (10)	0.0192 (2)
N3	0.2443 (2)	0.0843 (2)	1.09682 (12)	0.0160 (3)
C4	0.2482 (2)	−0.0776 (2)	1.08229 (14)	0.0159 (3)
O4	0.2372 (2)	−0.18135 (13)	1.18663 (10)	0.0199 (2)
C5	0.2629 (2)	−0.1110 (2)	0.94422 (14)	0.0170 (3)
C6	0.2636 (2)	0.0187 (2)	0.84334 (14)	0.0151 (3)
C7	0.2627 (2)	−0.0032 (2)	0.69617 (14)	0.0167 (3)
O5	0.2700 (2)	−0.14467 (13)	0.66634 (11)	0.0248 (3)
O6	0.2517 (2)	0.12889 (13)	0.61315 (10)	0.0187 (2)
O7	0.2571 (2)	0.53873 (15)	0.77327 (12)	0.0243 (3)
O8	0.2454 (2)	0.4782 (2)	0.48673 (12)	0.0243 (3)
O9	−0.0885 (2)	0.44763 (14)	0.74824 (11)	0.0179 (2)
O10	0.5826 (2)	0.26320 (13)	0.59877 (11)	0.0185 (2)
O1	0.1409 (2)	0.1414 (2)	0.37733 (13)	0.0407 (4)

Table 2. *Selected geometric parameters (Å, °)*

Mg1—O7	2.0128 (13)	C2—N3	1.385 (2)
Mg1—O8	2.0327 (13)	N3—C4	1.370 (2)
Mg1—O6	2.0393 (12)	C4—O4	1.249 (2)
Mg1—O9	2.1198 (13)	C4—C5	1.428 (2)
Mg1—O10	2.1295 (13)	C5—C6	1.358 (2)
Mg1—N1	2.1663 (14)	C6—C7	1.528 (2)
N1—C2	1.354 (2)	C7—O5	1.243 (2)
N1—C6	1.361 (2)	C7—O6	1.262 (2)
C2—O2	1.247 (2)		
O7—Mg1—O8	97.76 (6)	O2—C2—N1	122.90 (12)
O7—Mg1—O6	168.21 (5)	O2—C2—N3	118.75 (12)
O9—Mg1—O10	177.54 (4)	N1—C2—N3	118.35 (12)
O7—Mg1—N1	91.15 (5)	C4—N3—C2	125.30 (12)
O8—Mg1—N1	170.88 (5)	O4—C4—N3	119.46 (12)
O6—Mg1—N1	77.31 (5)	O4—C4—C5	125.64 (13)
O9—Mg1—N1	90.12 (6)	N3—C4—C5	114.90 (12)
O10—Mg1—N1	92.20 (6)	C6—C5—C4	118.40 (13)
C2—N1—C6	118.04 (12)	C5—C6—N1	124.96 (13)
C2—N1—Mg1	128.83 (9)		

All non-H atoms were refined anisotropically. H atoms were located from a difference Fourier map and refined isotropically.

Data collection: AFC-7S software. Cell refinement: *TEXSAN* (Molecular Structure Corporation, 1993). Data reduction: *TEXSAN*. Program(s) used to solve structure: *SHELXTL/PC* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *SHELXTL/PC*. Software used to prepare material for publication: *SHELXL93*.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: SK1023). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Tetrakis(1-methylimidazole-N^3)zinc(II) Diperchlorate

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Abstract

The structure of the title complex, [Zn(C₄H₆N₂)₄]-(ClO₄)₂, is comprised of discrete [Zn(MeIm)₄]²⁺ (MeIm is *N*-methylimidazole) cations and perchlorate anions. The Zn atom is coordinated by four MeIm ligands in a distorted tetrahedral arrangement, with a Zn—N distance of 1.991 (2) Å and N—Zn—N bond angles ranging from 103.00 (14) to 112.80 (8)°.