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The Crystal Structure of Triammine(orotato)zinc(II) Monohydrate

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Abstract

The crystal structure of triammine(orotato)Zn(II) monohydrate, $C_4H_{13}N_5O_5Zn$, has been determined by X-ray diffraction. The compound crystallizes in space group $P\bar{1}$ with cell parameters $a = 7.052(4)$, $b = 8.722(5)$, $c = 9.616(6)$ Å, $\alpha = 114.34(5)$, $\beta = 104.63(5)$, $\gamma = 92.43(5)°$, $V = 514.2(5)$ Å^3, $Z = 2$. The structure was refined on 1924 reflections to $R = 0.040$ and $R_w = 0.045$. The deprotonated orotato ligand coordinates to the Zn(II) ion by the N1 nitrogen and by the oxygen atom of the adjacent carboxylate group. The coordination sphere around the zinc is trigonal bipyramid with the carboxylate oxygen and one ammonia molecule occupying the axial sites and two ammonia molecules and the heterocyclic N1 nitrogen of the orotato anion at equatorial sites. The conformation of the orotato anion differs slightly from that of uncomplexed orotic acid, the C6–N1–C2 angle being 4.6° smaller and the adjacent angles 3.0° and 3.2° larger. The crystal structure is dominated by columnar packing of the complex molecules. The columns are held together by an extensive hydrogen bond network.

Introduction

Orotic acid, 2,6-dioxo-1,2,3,4-tetrahydro-4-pyrimidinecarboxylic acid, occupies biologically a unique position by being the only effective precursor in the biosyntheses 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 the orotic acid [1, 2].

The metal ion makes orotic acid available as N(3)H dianion where N1 is deprotonated and thus available for the phosphoribosylation. Thus, knowledge of the structural characteristics of the metal complexes of orotic acid helps in understanding the mechanism of the phosphoribosylation in biological systems.

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 is potentially a polydentate ligand since, especially above the deprotonation pH values, coordination may occur through the two heterocyclic nitrogen atoms of the pyrimidine ring, the carboxyl group and the exocyclic carbonyl oxygens [3–6]. The most potential coordination sites above deprotonation pH are the ring nitrogens, but once they are deprotonated or coordinated to a metal ion, the complexation of the exocyclic carbonyl oxygens is greatly enhanced [7–9]. In polymeric Co(III) and Ni(II) complexes orotic acid coordinates to metal ions via the N1 ring nitrogen and adjacent carboxylate oxygen and via the O2 oxygen, which is the more basic of the two exocyclic oxygens, to another metal ion [10]. Thus orotic acid is in these complexes a tridentate ligand and acts as a bridge between metal ions.

In Cu(II) [11, 12] and Ni(II) [13] complexes the interaction of the O2 oxygen with metal ions is small or there is no interaction at all. To Cd(II) and Ca(II) ions the orotato ligand coordinates by the N1 nitrogen and adjacent carboxylate group, but in contrast with the Co and Ni complexes, the O1 oxygen coordinates to other metal ions and O2 oxygen is involved only in hydrogen bond interactions [14]. This is in contrast with the predictions that the O2 atom should be the stronger donor in the pyrimidine group [15].

To study further the effects of metal ions on the complexation of orotic acid, we have prepared the triammine(orotato)zinc(II) monohydrate and determined its crystal structure by X-ray diffraction.

Experimental

The title compound was prepared by dissolving orotic acid in a solution of 50% ethanol and 50% 12 M aqueous NH_4OH and adding an equimolar amount of $ZnCl_2 \cdot H_2O$. The resulting solution was evaporated at 313 K and after a few days the complex precipitated as colourless prismatic crystals. A crystal of dimensions 0.45 × 0.4 × 0.4 mm was sealed in a capillary tube and used for X-ray measurements. Crystal data were measured at room temperature (291 K) on a Syntex $P2_1$ diffractometer using graphite monochromatized Mo Kα radiation

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($\lambda = 0.71069$ Å). The cell parameters were determined by least-squares treatment of the adjusted angular settings of 16 reflections ($7° < 2\theta < 23°$). The crystal data are $a = 7.052(7)$, $b = 8.722(5)$, $c = 9.616(6)$ Å, $\alpha = 114.34(5)$, $\beta = 104.63(5)$, $\gamma = 92.43(5)°$, $V = 514.2(5)$ Å^3, space group $P\bar{1}$, $D_{obs} = 1.86$ g cm^{-3}, $D_{calc} = 1.85$ g cm^{-3}, $Z = 2$, formula weight = 276.6 and $F(000) = 292$. The intensity data were collected by an ω–2θ scan technique at variable scan rate 2.5 to 29.3° min^{-1} depending on the number of counts measured in a fast preliminary scan. Up to a maximum value of $2\theta = 55°$, h, $\pm k$, $\pm l$ set with maximum absolute values 9, 11, 11, respectively, 2382 reflections were measured, resulting in a set of 2335 unique reflections. Of these, 1924 were considered as observed ($I_o > 3\sigma(I_o)$). The check reflection ($0\bar{3}1$), measured every 50 reflections, exhibited no variation during the data collection. The intensities were corrected for Lorentz and polarization effects but corrections for extinction and absorption ($\mu = 24.8$ cm^{-1}) were considered unnecessary.

The structure was solved by direct methods [16]. Successive Fourier calculations and full-matrix least-squares refinement with non-hydrogen atoms anisotropic and hydrogen atoms fixed with $U = 0.05$ Å^2 led to $R = 0.040$ and $R_w = 0.044$ ($R_w = [w(|F_o| - |F_c|)^2/w|F_o|]^{1/2}$, with $w = 1/\sigma^2(F_o)$). After the last cycle $(\Delta/\sigma)_{av} = 0.0005$ and $(\Delta/\sigma)_{max} = 0.007$. The $\Delta\rho$ peaks in the final difference map were 0.78 e Å^{-3} and -0.85 e Å^{-3} and these were situated in the vicinity of the Zn atom. Scattering factors were from Cromer and Mann [17] and the anomalous dispersion corrections were applied [18]. All calculations were carried out on a UNIVAC 1100/61 E computer with MULTAN [16] and X-RAY 76 [19] and for planes a program MPLN [20].

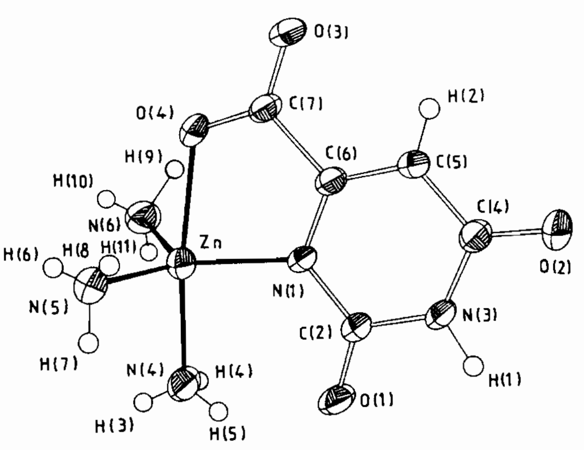

Fig. 1. ORTEP drawing and the numbering scheme of the triammine(orotato)Zn(II) complex molecule. The 50% thermal ellipsoids are shown for the non-hydrogen atoms.

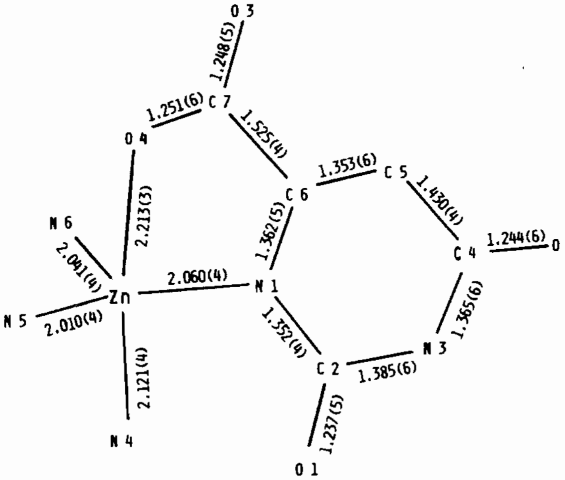

Fig. 2. Bond lengths (Å) for the Zn–orotato complex.

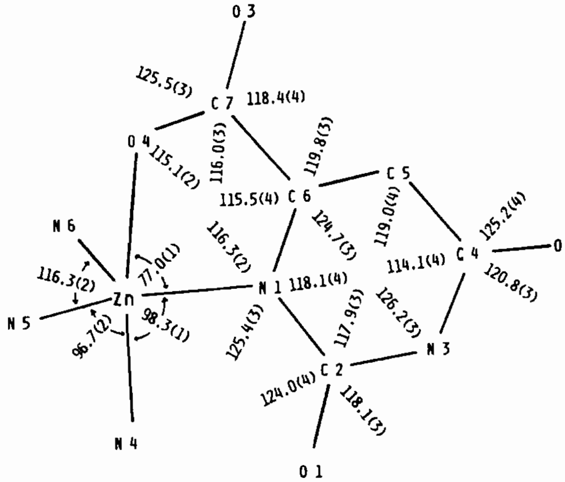

Fig. 3. Bond angles (°) for the Zn–orotato complex.

Results and Discussion

An ORTEP [21] drawing of the triammine(orotato)zinc(II) complex is shown in Fig. 1, the bond lengths in Fig. 2, angles in Fig. 3 and the packing of the molecules in Fig. 4. The atomic parameters are listed in Table I, conformational parameters in Table II and intermolecular distances in Table III.

Zinc Atom Coordination Sphere

The zinc(II) ion is involved in penta-coordinated trigonal bipyramid geometry. The carboxylate oxygen O4 of the orotato ligand occupies one axial site of the bipyramid and the other axial site is occupied by one ammonia molecule. The three equatorial sites are occupied by the N1 heterocyclic nitrogen of the orotato ligand and by two ammonia molecules.

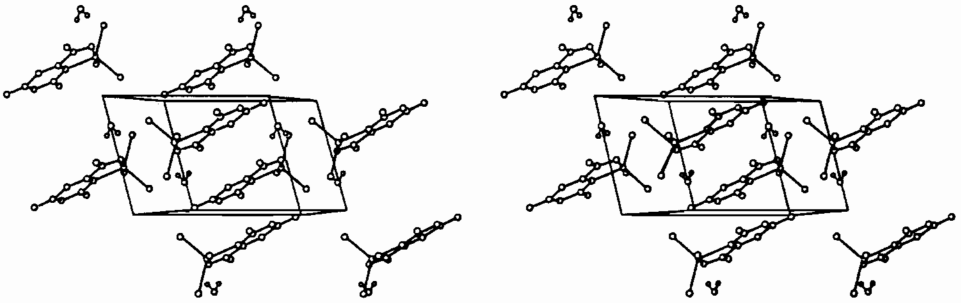

Fig. 4. The packing of the molecules.

The bond lengths are typical for this type of Zn complex [22]. As can be expected for a transition metal ion in d^{10} electronic configuration, the most electronegative carboxylate oxygen occupies the axial site. The zinc atom is out of the plane formed by equatorial ligands N5, N6 and N1 by 0.209(2) Å towards N4.

The angle formed by Zn and the axial ligands, 175.3(1)°, is typical for bipyramidal zinc complexes.

TABLE I. Fractional Atomic Coordinates (×10^4; ×10^3 for H) and U_{eq} (×10^3 Å^2)[a] with e.s.d.s in Parentheses

Atom	x	y	z	U_{eq}
Zn	6118(1)	7358(1)	2715(1)	30(3)
N1	7278(5)	6899(4)	4673(3)	26(2)
C2	8326(6)	8093(5)	6146(4)	27(2)
O1	8653(5)	9636(4)	6514(3)	48(2)
N3	9085(5)	7551(4)	7310(4)	28(2)
C4	8897(6)	5905(5)	7115(4)	27(2)
O2	9624(4)	5564(4)	8254(3)	41(2)
C5	7791(6)	4684(5)	5538(4)	28(2)
C6	7078(5)	5234(5)	4411(4)	24(2)
C7	5938(5)	3948(5)	2710(4)	27(2)
O3	5660(4)	2407(3)	2406(3)	39(2)
O4	5409(4)	4547(3)	1719(3)	36(2)
N4	6591(6)	10061(4)	3905(4)	47(2)
N5	7995(5)	7166(4)	1411(4)	36(2)
N6	3193(5)	7214(5)	1606(4)	40(2)
O5	2537(5)	–169(4)	–111(4)	54(2)
H1	988	841	825	50
H2	762	357	528	50
H3	677	1043	336	50
H4	767	1030	471	50
H5	573	1037	419	50
H6	876	646	155	50
H7	877	816	187	50
H8	753	692	63	50
H9	236	628	171	50
H10	273	823	205	50
H11	307	679	76	50
H12	337	71	65	50
H13	316	–74	–63	50

[a] $U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}\bar{a}_i{}^*\bar{a}_j{}^*\bar{a}_i\bar{a}_j$ [26].

The dihedral angle between the equatorial plane and the pyrimidine ring is 95.9(1)°.

Orotato Anion

Comparison of the structural parameters of the orotato anion of the title compound with uncoordinated orotic acid [23, 24] reveals that the changes are mainly the same as in other metal complexes of orotic acid [10–13]. The C6–N1–C2 angle is 4.6° smaller than in orotic acid due to the Zn coordination at N1. This causes widening of the adjacent N1–C6–C5 and N1–C2–N3 angles by 3.0° and 3.2°, respectively. The interatomic distances of the orotato ligand, Fig. 2, are normal. Deviations from the least-squares plane through the six atoms of the pyrimidine ring (Table II) reveal that the ring deviates only very slightly from planarity, much less than in related

TABLE II. The Least-squares Plane for the Pyrimidine Ring. The equation of the plane is expressed in direct space as $0.96595x + 0.01552y - 0.25827z = 2.67822$. Displacements from the plane (Å) with e.s.d.s in parentheses

N1[a]	–0.009(3)	C2[a]	0.003(4)	N3[a]	0.002(4)
C4[a]	–0.001(4)	C5[a]	–0.006(4)	C6[a]	0.011(4)
O1	0.026(6)	O2	–0.018(5)	Zn	0.085(6)

[a] Atoms included in the calculation of the plane.

TABLE III. Distances (Å) and Angles (°) with Interactions of the Type D– – –H···A

D	H	A	D–H	H··A	D··A	D–H··A
N3	H1	O5[a]	0.92	2.06	2.916(5)	154
N4	H3	O3[b]	0.75	2.34	2.960(6)	141
N5	H6	O2[c]	0.86	2.19	3.049(5)	177
N6	H10	O1[d]	0.93	2.25	3.148(5)	162
N6	H9	O2[e]	1.03	2.11	3.135(6)	173
O5	H13	O3[f]	0.78	2.12	2.894(5)	172

[a] $x + 1, y + 1, z + 1$. [b] $x, y + 1, z$. [c] $2 - x, 1 - y, 1 - z$. [d] $1 - x, 2 - y, 1 - z$. [e] $1 - x, 1 - y, 1 - z$. [f] $1 - x, -y, -z$.

complexes. As in other complexes, the exocyclic oxygens are out of the ring plane. The small deviations from planarity are probably a result of the fact that the Zn atom is only 0.085(6) Å out of the ring plane and thus the distortions caused by the coordination are small. The carboxylate group is twisted 4.0° and bent 3.0° in relation to the ring plane. These values are also smaller than in other metal complexes of orotic acid and even smaller than in uncoordinated orotic acid.

Crystal Packing

The principal feature of the packing is the columnar stacking of the complex molecules. The overlap of the molecules in these columns is similar to that found in molecular systems with extended π-networks [25] and the distance of 3.34 Å between the stacking pyrimidine rings is also normal.

The columnar stacks are held together by an extensive intermolecular hydrogen bond network (Table III). The water molecules are acceptors from the N3 nitrogen of the pyrimidine ring and donors to the O3 carboxylate oxygen and thus connect the adjacent complex molecules within the columns.

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