metal-organic papers

Diaqua(2,6-dioxo-1,2,3,6-tetrahydro-pyrimidine-4-carboxylato-κN^3)(1,10-phenanthroline)zinc(II) dihydrate

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In the title compound, $[Zn(C_5H_2N_2O_4)(C_{12}H_8N_2)(H_2O)_2]\cdot 2H_2O$, the Zn atom is coordinated by N and O atoms from the orotate (2,6-dioxo-1,2,3,6-tetrahydropyrimidine-4-carboxylate) ligand, two N atoms from 1,10-phenanthroline and two aqua O atoms in a distorted octahedral geometry. The presence of intermolecular N—H···O and O—H···O hydrogen bonds and π–π-stacking interactions between the phenanthroline ligands results in a three-dimensional structure.

Comment

Orotic acid (2,6-dioxo-1,2,3,6-tetrahydropyrimidine-4-carboxylic acid; vitamin B_{13}; H_3dtpc) is an important pyrimidine derivative, as the effective precursor in the biosynthesis of pyrimidine base of nucleic acids in living organisms, and so it occupies a unique role in bio-inorganic and pharmaceutical studies (Leberman *et al.*, 1955). Aside from the biological interest, orotic acid is also a good organic building block in coordination chemistry. Its ketonic and enolic tautomers, along with its asymmetric geometry, make it a versatile multidentate organic ligand (Karipides & Thomas, 1986). It contains a potential hydrogen-bond acceptor and hydrogen-bond donor, and can display different hydrogen-bonding interactions in supramolecular complexes (Xu *et al.*, 2000). Many complexes of orotate ligand have been reported in the past decade (Hambley *et al.*, 1995). The structure of the title compound, (I), has been determined in order to study further the coordination chemistry of orotic acid.


(I)
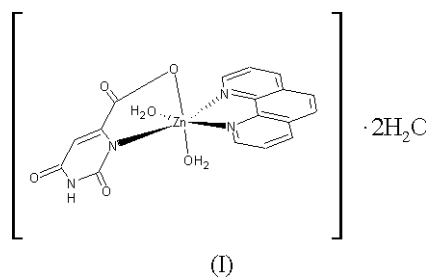
The title complex is mononuclear, as shown in Fig. l. The central Zn^{II} atom is coordinated by two water molecules, two N atoms from 1,10-phenanthroline, and by N and carboxylate O atoms from the orotate ligand, forming a distorted octahedral coordination geometry. The Zn—O6 and Zn—N3 bond lengths are significantly longer than the corresponding distances (Zn—5 and Zn—N4), suggesting that this is more likely to do with relative trans influences of orotic and phenanthroline ligands. The angles of N3—Zn—O6, N1—
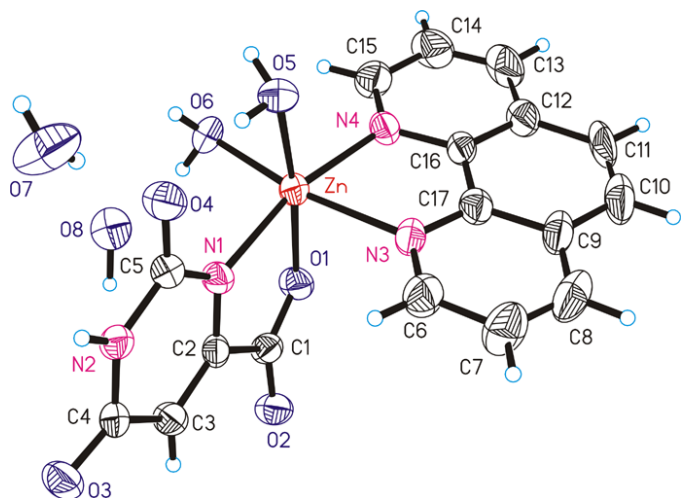
Figure 1
A view of the title compound (I), with displacement ellipsoids drawn at the 50% probability level.
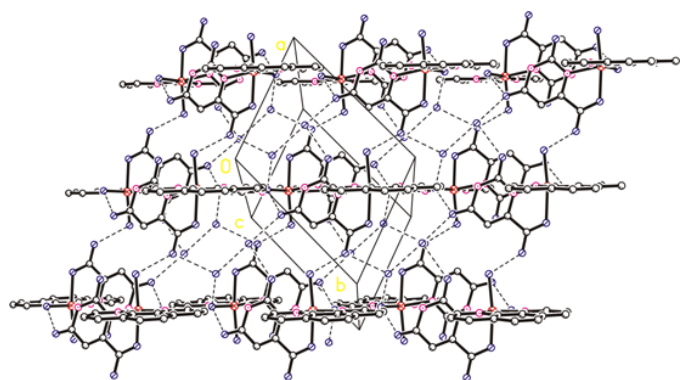
Figure 2
Two-dimensional structure of (I), showing the hydrogen-bonding interactions as dashed lines.
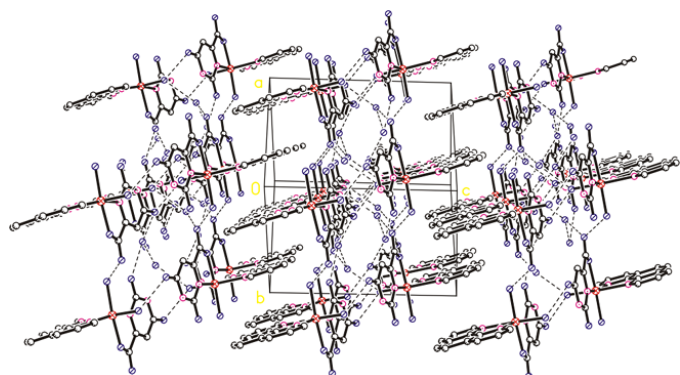
Figure 3
The three-dimensional structure of (I), formed through π–π-stacking and hydrogen-bonding interactions.

Zn—N4 and O5—Zn—O1 are 167.46 (19), 166.67 (18) and 171.39 (18)°, respectively.

There are intermolecular N—H⋯O and O—H⋯O hydrogen-bonding interactions (Table 2), which result in a two-dimensional layer structure (Fig. 2). A three-dimensional structure (Fig. 3) is finally formed by face-to-face π–π-stacking interactions between the 1,10-phenanthroline ligands of neighboring layers, with distances between the aromatic rings ranging from 3.20 to 3.60 Å.

Experimental

A mixture of orotic acid (0.3 mmol, 0.052 g) and Zn(CH3COO)2·2H2O (0.3 mmol, 0.066 g) in 30 ml of EtOH–water (1:3 v/v) was heated with stirring; the pH of the reaction solution was adjusted to 6 using a dilute aqueous solution of ammonia. After evaporation of the solution for two weeks, colorless block-like crystals of (I) were isolated by filtration (yield, 65%).

Crystal data

[Zn(C5H2N2O4)(C12H8N2)-(H2O)2]·2H2O	$Z = 2$
$M_r = 471.72$	$D_x = 1.655$ Mg m^{-3}
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 7.9351$ (6) Å	Cell parameters from 2440
$b = 10.1874$ (8) Å	reflections
$c = 12.6841$ (10) Å	$\theta = 1.6$–25.1°
$\alpha = 91.834$ (2)°	$\mu = 1.35$ mm^{-1}
$\beta = 94.264$ (2)°	$T = 293$ (2) K
$\gamma = 111.915$ (1)°	Block, colorless
$V = 946.65$ (13) Å^3	$0.26 \times 0.20 \times 0.12$ mm

Data collection

Siemens CCD area-detector diffractometer	3303 independent reflections
	2680 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{int} = 0.040$
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	$\theta_{max} = 25.1°$
	$h = -5 \rightarrow 9$
$T_{min} = 0.593$, $T_{max} = 0.850$	$k = -12 \rightarrow 11$
4875 measured reflections	$l = -14 \rightarrow 15$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0626P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.066$	$+ 4.4071P]$
$wR(F^2) = 0.166$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.12$	$(\Delta/\sigma)_{max} = 0.055$
3303 reflections	$\Delta\rho_{max} = 0.73$ e Å^{-3}
303 parameters	$\Delta\rho_{min} = -0.80$ e Å^{-3}
H atoms treated by a mixture of independent and constrained refinement	

Table 1
Selected geometric parameters (Å, °).

Zn—O1	2.084 (4)	Zn—O5	2.122 (5)
Zn—O6	2.101 (5)	Zn—N4	2.140 (5)
Zn—N1	2.116 (5)	Zn—N3	2.226 (5)
O1—Zn—O6	90.1 (2)	N1—Zn—N4	166.67 (18)
O1—Zn—N1	78.07 (16)	O5—Zn—N4	95.33 (19)
O6—Zn—N1	99.13 (19)	O1—Zn—N3	89.30 (18)
O1—Zn—O5	171.39 (18)	O6—Zn—N3	167.46 (19)
O6—Zn—O5	90.4 (2)	N1—Zn—N3	93.00 (18)
N1—Zn—O5	93.37 (19)	O5—Zn—N3	92.01 (19)
O1—Zn—N4	93.25 (17)	N4—Zn—N3	76.64 (19)
O6—Zn—N4	90.89 (19)		

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N2—H2A···O8^i	0.88	2.10	2.971 (5)	172
O5—H5A···O2^{ii}	0.88 (8)	1.85 (8)	2.708 (7)	166 (7)
O5—H5B···O4	0.84 (8)	1.85 (8)	2.678 (7)	167 (9)
O6—H6B···O3^i	0.73 (10)	2.08 (9)	2.776 (7)	162 (10)
O6—H6C···O8	0.92 (11)	1.85 (11)	2.741 (9)	164 (9)
O7—H7B···O4	0.89 (10)	1.94 (11)	2.789 (9)	160 (10)
O7—H7C···O3^{ii}	0.75 (10)	2.11 (10)	2.844 (9)	166 (8)
O8—H8B···O7^i	1.04 (13)	1.79 (12)	2.715 (10)	146 (8)
O8—H8C···O2^{iii}	0.70 (7)	2.14 (7)	2.836 (7)	171 (9)

Symmetry codes: (i) $-1-x, -1-y, 1-z$; (ii) $1+x, y, z$; (iii) $-1-x, -y, 1-z$.

The H atoms of the water molecules (free and coordinated) were located in a difference electron-density map and refined isotropically. The O—H bond lengths are in the range 0.70 (7)–1.04 (11) Å. The H atoms of C—H and N—H groups were placed in calculated positions and were allowed to ride on their parent C and N atoms.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SMART*; data reduction: *SAINT* (Siemens, 1994); program(s) used to solve structure: *SHELXTL* (Siemens, 1994); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

References

Hambley, T. W., Christopherson, R. I. & Zvargulis, E. S. (1995). *Inorg. Chem.* **34**, 6550–6552.
Karipides, A. & Thomas, B. (1986). *Acta Cryst.* C**42**, 1705–1707.
Leberman, L., Kornberg, A. & Simms, E. S. (1955). *J. Biol. Chem.* **215**, 403.
Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
Siemens (1994). *SAINT* and *SHELXTL* (Version 5). Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Siemens (1996). *SMART*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Xu, X. L., James, S. L., Mingos, D. M. P., White, A. J. P. & Williams, D. J. (2000). *J. Chem. Soc. Dalton Trans.* pp. 3783–3790.