

Synthesis, Crystal Structure, Spectral and Thermal Characterization of *cis*-Diaquabis(1,10-phenanthroline)zinc(II) Diorotate Hydrate, *cis*-[Zn(H₂O)₂(phen)₂](H₂Or)₂·(H₂O)_{2.125}

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Preparation, X-ray crystal structure, thermal behavior, and IR spectroscopic studies of *cis*-diaquabis(1,10-phenanthroline)zinc(II) diorotate hydrate are described. In the compound [Zn(H₂O)₂(C₁₂H₈N₂)₂](C₅H₃N₂O₄)₂·(H₂O)_{2.125} (**1**), the zinc ion, located on a twofold axis, is coordinated by two aqua ligands together with a pair of bidentate 1,10-phenanthroline (phen) molecules, and exhibits a distorted octahedral coordination. The orotate anions have a single negative charge each. The metal-coordinated water molecules link the orotate ions to the metal complex *via* O–H···O hydrogen bonds. Also the uncoordinated water molecules are bonded to orotate ions through O–H···O hydrogen bonds. Thus, an extensive network of hydrogen bonds together with π - π , and π -ring interactions stabilize the crystal structure and form an infinite three dimensional structure. The thermal decomposition pathway of **1** has been investigated by the help of thermal analysis data (TG, DTG and DTA).

Key words: Orotic Acid, 1,10-Phenanthroline, Thermal Decomposition

Introduction

Orotic acid (1,2,3,6-tetrahydro-2,6-dioxo-4-pyrimidine carboxylic acid, vitamin B13, H₃Or, Fig. 1) and its metal-ion complexes continue to attract attention due to their multidentate functionality and their crucial role in many living organisms [1, 2]. Besides being a biologically important agent, orotic acid and its anions, H₂Or[−], HO^{2−} and Or^{3−}, are also rich in donor sites. Mixed ligand complexes with 1,10-phenanthroline are also interesting due to their potential role as models for biological systems such as binding of small molecules to DNA [3].

It is worth mentioning that most of the studies of the complexes in the solid phase have used orotic acid in its dianionic form. On the other hand orotic acid is in the monoanionic form in living organisms due to the neutral pH. It is, therefore, of great interest to examine its coordinating properties at neutral or slightly acidic pH [4].

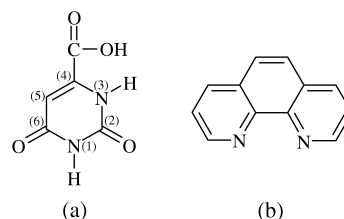


Fig. 1. (a) Orotic acid, H₃Or; (b) 1,10-phenanthroline, phen.

The orotato anion is known to exhibit diverse coordinating modes such as monodentate (Orotato-O_{acid}) [4–6], bidentate (Orotato-N(3),O_{acid}) [4, 7–23], bridging (Orotato-N(3),O_{acid}, O(6) and O(2)) [24–27], but less has been written about the equally important complexes with orotate counter anions [28–31]. In recent years, we have studied the synthesis, spectral, thermal and crystallographic properties of metal-orotate complexes with various ligands [8–12,31], and the first complexes of neutral orotic acid [32]. As part of our on going research, in

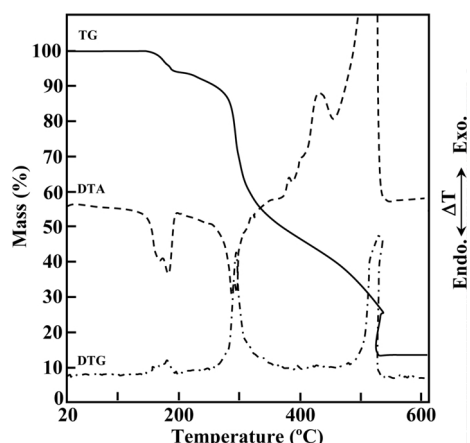


Fig. 2. TG, DTG and DTA curves of $[\text{Zn}(\text{H}_2\text{O})_2(\text{phen})_2](\text{H}_2\text{Or})_2 \cdot (\text{H}_2\text{O})_{2.125}$.

this study, we describe a Zn(II) complex with 1,10-phenanthroline ligands and orotate anions (Fig. 1).

Results and Discussion

Structures of the complexes

The title complex has octahedral geometry with two phen molecules coordinated to the Zn(II) ion as chelating ligands and two aqua ligands in the *cis* positions. The H_2Or^- anion does not coordinate to the Zn(II) ion and is present as the counter-ion. This result was supported by conductivity measurements. The molar conductance $\Lambda_M = 119 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ confirmed that the Zn(II) complex is a 1 : 2 electrolyte in aqueous solutions. Magnetic moment measurements showed that the complex is diamagnetic as expected. The complex shows broad bands in the UV region with three maxima at 216, 294 and 310 nm, being due to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ intraligand transitions of the H_2Or^- anion and the phen ligand. d-d bands were not observed as expected.

IR spectroscopic investigation

The strong and broad absorptions at *ca.* 3500 cm^{-1} are attributed to the $\nu(\text{OH})$ vibrations of coordinated and crystal water molecules. The bands between 3000 and 3300 cm^{-1} correspond to NH groups of H_2Or^- . The weak bands in the $3000\text{--}2900 \text{ cm}^{-1}$ range are due to $\nu(\text{CH})$ stretching absorptions.

IR vibration modes of the carboxyl group of the orotic acid gives valuable information about the coordination behavior of orotic acid in its metal complexes. The carbonyl groups give rise to two main peaks

Table 1. Crystallographic data for the title compound.

Formula	$\text{C}_{34}\text{H}_{30.25}\text{N}_8\text{O}_{12.125}\text{Zn}$
Colour	Colorless
Molecular weight	810.29
Temperature	296 K
Wavelength	0.71073
Crystal system	monoclinic
Space group	$C2/c$
Unit cell dimensions	
a (Å)	16.1839(9)
b (Å)	12.5470(8)
c (Å)	16.5634(9)
β (°)	92.579(5)
Volume (Å ³)	3359.9(3)
Z	4
Calculated density (g/cm ³)	1.597
μ (mm ⁻¹)	0.812
Crystal size (mm)	$0.35 \times 0.25 \times 0.15$
θ_{max}	28.33°
Index ranges	
h	$-21 \rightarrow 21$
k	$-16 \rightarrow 16$
l	$-22 \rightarrow 21$
Reflections collected	29616
Independent reflections	4191
Reflections observed ($> 2\sigma$)	2817
Absorption correction	integration
Max. and min. Transmission	0.91 0.73
w	$1/[\sigma^2(F_o^2) + (0.0562P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
Goodness-of-fit on F^2	0.921
$R[F^2 > 2\sigma(F^2)]$	$R_1 = 0.0357$, R_1 (all data) = 0.0578
$wR(F^2)$	0.0898
Largest diff. peak and hole (eÅ ⁻³)	0.25, -0.69
CCDC deposition no.	283420

at 1700 cm^{-1} [$\nu_{\text{C}=\text{O}(\text{acid})} + \nu_{\text{C}(2)=\text{O}}$] and 1660 cm^{-1} [$\nu_{\text{C}(6)=\text{O}} + \nu_{\text{C}=\text{C}}$] for free H_3Or [4]. These values shift to 1704 and 1674 cm^{-1} for the complex the monoanionic orotate anion does not coordinate to the metal ion. The medium intensity band at 1625 cm^{-1} is assigned to the ν_{CN} vibration in the rings of the phen ligands. $\nu_{\text{C}(4)-\text{C}(5)}$ which appears as a main band at 1295 cm^{-1} for the free H_3Or [4], was observed at 1330 cm^{-1} for the complex. The low intensity bands at 543 and 640 cm^{-1} are attributed to $\nu_{\text{Zn}-\text{N}}$ and $\nu_{\text{Zn}-\text{O}}$ vibrations, respectively.

Thermal studies

Thermal decomposition of **1** proceeds in four stages (Fig. 2). In the first stage, the endothermic peaks in the temperature range $33\text{--}193^\circ\text{C}$ correspond to the loss of coordinated and crystallization water. In the second and third stages, two moles of phen and

Table 2. Selected bond lengths (Å) and bond angles (°).

Zn(1) – O(1)	2.124(2)	Zn(1) – N(2)	2.146(2)
Zn(1) – N(1)	2.143(2)		
O(1) – Zn(1) – N(1)	165.72(6)	N(1) – Zn(1) – N(2) ⁱ	100.24(6)
O(1) – Zn(1) – N(2)	89.08(6)	O(1) ⁱ – Zn(1) – N(2)	93.08(6)
O(1) – Zn(1) – O(1) ⁱ	83.34(9)	N(1) ⁱ – Zn(1) – N(2)	100.24(6)
O(1) – Zn(1) – N(1) ⁱ	91.69(6)	N(2) – Zn(1) – N(2) ⁱ	177.11(8)
O(1) – Zn(1) – N(2) ⁱ	93.08(6)	O(1) ⁱ – Zn(1) – N(1) ⁱ	165.75(7)
N(1) – Zn(1) – N(2)	77.96(6)	O(1) ⁱ – Zn(1) – N(2) ⁱ	89.08(7)
O(1) ⁱ – Zn(1) – N(1)	91.69(6)	N(1) ⁱ – Zn(1) – N(2) ⁱ	77.79(6)
N(1) – Zn(1) – N(1) ⁱ	96.10(9)		

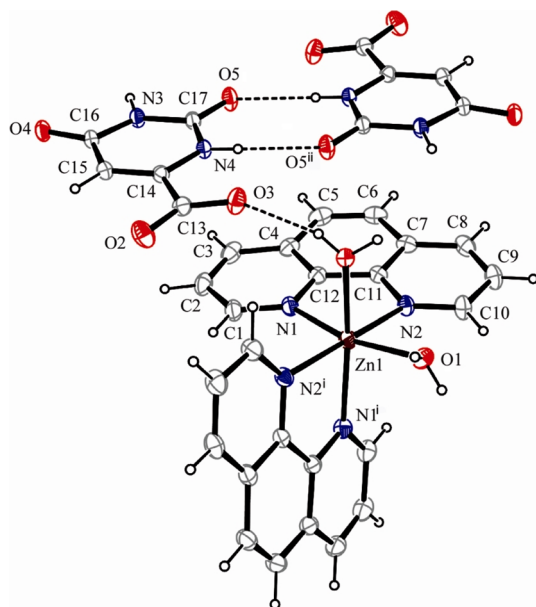
Symmetry code: ⁱ $-x, y, 1/2 - z$.

Fig. 3. A view of the zinc coordination, with the atom labeling scheme. Displacement ellipsoids are drawn at the 30% probability level. The crystal water molecules are omitted for clarity. Dashed lines indicate hydrogen bonds (symmetry code; ⁱ $-x, y, -z + 1/2$; ⁱⁱ $-x + 1/2, -y + 1/2, -z$).

the CO₂ from the decarboxylation of orotate are released by endothermic and then exothermic decomposition processes, respectively (DTG_{max}: 292, 325, 386 °C). This type of behaviour has been reported earlier for the saccharinato [33,34], salicylato [35], isoorotato and 2-thioisoorotato [36] complexes. In the last stage, remaining organic parts are abruptly burnt (DTG_{max}: 504 °C), leading finally to ZnO (found 89.52, calcd. 89.96%), identified by IR spectroscopy.

Crystallographic analysis

Details of the crystal structure are given in Table 1 and selected bond distances and angles are listed in Ta-

ble 2. The crystal structure of the Zn(II) complex is presented in Fig. 3 [37]. The title compound has a distorted octahedral coordination geometry comprised of four N atoms from two chelating phen molecules together with two water molecules. The coordinated water molecule [2.124(2) Å for Zn1-O1] and three phen N atoms [varying in the range of 2.143(2)–2.146(2) Å for Zn1-N] form the equatorial plane, whereas the symmetry related fourth phen N atom and the second water molecule are in apical positions [Zn1-N2ⁱ = 1.146(2) Å; symmetry code: (i) $1 - x, y, 0.5 - z$]. These values are in agreement with those previously reported for other phen-containing zinc(II) metal complexes [38,39]. The equatorial plane is approximately planar with a r.m.s. deviation of 0.0625 Å and the largest deviation from the mean plane of 0.0759(8) Å for the N1 atom. The phen ligand is essentially planar and the largest deviation from the mean plane is 0.094(2) Å for the C2 atom. The dihedral angles between the zinc(II) basal equatorial plane and phen ligands are 11.92(6) and 82.79(3)°. The dihedral angle between the two phen molecules is 75.08(2)°. The unique orotate anion in the asymmetric unit carries a single negative charge and is not coordinated to the Zn(II) ion.

It is essentially planar, with a slight deviation from planarity arising from the small non-zero torsion angle between the carboxylate group and the ring [N4-C14-C13-O3 = 5.2(3)°]. The dihedral angles between the orotate anion and the phen ligands are 2.99(5) and 77.92(2)°. The angles formed at the amide C=O group of the urea fragment, N4-C17-O5- and N3-C17-O5, are essentially equal, but as the chemical environment of the carbonyl group (C16=O4) is not symmetrical, the angles around it are quite different [N3-C16-O4 = 118.94(18)° and C15-C16-O4 = 126.10(18)°]. A similar behaviour was also observed in the structure of the ammonium orotate [40].

The orotate counter anion seems to be quite flexible: In the Ni [13,41], Cu [20], and Zn [14] complexes of HOR²⁻, the C14-N4-C17 angle is smaller [118.3(3), 119.0(1), 117.9(2), and 118.1(4)°, respectively) than that found in orotic acid 123.07(14)° [31], 122.8(3)° [30], and 122.92(15)° for **1**. The carboxylate C-O distances also display some variability depending on their environment. These distances are practically equal when the orotate ligand acts as a counter ion [C13-O3 = 1.241(2), C13-O2 = 1.236(2) Å] [30,31]. However, in the Co(II), Cu(II) [8], Mg(II) [17] complexes of HOR²⁻, the carboxylate group [C-

Table 3. The hydrogen bonding geometry (Å, °).

D–H...A	D–H	H...A	D...A	D–H...A
N(4)–H(4)···O(3)	0.8(2)	2.29(2)	2.640(2)	107.0(2)
N(4)–H(4)···O(5) ⁱⁱ	0.8(2)	2.06(2)	2.875(2)	167(2)
O(6)–H(6)A···O(2)	0.83(3)	1.99(4)	2.794(3)	161(3)
O(6)–H(6)B···O(5) ⁱⁱⁱ	0.93(5)	2.36(5)	3.109(3)	138(4)
O(1)–H(11)A···O(4) ^{iv}	0.83(3)	1.98(3)	2.809(2)	176(3)
O(1)–H(11)B···O(3) ^v	0.83(3)	1.93(3)	2.745(2)	155(3)
N(3)–H(17)···O(4) ^{vi}	0.88(2)	1.99(2)	2.874(2)	178(2)

Symmetry codes: ⁱⁱ $1/2 - x, 1/2 - y, -z$; ⁱⁱⁱ $x, -y, 1/2 + z$; ^{iv} $1/2 - x, 1/2 + y, 1/2 - z$; ^v $1 - x, y, 1/2 - z$; ^{vi} $-x, -y, -z$.

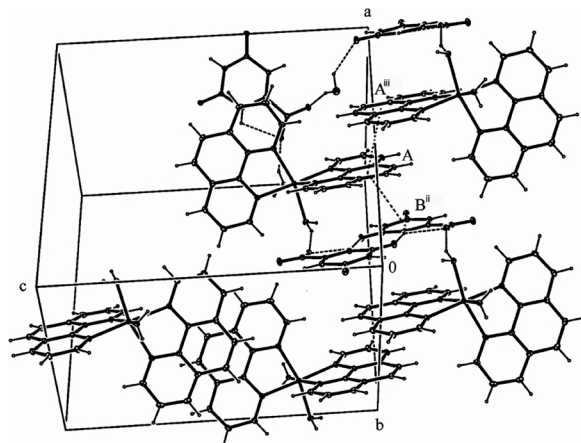


Fig. 4. The unit-cell packing of the complex $[\text{Zn}(\text{H}_2\text{O})_2(\text{phen})_2](\text{H}_2\text{O})_2 \cdot (\text{H}_2\text{O})_{2.125}$. Dashed lines indicate π - π and hydrogen bonding interactions (symmetry code ii: $-x + 1/2, -y + 1/2, -z$; iii: $1 - x, -y, -z$).

$\text{O} = 1.278(2) - 1.223(3) \text{ \AA}, 1.270(4) - 1.240(4) \text{ \AA}, 1.262(2) - 1.243(2) \text{ \AA}]$ is rather asymmetric.

The packing in the unit cell is based on intra- and intermolecular hydrogen bonding together with π - π , and π -ring interactions. It can be seen from Fig. 4 that two orotate anions are joined by two N4–H4···O5 hydrogen bonds (Table 3) which lead to the formation of a centrosymmetric dimer. The water ligand and lattice water molecules also form intermolecular hydrogen-bonds through the carboxylate O2, O3 atoms and exocyclic carbonyl O4, O5 atoms (see Table 3 for details). In the extended structure of **1**, shown in Fig. 4, there are also π - π , and π -ring interactions. An intermolecular π - π contact occurs between two symmetry-related phen rings (C4, C5, C6, C7, C11, C12; hereafter A) of neighbouring molecules. Ring A is oriented in such a way that the perpendicular distance from A to Aⁱⁱⁱ is 3.282 Å, the closest interatomic distance being C4...C6ⁱⁱⁱ [3.330(3) Å; symmetry code: (iii) $1 - x, -y, -z$]. The distance between the ring centroids is 3.5655(12) Å. Ring A forms also an in-

termolecular π - π contact with the uracilate ring (B) of the orotate counterion. Rings A and B are oriented in such a way that the perpendicular distance from A to Bⁱⁱ is 3.349(3) Å, the closest interatomic distance being C6...N4ⁱⁱ [3.349(3) Å; symmetry code: (ii) $-x + 0.5, -y + 0.5, -z$]. The dihedral angle between the planes of rings is 2.37°, the distance between the ring centroids is 3.8246(11) Å. Apart from that there is also an intra-molecular π -ring interaction between the H11B atom of the aqua ligand and the five-membered chelate ring. The distance between atom H11B and the centre of the ring is 2.95 Å. The distance between atom H11B and the plane of the chelate ring is 2.570 Å, and the O1–H11B...(chelate ring) angle is 71.0(18)°. All these hydrogen bonds, π - π , and π -ring interactions stabilize the crystal structure and form an infinite three-dimensional structure.

Experimental Section

Materials and instrumentation

All chemicals used were analytical reagent products. Elemental analysis for C, H, and N was carried out at the TÜBİTAK Marmara Research Centre in Turkey. Magnetic susceptibility measurement at room temperatures was performed using a Sherwood Scientific MXI model Gouy magnetic balance. The UV vis spectrum was obtained from the aqueous solution of the complex with a Unicam UV2 spectrometer in the range 900–190 nm. The IR spectrum was recorded in the 4000–200 cm^{-1} region with a Mattson 1000 FT IR spectrometer using KBr pellets. A Rigaku TG8110 thermal analyzer was used to record simultaneous TG, DTG and DTA data in static air atmosphere at a heating rate of 10 K min^{-1} in the temperature range 20–600 °C using platinum crucibles. Highly sintered α - Al_2O_3 was used as a reference. The DTG sensitivity was 0.05 mg s^{-1} . The conductance value was measured on a 522 CRISON conductometer.

A suitable single crystal was mounted on a glass fibre and data collection was performed on a STOE IPDSII image plate detector using Mo- $\text{K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). Data collection: Stoe X-AREA [42]. Cell refinement: Stoe X-AREA [42]. Data reduction: Stoe X-RED [42]. The structure was solved by direct methods using SIR97 [43], and anisotropic displacement parameters were applied to non-hydrogen atoms in a full-matrix least-squares refinement based on F^2 using SHELXL-97 [44]. H atoms attached to the O1, O6 atoms of water and the N atom were located in a difference Fourier map and their coordinates and U_{iso} parameters were refined freely. The remaining H atoms were placed geometrically and allowed to ride on their parent atoms, with C–H = 0.93 Å and $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C})$. At

this stage, the maximum difference density of 1.37 eÅ^{-3} (the ratio of maximum / minimum residual density is 2.87) indicated the presence of a possible atom site. A check for the solvent-accessible volume using PLATON [45] 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 0.114(5). The occupancy was later fixed at 0.125 to result in half water (O7) per unit cell. H atoms attached to O7 were not located.

Synthesis of $[\text{Zn}(\text{HOR})(\text{H}_2\text{O})_4] \cdot \text{H}_2\text{O}$

The mixture of a solution of ZnCl_2 (0.85 g, 5 mmol) in water (25 ml) and of NaHCO_3 (0.42 g, 5 mmol) in water (25 ml) was dropped with stirring into an aqueous (25 ml) suspension of orotic acid (0.87 g, 5 mmol) at 80°C . The suspension was refluxed and stirred for 10 h at 80°C in a temperature-controlled bath. After degassing to remove CO_2 , the clear solution was cooled to room temperature. The colorless crystals of the zinc(II) complex were filtered off and washed with 10 ml- portions of cold distilled water and acetone and dried *in air*.

Synthesis of $[\text{Zn}(\text{phen})_2(\text{H}_2\text{O})_2](\text{H}_2\text{O})_2 \cdot (\text{H}_2\text{O})_{2.125}$

The solution of phen (0.73 g, 4 mmol) in ethanol (10 ml) was dropped into a stirred solution of $[\text{Zn}(\text{HOR})(\text{H}_2\text{O})_4] \cdot \text{H}_2\text{O}$

(0.63 g, 2 mmol) in water (25 ml). The solution was heated to 60°C in a temperature-controlled bath and then refluxed and stirred for 12 h at 60°C . The colorless crystals formed were filtered and washed with 10 ml of cold distilled water and ethanol and dried *in air*. – UV/vis (H_2O): $\lambda_{\text{max}} = 216$, 297 and 310 nm. – IR (KBr): $\nu = 3500 \text{ (cm}^{-1}\text{)}$ (O-H), 1700 (vs) ($\text{C}=\text{O}_{(\text{acid})} / \text{C}_{(2)}=\text{O}$), 1650 (cm^{-1}) (vs) ($\text{C}_{(6)}=\text{O} / \text{C}=\text{C}$), 1625 (cm^{-1}) (vs) (CN), 1295 (cm^{-1}) ($\text{C}_{(4)}-\text{C}_{(5)}$). – $\text{C}_{34}\text{H}_{30.25}\text{N}_8\text{O}_{12.125}\text{Zn}$ (810.29): calcd. C 50.39, H 3.73, N 13.82; found C 49.96, H 4.09, N 13.50.

Supplementary Data

Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as the supplementary publication no CCDC 283420. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).

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