

# Synthesis, Crystal Structure and Thermal Properties of Copper(II) Orotato Complex with 2,2'-Bipyridine

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A mixed-ligand orotato (HOr) complex of Cu(II) with 2,2'-bipyridine (bipy) was synthesized and characterized by elemental analysis, magnetic susceptibility, UV-vis and FT-IR spectroscopy, TG / DTA techniques and X-ray diffraction analysis. X-Ray diffraction analysis has shown that the square-pyramidal five-coordinate copper atom is chelated by the deprotonated N3 pyrimidine atom and the carboxylate oxygen atom of the bidentate orotato dianion, and to the two nitrogen atoms of the 2,2'-bipyridine molecule. A water molecule is attached above the N<sub>3</sub>O plane. Thermal analyses showed that the title compound decomposes in two steps over the range 20–1000 °C on heating in a static air atmosphere. Intermolecular hydrogen-bonds and  $\pi$ -ring interactions lead to the formation of a three-dimensional network.

**Key words:** Orotato Complexes, 2,2'-Bipyridine, Spectrothermal Analysis

## Introduction

Orotic acid (1,2,3,6-tetrahydro-2,6-dioxo-4-pyrimidine carboxylic acid, vitamin B<sub>13</sub>, H<sub>3</sub>Or; Fig. 1a) is a precursor in the biosynthesis of pyrimidine bases and nucleic acids in living organisms and has been widely exploited in medicine [1]. Its metal complexing properties are responsible for the successful application of orotato complexes in curing syndromes associated with deficiency of various metal ions. Some metal complexes of orotic acid display therapeutic properties and are used as drugs as well as for other purposes [2]. Moreover, platinum, palladium and nickel orotato complexes have been screened as therapeutic agents for cancer [3]. Besides its biological importance, orotic acid is an interesting ligand. Since it is potentially multidentate, the coordination may occur through the heterocyclic nitrogen atoms of the pyrimidine ring, the exocyclic carbonyl oxygen atoms, and the carboxylic group [2–5]. The literature lists many reports on the coordinating preferences of the orotato moiety in metal complexes. It was found that in solutions with neutral or slightly acidic pH, metal ions are coordinated through the carboxylate group [2]. Bidentate binding through N3 and the carboxylate group was observed by several crystal structure determinations [6–21]. Despite its polydentate nature only a few polymeric complexes of orotic acid have been observed. These

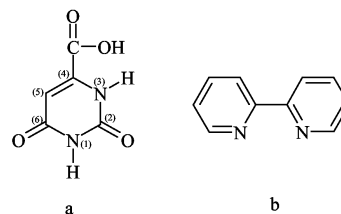


Fig. 1. Orotic acid (a) and 2,2'-Bipyridine (b).

include Co(II) [4, 5, 10], Co(III) [22], Ni(II) [5, 22], Cu(II) [23] and Mn(II) [3, 5] complexes in which it acts as a tridentate ligand and bridges metal-ions forming polymer chains. In some transition metal complexes, the orotate acts as a counter ion [24–26]. We have recently synthesized first complexes of neutral orotic acid and characterized them by spectroscopic and thermal methods [27].

The aim of this work was to prepare a new mixed-ligand orotato complex of Cu(II) with 2,2'-bipyridine (Fig. 1b) ligand in order to study further the complexation properties of orotic acid and undertake its crystal structure and spectrothermal analysis.

## Results and Discussion

The molar conductance value of the title complex ( $\Lambda_M = 21 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ ) indicated that [Cu(HOr)(H<sub>2</sub>O)(bipy)] is a non-electrolyte. The

magnetic moment value of the complex is 1.40 BM corresponding to one unpaired electron.

#### UV-vis spectra

The electronic spectrum of an aqueous solutions of [Cu(HOr)(H<sub>2</sub>O)(bipy)] is compatible with a distorted square-pyramidal configuration. The  $\lambda_{\text{max}}$  value of the absorption band is at 740 nm and the corresponding  $\epsilon$  value is 74.0 Lmol<sup>-1</sup>cm<sup>-1</sup>. The  $\lambda_{\text{max}}$  value was assigned to the  $a_1 \rightarrow b_1$  d-d transition [28].

#### IR spectra

The stretching mode of coordinated water in [Cu(HOr)(H<sub>2</sub>O)(bipy)] appears at 3385 cm<sup>-1</sup>, similar to data for the [Mn(HOr)(bipy)(H<sub>2</sub>O)] complex [5]. The most common coordination mode of orotic acid was observed for the bidentate form after deprotonation of both the N<sub>(3)</sub>H and the carboxylate group. In the IR spectrum, the O-H vibration of the carboxyl group, which was observed for the free orotic acid at 2500 cm<sup>-1</sup>, has disappeared. The N<sub>(3)</sub>H vibration bands which appear at 3170, 1431 cm<sup>-1</sup> for the free orotic acid are not observed in the complex. The carbonyl groups give rise to two main peaks at 1700 cm<sup>-1</sup> [ $\nu_{\text{C=O(acid)}} + \nu_{\text{C(2)=O}}$ ] and 1660 cm<sup>-1</sup> [ $\nu_{\text{C(6)=O}} + \nu_{\text{C=C}}$ ] for the free H<sub>3</sub>Or [2]. The carbonyl stretching modes in the title complex were observed at 1667 and 1647 cm<sup>-1</sup>.

#### Thermal analysis

The thermal decomposition of the title complex, [Cu(HOr)(H<sub>2</sub>O)(bipy)], presented in Fig. 2, is well-defined, consisting of two stages. In the first step, dehydration of the complex occurs in the temperature interval 88–177 °C. Release of the coordinated water gives

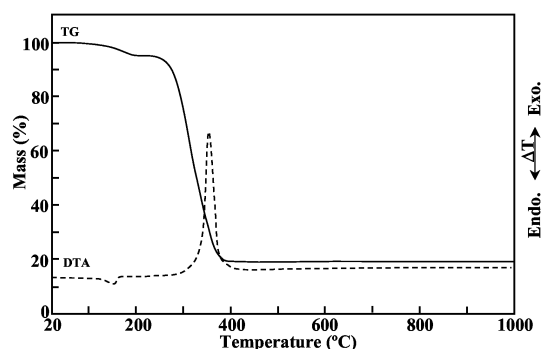


Fig. 2. TG, DTG and DTA curves of [Cu(HOr)(H<sub>2</sub>O)(bipy)].

Table 1. Crystallographic data for the title compound.

Formula	C <sub>15</sub> H <sub>12</sub> CuN <sub>4</sub> O <sub>5</sub>
Colour	green
Molecular weight	391.83
Temperature	296 K
Wavelength	0.71073
Crystal system	triclinic
Space group	<i>P</i> 1
Unit cell dimensions	
<i>a</i> (Å)	7.0275 (13)
<i>b</i> (Å)	9.760 (2)
<i>c</i> (Å)	10.9976 (19)
$\alpha$ (°)	80.703 (15)
$\beta$ (°)	86.029 (14)
$\gamma$ (°)	82.219 (16)
Volume (Å <sup>3</sup> )	736.7 (2)
<i>Z</i>	2
Calculated density (Mgm <sup>-3</sup> )	1.766
$\mu$ (mm <sup>-1</sup> )	1.521
Crystal size	0.30 × 0.22 × 0.15 mm <sup>3</sup>
$\theta$ Range	1.88–28.96°
Index ranges	
<i>h</i>	–8 → 8
<i>k</i>	–12 → 12
<i>l</i>	–13 → 13
Reflections collected	10497
Independent reflections	2901 ( $R_{\text{int}} = 0.0821$ )
Reflections observed ( $> 2\sigma$ )	2249
Absorption correction	integration
Max. and min. Transmission	0.9147 and 0.7240
Refinement method	$F^2$
<i>w</i>	$1/[2\sigma(F_o^2) + (0.0749P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
Goodness-of-fit on $F^2$	0.986
$R[F^2 > 2\sigma(F^2)]$	0.0442
$wR(F^2)$	0.1184
Largest diff. peak and hole (eÅ <sup>-3</sup> )	–0.804 to 0.422
CCDC deposition no.	CCDC 267852

an endothermic effect at 157 °C (DTA curve). A good agreement between the experimental and calculated values was observed for the mass loss (exp. 4.35%; calc. 4.55%). The anhydrous complex is stable in air up to 228 °C and decomposes in one step in the temperature range of 229–406 °C. The final decomposition product, CuO, was identified by IR spectroscopy. The overall weight loss (79.30, calc. 79.70%) agrees with the propose composition.

#### Crystallography

The structure of the title complex, [Cu(HOr)(H<sub>2</sub>O)(bipy)], is shown in Fig. 3 and the crystallographic data are summarized in Table 1. Table 2 and 3 list bond lengths and angles and hydrogen-bonding geometries. The Cu ion is coordinated to the N2 and N4 atoms of 2,2'-bipyridine, the

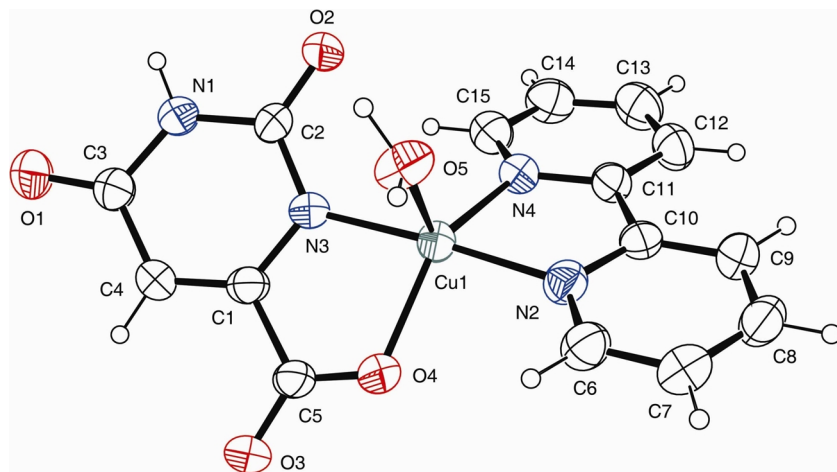


Fig. 3. A view of the copper coordination, with the atom labeling scheme. Displacement ellipsoids are drawn at the 50% probability level.

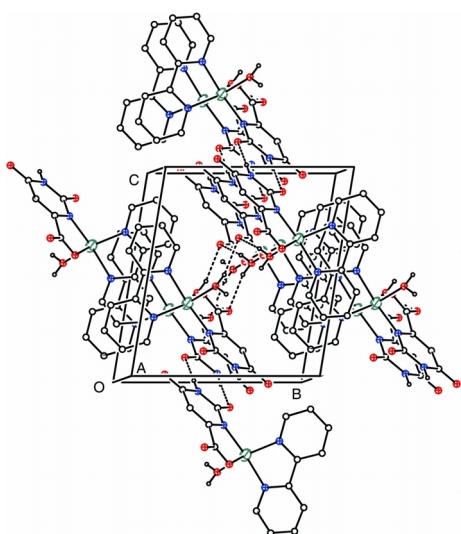


Fig. 4. The packing of the  $[\text{Cu}(\text{HOr})(\text{H}_2\text{O})(\text{bipy})]$  complex with the unit cell.

N3 and O2 atoms of the orotate anion, and O5 of a water molecule forming a distorted square pyramidal geometry. The 2,2'-bipyridine and pyrimidine ring are essentially planar and the dihedral angle between them is  $46.40(12)^\circ$ . The largest deviations from the mean planes are  $-0.043(4)$  Å for atom C11 and  $-0.030(3)$  Å for atom C4.

The crystal packing of the title complex is formed by intermolecular N-H...O and O-H...O hydrogen bonding (Table 3.) and  $\pi$ -ring interactions (Fig. 4). The C7-H7...CgA (CgA with symmetry code:  $1-x, -y, 1-z$  is the centroid of N4, C11-C15)  $\pi$ -ring contact distance and angle are  $3.345(5)$  Å and  $87.36^\circ$ , respectively. The same parameters for the C9-H9...CgB

Table 2. Selected bond lengths (Å) and bond angles ( $^\circ$ ).

Cu(1)-N(3)	1.934 (3)	Cu(1)-O(5)	2.261 (3)
Cu(1)-N(2)	1.974 (3)	Cu(1)-O(4)	2.000 (2)
Cu(1)-N(4)	2.028 (3)		
N(3)-Cu(1)-N(2)	174.48 (11)	O(4)-Cu(1)-N(4)	139.15 (12)
N(3)-Cu(1)-O(4)	82.94 (10)	N(3)-Cu(1)-O(5)	89.08 (12)
N(3)-Cu(1)-N(4)	104.54 (11)	N(2)-Cu(1)-O(5)	88.24 (12)
N(2)-Cu(1)-N(4)	80.98 (11)	O(4)-Cu(1)-O(5)	102.27 (12)
N(2)-Cu(1)-O(4)	92.92 (11)	N(4)-Cu(1)-O(5)	117.73 (12)

Table 3. Hydrogen bonding geometry (Å,  $^\circ$ ).

D-H...A	D-H	H...A	D...A	D-H...A
N1-H1...O2 <sup>i</sup>	0.86	1.98	2.837 (4)	177.7
O5-H5A...O3 <sup>ii</sup>	0.94 (6)	1.91 (6)	2.836 (4)	170 (5)
O5-H5B...O3 <sup>iii</sup>	0.77 (6)	2.06 (6)	2.810 (4)	164 (6)

Symmetry codes: <sup>i</sup>  $2-x, 1-y, -z$ ; <sup>ii</sup>  $1+x, y, z$ ; <sup>iii</sup>  $1-x, 1-y, 1-z$ .

(CgB with symmetry code:  $2-x, -y, 1-z$  is the centroid of N1, C2, N3, C1, C4, C3)  $\pi$ -ring interaction are  $3.370(4)$  Å and  $90.54^\circ$ .

## 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. Conductivity was measured by using a Crison conductimeter, model 522. Magnetic susceptibility measurement at room temperature was performed using a Sherwood Scientific MXI model Gouy magnetic balance. The UV-vis spectrum was obtained from the aqueous solution ( $10^{-3}$  M) of the title complex with a Unicam UV2 spectrometer in the range of 900–190 nm. The IR spectrum was recorded in the  $4000-200\text{ cm}^{-1}$  region with a Mattson 1000 FT IR spec-

trometer using KBr pellets. A Rigaku TG8110 thermal analyzer was used to record TG, DTG and DTA curves in static air atmosphere at a heating rate of  $10\text{ K min}^{-1}$  in the temperature range of  $20\text{--}1000\text{ }^{\circ}\text{C}$  using platinum crucibles. Highly sintered  $\alpha\text{-Al}_2\text{O}_3$  was used as a reference, and the DTG sensitivity was  $0.05\text{ mg s}^{-1}$ .

Data collection was performed on a STOE IPDSII image plate detector using  $\text{Mo-K}\alpha$  radiation ( $\lambda = 0.71073\text{ \AA}$ ). Intensity data were collected in the  $\theta$  range  $1.88\text{--}28.96^{\circ}$  at  $296\text{ K}$ . Details of crystal structures are given in Table 1. Data collection: Stoe X-Area [29]. Cell refinement: Stoe X-Area [29]. Data reduction: Stoe X-RED [29]. The structure was solved by direct methods using SIR97 [30] and anisotropic displacement parameters were applied to non-hydrogen atoms in a full-matrix least-squares refinement based on  $F^2$  using SHELXL-97 [31]. All hydrogen atoms except those bound to O5 were positioned geometrically and refined by a riding model with  $U_{\text{iso}}$  1.2 times that of the attached atom. Molecular drawings were obtained using ORTEP-III [32].

#### Synthesis of $[\text{Cu}(\text{HOR})(\text{H}_2\text{O})(\text{bipy})]$

The complex  $[\text{Cu}(\text{HOR})(\text{H}_2\text{O})_4]\cdot\text{H}_2\text{O}$ , was prepared by the method reported earlier [7,8]. A solution of 2,2'-bipyridine ( $0.25\text{ g}$ ,  $2\text{ mmol}$ ) in ethanol ( $10\text{ ml}$ )

was added drop wise with stirring to a solution of  $[\text{Cu}(\text{HOR})(\text{H}_2\text{O})_4]\cdot\text{H}_2\text{O}$  ( $0.75\text{ g}$ ,  $2\text{ mmol}$ ) in distilled water ( $50\text{ ml}$ ). The solution was heated to  $60\text{ }^{\circ}\text{C}$  in a temperature-controlled bath and stirred for  $4\text{ h}$  at  $60\text{ }^{\circ}\text{C}$ . The reaction mixture was then cooled to room temperature. The green crystals were filtered and washed with  $10\text{ ml}$  of cold distilled water and acetone and dried *in vacuo*. UV/vis ( $\text{H}_2\text{O}$ ):  $\lambda_{\text{max}}(\epsilon) = 740\text{ nm}$  ( $74.0\text{ L mol}^{-1}\text{cm}^{-1}$ ). –IR (KBr):  $\nu = 3385\text{ (m)}$  (O–H),  $1667\text{ (vs)}$  ( $\nu_{\text{C=O(acid)}} + \nu_{\text{C(2)=O}}$ ),  $1647\text{ (vs)}$  ( $\nu_{\text{C(6)=O}}$ )  $\text{cm}^{-1}$ .  $\text{C}_{15}\text{H}_{12}\text{N}_4\text{O}_5\text{Cu}$  ( $391.8$ ): calcd. C  $46.01$ , H  $3.14$ , N  $14.32$ ; found C  $45.59$ , H  $2.98$ , N  $14.02$ .

#### Supplementary Data

Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as the supplementary publication No. CCDC 267852. 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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