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SYNTHESIS AND CRYSTAL STRUCTURE OF CUPPER(II) ((*E*)-2-HYDROXYBENZALDEHYDE OXIME)$_2$

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*Abstract:*The central Cu^{II} atom in the title complex, $C_{14}H_{12}CuN_2O_4$ is located on an inversion center and adopts a roughly square- planar coordination environment defined by two chelating N, S donor set of two symmetry – related ligands in a Trans configuration. In the molecular complex, the Ni^{2+} cation is situated at an inversion centre and displays a square planar coordination environment. The N1-N and N1-S bond length are 1.9193(14)Å and 2.1788(5)Å, respectively. However, the chelating N, S bond angles in these complexes are similar within their standard deviations and fall into the range 85.67(5) – 86.40(5)°.

Index Terms - copper(II); crystal structure; (e)-2-hydroxybenzaldehyde oxime; square pyramidal; tetrahedral; O-H…O; C-H…O; hydrogen bonds; π-stacking; T = 295 K; R factor = 0.0751; wR factor = 0.1973; data-to-parameter ratio = 9.05.

I. INTRODUCTION

Phenolic oximes are widely used in industrial copper extraction process from waste streams, and as corrosion protectors in protective coatings. They exhibit selective preference for copper (II) over the other metals, particularly over iron present in pregnant leach solutions. The large selectivity for copper (II) is due to the fact that it perfectly fits in the cavity created by two hydrogen bonded ligands, producing a stable pseudo-macrocyclic monomer (Scheme 1). Mononuclear complexes of Co(II), Ni(II), Cu(II), and Zn(II) with these phenolic oximes are also known to be formed. One more important aspect of phenolic oximes is the capability to form polynuclear complexes since both the oximate and phenolate groups be able to bridge the metals[1]. Copper (II) complexes coordinated to polydentate pyrazole-based ligands have been proposed as models for the type-3 active-site of the copper proteins hemocyanin and tyrosinase [2], [3], [4]. The role of these proteins [5], [6] is to bind and transport dioxygen. In addition, tyrosinase has both catecholase and cresolase activity [7]. Enzymatic syntheses often proceed under mild conditions and are very selective. It is therefore interesting to study and to model these bio-catalysts in order to use them as effective chemical tools for common reactions.

II. Experimental

The title compound (*E*)-2-hydroxybenzaldehyde oxime and their corresponding copper(II) complex was synthesized using reported method[8,9].

[8] Heliyon 6 (2020) e04942

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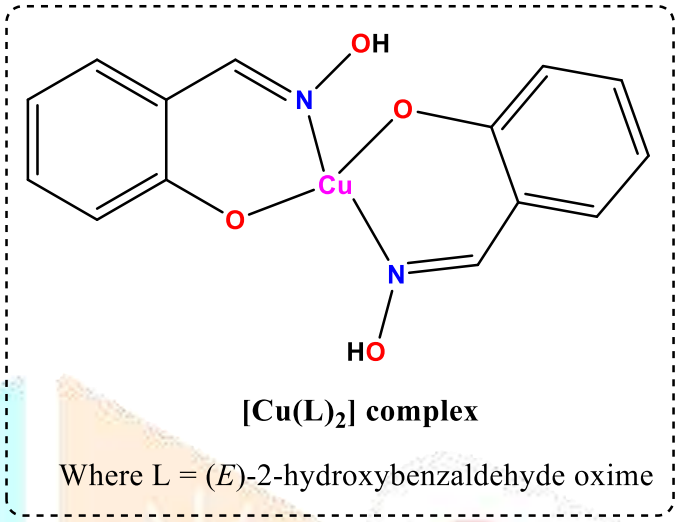

[Cu(L)$_2$] complex

Where L = (*E*)-2-hydroxybenzaldehyde oxime

Scheme 1. Structure of copper complex

III. Data collection

Data collection: APEX3 (Bruker, 2016)[10]; cell refinement: SAINT (Bruker, 2016); data reduction: SAINT (Bruker, 2016); program(s) used to solve structure: SHELXT (Sheldrick, 2015a)[11]; program(s) used to refine structure: SHELXL2018/3 (Sheldrick, 2015b)[12]; molecular graphics: DIAMOND (Brandenburg & Putz, 2012)[13], PLATON (Spek, 2020)[14]; software used to prepare material for publication: SHELXL2018/3 (Sheldrick, 2015b), PLATON (Spek, 2020) and publCIF (Westrip, 2010)[15].

IV. Refinement

Crystal data, data collection, and structure refinement details are summarized in Table 3. For both compounds, initial structure solution identified positions of all non-H atoms except those of the anti conformation. Prominent electron density difference map peaks then identified atoms of the anti conformation. Common site occupation factors for each conformation were refined with the constraint that their sum equal 1.0. H-atom positions were visible on the electron density difference map, but were calculated and refined using a riding model for those bound to C with isotropic displacement parameters set to 1.2 or 1.5U_{iso} of the parent atom for methylene or methyl H atoms, respectively. The H atom bound to N was freely refined to a reasonable N—H bond length and the N1—C1A distance was constrained to a chemically reasonable distance (1.50± 0.01Å) using the DFIX command in SHELX.

V. Structural Commentary

The molecular structure of the title compound consists of a tridentate ligand synthesized (e)-2-hydroxybenzaldehyde oxime molecule coordinating by the copper(II) ion (Fig. 1). The planarity of the π-electron system allows for the acquisition of large resonance energies due to the overlap of orbitals, resulting in a planar structure. The azo group is in a Tran's conformation. The molecular structure of the title complex is illustrated in Fig. 1. The Cu^{II} atom has a distorted octahedral coordination sphere, reflecting the characteristic Jahn–Teller distortion. It is coordinated by the N atoms of two propane-1,3-diamine ligands in the equatorial plane with Cu—N bond lengths varying between 2.003 (4)–2.023 (3) Å. The Cu1—O1 Cu1—O2 bonds lengths are 1.947 (3) and 1.904 (3) A˚ , respectively, close to a typical Cu—O bond length. The Cu1—N1 and Cu1—N2 bonds lengths of 1.928 (4) and 1.949 (4) Å corresponds to the typical Cu—N bond length.

VI. Superamolecular features

Fig. 3 shows the packing in the unit cell. There are no significant intermolecular interactions. However, the structure displays hydrogen-bonding interactions within the molecule, which are those between the aromatic OH groups and an oxygen atom of the carboxylate group within the 3,5-DIPS ligand. The hydrogen bond O-H…O distances and angles for O1-H…O2 and N1-H1…O1 are reported in Table 2 and Fig. 3. Numerous intermolecular hydrogen bonds of the type C-H…O (Table 3) connect adjacent units, resulting in a three-dimensional network (Fig. 4).

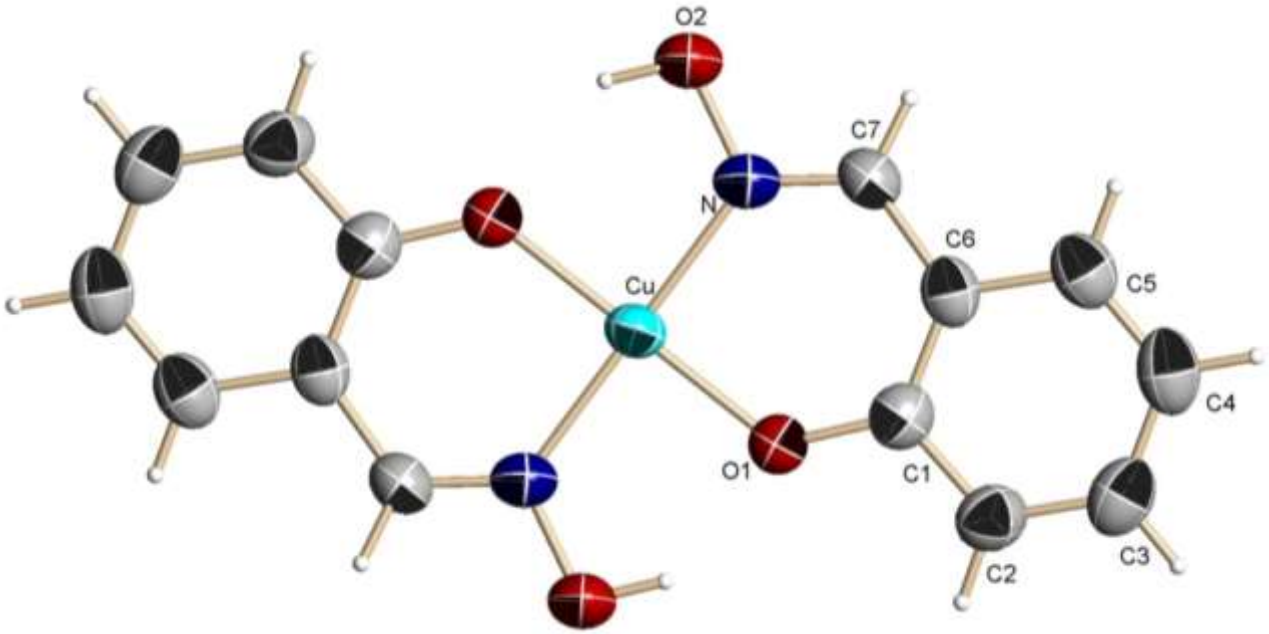

Figure 2 A view of the title compound, showing the atom-labeling scheme. Displacement ellipsoids are plotted at the 50% probability level.

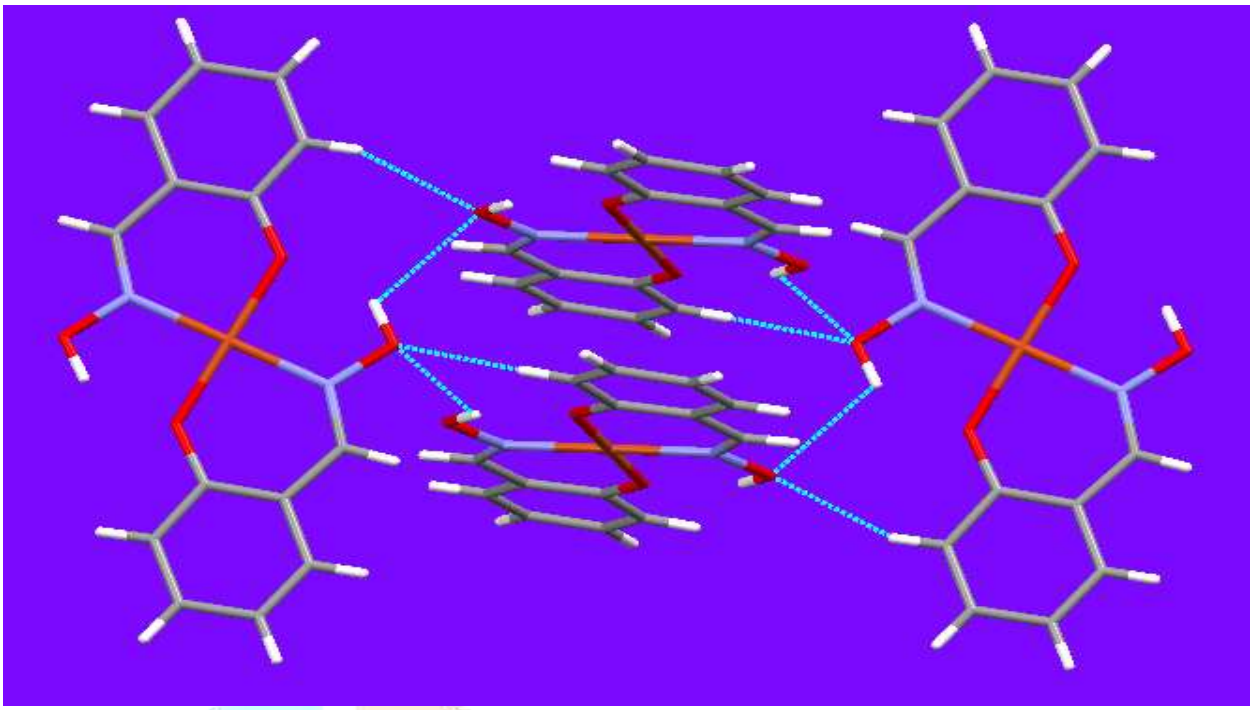

Figure 3 Fragment of a [010] polymeric chain in the crystal structure of the title compound.

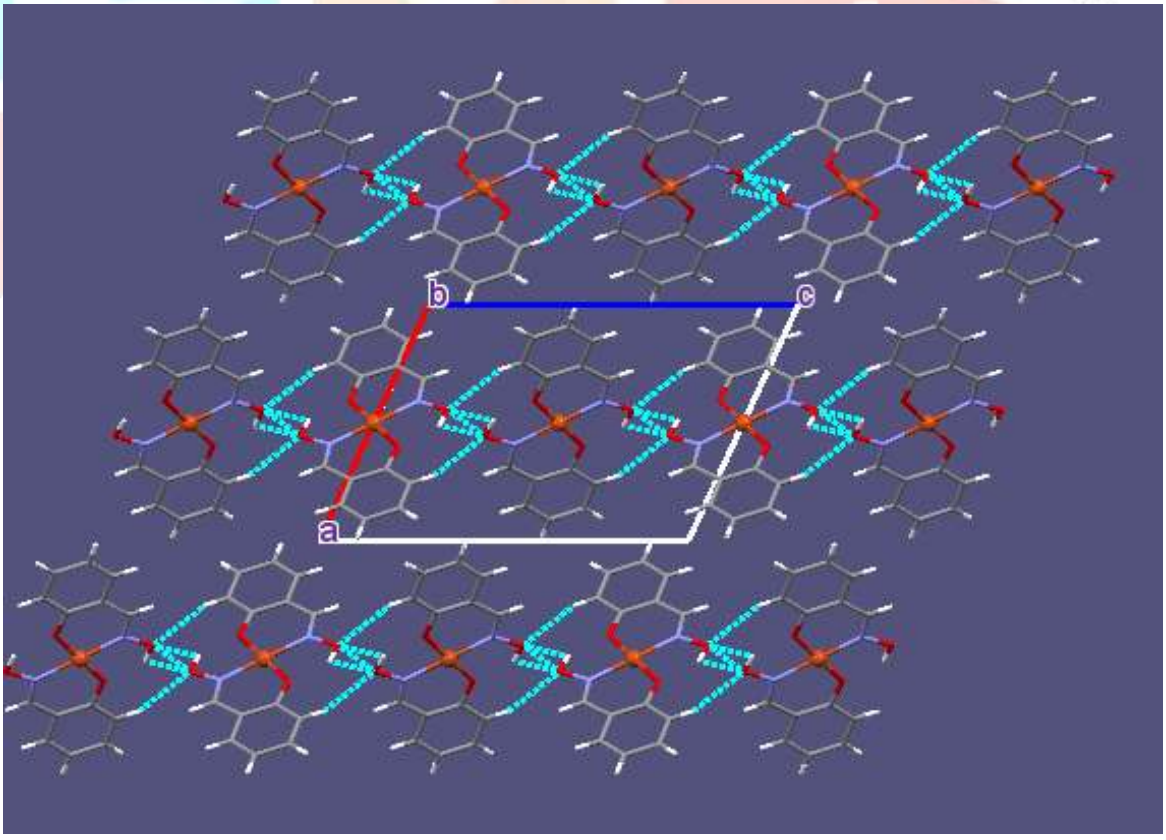

Figure 4 The packing in the crystal of the title complex, viewed along the b axis.

VII. Table: 1

Crystal Data and Details of the Structure Determination

Parameters	Title of compound
Empirical formula	$C_{14}H_{12}CuN_2O_4$
Formula weight	335.8
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	*P21/c*
Unit cell dimensions	a = 10.2470(6) Å, α= 90°
	b = 4.938(1) Å, β= 113.900(8)°
	c = 13.970(1) Å, γ = 90°
Volume	646.27(15) $Å^3$
Z	2
Density (calculated)	1.726 g/cc
Absorption coefficient	1.708 mm^{-1}
F(000)	342
Crystal size	0.32 x 0.22 x 0.18 mm^3
Theta range for data collection	2.17 to 24.99°.
Index ranges	-1<=h<=12, -5<=k<=1, -16<=l<=15
Reflections collected	1593
Independent reflections	1009 [R(int) = 0.0757]
Completeness to theta = 24.99°	89.10%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7486 and 0.6077
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1009 / 0 / 97
Goodness-of-fit on F2	1.114
Final R indices [I>2sigma(I)]	R1 = 0.0689, wR2 = 0.1853
R indices (all data)	R1 = 0.0751, wR2 = 0.1973
Largest diff. peak and hole	0.706d -1.520 e.$Å^{-3}$

VIII. Table 2

The selected Bond length (Å) and Bond angles (°)

Atom	Length(Å)	Atom	Angles(°)
Cu-O1	1.899(3)	O(1)-Cu-O(1)	180
Cu-O1	1.899(3)	O(1)-Cu-N1	91.58(13)
Cu-N1	1.937(3)	O(1)-Cu-N1	88.42(13)
Cu-N	1.937(3)	O(1)-Cu-N	88.42(13)
O1-C1	1.320(6)	O(1)-Cu-N	91.58(13)
O2-N	1.392(5)	N1-Cu-N	180.000(1)
N-C7	1.281(5)	C(1)-O(1)-Cu	128.6(3)
C1-C6	1.391(8)	C(7)-N-O(2)	114.4(3)
C1-C2	1.413(6)	C(7)-N-Cu	128.2(3)
C2-C3	1.376(6)	O(2)-N-Cu	117.5(3)
C3-C4	1.392(7)	O(1)-C(1)-C(6)	124.3(4)
C4-C5	1.365(7)	O(1)-C(1)-C(2)	118.7(4)
C5-C6	1.412(6)	C(6)-C(1)-C(2)	117.0(4)
C6-C7	1.445(7)	C(3)-C(2)-C(1)	122.1(4)

IX. Table 3

Hydrogen-bond geometry (Å ,°).

D-H…A	D-H	H…A	D…A	D-H…A
O1-H1…O2[I]	0.89	2.59	3.017(6)	110
C2-H10…O2[ii]	0.93	2.55	3.424(6)	157

Symmetry codes: i= 1-x,1/2+y,3/2-z
ii = x,3/2-y,-1/2+z

X. Acknowledgment

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