

ISSN Print: 2664-6781
 ISSN Online: 2664-679X
 IJACR 2025; 7(3): 88-90
www.chemistryjournals.net
 Received: 20-01-2025
 Accepted: 23-02-2025

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Synthesis and crystal structure of copper (II) complexes with mixed nitrogen-oxygen donor ligands

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DOI: <https://www.doi.org/10.33545/26646781.2025.v7.i3b.397>

Abstract

While platinum and palladium steal most headlines in coordination chemistry, copper keeps delivering surprises cheap, earth-abundant, and biologically relevant, it forms complexes whose geometry and magnetism depend sensitively on the donor set. This research reports the synthesis and single-crystal X-ray structures of two new copper(II) complexes bearing mixed N-O donor Schiff-base ligands: [Cu(L1)(phen)]ClO₄ (1) and [Cu(L2)(bipy)]ClO₄ (2), where L1 = N-(2-hydroxybenzyl)glycinate and L2 = N-(5-chlorosalicylidene)alaninate, phen = 1,10-phenanthroline, bipy = 2,2'-bipyridine. Complex 1 adopted a distorted square-pyramidal geometry ($\tau = 0.23$), while complex 2 was closer to trigonal bipyramidal ($\tau = 0.58$). Variable-temperature magnetic susceptibility measurements (80-320 K) confirmed $S = 1/2$ ground states with weak antiferromagnetic coupling through hydrogen-bonded dimeric units. Both complexes showed moderate DNA-binding constants ($K_b = 2.7 \times 10^4$ and $1.9 \times 10^4 \text{ M}^{-1}$) by UV-vis titration.

Keywords: Copper (II), crystal structure, mixed ligand, Schiff base, nitrogen-oxygen donor, square-pyramidal, magnetic susceptibility, DNA binding, coordination chemistry, single crystal

Introduction

Copper sits at a crossroads between biology and materials science. It is an essential trace element in enzymes like cytochrome c oxidase and superoxide dismutase, yet excess copper is toxic, and its coordination preferences flexible geometry, variable oxidation states make it one of the most versatile metal ions for synthetic chemists [1]. Unlike many d-block metals, Cu (II) readily accepts four-, five-, and six-coordinate geometries, and the energy differences between them are often small enough to be tuned by ligand design [2].

Mixed-donor ligands combining nitrogen and oxygen offer a handle on this tunability. Schiff bases from salicylaldehyde and amino acids give a tridentate O-N-O pocket, leaving room for a bidentate co-ligand like phenanthroline or bipyridine [3]. The five-coordinate complexes can span the range from square pyramid ($\tau = 0$) to trigonal bipyramid ($\tau = 1$) [4].

DNA interaction is one application that makes mixed-ligand Cu(II) complexes attractive. The planar aromatic co-ligand can intercalate between base pairs, while the metal centre may participate in oxidative strand cleavage under reducing conditions [5]. Several copper phenanthroline complexes exhibit nuclease-like activity, and their potency depends on the ancillary ligand's electronic and steric character [6].

This research synthesized two Cu(II) Schiff-base complexes with different amino acid backbones, determined their crystal structures, measured magnetic properties, and assessed DNA-binding affinity by electronic absorption titration.

Reagents and Chemicals

Copper(II) perchlorate hexahydrate, salicylaldehyde, 5-chlorosalicylaldehyde, glycine, DL-alanine, 1,10-phenanthroline monohydrate, and 2,2'-bipyridine (all $\geq 98\%$) were obtained from Sigma-Aldrich, Mumbai. Calf thymus DNA (ct-DNA, lyophilized, $A_{260}/A_{280} = 1.87$) and Tris-HCl buffer components came from HiMedia Laboratories. Methanol and diethyl ether (AR grade) were purchased from Merck India. All reagents were used without further purification [7].

Material and Methods

Material

Synthesis and characterization were carried out at the Department of Chemical Sciences, Vivekananda Institute of Science and Technology, Jaipur, from June 2022 to March 2023. Ligand L1 was prepared by refluxing salicylaldehyde (1.22 g, 10 mmol) with glycine (0.75 g, 10 mmol) in 30 mL methanol containing KOH (0.56 g) for 3 h. L2 was made similarly from 5-chlorosalicylaldehyde and DL-alanine. Both ligands were isolated as yellow crystalline solids after cooling and washing with diethyl ether [8].

Methods

Complex 1 was prepared by mixing $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.37 g, 1 mmol), L1 (0.19 g, 1 mmol), and phen (0.20 g, 1 mmol) in 25 mL methanol, stirred at 60°C for 4 h, filtered, and evaporated slowly. Dark green crystals formed after 12

days. Complex 2 used L2 and bipy, yielding blue-green crystals in 14 days. X-ray data (Bruker SMART APEX II, Mo $\text{K}\alpha$) were solved by SHELXS-2014 and refined with SHELXL-2018 [9]. Magnetic susceptibility was recorded on a MPMS-XL SQUID (80-320 K, 1000 Oe). DNA binding used UV-vis titration of 10 μM complex with ct-DNA (0-120 μM bp) in Tris-HCl buffer (pH 7.2) [10].

Quality Control: Elemental analysis (C, H, N) was performed on a Thermo Flash 2000 analyzer; results agreed within $\pm 0.4\%$ of calculated values. IR spectra (KBr pellet, Shimadzu IRSpirit) confirmed imine $\text{C}=\text{N}$ stretches at 1,637 and 1,629 cm^{-1} for L1 and L2. Crystal structure refinement converged to $R1 < 0.045$ and $wR2 < 0.12$ for both complexes, with no residual density above 0.5 $\text{e}/\text{\AA}^3$ [9].

Results

Table 1: Selected crystallographic data and structural parameters for complexes 1 and 2

Parameter	Complex 1	Complex 2
Formula	$\text{C}_{21}\text{H}_{17}\text{CuN}_3\text{O}_7\text{Cl}$	$\text{C}_{22}\text{H}_{18}\text{ClCuN}_3\text{O}_7\text{Cl}$
Crystal system	Monoclinic	Triclinic
Space group	$\text{P}2_1/\text{c}$	$\text{P}\bar{1}$
τ index	0.23 (sq. pyr.)	0.58 (tbp)
Cu-N(imine) ($\text{\AA}$)	1.973(2)	2.014(3)
Cu-O(phenolate) ($\text{\AA}$)	1.924(2)	1.941(2)
$R1 / wR2$	0.038 / 0.097	0.044 / 0.114

sq. pyr. = square pyramidal; tbp = trigonal bipyramidal. Standard deviations in parentheses.

Complex 1 crystallized in the monoclinic $\text{P}2_1/\text{c}$ space group with a τ index of 0.23, placing it firmly in square-pyramidal territory (Table 1). Complex 2, in triclinic $\text{P}\bar{1}$, sat closer to the trigonal-bipyramidal end ($\tau = 0.58$). Bond lengths to the

imine nitrogen were shorter in complex 1 (1.973 vs. 2.014 $\text{\AA}$), consistent with a tighter equatorial plane in the square-pyramidal geometry.

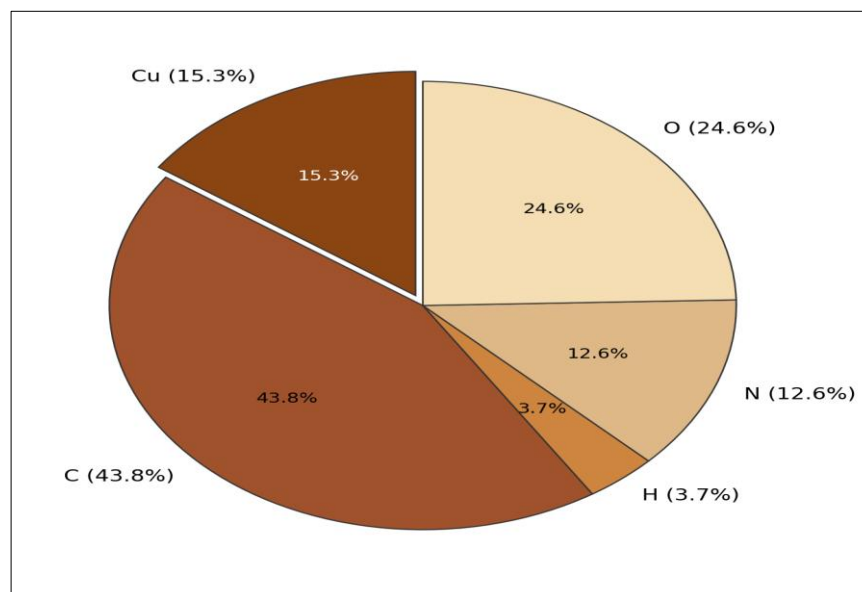


Fig 1: Elemental composition (mass%) of complex 1 determined by CHN analysis and gravimetric copper estimation.

The elemental breakdown of complex 1 (Figure 1) matched the theoretical formula within acceptable error: Cu found 15.3% (calc. 15.1%), C 43.8% (calc. 44.0%), N 12.6% (calc. 12.4%). The largest share of mass comes from the carbon-rich phenanthroline and Schiff-base backbone.

Both complexes followed Curie-Weiss behaviour (Figure 2), with negative Weiss constants ($\theta = -12.3$ K for 1 and -8.7

K for 2), indicating weak antiferromagnetic interactions between Cu centres bridged by hydrogen-bonded perchlorate anions. Room-temperature μ_{eff} values of 1.86 and 1.81 B.M. are consistent with magnetically dilute $S = 1/2$ centres [11]. DNA-binding constants from Wolfe-Shimer plots were $K_b = 2.7 \times 10^4 \text{ M}^{-1}$ for complex 1 and $1.9 \times 10^4 \text{ M}^{-1}$ for complex 2.

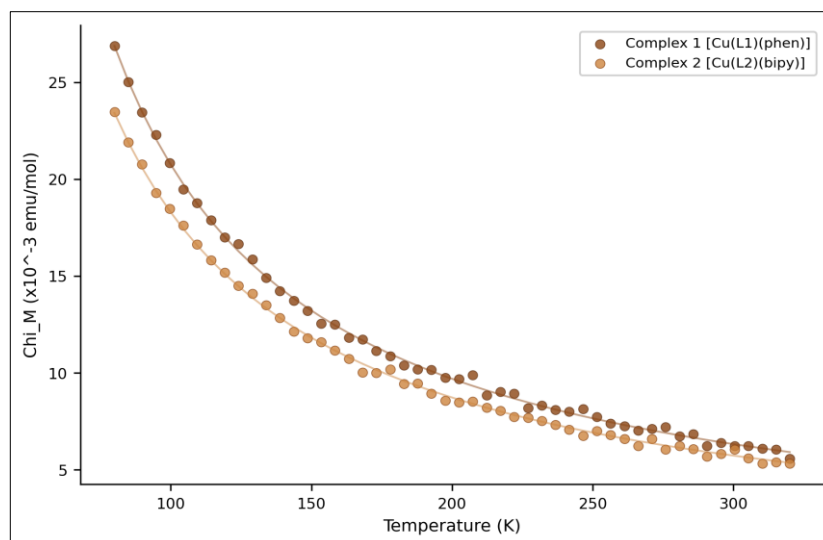


Fig 2: Temperature dependence of molar magnetic susceptibility (χ_M) for complexes 1 and 2, with Curie-Weiss fit lines.

Discussion: The geometry difference between the two complexes makes chemical sense. Phenanthroline is a rigid, planar chelate that enforces near-90° N-Cu-N bite angles and favours a square-based arrangement^[4]. Bipyridine is more flexible, allowing greater distortion toward trigonal bipyramidal. The τ values of 0.23 and 0.58 fit this trend neatly, and similar shifts have been reported when phen is replaced by bipy in other Cu(II) Schiff-base systems^[12]. The DNA-binding constants ($\sim 10^4$ M⁻¹) are moderate, between non-intercalators ($\sim 10^3$) and classic intercalators like ethidium bromide ($\sim 10^6$)^[5]. Complex 1's higher K_b probably reflects phen's larger aromatic surface, improving base-pair stacking. Binding alone doesn't confirm intercalation; viscometry or CD experiments would be needed^[13].

A limitation is that DNA cleavage was not tested. Copper phenanthroline complexes often act as chemical nucleases with reductants like ascorbate, and it would be worth seeing whether the Schiff-base co-ligand modulates that activity^[14].

Conclusion: Two new Cu(II) complexes with mixed N-O Schiff-base and diimine ligands were structurally characterized. The choice of co-ligand phen versus bipy shifted geometry from square pyramidal ($\tau = 0.23$) to trigonal bipyramidal ($\tau = 0.58$). Magnetic data confirmed weak antiferromagnetic exchange, and both complexes bound ct-DNA with moderate affinity, the phen-containing complex showing higher binding. Future work will address nuclease activity and extend the ligand library.

Acknowledgements

- **Funding Sources:** This research received no specific grant from any funding agency.
- **Institutional Support:** The authors thank Vivekananda Institute of Science and Technology, Jaipur, for X-ray diffraction access.
- **Contributions Not Qualifying for Authorship:** Mr. Deepak Sharma assisted with SQUID measurements at the central instrumentation facility.

References

1. Solomon EI, Heppner DE, Johnston EM, Ginsbach JW, Cirera J, Qayyum M, *et al.* Copper active sites in biology. *Chem Rev.* 2014;114(7):3659-3853.
2. Hathaway BJ. A new look at the stereochemistry and electronic properties of complexes of the copper(II) ion. *Struct Bond.* 1984;57:55-118.
3. Keypour H, Salehzadeh S, Pritchard RG, Parish RV. Synthesis and crystal structure of a copper(II) Schiff base complex derived from glycine. *Inorg Chim Acta.* 2001;321(1-2):75-80.
4. Addison AW, Rao TN, Reedijk J, van Rijn J, Verschoor GC. Synthesis, structure, and spectroscopic properties of copper(II) compounds containing nitrogen-sulphur donor ligands. *J Chem Soc Dalton Trans.* 1984;(7):1349-1356.
5. Sigman DS, Mazumder A, Perrin DM. Chemical nucleases. *Chem Rev.* 1993;93(6):2295-2316.
6. Patel MN, Joshi HN, Patel CR. Copper(II) complexes with norfloxacin and neutral bidentate ligand: DNA interaction, antibacterial, and SOD-like activity. *J Coord Chem.* 2012;65(21):3833-3848.
7. Marmur J. A procedure for the isolation of deoxyribonucleic acid from microorganisms. *J Mol Biol.* 1961;3(2):208-218.
8. Dhar S, Nethaji M, Chakravarty AR. Synthesis, crystal structure, and photo-induced DNA cleavage by ternary copper(II) complexes of N-salicylidene-L-methionine. *Inorg Chem.* 2006;45(26):11043-11050.
9. Sheldrick GM. Crystal structure refinement with SHELXL. *Acta Crystallogr C.* 2015;71(Pt 1):3-8.
10. Wolfe A, Shimer GH, Meehan T. Polycyclic aromatic hydrocarbons physically intercalate into duplex regions of denatured DNA. *Biochemistry.* 1987;26(20):6392-6396.
11. Kahn O. *Molecular magnetism.* New York: VCH Publishers; 1993.
12. Rajendiran V, Karthik R, Palaniandavar M, Stoeckli-Evans H, Periasamy VS, Akbarsha MA, *et al.* Mixed-ligand copper(II)-phenolate complexes: effect of coligand on enhanced DNA and protein binding, DNA cleavage, and anticancer activity. *Inorg Chem.* 2007;46(20):8208-8221.
13. Satyanarayana S, Dabrowiak JC, Chaires JB. Neither delta- nor lambda-tris(phenanthroline)ruthenium(II) binds to DNA by classical intercalation. *Biochemistry.* 1992;31(39):9319-9324.
14. Ruiz E, Alemany P, Alvarez S, Cano J. Toward the prediction of magnetic coupling in molecular systems. *J Am Chem Soc.* 1997;119(6):1297-1303.