



## A copper(II)-Schiff base complex: Synthesis, structural characterization and catalytic oxidative coupling of 2-aminophenol

Shreya Mahato and Bhaskar Biswas\*

Department of Chemistry, University of North Bengal, Darjeeling-734 013, West Bengal, India

E-mail: icbbiswas@gmail.com, bhaskarbiswas@nbu.ac.in

Manuscript received online 30 January 2020, revised and accepted 28 May 2020

This present study reports the synthesis, X-ray structural analysis, supramolecular architectures and oxidative coupling of 2-aminophenol of a copper(II)-Schiff base complex,  $[\text{Cu}(\text{L})](\text{H}_2\text{O})$  (**1**) containing a previously reported Schiff base,  $\text{H}_2\text{L} = 2,2'$ -((1,2-phenylenebis(azanylylidene))bis(methanylylidene))diphenol. Crystal structure analysis reveals that Cu(II) centre adopts a square planar coordination geometry with  $R\text{-}3$  space group. Investigation on self-assembled crystalline architecture displays that the aqua molecule in crystal lattice involves in significant intermolecular H-bonding to lead the formation of water mediated dimeric unit of Cu(II) complex. Noteworthy  $\pi\cdots\pi$  interactions are operative strongly among the centroids of ligands to assemble Cu(II) complex in a zigzag 1D chain. The red highlighted spots in Hirshfeld surface suggests the active involvement of C-H $\cdots$ O, O-H $\cdots$ O types H-bonding and  $\pi\cdots\pi$  interactions. The catalytic aspects of Cu(II) complex has been evaluated towards oxidative dimerization of 2-aminophenol (2-AP) in methanol and found high catalytic efficiency,  $k_{\text{cat}}/K_{\text{M}}$  ( $\text{h}^{-1}$ ) as  $2.14 \times 10^5$ . Mass spectrometry studies of the Cu(II) complex with 2-AP ensures that the course of catalysis undergoes through enzyme-substrate adduct formation in solution phase.

Keywords: Copper(II), Schiff base, Hirshfeld surface analysis, X-ray structure, phenoxazinone synthase activity.

### Introduction

Now-a-days, copper(II)-Schiff base chelates exhibit their potential uses in designing important catalysts of industrial and biological significance, functional materials with potential magnetic and conducting properties, optical materials and others<sup>1-5</sup>. In biology, copper based metallo-proteins and enzymes play significant roles, like in hemocyanin<sup>6</sup> as dioxygen transporter, copper dependent oxidase and oxygenase enzymes such as tyrosinase<sup>7</sup>, catechol oxidase<sup>8</sup> and quercetin 2,3-dioxygenase<sup>9-11</sup>, galactose and glyoxal oxidases<sup>12-15</sup>, methane monooxygenase and so on<sup>16-18</sup>. Several copper dependent metallo-proteins are available in living system, however, phenoxazinone synthase<sup>19</sup>, a copper-based oxidase enzyme holds a great promise in producing final product (2-aminophenoxazinone species) of the catalytic reactions with great therapeutic value<sup>19-22</sup>. Focusing on the of bio-catalytic importance of the Cu(II) complexes as well as their potential applications of modern use, different scientific groups across the globe have been pursuing their research activities based on copper(II) based coordination compound<sup>23,24</sup>.

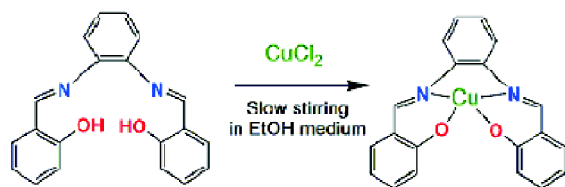
It is also been observed that, this Cu(II) complex with chloroform as solvate molecule has been previously published by Marinovich *et al.*<sup>25</sup>. In this context, attempts were made to isolate the single crystals of same copper(II) compound with an aim to prepare the isostructural mononuclear copper(II)-Schiff base complex in ethanol as a green solvent. We are able to synthesize this same complex with aqueous molecule as a solvent. Herein, we address the synthesis, X-ray structural analysis, supramolecular architectures, crystal surface analysis and aminophenol oxidation study of a copper(II)-Schiff base complex,  $[\text{Cu}(\text{L})](\text{H}_2\text{O})$  with high catalytic efficacy.

### Results and discussion

#### *Synthesis and formulation of the $[\text{Cu}(\text{L})](\text{H}_2\text{O})$ :*

The mononuclear copper(II)-Schiff base was prepared by mixing of  $\text{CuCl}_2$  to Schiff base in ethanol (Scheme 1). The structural aspects of Cu(II) complex was described by different analytical techniques and crystal structure analysis. The same Cu(II) complex can be synthesized in methanol-

dichloromethane solvent mixture using different Cu(II) salts with H<sub>2</sub>L ligand.



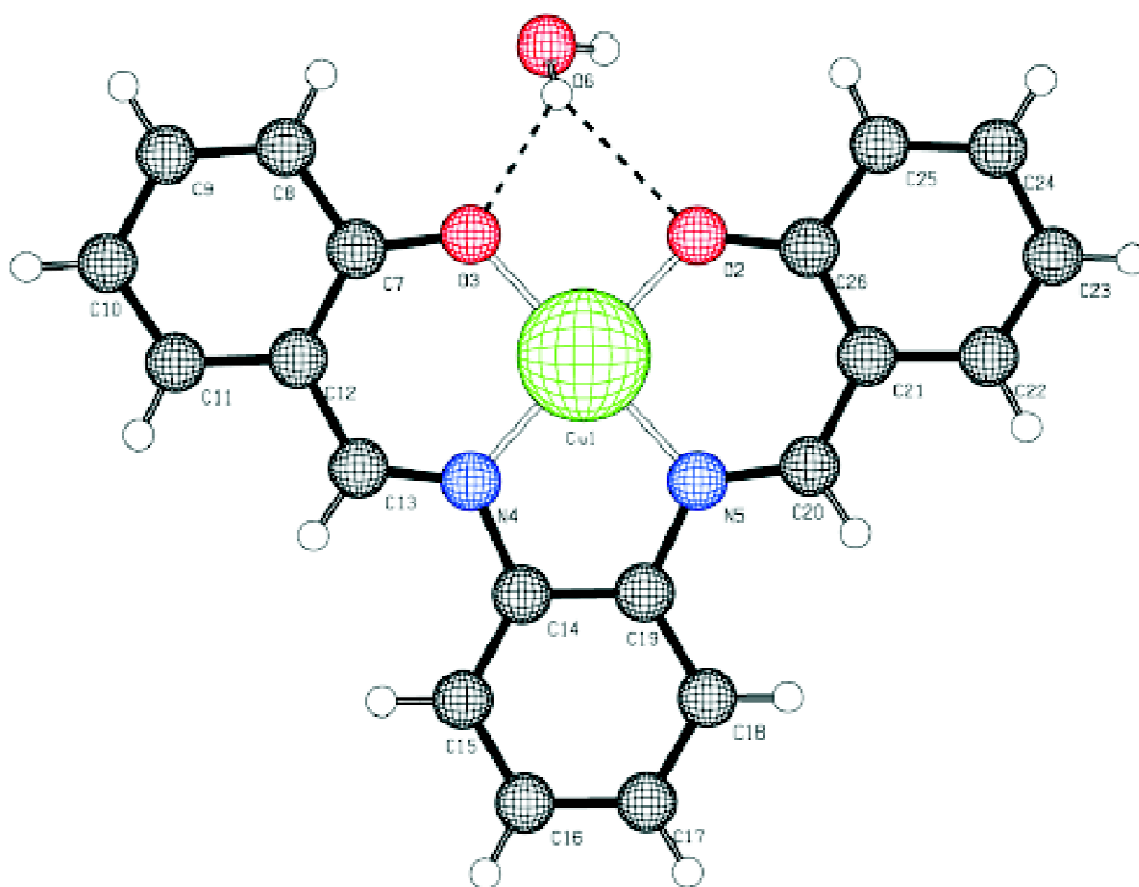
**Scheme 1.** Preparative route of the Cu(II) complex.

*Description of the crystal structure:*

Single crystal structural study indicates that copper(II)-Schiff base crystallizes in a trigonal system with *R*-3 space group. An ORTEP diagram of Cu(II) complex is displayed in Fig. 1. The crystallographic parameters are presented in Table 1 and bond angles as well as bond distances are tabulated in Table S1. The Cu(II) centre in **1** adopts a square planar

coordination geometry with two longer Cu(II)-N bond distances (Cu1-N4, 1.937 Å; Cu1-N5, 1.943 Å) and two shorter Cu(II)-O bond distances (Cu1-O2, 1.906 Å; Cu1-O3, 1.899 Å). The bond angle values around Cu(II) centre make an evidence for the deviation from ideal square planar geometry (Table S1). This coordination geometry of the copper(II) centre resembles well to previously reported square planar coordination geometry, [Cu(L)](CHCl<sub>3</sub>), except the solvent of crystallization<sup>25</sup>. The coordination linkages and bond angles of the reported Cu(II) complex resemble closely to the synthesized structure perhaps the crystal system as well as space group are found different. The *R*-factor of the previously reported structure is slightly lower compared to the synthesized copper(II)-Schiff base complex (Table 1).

The crystallographic packing is viewed over Mercury software to comprehend the packing nature of asymmetric Cu(II) complex unit along *ab* plane by varying molecular style model



**Fig. 1.** An ellipsoidal plot of [Cu(L)](H<sub>2</sub>O) (**1**) (30% ellipsoid probability).

Table 1. Crystallographic refinement parameters of [Cu(L)](H <sub>2</sub> O) (1)	
Parameters	Cu(II) compound
Empirical formula	C <sub>20</sub> H <sub>16</sub> N <sub>2</sub> O <sub>3</sub> Cu
Formula weight	395.89
Temperature (K)	293
Crystal system	Trigonal
Space group	<i>R</i> -3
<i>a</i> (Å)	30.969(2)
<i>b</i> (Å)	30.969(2)
<i>c</i> (Å)	9.1125(6)
Volume (Å <sup>3</sup> )	7568.7(9)
<i>Z</i>	18
$\rho$ (g cm <sup>-3</sup> )	1.564
$\mu$ (mm <sup>-1</sup> )	1.321
<i>F</i> (000)	3654
$\theta$ ranges (°)	2.16 to 32.8°
<i>R</i> <sub>int</sub>	0.147
<i>R</i> (reflections)	35847
<i>wR</i> 2 (reflections)	6056
Final <i>R</i> indices	0.0890, 0.2676
Largest peak and hole (eÅ <sup>-3</sup> )	2.79, -0.68

and presented in Fig. S1. The solvate water in crystal lattice exhibits significant intermolecular H-bonding in the formation of water mediated dimeric unit (Fig. 2) and noteworthy  $\pi \cdots \pi$  interactions are operative in assembling asymmetric Cu(II) complex units to lead a zigzag 1D chain in crystalline state (Fig. 3). The oxygen atom (O6) of lattice water acts as a donor towards one H atom of phenyl ring in one Cu(II) complex unit on the contrary one of the two H atoms attached to same O6 atom plays a role of acceptor in a bifurcated fashion towards two phenolate oxygen ions (O2, O3) of the ligand

in assembling two Cu(II) complex units (Tables S2, S3). The  $\pi \cdots \pi$  interactions involving the different centroids of Schiff bases in Cu(II) complex are found as strong forces which exhibit a unique mode of growth (zigzag 1D) for the Cu(II) complex in crystalline phase (Fig. 3).

The crystalline phase morphology of the Cu(II) complex was examined by Hirshfeld surface analysis (Fig. 4). The surface volume and surface area were calculated as 412.82 Å<sup>3</sup> and 376.73 Å<sup>2</sup> respectively. The intermolecular interactions of Cu(II) complex is manifested by generation of fingerprint plots (Fig. S2). This plot exhibits a mapping over a definite  $d_{\text{norm}}$ , curvedness and shape index in the crystal (Fig. 4). The  $d_{\text{norm}}$  surface in 3D is plotted over a fixed scale of colour from -0.1363 (red) to 1.0474 (blue) a.u. where area of red spots expresses the area of  $d_{\text{norm}}$ . The negative values in  $d_{\text{norm}}$  on the surface highlight C-H $\cdots$ O and O-H $\cdots$ O intermolecular interactions (Table S2). The % share of individual

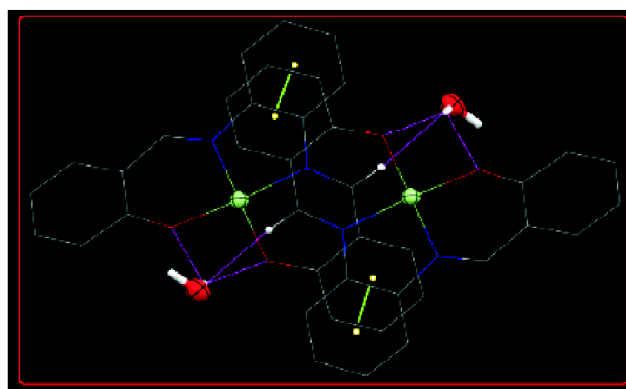


Fig. 2. Intermolecular O $\cdots$ H (purple dot) and  $\pi \cdots \pi$  (green line) interactions mediated dimer formation of [Cu(L)](H<sub>2</sub>O) (1) in crystalline phase.

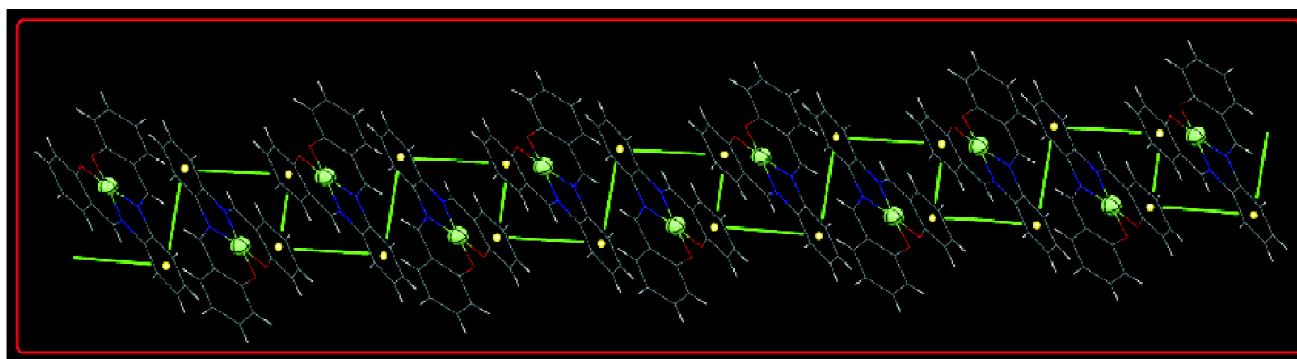
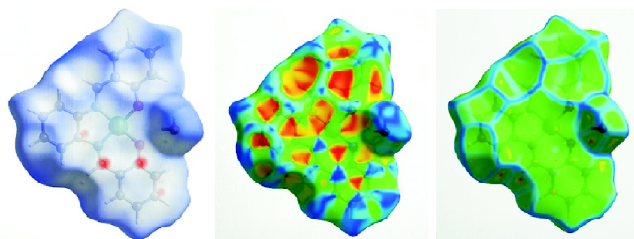


Fig. 3. Formation of 1D zigzag chain through purely  $\pi \cdots \pi$  (green line) interactions in the growth of [Cu(L)](H<sub>2</sub>O) (1) in ac plane.



**Fig. 4.** The Hirshfeld surfaces of Cu(II)-Schiff base complex mapped over  $d_{\text{norm}}$ , shape index and curvedness.

elements with other elements in the formation of crystalline architecture is summarized in Table S4. This Cu(II)-Schiff base is interacted by adjacent units by C-H $\cdots$ O/O-H $\cdots$ O and  $\pi\cdots\pi$  interactions as evident in Fingerprint plots (Fig. S2).

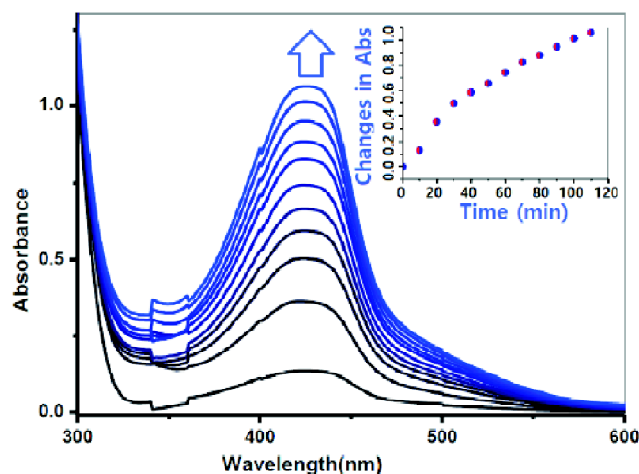
#### *Solution phase property:*

The solution phase behaviour of the Cu(II) complex was examined by electronic and EPR spectral analysis. The electronic spectrum in methanol exhibits the characteristics transitions at 240, 300 and 418 nm (Fig. S2). The electronic transitions in high energy wavelength region may be attributed to the intraligand electronic transitions<sup>26</sup> while a low energetic and broad electronic band at 418 nm ensures the presence of phenoxo to copper(II) ion electronic transition in solution phase<sup>27</sup>. The d-d electronic transition of Cu(II) complex is not observed in this case<sup>27</sup>. The Cu(II)-Schiff base exhibits poor conductance value ( $3.5 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ ) in methanol and may be considered as a non-electrolyte in solution<sup>28</sup>.

#### *Catalytic oxidation of 2-aminophenol:*

The catalytic efficacy of the copper(II)-Schiff base towards phenoxazinone synthase activity was examined by treating 2-AP as a model substrate in methanol. To carry out the biomimetic oxidation, a reaction mixture containing  $1 \times 10^{-3} \text{ M}$  Cu(II) complex solution with  $1 \times 10^{-2} \text{ M}$  2-AP was prepared and spectrophotometer was employed to monitor the course of the reaction for 2 h.

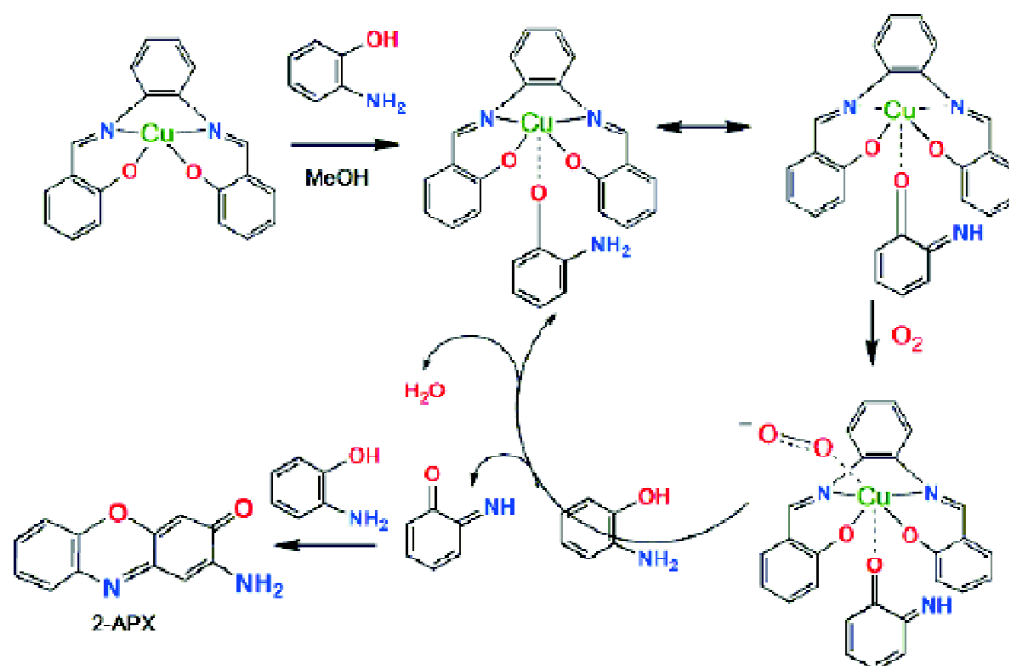
Three characteristic optical bands at 240, 300 and 418 nm were developed for Cu(II)-Schiff base in UV-Vis spectrum and 2-AP displayed one electronic band at 267 nm. It was observed that treatment of catalytic amount of Cu(II)



**Fig. 5.** Monitoring of growth of aminophenoxazinone species at 430 nm upon addition of  $10^{-4} \text{ M}$  solution of Cu(II) complex to  $10^{-2} \text{ M}$  2-AP in MeOH. The spectra were recorded after every 10 min. Inset: Plot of time vs Abs.

complex to 10 equivalent 2-AP in methanol, a characteristic electronic band corresponding to amino-phenoxazinone (APX) species<sup>29–34</sup> started to develop at 430 nm (Fig. 5). Extraction of phenoxazinone compound (77.9% for Cu(II) complex) was performed with column chromatographic technique. The proton signals in  $^1\text{H}$  NMR spectrum were well indexed with the reported values<sup>33</sup>.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta_{\text{H}}$ : 7.67 (m, 1H), 7.47 (m, 3H), 6.42 (s, 1H), 6.35 (s, 1H).

The efficiency of 2-AP oxidation by Cu(II) complex was measured by kinetic studies following the method of initial rates<sup>29–34</sup> under aerobic atmosphere. The growth of aminophenoxazinone compound in solution was monitored at 430 nm with the progress of time (Fig. S4)<sup>29–34</sup>. The kinetic parameter was determined from the plot of rate constants vs concentration of the substrate employing Michaelis-Menten equation of enzymatic kinetics. The maximum velocity of the reaction,  $V_{\text{max}} (\text{MS}^{-1})$  and Michaelis-Menten constant were calculated as  $2.386 \times 10^{-5}$  (Sd. Error,  $3.75 \times 10^{-6}$ ) and  $K_{\text{M}} = 3.99 \times 10^{-3}$  (Sd. Error,  $9.54 \times 10^{-4}$ ) respectively while the turnover number was determined as  $k_{\text{cat}} = 5.89 \times 10^2 \text{ h}^{-1}$ . The catalytic efficiency of the biomimetic oxidation is expressed as  $k_{\text{cat}}/K_{\text{M}} = 2.14 \times 10^5$  which accounts on high level of activity of the Cu(II) complex.



**Scheme 2.** Plausible catalytic cycle for oxidative coupling of 2-AP.

Previously, phenoxazinone synthase activity of few Cu(II) complexes was evaluated by the renowned scientist Chaudhury *et al.*<sup>35</sup> and Begley *et al.*<sup>36</sup>. Chaudhury and group<sup>35</sup> evaluated the bio-mimetic phenoxazinone synthase activity of a tetranuclear copper complex through “on-off” mechanism. They suggested the active involvement of Cu(II) centre and radical generation in the course of oxidative catalysis. Begley and group<sup>36</sup> ensured the production of oxidation product through sequential three consecutive 2e oxidations. In this case, *in situ* mass spectrum of Cu(II)-Schiff base complex with 2-AP was recorded in methanol to understand the oxidative coupling of 2-AP (Scheme 2).

The mass spectrum provides valuable information about the course of catalytic oxidation. The mass spectrum exhibits the characteristic signals at  $m/z$  212.99 and 502.24 (Fig. S5) which corroborated the production of [(2-amino-3H-phenoxazine-3-ones) + H<sup>+</sup>] and [[Cu(L)(2-AP)] + H<sup>+</sup>] respectively. Thus, course of oxidative catalysis undergoes through enzyme-substrate adduct formation. Thereafter, the adduct reacts with molecular oxygen to form reactive intermediate and subsequently released 2-APX and water as products. A comparison of reactivity for aminophenol oxidation is drawn between the copper(II)-Schiff base and few previously reported Cu(II) complexes (Table 2)<sup>37–40</sup>.

**Table 2.** Comparison of  $k_{\text{cat}}$  ( $\text{h}^{-1}$ ) values for catalytic oxidation of 2-AP by reported copper(II) compounds and **1**

Complex	$k_{\text{cat}}$ ( $\text{h}^{-1}$ ) (Solvent)	CCDC No.	Ref.
[Cu <sub>4</sub> (L <sup>1</sup> ) <sub>4</sub> ]	86.3 (CH <sub>3</sub> OH)	1507035	[43]
[Cu <sub>4</sub> (L <sup>2</sup> ) <sub>4</sub> ]	340.26 (CH <sub>3</sub> OH)	1507036	[43]
[Cu <sub>4</sub> (L <sup>3</sup> ) <sub>4</sub> ]	1.21 × 10 <sup>5</sup> (CH <sub>3</sub> OH)	1455999	[44]
[Cu(bpy)Cl <sub>2</sub> ]	5.40 × 10 <sup>3</sup> (CH <sub>3</sub> OH)	1524681	[45]
[(CH <sub>3</sub> CN)Cu(L <sub>s</sub> ) <sub>2</sub> Cu] <sup>2+</sup>	11.1 (CH <sub>3</sub> OH)	1940162	[46]
[Cu(L)](H <sub>2</sub> O) ( <b>1</b> )	8.59 × 10 <sup>2</sup> (CH <sub>3</sub> OH)	1981345	This work

L<sup>1</sup> = (E)-4-Chloro-2-((thiazol-2-ylimino)methyl)phenol, L<sup>2</sup> = (E)-4-Bromo-2-((thiazol-2-ylimino)methyl)phenol, L<sup>3</sup> = N-(2-hydroxyethyl)-3-methoxysalicylalimine.

## Experimental

*Preparation of the Schiff base and mononuclear Cu(II) complex:*

*Chemicals, solvents and starting materials:*

Salisaldehyde (E. Merck, India), *o*-phenylenediamine (Aldrich, UK), copper(II) chloride dihydrate (E. Merck, India) were purchased from reputed sources and used without purification. All the reagents and solvents were of analytical grade (A.R. grade).

*Synthesis of the Schiff base, H<sub>2</sub>L and [Cu(L)](H<sub>2</sub>O):*

The Schiff base, H<sub>2</sub>L was previously synthesized by some other scientific groups as well as our group following reported procedure<sup>25,41</sup>. The structural composition was confirmed by <sup>1</sup>H NMR and HRMS spectral analyses.

The Cu(II)-Schiff base compound was synthesized by dropwise addition of 1 mole of CuCl<sub>2</sub> (0.134 g in 10 ml) to 1 mole of H<sub>2</sub>L (0.316 g in 1 mmol) in ethanol medium. The bright yellow coloured solution of H<sub>2</sub>L was immediately turned into green colored solution. Then, the solution was kept on magnetic stirrer for another 30 min followed by filter. Green coloured single crystals were appeared after 5-7 days from the reaction mixture. Yield: 0.453 g (69% based on metal salt). Anal. Calcd. for C<sub>20</sub>H<sub>16</sub>N<sub>2</sub>O<sub>3</sub>Cu (1). IR (KBr, cm<sup>-1</sup>): 1595 (ν<sub>C=N</sub>); UV-Vis (λ<sub>max</sub>, nm, 10<sup>-4</sup> M MeOH): 284,425.

*Physical measurements:*

FT-IR spectra (KBr) of the compounds were recorded with an FTIR-8400S SHIMADZU spectrophotometer (400–3600 cm<sup>-1</sup>, KBr pellet). <sup>1</sup>H NMR spectrum in CDCl<sub>3</sub> was recorded on a Bruker Advance 400 MHz spectrometer. All the electronic spectra and kinetic analysis were carried on a JASCO V-730 UV-Vis spectrophotometer. Mass spectrum was obtained from Q-TOF-micro quadrupole mass spectrometer.

*X-Ray diffraction study and Hirshfeld surface analysis of the copper(II) compound:*

Single crystal X-ray diffraction data of the [Cu(L)](H<sub>2</sub>O) complex was collected using a RigakuXtaLABmini diffractometer equipped with Mercury CCD detector. The diffraction data were recorded with graphite monochromated Mo-Kα radiation (λ = 0.71073 Å) at 293 K using ω scans. The data were reduced using CrysAlisPro 1.171.38.46<sup>42,43</sup> and the space group determination was done using Olex2. The structure was resolved by direct method and refined by full-matrix least-squares procedures using the SHELXL-2014/

7 software package using OLEX2 suite<sup>44</sup>.

Crystal Explorer 17.5<sup>45a</sup> programme package was employed to generate Hirshfeld surfaces<sup>45b</sup> and 2D fingerprint plots<sup>45c,d</sup> of **1** using its single crystal X-ray diffraction data. The function *d*<sub>norm</sub> is a ratio of the distances of any surface point to the nearest interior (*d*<sub>i</sub>) and exterior (*d*<sub>e</sub>) atom and the van der Waals radii of the atoms<sup>46</sup>. The details of analysis are reported elsewhere<sup>45,46</sup>.

*Catalytic oxidation of 2-aminophenol:*

The catalytic oxidation of 2-AP was carried out by the treatment of 1×10<sup>-3</sup> M solution of Cu(II) complex with 10 equiv. of 2-AP (1×10<sup>-2</sup> M) in methanol. Absorbance vs wavelength (wavelength scans) of the solution was recorded at a regular time interval of 10 min for oxidation of 2-AP in the wavelength with a range 300–800 nm. Kinetic experiments were performed spectrophotometrically<sup>29–34</sup> with Cu(II) complex and 2-AP in MeOH at 25°C for aminophenol oxidation activity. 0.04 mL of the complex solution, with a constant concentration of 1×10<sup>-3</sup> M, was added to 2 mL of 2-AP of a particular concentration (varying its concentration from 1×10<sup>-3</sup> M to 1×10<sup>-2</sup> M) to achieve the ultimate concentration of the complex as 1×10<sup>-3</sup> M. The conversion of 2-AP to 2-amino-phenoxazine-3-one (2-APX) was monitored with time at a wavelength of 430 nm (time scan)<sup>33,34</sup> in MeOH. The nature of dependence of rate on the concentration of substrate and kinetic parameter were determined through kinetic analyses. The kinetic analyses were performed in triplicate.

## Conclusion

This research work addresses the synthesis, crystal structure, supramolecular architectures and oxidative coupling of 2-AP of a copper(II)-Schiff base complex, [Cu(L)](H<sub>2</sub>O). Crystal structure analysis indicates that Cu(II) centre in complex exists in square planar geometry. Aqua molecule in crystal lattice plays significant role to form a dimeric unit of Cu(II) complex. Noteworthy π...π interactions are strongly operative among the centroids of Schiff base of Cu(II) complex leading to a zigzag 1D chain in crystalline phase. Hirshfeld surface analysis ensures the correspondence of active participation of intermolecular O-H...O, C-H...O H bonding as well as π...π interactions. This Cu(II) complex has been evaluated as a bio-inspired catalyst for the oxidative cyclisation of 2-AP with high turnover number, 5.89×10<sup>2</sup> h<sup>-1</sup>. Electrospray ionization mass spectrometry of



Cu(II) complex in presence of 2-AP suggests that the course of catalytic oxidative coupling of 2-AP proceeds through enzyme-substrate adduct. The crystal structure and structural aspects of this Cu(II) complex was previously reported perhaps we are able to produce the same Cu(II)-Schiff base complex using ethanol as a green solvent and explored its catalytic activity towards oxidative coupling of 2-AP with high catalytic efficiency in methanolic medium. This copper(II)-Schiff base complex may be useful as a metallo-ligand to develop multinuclear Cu(II) complex.

### Acknowledgement

BB thanks SERB, India for financial support under the Teachers Associateship for Research Excellence (TAR/000473/2018).

### Supplementary data

CCDC 1981345 contains the supplementary crystallographic data for **1**. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html> or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk). Experimental information such as molecular packing, fingerprint plot, IR and UV-Vis spectra, rate vs [substrate] plot, ESI mass spectrum, bond distance, bond angle and H-bonded interactions as well as  $\pi \cdots \pi$  interaction parameter are given here.

### References

- (a) W. Kaim and B. Schwederski, "Bioanorganische Chemie, Teubner, Stuttgart, Bioinorganic Catalysis", ed. J. Reedijk, Marcel Dekker, New York; (b) E. I. Solomon, U. Sundaram and T. E. Machonkin, *Chem. Rev.*, 1996, **96**, 2563.
- A. A. Amer, H. Ilikti, C. Beyens, J. Lyskawa and U. Maschke, *Eur. Polym. J.*, 2019, **112**, 569.
- G. Ahumada, J. Oyarce, T. Roisnel, S. Kahlal, M. A. del Valle, D. Carrillo, J. Y. Saillard, J. R. Hamon and C. Manzur, *New J. Chem.*, 2018, **42**, 19294.
- Y. Guo, X. Hu, X. Zhang, X. Pu and Y. Wang, *RSC Adv.*, 2019, **9**, 41737.
- V. Chhabra, B. K. Kundu, R. Ranjan, Pragti, S. M. Mobin and S. Mukhopadhyay, *Inorg. Chim. Acta*, 2020, **502**, 11938.
- K. A. Magnus, H. Ton-That and J. E. Carpenter, *Chem. Rev.*, 1994, **94**, 727.
- A. Sanchez-Ferrer, J. N. Rodriguez-Lopez, F. Garcia-Canovas and F. Garcia-Carmona, *Biochim. Biophys. Acta*, 1995, **1**, 1247.
- C. Gerdemann, C. Eicken and B. Krebs, *Acc. Chem. Res.*, 2002, **35**, 183.
- F. Fusetti, K. H. Schröter, R. A. Steiner, P. I. van Noort, T. Pijning, H. J. Rozeboom, K. H. Kalk, M. R. Egmond and B. W. Dijkstra, *Structure*, 2002, **10**, 259.
- R. A. Steiner, I. M. Kooter and B. W. Dijkstra, *Biochemistry*, 2002, **41**, 7955.
- I. M. Kooter, R. A. Steiner, B. W. Dijkstra, P. I. van Noort, M. R. Egmond and M. Huber, *Eur. J. Biochem.*, 2002, **269**, 2971.
- J. W. Whittaker, *Chem. Rev.*, 2003, **103**, 2347.
- M. Halcrow, S. Phillips and P. Knowles, in: "Subcellular Biochemistry, 35, Enzyme-Catalyzed Electron and Radical Transfer", eds. A. Holzenburg and N. S. Scrutton, Plenum, New York, 2000, 183.
- M. M. Whittaker, P. J. Kersten, N. Nakamura, J. Sanders-Loehr, E. S. Schweizer and J. W. Whittaker, *J. Biol. Chem.*, 1996, **271**, 681.
- M. M. Whittaker, P. J. Kersten, D. Cullen and J. W. Whittaker, *J. Biol. Chem.*, 1999, **274**, 36226.
- H.-H. T. Nguyen, K. H. Nakagawa, B. Hedman, S. J. Eliot, M. E. Lidstrom, K. O. Hodgson and S. I. Chan, *J. Am. Chem. Soc.*, 1996, **118**, 12766.
- S. J. Elliott, D. W. Randall, R. D. Britt and S. I. Chan, *J. Am. Chem. Soc.*, 1998, **120**, 3247.
- R. L. Lieberman, D. B. Shrestha, P. E. Doan, B. M. Hoffman, T. L. Stemmler and A. C. Rosenzweig, *Proc. Natl. Acad. Sci.*, 2003, **100**, 3820.
- E. Katz, "Biosynthesis of secondary metabolites: roles of trace metals Antibiotics II", eds. D. Gottlieb and P. D. Shaw, Springer, New York, 1967, p. 276.
- (a) U. Hollstein, *Chem. Rev.*, 1974, **74**, 625; (b) L. I. Simandi, S. Nemeth and N. Rumlis, *J. Mol. Catal.*, 1987, **42**, 357.
- (a) A. Butenandt, *Angew. Chem.*, 1957, **69**, 16; (b) T. M. Simándi, L. I. Simándi, M. Gyór, A. Rockenbauer and A. Gömöry, *Dalton Trans.*, 2004, 1056.
- (a) G. W. K. Cavill, P. S. Clezy, J. R. Tetaz and R. L. Werner, *Tetrahedron.*, 1959, **5**, 275; (b) J. Kaizer, R. Csonka and G. Speier, *J. Mol. Catal. A: Chem.*, 2002, **180**, 91.
- (a) S. S. Massoud, C. C. Ledet, T. Junk, S. Bosch, P. Comba, R. Herchel, J. Hošek, Z. Trávníček, R. C. Fischer and F. A. Mautner, *Dalton Trans.*, 2016, **45**, 12933; (b) S. S. Massoud, A. A. Gallo, M. J. Dartez, J. G. Gautreaux, R. Vicente, J. H. Albering and F. A. Mautner, *Inorg. Chem. Commun.*, 2014, **43**, 35; (c) S. S. Massoud, T. Junk and F. A. Mautner, *RSC Adv.*, 2015, **5**, 87139.
- (a) S. Cao, R. Cheng, D. Wang, Y. Zhao, R. Tang, X. Yang and J. Chen, *J. Inorg. Biochem.*, 2019, **192**, 126; (b) P. Kar, A. Franconetti, A. Frontera and A. Ghosh, *Cryst. Eng. Comm.*, 2019, **21**, 6886; (c) A. Shirvan, H. Golchoubian and E. Bouwman, *J. Mol. Struct.*, 2019, **1195**, 769; (d) A. Hussain, M. F. AlAjmi, M. T. Rehman, S. Amir, F. M. Husain, A. Alsalmeh, M. A. Siddiqui, A. A. AlKhedhairi and

- R. A. Khan, *Sci. Rep.*, 2019, **9**, 5237; (e) Y.-X. Sun, Y.-Q. Pan, X. Xu and Y. Zhang, *Crystals*, 2019, **9**, 607.
25. A. F. Marinovich, R. S. O'Mahony, J. M. Waters and T. N. M. Waters, *Croat. Chem. Acta*, 1999, **72**, 685.
  26. S. Das, A. Sahu, M. Joshi, S. Paul, M. Shit, A. R. Choudhury and B. Biswas, *ChemistrySelect*, 2018, **3**, 10774.
  27. P. K. Mudi, N. Bandopadhyay, M. Joshi, M. Shit, S. Paul, A. R. Choudhury and B. Biswas, *Inorg. Chim. Acta*, 2020, **505**, 119468.
  28. W. J. Geary, *Coord. Chem. Rev.*, 1971, **7**, 81.
  29. "Biomimetic oxidations catalyzed by transition metal complexes", in: B. Meunier (ed.), 'Biomimetic Oxidations Catalyzed by Transition Metal Complexes', Imperial College Press, London.
  30. (a) U. Hollstein, *Chem. Rev.*, 1974, **74**, 625; (b) L. I. Simandi, S. Nemeth and N. Rumlis, *J. Mol. Catal.*, 1987, **42**, 357.
  31. (a) A. Butenandt, *Angew. Chem.*, 1957, **69**, 16; (b) T. M. Simandi, L. I. Simandi, M. Gyor, A. Rockenbauer and A. Gomory, *Dalton Trans.*, 2004, **7**, 1056.
  32. (a) G. W. K. Cavill, P. S. Clezy, J. R. Tetaz and R. L. Werner, *Tetrahedron*, 1959, **5**, 275; (b) J. Kaizer, R. Csonka and G. Speier, *J. Mol. Catal. A: Chem.*, 2002, **180**, 91.
  33. B. Chowdhury, B. Bhowmik, A. Sahu, M. Joshi, S. Paul, A. R. Choudhury and B. Biswas, *J. Chem. Sci.*, 2018, **130**, 161.
  34. M. Garai, A. Das, M. Joshi, S. Paul, M. Shit, A. R. Choudhury and B. Biswas, *Polyhedron*, 2018, **156**, 223.
  35. C. Mukherjee, T. Weyhermuller, E. Bothe, E. Rentschler and P. Chaudhury, *Inorg. Chem.*, 2007, **46**, 9895.
  36. C. E. Barry, P. G. Nayar and T. G. Begley, *Biochemistry*, 1989, **28**, 6323.
  37. S. Sagar, S. Sengupta, A. J. Mota, S. K. Chattopadhyay, A. E. Ferao, E. Riviere, W. Lewis and S. Naskar, *Dalton Trans.*, 2017, **46**, 1249.
  38. M. Mitra, T. Kundu, G. Kaur, G. Sharma, A. R. Choudhury, Y. Singh and R. Ghosh, *RSC Adv.*, 2016, **6**, 58831.
  39. M. Garai, D. Dey, H. R. Yadav, A. R. Choudhury, M. Maji and B. Biswas, *ChemistrySelect*, 2017, **2**, 11040.
  40. T. Dutta, S. Mirdya, P. Giri and S. Chattopadhyay, *Polyhedron*, 2020, **175**, 114164.
  41. (a) T. Khan and A. Datta, *J. Phys. Chem. C.*, 2017, **121**, 2410; (b) B. Chowdhury, M. Karar, S. Paul, M. Joshi, A. R. Choudhury and B. Biswas, *Sens. Actuators, B.*, 2018, **276**, 560.
  42. CrystalClear 2.0; Rigaku Corporation, Tokyo, Japan.
  43. G. M. Sheldrick, *Acta Cryst. A.*, 2008, **64**, 112.
  44. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Cryst.*, 2009, **42**, 339.
  45. (a) M. J. Turner, J. J. McKinnon, S. K. Wolff, D. J. Grimwood, P. R. Spackman, Jayatilaka D and M. A. Spackman, (2017) Crystal Explorer, University of Western Australia, <http://hirshfeldsurface.net/17>; (b) M. A. Spackman and D. Jayatilaka, *Cryst. Eng. Com.*, **11**, 2009, 19; (c) S. K. Seth, V. S. Lee, J. Yana, S. M. Zain, A. C. Cunha, V. F. Ferreira, A. K. Jordao, M. C. B. V. de Souza, S. M. S. V. Wardell, J. L. Wardell and E. R.T. Tiekink, *Cryst. Eng. Comm.*, 2015, **17**, 2255; (d) M. N. Ahamad, M. Kumar, A. Ansari, I. Mantasha, M. Ahmad and M. Shahid, *New. J. Chem.*, 2019, **43**, 14074.
  46. (a) M. A. Spackman and D. Jayatilaka, *Cryst. Eng. Comm.*, 2009, **11**, 19; (b) M. A. Spackman and J. J. McKinnon, *Cryst. Eng. Comm.*, 2002, **4**, 378; (c) H. Yamatera, *Acta Chem. Scand. A.*, 1979, **33**, 107.