

# Synthesis, Spectroscopic Studies And X-Ray Structure Determination Of A Tetranuclear Copper Complex Derived From The Schiff Base Ligand *N,N'*-Bis(Salicylidene)Diaminobenzene

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## Abstract:

The reactions of the Schiff base *H*<sub>2</sub>salophen (*H*<sub>2</sub>salophen = *N,N'*-Bis(salicylidene)diaminobenzene), with Chloride copper (II) salt afforded the mononuclear complexes formulated respectively as [Cu(L)]<sub>4</sub>·16H<sub>2</sub>O (**1**). The compound has been studied and characterized by elemental analysis, IR and UV-Vis spectroscopies, molar conductivity, and room temperature magnetic measurements. The structure of the complex has been resolved by X-ray crystallography technique. The complex (**1**) crystallises in the monoclinic space group *P*21/*c* with the following unit cell parameters *a* = 11.7571(2) Å, *b* = 16.8082(2) Å, *c* = 36.5351(5) Å, β = 94.9540(10)°, *V* = 7192.94(18) Å<sup>3</sup>, *Z* = 16, *Z'* = 4, *R*<sub>1</sub> = 0.0493 and *wR*<sub>2</sub> = 0.0568. In the complex the ligand acts in tetradentate fashion, and the coordination environment of the copper atom can be described as distorted square planar geometry. Numerous hydrogen bonds stabilise the structure in a three-dimensional network.

**Keywords:** Schiff base; 1,2-diaminobenzene; 2-hydroxy benzaldehyde; X-ray; Copper (II)

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## I. Introduction

The coordination chemistry of transition metal complexes has been the subject of much work since the early 2000s. A good part of these studies have focused on the role of the central metal in the activity of the complexes [1–4]. The authors were interested in the synthesis of complexes aimed at understanding the roles of the metal in metallo-enzymes [5–7], in catalysis [8,9], in the treatment of certain diseases such as cancer [10,11], tuberculosis [12,13] and bacterial infections [14–16]. Copper Schiff base complexes are of particular interest and are considered good models in the study of metal center reactivity in metalloenzymes [17,18]. Typical [Cu<sup>II</sup>(salen)] complexes (salen=*N,N'*-bis(salicylideneiminato)ethylene) are widely studied and several physical properties are attributed to them. In the field of optical [19,20] and of magnetism [21,22], mention may be made of the salen-type complexes. Symmetric and dissymmetric salen Schiff base ligand are reported [23,24]. Their complexes are synthesized using direct method or template method [25–27].

Herein, based on the diamine precursor *H*<sub>2</sub>salophen (*H*<sub>2</sub>salophen = *N,N'*-Bis (salicylidene) diaminobenzene), we report the synthesis of the following complex [ Cu<sup>II</sup> (salophen) ]<sub>4</sub>·16H<sub>2</sub>O in a methanol solution and its structural characterization.

## II. Experimental Section

### Starting materials and Instrumentations

All chemicals and solvents were of analytical reagent grade and were used directly without further purification. Elemental analyses of C, H and N were recorded on a VxRio EL Instrument. Infrared spectra were obtained on a FTIR Spectrum Two of Perkin Elmer spectrometer in the 4000-400 cm<sup>-1</sup> region. The UV-Visible spectra were recorded on a Perkin Elmer Lambda UV-Vis spectrophotometer. The molar conductance of 1×10<sup>-3</sup> M in DMF solutions of the metal complexes was measured at 25 °C using a WTW LF-330 conductivity meter with a WTW conductivity cell. Room temperature magnetic susceptibilities of the powdered samples were measured using a Johnson Matthey scientific magnetic susceptibility balance (Calibrant: Hg[Co(SCN)<sub>4</sub>]).

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### Synthesis of the ligand *N,N'*-Bis(salicylidene)diaminobenzene (**H<sub>2</sub>salophen**) **H<sub>2</sub>L**

The ligand is synthesized according to the procedure reported in literature with slight modification [28]. 1,2-diaminobenzene (1.08 g, 10 mmol) was introduced into a 100 mL flask containing 20 mL of methanol. To the resulting suspension was added a methanolic solution containing 2-hydroxy benzaldehyde (2.42 g, 20 mmol) and two drops of glacial acetic acid. The mixture was stirred under reflux for 2 h. The yielded orange precipitate was recovered by filtration. The solid was washed successively with cold ethanol (2 x 10 mL) and diethyl ether (2 x 10 mL) before being dried under P<sub>2</sub>O<sub>5</sub>. M.p. 163°C, yield 89.7 %. Analysis calculated for [C<sub>20</sub>H<sub>16</sub>N<sub>2</sub>O<sub>2</sub>] C, 75.93; H, 4.83; N, 8.86. Found: 75.91; H, 4.80; N, 8.88. IR (cm<sup>-1</sup>): 3254, 1610, 1597, 1558, 1480, 1361, 1275, 1190, 909, 787, 639. <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, d(ppm)): 6.97–7.66 (m, 12H, H<sub>Ph</sub>); 8.12 (s, 1H, H—C=N); 8.94 (s, 2H, H—C=N); 12.93 (s, 2H, —OH). <sup>13</sup>C NMR (DMSO-d<sub>6</sub>, d(ppm)): 164 (C=N); 160 (C<sub>ipso</sub>—OH); 142.25 (C<sub>Ar</sub>); 133.40 (C<sub>Ar</sub>); 132.42 (C<sub>Ar</sub>); 127.77 (C<sub>Ar</sub>); 119.73 (C<sub>Ar</sub>); 119.47 (C<sub>Ar</sub>); 119.05 (C<sub>Ar</sub>); 116.64 (C<sub>Ar</sub>).

### Synthesis of the complex (**1**)

The title complex was prepared by mixing a solution of H<sub>2</sub>L (316 mg, 1 mmol) in 10 mL of methanol and a methanolic solution of CuCl<sub>2</sub>·2H<sub>2</sub>O (168 mg, 1.25 mmol). A green solution was obtained after refluxing for 1 h. The solution was filtered, and the filtrate left for slow evaporation. After two weeks, green crystals suitable for X-ray diffraction were collected, yield 70 %. Analysis calculated for [C<sub>20</sub>H<sub>18</sub>CuN<sub>2</sub>O<sub>4</sub>] C, 58.03; H, 4.38; N, 6.77. Found: C, 58.00; H, 4.348; N, 6.75. Λ (S cm<sup>2</sup> mol<sup>-1</sup>): 167. IR (ν, cm<sup>-1</sup>): 1607, 1581, 1532, 1463, 1444, 1313, 1192, 1154, 923, 750. UV-vis (Solution, DMF, λ (nm)): 277, 309, 426, 589. μ<sub>eff</sub> (μ<sub>B</sub>) = 2.93.

### Crystal structure determination

Crystals suitable for single-crystal X-ray diffraction, of the reported compound (**1**), were grown by slow evaporation of MeOH solution of the complex. Details of the crystal structure solution and refinement are given in Table 1. Diffraction data were collected using a Rigaku FRE+ equipped with Varimax confocal mirrors and UG2 Universal goniometer with graphite monochromatized CuKα radiation (λ = 1.54178 Å). All data were corrected for Lorentz and polarization effects. Complex scattering factors were taken from the program package SHELXTL [29]. The structures were solved by direct methods which revealed the position of all non-hydrogen atoms. All the structures were refined on *F*<sup>2</sup> by a full-matrix least-squares procedure using anisotropic displacement parameters for all non-hydrogen atoms [30]. H atoms (NH, OH, CH and CH<sub>3</sub> groups) were geometrically optimized and refined as riding model by AFIX instructions. Molecular graphics were generated using ORTEP [31].

**Table-1. Crystallographic data and refinement parameter for the Mn(II) complex.**

Chemical formula	C <sub>20</sub> H <sub>18</sub> CuN <sub>2</sub> O <sub>4</sub>
Mr	413.90
Crystal system	Monoclinic
Space group	P21/c
Temperature (K)	100
<i>a</i> (Å)	11.7571 (2)
<i>b</i> (Å)	16.8082 (2)
<i>c</i> (Å)	36.5351 (5)
$\beta$ (°)	94.954 (1)
<i>V</i> (Å <sup>3</sup> )	7192.94 (18)
<i>Z</i>	16
$\rho_{\text{calc}}$ (g/cm <sup>3</sup> )	1.529
$\mu$ (mm <sup>-1</sup> )	1.967
F(000)	3088
Crystal size (mm <sup>3</sup> )	0.1 × 0.04 × 0.03
CuK $\alpha$ (Å)	1.54178
2 $\theta$ range for data collection (°)	2.428-74.486
<i>h k l</i> ranges	-14 ≤ <i>h</i> ≤ 14 ; -20 ≤ <i>k</i> ≤ 21 ; -44 ≤ <i>l</i> ≤ 45
<i>T</i> <sub>min</sub> , <i>T</i> <sub>max</sub>	0.857, 0.950
No. of measured reflections	172351
No. of independent reflections	14664
No. of observed [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )] reflections	12330
<i>R</i> <sub>int</sub>	0.035
<i>R</i> [ <i>F</i> <sup>2</sup> > 2 $\sigma$ ( <i>F</i> <sup>2</sup> )], <i>wR</i> ( <i>F</i> <sup>2</sup> )	0.049, 0.1364
Final <i>R</i> indexes [all data]	0.0568, 0.1429
GOF	1.039
Parameters / restraints	901 / 0
$\Delta\rho_{\text{max}}$ , $\Delta\rho_{\text{min}}$ (e Å <sup>-3</sup> )	1.09, -1.31

### III. Results and Discussion

#### General study

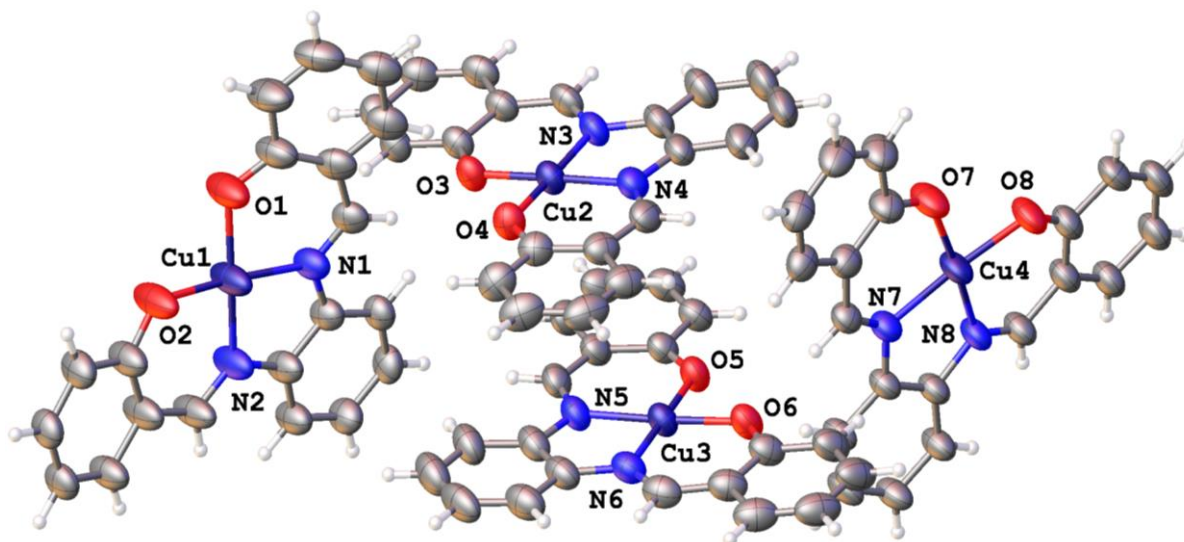
The IR spectrum of the ligand H<sub>2</sub>L shows a band of medium intensity at *ca.* 1610 cm<sup>-1</sup> which is attributed to the  $\nu_{\text{C=N}}$  absorption. The absence of the bands due to the  $\nu_{\text{C=O}}$  and  $\nu_{\text{N-H}}$  vibrations of the amine group combined to the apparition of the  $\nu_{\text{C=N}}$  band are indicative of the success of the condensation reaction. The band which appears at 1190 cm<sup>-1</sup> is assigned to the  $\nu_{\text{O-H}}$  vibration of the phenolic group. The band pointed at 3254 cm<sup>-1</sup> is attributed to the  $\nu_{\text{O-H}}$ . The bands due to  $\nu_{\text{C}_{\text{Ar}}=\text{C}_{\text{Ar}}}$  vibrations are pointed in the range 1479–1600 cm<sup>-1</sup>. The condensation reaction is confirmed by the NMR spectra analyses. The signal pointed at 8.12 ppm in the <sup>1</sup>H NMR spectrum and the signal at 164 ppm in the <sup>13</sup>C spectrum are, respectively, due the proton atom H—C=N— and the carbon atom H—C=N— of the azomethine group formed after condensation. The signal at 12.93 ppm is attributed to the phenolic proton. The signals that appear in the 6.97-7.66 ppm region are due to the protons of the aromatic ring. The carbon NMR spectrum shows characteristic signals from the carbon atoms of C<sub>ipso</sub>—OH carbon atoms

at 160 ppm.

Upon coordination to the copper(II) ion, the band due to  $\nu_{C=N}$  was slightly shifted to low frequencies at  $1607\text{ cm}^{-1}$ . The complex formed is essentially neutral, with molar conductivity value of  $16.3\text{ S cm}^2\text{ mol}^{-1}$  [32]. The electronic spectrum of the complex (1) recorded with millimolar DMF solution reveals, an absorption band centered at 426 nm attributed to the ligand  $\rightarrow$  metal charge transfer. Two other absorption bands due to  $\pi\rightarrow\pi^*$  and  $n\rightarrow\pi^*$  transitions of the ligand are pointed, respectively, at 277 nm and 309 nm. The absorption band pointed at 589 nm is attributed to the  $d\rightarrow d$  transition ( ${}^2B_{1g}\rightarrow{}^2A_{1g}$ ) of a Cu(II) ion in square planar geometry [33]. The value of the magnetic moment at room temperature of the complex of 2.93 B.M. is consistent with the presence of more than one Cu(II) ion.

### Structure description of the complex

Complex **1** crystallizes in the monoclinic  $P2_1/c$  space group. Selected bond length and angles are listed in Table 2. The ORTEP view is plotted in Figure 1. The asymmetric unit consists of four crystallographically independent Cu centers, with square planar geometries. The geometry around the Cu atoms, which are tetracoordinate, is determined by the distortion index or tetragonality parameter [34]  $\tau_4 = (360^\circ - \alpha - \beta)/141^\circ$  where  $\alpha$  and  $\beta$  are the two largest angles around the latter. The expected values for  $\tau_4$  are zero for a perfect square plane and one for a perfect tetrahedron. The value of  $\tau_4$ , which is 0.100 (Cu1), 0.037 (Cu2), 0.036 (Cu3) and 0.075 (Cu4) suggests a distorted square planar geometry [35]. Each Cu ion is coordinated to the two azomethine nitrogen atoms and to the two phenoxo oxygen atoms. The bond lengths in the square plane around Cu are nearly equal in both cases. The O—Cu and O—N are respectively in the range [1.891(2)—1.917(2) Å] and [1.936(2)—1.954(2) Å]. These values are comparable to those reported for a similar complex [36]. The O—Cu—O and N—Cu—N angles values are, respectively, in the range  $83.71(10)$ — $84.17(11)^\circ$  and  $86.51(8)$ — $89.98(10)^\circ$ . The O—Cu—N are the largest *cisoid* angles values around the Cu atoms [ $92.90(10)$ — $95.10(9)^\circ$ ]. Each ligand forms, upon coordination, two six-membered rings of type CuOCCCN and one five-membered ring CuNCCN. The *transoid* angles values O—Cu—N are in the range [ $171.34(15)$ — $178.76(9)^\circ$ ]. As can be seen in Figure 1, the packing of the components leads to voids that are large enough to host solvent molecules of water or methanol.



**Figure 1.** The asymmetric unit of **1**, thermal ellipsoids drawn at the 50% probability level, the minor positions of the disordered atoms are not shown.

There are also highly disordered solvent molecules (presumably water and/or methanol) in the crystal structure. As it was impossible to refine these molecules was not possible, the content of the voids was taken into account using reverse Fourier transform methods [SQUEEZE procedure in PLATON] [37]. The given chemical formula and other crystal data do not consider the unknown solvent molecule(s). The solvent accessible volume in the structure of the title compound as calculated by PLATON is  $1208\text{ Å}^3$  (16.8 %) and the total calculated electron count was 324 (Figure 2).

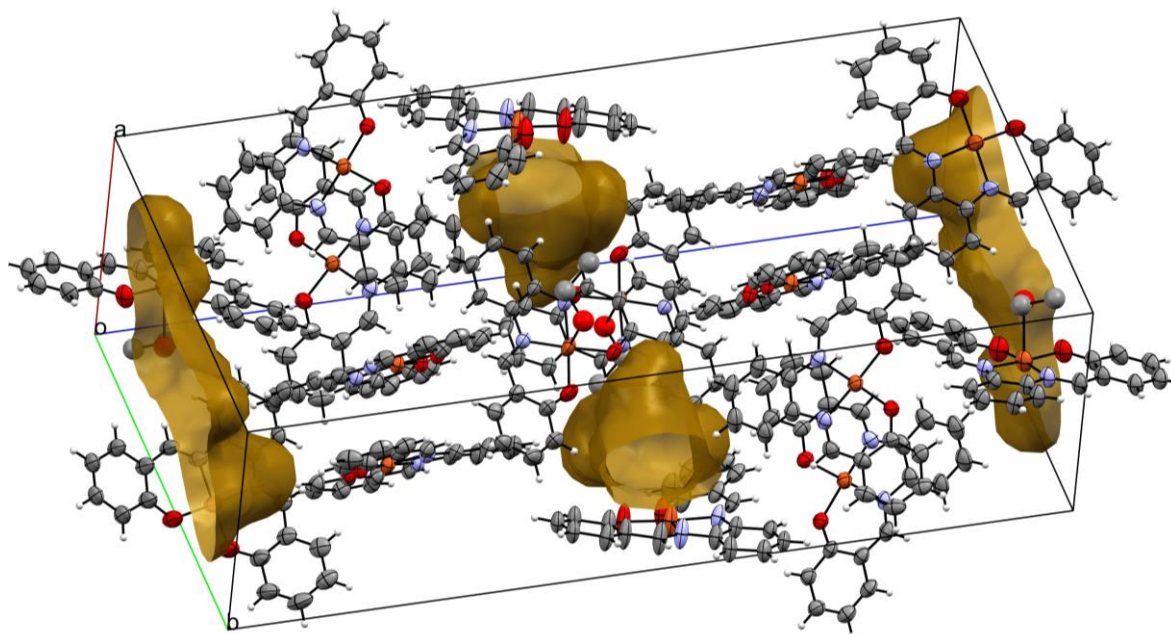


Figure 2: The calculated solvent voids (encapsulated within the gold surfaces) within 1 thermal ellipsoid drawn at the 50% probability level.

Table 2. Selected bond length [Å] and angles (°) for the Cu(II) complex.

Cu1—N1	1.948 (2)	O1—Cu1—N1	92.90 (10)
Cu1—N2	1.947 (3)	O1—Cu1—N2	171.34 (15)
Cu1—O1	1.917 (2)	O2—Cu1—N1	174.56 (14)
Cu1—O2	1.909 (2)	O2—Cu1—N2	94.07 (10)
Cu2—N3	1.954 (2)	O2—Cu1—O1	89.98 (10)
Cu2—N4	1.936 (2)	O3—Cu2—N3	94.82 (9)
Cu2—O3	1.893 (2)	O3—Cu2—N4	177.89 (9)
Cu2—O4	1.903 (2)	O3—Cu2—O4	86.51 (8)
Cu3—N5	1.949 (2)	O4—Cu2—N3	176.86 (9)
Cu3—N6	1.938 (2)	O5—Cu3—N5	95.02 (9)
Cu3—O5	1.891 (2)	O5—Cu3—N6	178.76 (9)
Cu3—O6	1.901(2)	O6—Cu3—N5	176.16 (9)
Cu4—N7	1.953 (2)	O6—Cu3—N6	95.10 (9)
Cu4—N8	1.937 (2)	O7—Cu4—N7	93.84 (9)
Cu4—O7	1.893 (2)	O7—Cu4—N8	173.90 (12)
Cu4—O8	1.913 (2)	O8—Cu4—N7	175.51 (11)

#### IV. Conclusion

Chelate complex of copper (II) with *N,N'*-Bis(salicylidene)diaminobenzene have been synthesized and characterized by FTIR and UV-visible spectroscopies and magnetic and conductance measurements. The structure is confirmed by X-ray diffraction technique. Each Cu(II) ion is coordinated by one ligand molecule which acts in tetradentate fashion through two azomethine nitrogen atoms and two phenoxo oxygen atoms. The coordination polyhedron around each Cu(II) center is best described as a distorted square planar geometry. The highly disordered solvent molecules in the crystal structure were squeezed.

## V. Supplementary Materials

CCDC-2251815 contains the supplementary crystallographic data for this paper. 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; e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk) (or [www:ccdc.cam.ac.uk](http://www.ccdc.cam.ac.uk)).

## References

- [1] Kanso, H., Clarke, R. M., Kochem, A., Arora, H., Philouze, C., Jarjayes, O., Storr, T., Thomas, F. (2020). Effect of Distortions on the Geometric and Electronic Structures of One-Electron Oxidized Vanadium(IV), Copper(II), and Cobalt(II)/(III) Salen Complexes. *Inorganic Chemistry*, 59(7), 5133–5148. <https://doi.org/10.1021/acs.inorgchem.0c00381>
- [2] Mazzoni, R., Roncaglia, F., Rigamonti, L. (2021). When the Metal Makes the Difference: Template Syntheses of Tridentate and Tetradentate Salen-Type Schiff Base Ligands and Related Complexes. *Crystals*, 11(5). <https://doi.org/10.3390/cryst11050483>
- [3] Colon, M. L., Qian, S. Y., Vanderveer, D., Bu, X. R. (2004). Chiral bimetallic complexes from chiral salen metal complexes and mercury (II) halides and acetates: the anionic groups interact with Cu(II) in apical position. *Inorganica Chimica Acta*, 357(1), 83–88. [https://doi.org/10.1016/S0020-1693\(03\)00426-2](https://doi.org/10.1016/S0020-1693(03)00426-2)
- [4] Li, X., Hu, Z.-F., Gan, L.-L., Deng, Y.-H., Dong, W.-K. (2023). Paradoxical fluorescein-naphthalene Salamo-Salen-Salamo Zn(II) complex as a H<sub>2</sub>PO<sub>4</sub><sup>-</sup>-targeted chemosensor and its application in water samples. *Journal of Molecular Structure*, 1278, 134968. <https://doi.org/10.1016/j.molstruc.2023.134968>
- [5] Wang, W., Wang, J., Li, S., Li, C., Tan, R., Yin, D. (2020). Iron(II)-folded single-chain nanoparticles: a metalloenzyme mimicking sustainable catalyst for highly enantioselective sulfa-Michael addition in water. *Green Chemistry*, 22(14), 4645–4655. <https://doi.org/10.1039/D0GC00949K>
- [6] Shahraki, S. (2022). Schiff base compounds as artificial metalloenzymes. *Colloids and Surfaces B: Biointerfaces*, 218, 112727. <https://doi.org/10.1016/j.colsurfb.2022.112727>
- [7] Mirts, E. N., Bhagi-Damodaran, A., Lu, Y. (2019). Understanding and Modulating Metalloenzymes with Unnatural Amino Acids, Non-Native Metal Ions, and Non-Native Metallocofactors. *Accounts of Chemical Research*, 52(4), 935–944. <https://doi.org/10.1021/acs.accounts.9b00011>
- [8] Provis-Evans, C. B., Lau, S., Krewald, V., Webster, R. L. (2020). Regioselective Alkyne Cyclotrimerization with an In Situ-Generated [Fe(II)H(salen)]-Bpin Catalyst. *ACS Catalysis*, 10(17), 10157–10168. <https://doi.org/10.1021/acscatal.0c03068>
- [9] Sharghi, H., Aboonajmi, J., Aberi, M. (2020). One-Pot Multicomponent Reaction of Catechols, Ammonium Acetate, and Aldehydes for the Synthesis of Benzoxazole Derivatives Using the Fe(III)–Salen Complex. *The Journal of Organic Chemistry*, 85(10), 6567–6577. <https://doi.org/10.1021/acs.joc.0c00560>
- [10] Mohan, N., Vidhya, C. V., Suni, V., Mohamed Ameer, J., Kasoju, N., Mohanan, P. V., Sreejith, S. S., Prathapachandra Kurup, M. R. (2022). Copper(II) salen-based complexes as potential anticancer agents. *New Journal of Chemistry*, 46(26), 12540–12550. <https://doi.org/10.1039/D2NJ02170F>
- [11] Kumar, S., Choudhary, M. (2022). Copper(II) Schiff base complex derived from salen ligand: structural investigation, Hirshfeld surface analysis, anticancer and anti-SARS-Co Journal of Biomolecular Structure and Dynamics. Retrieved from <https://www.tandfonline.com/doi/abs/10.1080/07391102.2022.2076155>
- [12] Sinha, A., Chaudhary, R., Reddy, D. S., Kongot, M., Kurjogi, M. M., Kumar, A. (2022). ON donor tethered copper (II) and vanadium (V) complexes as efficacious anti-TB and anti- fungal agents with spectroscopic approached HSA interactions. *Heliyon*, 8(8), e10125. <https://doi.org/10.1016/j.heliyon.2022.e10125>
- [13] Avcu Altıparmak, E., Erdemir, G., Özdemir, N., Kuruca, S. E., Bal-Demirci, T. (2020). Cu(II) salen and 1,2,4-triazole complexes from thiosemicarbazone: synthesis, physicochemical and structural properties and cytotoxic activities. *New Journal of Chemistry*, 44(14), 5333–5342. <https://doi.org/10.1039/C9NJ04455H>
- [14] Baecker, D., Sesli, Ö., Knabl, L., Huber, S., Orth-Höller, D., Gust, R. (2021). Investigating the antibacterial activity of salen/salophene metal complexes: Induction of ferroptosis as part of the mode of action. *European Journal of Medicinal Chemistry*, 209, 112907. <https://doi.org/10.1016/j.ejmech.2020.112907>
- [15] Gur'eva, Y. A., Zalevskaya, O. A., Shevchenko, O. G., Slepukhin, P. A., Makarov, V. A., Kuchin, A. V. (2022). Copper(II) complexes with terpene derivatives of ethylenediamine: synthesis, and antibacterial, antifungal and antioxidant activity. *RSC Advances*, 12(15), 8841–8851. <https://doi.org/10.1039/D2RA00223J>
- [16] Das, K., Goswami, S., Beyene, B. B., Yibeltal, A. W., Massera, C., Garrriba, E., Frontera, A., Cantürk, Z., Askun, T. Datta, A. (2019). Spectral, electrochemical and DFT studies of a trimetallic CuII Derivative: Antimycobacterial and cytotoxic activity. *Inorganica Chimica Acta*, 490, 155–162. <https://doi.org/10.1016/j.ica.2019.03.014>
- [17] Liu, X.-H., Yu, H.-Y., Huang, J.-Y., Su, J.-H., Xue, C., Zhou, X.-T., He, Y.-R., He, Q., Xu, D.-J., Xiong, C., Ji, H.-B. (2022). Biomimetic catalytic aerobic oxidation of C–sp(3)–H bonds under mild conditions using galactose oxidase model compound Cu<sup>II</sup>L. *Chemical Science*, 13(33), 9560–9568. <https://doi.org/10.1039/D2SC02606F>
- [18] Reed, C. J., Lam, Q. N., Mirts, E. N., Lu, Y. (2021). Molecular understanding of heteronuclear active sites in heme–copper oxidases, nitric oxide reductases, and sulfite reductases through biomimetic modelling. *Chemical Society Reviews*, 50(4), 2486–2539. <https://doi.org/10.1039/D0CS01297A>
- [19] Duarte, L. G. T. A., Coelho, F. L., Germino, J. C., Costa, G. G. da, Berbigier, J. F., Rodembusch, F. S., Atvars, T. D. Z. (2020). A selective proton transfer optical sensor for copper<sup>II</sup> based on chelation enhancement quenching effect (CHEQ). *Dyes and Pigments*, 181, 108566. <https://doi.org/10.1016/j.dyepig.2020.108566>
- [20] Rigamonti, L., Forni, A., Cariati, E., Malavasi, G., Pasini, A. (2019). Solid-State Nonlinear Optical Properties of Mononuclear Copper(II) Complexes with Chiral Tridentate and Tetradentate Schiff Base Ligands. *Materials*, 12(21). <https://doi.org/10.3390/ma12213595>
- [21] Schreck, C., Weihermüller, J., Thoma, P., Rosenfeldt, S., Drechsler, M., Förster, C., Heinze, K., Hörner, G. Weber, B. (2022). Solvent-Dependent Self-Assembly of an Amphiphilic Copper(II) Complex with Bulky Head Groups. *European Journal of Inorganic Chemistry*, 2022(27), e202200341. <https://doi.org/10.1002/ejic.202200341>
- [22] Sobel, S. G., Kimura, M. W., Laxdal, C. (2020). Investigating Periodic Trends in M-SALEN Complexes: An Open-Ended Lab Experience. In *Advances in Teaching Inorganic Chemistry Volume 2: Laboratory Enrichment and Faculty Community* (Vols. 1-0, Vol. 1371, pp. 1–12). American Chemical Society. <https://doi.org/10.1021/bk-2020-1371.ch001>

- [23] Ding, L., Liang, S., Zhang, J., Ding, C., Chen, Y., Lü, X. (2014). Cu<sup>2+</sup>-templated self-assembly of an asymmetric Salen–Cu(II) complex and its application in catalytic polymerization of methyl methacrylate (MMA). *Inorganic Chemistry Communications*, 44, 173–176. <https://doi.org/10.1016/j.inoche.2014.03.025>
- [24] Weberski, M. P., McLauchlan, C. C., Hamaker, C. G. (2006). Synthesis and X-ray structural characterization of M(3,5-tBu<sub>2</sub>-salophen) (M=Cu, VO). *Polyhedron*, 25(1), 119–123. <https://doi.org/10.1016/j.poly.2005.07.018>
- [25] Kaczmarek, M. T., Strzelec, J., Kubicki, M., Kováč, J., Jastrzab, R. (2021). Template condensation reactions of 5-methylsalicylaldehyde with 4,5-dimethyl-1,2-phenylenediamine in the presence of copper(II) and selected lanthanide(III) ions. *Polyhedron*, 203, 115236. <https://doi.org/10.1016/j.poly.2021.115236>
- [26] Middy, P., Saha, A., Chattopadhyay, S. (2023). A comprehensive overview on the synthesis, structures, and applications of mononuclear transition metal complexes with asymmetrically substituted ‘salen-type’ Schiff bases. *Inorganica Chimica Acta*, 545, 121246. <https://doi.org/10.1016/j.ica.2022.121246>
- [27] Lin, H., Wang, J.-G., Shi, H.-T., Chen, Q., Zhang, Q.-F. (2013). Chlorido[2,2’-[1,2-phenylenebis (nitrilomethanylylidene)] diphenolato-κ<sup>4</sup>O,N,N’,O’] manganese (III) methanol monosolvate. *Acta Crystallographica Section E*, 69(7), m404. <https://doi.org/10.1107/S1600536813016450>
- [28] Holm, R. H. (1960). Studies on Ni(II) Complexes. I. Spectra of Tricyclic Schiff Base Complexes of Ni(II) and Cu(II). *Journal of the American Chemical Society*, 82(21), 5632–5636. <https://doi.org/10.1021/ja01506a020>
- [29] Sheldrick, G. M. (2015). SHELXT – Integrated space-group and crystal-structure determination. *Acta Crystallographica Section A*, 71(1), 3–8. <https://doi.org/10.1107/S2053273314026370>
- [30] Sheldrick, G. M. (2015). Crystal structure refinement with SHELXL. *Acta Crystallographica Section C*, 71(1), 3–8. <https://doi.org/10.1107/S2053229614024218>
- [31] Farrugia, L. J. (2012). WinGX and ORTEP for Windows: an update. *Journal of Applied Crystallography*, 45(4), 849–854. <https://doi.org/10.1107/S0021889812029111>
- [32] Geary, W. J. (1971). The use of conductivity measurements in organic solvents for the characterisation of coordination compounds. *Coordination Chemistry Reviews*, 7(1), 81–122. [https://doi.org/10.1016/S0010-8545\(00\)80009-0](https://doi.org/10.1016/S0010-8545(00)80009-0)
- [33] Ünver, H., Hayvali, Z. (2010). Synthesis, spectroscopic studies, and structures of square-planar nickel(II) and copper(II) complexes derived from 2-(Z)-[furan-2-ylmethyl]imino]methyl-6-methoxyphenol. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 75(2), 782–788. <https://doi.org/10.1016/j.saa.2009.11.055>
- [34] Singh, Y. P., Patel, R. N., Singh, Y., Choquesillo-Lazarte, D., Butcher, R. J. (2017). Classical hydrogen bonding and stacking of chelate rings in new copper(ii) complexes. *Dalton Transactions*, 46(9), 2803–2820. <https://doi.org/10.1039/C6DT04661D>
- [35] Biswas, S., Ghosh, A. (2012). A novel 1D chain of azido bridged copper(II) with a salen-type di-Schiff base ligand. *Journal of Molecular Structure*, 1019, 32–36. <https://doi.org/10.1016/j.molstruc.2012.03.030>
- [36] Diouf, N., Thiam, I. E., Sylla-Gueye, R., Retailleau, P., Gaye, M. (2022). Syntheses, Characterization, and X-Ray Crystal Structure of a Co-Crystal Containing One Neutral Mononuclear Copper (II) Unit and One Cationic Dinuclear Copper (II) Unit Assembled with Schiff Base and Perchlorate Copper(II) Salt. *Earthline Journal of Chemical Sciences*, 8(1), 35–52. <https://doi.org/10.34198/ejcs.8122.3552>
- [37] Spek, A. L. (2015). PLATON SQUEEZE: a tool for the calculation of the disordered solvent contribution to the calculated structure factors. *Acta Crystallographica Section C*, 71(1), 9–18. <https://doi.org/10.1107/S2053229614024929>

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