

## Synthesis, Spectral Studies and Crystal Structure of a New Trinuclear Copper(II) Schiff Base Complex

Santarupa Thakurta\*

### Abstract

A new linear trinuclear complex  $[\text{Cu}_3\text{L}_2(\text{CCl}_3\text{COO})_2]$  (**1**) [ $\text{H}_2\text{L} = \text{N,N}'\text{-bis(2-hydroxyacetophenone)propylenediimine}$ ] has been synthesized and characterized by IR and UV/vis spectroscopic studies. The crystal structure of the complex, determined by X-ray single-crystal diffraction, consists of strictly linear trimer of copper atoms. The adjacent copper(II) centers are linked by double phenoxo bridges and a carboxylato bridge. The central copper atom adopts distorted octahedral geometry while each terminal copper atom has square-pyramidal geometry.

### Keywords:

Trinuclear;  
Copper(II);  
Schiff Base;  
Crystal Structure;  
Spectroscopy.

Copyright © 2018 International Journals of Multidisciplinary Research Academy. All rights reserved.

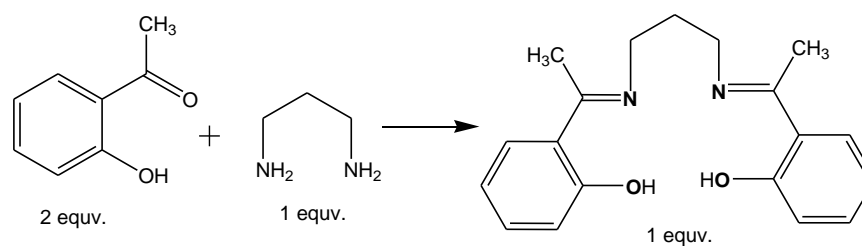
### Author correspondence:

Santarupa Thakurta,  
Department of Chemistry,  
Prabhu Jagatbandhu College, Howrah  
West Bengal, India  
Email: [sthakurtaju@yahoo.co.in](mailto:sthakurtaju@yahoo.co.in)

### 1. Introduction

The study of trinuclear copper(II) systems assumes a special position in coordination chemistry due to their novel structural and magnetic properties [1]-[5]. In addition, such complexes have gained attention as potential biomimic models after the discovery of tricopper active sites in several copper oxidase like laccase or ascorbate oxidase [6],[7]. The use of bis(salicylidene) ligands with polymethylene spacers of varying flexibility allowed us to regulate their electronic and steric demands which could effectively modulate structural versatility enlightening spin and valence change phenomena. Previously our research group reported the magneto-structural correlation of some phenoxo-bridged linear trinuclear copper(II) complexes [8],[9] of the symmetrical  $\text{N}_2\text{O}_2$  donor Schiff Base  $\text{H}_2\text{L}$ ,  $\text{N,N}'\text{-bis(2-hydroxyacetophenone)propylenediimine}$ , derived from 2:1 condensation of 2-hydroxyacetophenone and 1,3-diaminopropane (Scheme 1). In continuation of my research on linear trinuclear copper(II) complexes, a new complex  $[\text{Cu}_3\text{L}_2(\text{CCl}_3\text{COO})_2]$  (**1**) has been synthesized and this paper describes spectral characterization and structural features of this complex.

\* Department of Chemistry, Prabhu Jagatbandhu College, Howrah, West Bengal, India



Scheme 1.

## 2. Experimental Section

### 2.1. Materials and Methods

All the chemicals were purchased from Aldrich Chemical Co. and were used as received without further purification. All the solvents were of reagent grade. Copper(II) trichloroacetate was prepared by the treatment of basic copper(II) carbonate,  $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$  with 60% trichloroacetic acid followed by slow evaporation on a steam bath.

The Fourier transform infrared spectra were recorded on a Perkin Elmer RX I FT-IR spectrometer with a KBr disc in the range  $4000\text{--}200\text{ cm}^{-1}$ . The electronic spectra were recorded on a Perkin Elmer Lambda 40 UV/Vis spectrophotometer using HPLC grade acetonitrile in the range  $200\text{--}800\text{ nm}$ . Elemental analyses (C, H, N) were carried out using a Perkin Elmer 2400 II elemental analyser.

### 2.2. Synthesis of the Complex

The Schiff base ligand  $\text{H}_2\text{L}$  was prepared following the procedure described earlier [9]. The methanolic solution of 2 mmol (0.621 g)  $\text{H}_2\text{L}$  was added to a methanolic solution of  $\text{Cu}(\text{CCl}_3\text{COO})_2$  (1.165 g, 3 mmol). The mixture was refluxed for 45 minutes at  $65^\circ\text{C}$ . After 3 days block shaped single crystals were isolated from the filtrate. Anal. Calcd for  $\text{C}_{42}\text{H}_{40}\text{Cl}_6\text{Cu}_3\text{N}_4\text{O}_8$ : C, 44.54; H, 3.56; N, 4.95%. Found: C, 44.48; H, 3.50; N, 4.82%.

### 2.3. X-ray Structure Determination

The air stable single crystal of complex **1** ( $\text{C}_{42}\text{H}_{40}\text{Cl}_6\text{Cu}_3\text{N}_4\text{O}_8$ ,  $M = 1132.10$ ) has dimension of  $0.32 \times 0.25 \times 0.12\text{ mm}^3$  with triclinic crystal system and  $P-1$  space group:  $a = 10.6287(5)\text{ \AA}$ ,  $b = 10.9526(6)\text{ \AA}$ ,  $c = 19.3643(11)\text{ \AA}$ ,  $\alpha = 75.552(2)^\circ$ ,  $\beta = 87.424(2)^\circ$ ,  $\gamma = 81.380(2)^\circ$ ,  $V = 2158.2(2)\text{ \AA}^3$ ,  $Z = 2$ ,  $D_{\text{calc}} = 1.742\text{ g cm}^{-3}$ ,  $\mu = 1.895\text{ mm}^{-1}$ ,  $F(000) = 1146$ .

Intensity data were collected on single crystals at 100 K on a Bruker X8 Apex 2 CCD diffractometer equipped with a graphite monochromator and Mo- $K\alpha$  radiation ( $\lambda = 0.71073\text{ \AA}$ ). The structure was refined by full-matrix least-squares methods on  $F^2$  with SHELXTL program [10]. Multiscan absorption correction was applied using SADABS [11]. All non-hydrogen atoms were refined anisotropically.

CCDC 1823836 contains the supplementary crystallographic data for **1**. This can be obtained free of charge from the Cambridge Crystallographic Data Center via [http://www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

## 3. Results and Discussion

### 3.1. Crystal Structure

The perspective view of **1** with the atom labeling scheme is shown in Figure 1. The adjacent  $\text{Cu}^{\text{II}}$  ions in the linear trinuclear array of complex **1** are bridged by two  $\mu$ -phenolato oxygen atoms of the deprotonated Schiff base ligand  $\text{L}^{2-}$  and one bidentate

bridging  $\text{CCl}_3\text{COO}^-$  anion. Both the carboxylates bridge the terminal Cu2 and central Cu1 centers in a *syn-syn* fashion but are mutually *trans*- to each other owing to the centrosymmetric nature of the complex. Selected bond lengths and angles of **1** are summarized in Table 1. The coordination sphere of central Cu1 in complex **1** can be described as distorted octahedral since the equatorial Cu-O bond lengths are distinctly shorter than the axial Cu-O bond lengths. The equatorial plane of the central Cu1 is constructed by two bridging phenoxo oxygen atoms (O1A and its symmetry related counterpart) from two Schiff base ligands and two oxygen atoms (O3A and its symmetry related counterpart) from the two bridging carboxylates, while the apical positions of the octahedron are occupied by the other two bridging phenoxo oxygen atoms (O2A and its symmetry related counterpart). Since the central Cu1 atom is located on an inversion center, all the three *trans*- angles are  $180^\circ$ . Two pentacoordinated terminal copper atoms have an identical environment, owing to the crystallographic inversion symmetry. For a pentacoordinated metal center, the distortion of structure from trigonal bipyramidal (TBP) to square pyramidal (SP) can be evaluated by the Addison distortion index,  $\tau$ , defined as  $\tau = [|\theta - \Phi|/60]$ , where  $\theta$  and  $\Phi$  are the two largest coordination angles;  $\tau = 0$  for perfect SP and 1 for ideal TBP [12]. In complex **1** the calculated  $\tau$  value of 0.04 suggests an almost perfect square pyramidal geometry for the terminal copper atoms. The equatorial plane of each of the two equivalent terminal copper atoms is formed by the two imine nitrogen atoms and two phenolic oxygen atoms. The apical position is occupied by an oxygen atom from the bridging carboxylate group. Cu2 is displaced from the mean equatorial plane constructed by  $\text{N}_2\text{O}_2$  donor set of the Schiff base ligand by  $0.156(3)$  Å towards the axial oxygen O5A#.

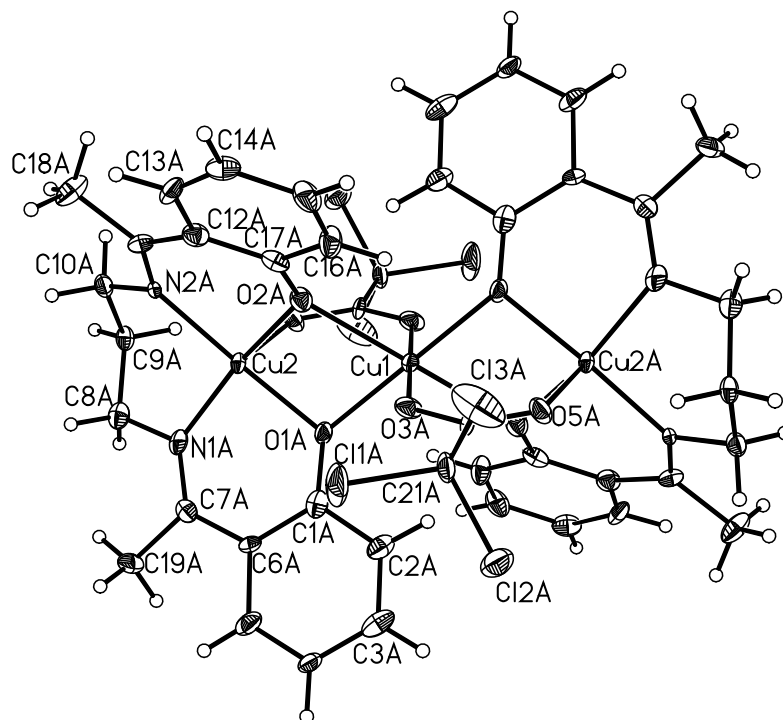


Figure 1. ORTEP view of **1** with atom labeling scheme. Ellipsoids are at the 50% probability level. (Symmetry code: #  $-x+1, -y+2, -z$ ).

The title complex  $[\text{Cu}_3\text{L}_2(\text{CCl}_3\text{COO})_2]$  (**1**) is isostructural with the complexes  $[\text{Cu}_3\text{L}_2(\text{CH}_3\text{COO})_2]$  and  $[\text{Cu}_3\text{L}_2(\text{CF}_3\text{COO})_2]$  which were reported earlier by our research group. In this series of complexes the versatility of the bridging carboxylates present are greatly enhanced due to different groups as substituents ( $\text{RCOO}^-$ ; R=  $\text{CH}_3$ ,  $\text{CF}_3$ ,  $\text{CCl}_3$ ).

This provides us a scope to analysis the effect of electron withdrawing group of the on the structures. With increasing electron withdrawing nature of the substituents i.e.,  $\text{CH}_3 < \text{CCl}_3 < \text{CF}_3$ , the geometry of terminal copper(II) centers tends to perfect square pyramidal (as shown in Table 2).

Table 1. Selected bond lengths (Å) and bond angles (°) for **1**

Bond Lengths (Å)		Bond Angles (°)	
Cu(1)-O(3A)	1.999(7)	O(3A)#-Cu(1)-O(1A)	91.2(3)
Cu(1)-O(1A)	2.066(7)	O(3A)-Cu(1)-O(1A)	88.8(3)
Cu(1)-O(2A)	2.261(7)	O(3A)-Cu(1)-O(2A)	88.9(3)
Cu(2)-O(2A)	1.934(7)	O(1A)-Cu(1)-O(2A)	73.8(3)
Cu(2)-O(1A)	1.984(7)	O(1A)#-Cu(1)-O(2A)	106.2(3)
Cu(2)-N(2A)	1.995(8)	O(2A)-Cu(2)-O(1A)	83.2(3)
Cu(2)-N(1A)	2.004(8)	O(2A)-Cu(2)-N(2A)	89.6(3)
Cu(2)-O(5A)#	2.273(7)	O(1A)-Cu(2)-N(2A)	170.1(3)
		O(2A)-Cu(2)-N(1A)	167.6(3)
		O(2A)-Cu(2)-O(5A)#	90.7(3)
		N(2A)-Cu(2)-O(5A)#	99.8(3)

Symmetry code: # -x+1,-y+2,-z

Table 2. Comparative analysis among three trinuclear complexes

	Cu (Terminal) – O (acetate) Bond length (Å)	$\tau$	Geometry of terminal copper(II) center
$[\text{Cu}_3\text{L}_2(\text{CH}_3\text{COO})_2]$	2.2305(18)	0.32	Distorted Square pyramidal
$[\text{Cu}_3\text{L}_2(\text{CCl}_3\text{COO})_2]$	<b>2.273(7)</b>	<b>0.04</b>	<b>Almost perfect Square pyramidal</b>
$[\text{Cu}_3\text{L}_2(\text{CF}_3\text{COO})_2]$	2.312(3)	0.01	Perfect Square pyramidal

### 3.2. IR Spectra

The solid state Fourier transform infrared spectrum of complex **1** is fully consistent with its single crystal structure (Figure 2). A strong sharp absorption band around  $1625 \text{ cm}^{-1}$  in the spectrum of the Schiff base ligand may be assigned for the imine stretching frequency. This band is shifted to the lower wave numbers upon complexation with the metal by  $35 \text{ cm}^{-1}$ , which can be attributed to the coordination of the nitrogen atom of the imine group to the metal ion [13]. Ligand coordination to metal center is substantiated by prominent bands appearing at nearly  $455$  and  $375 \text{ cm}^{-1}$  which can be attributed to  $\nu(\text{M}-\text{N})$ , and  $\nu(\text{M}-\text{O})$ , respectively. The asymmetric and symmetric stretching vibrations of trichloroacetate appear at  $1580 \text{ cm}^{-1}$  and  $1435 \text{ cm}^{-1}$  respectively. The separation value between  $\nu_{\text{asym}}(\text{COO}^-)$  and  $\nu_{\text{sym}}(\text{COO}^-)$ :  $\Delta\nu \sim 145 \text{ cm}^{-1}$ , which is smaller than  $164 \text{ cm}^{-1}$  observed in free trichloroacetate ion, is a clear indication of the bidentate *syn-syn* bridging mode of the carboxylate [14].

### 3.3. Electronic Spectrum

The electronic spectral data for complex **1** in HPLC grade acetonitrile solvent are in good agreement with its geometry. Complex **1** shows a broad band centered at  $650 \text{ nm}$  which is a typical *d-d* band for copper(II) complex [15]. The intense band at  $325-360 \text{ nm}$  region can be attributed to the charge transfer transition from the coordinated unsaturated ligand to the metal ion (LMCT) [16].

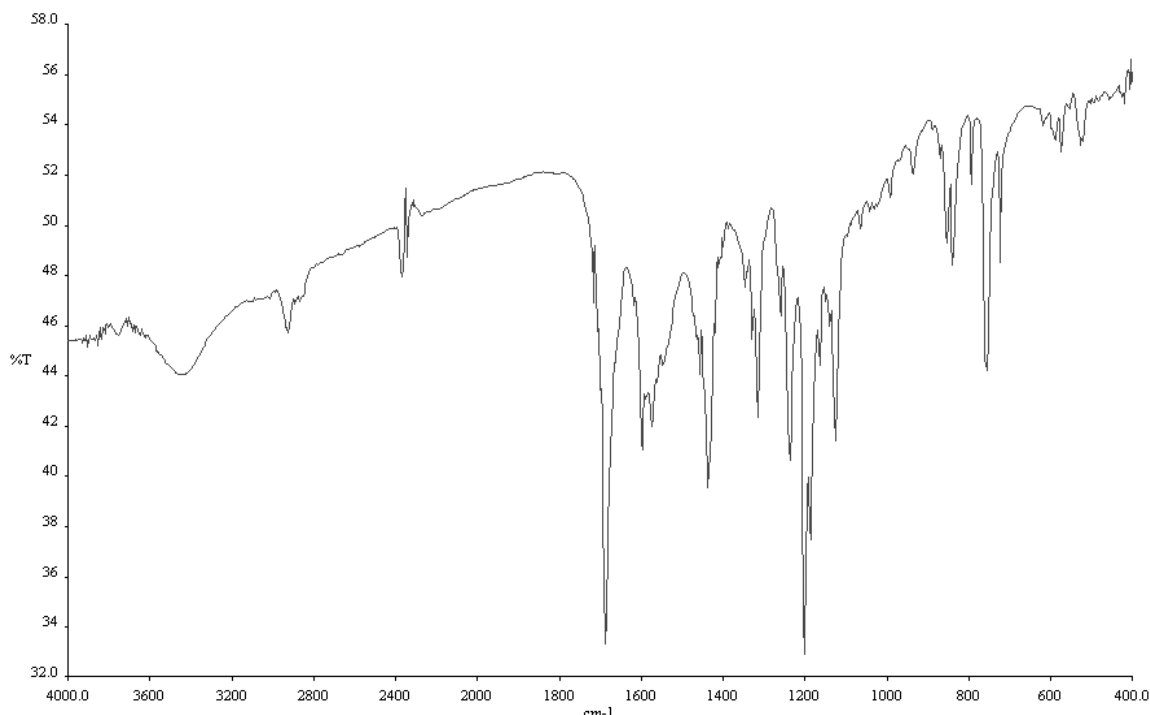


Figure 2. IR spectrum of 1.

#### 4. Conclusion

In this paper I have reported the crystal structure of a new complex  $[\text{Cu}_3\text{L}_2(\text{CCl}_3\text{COO})_2]$  as a part of our research in the series of linear trinuclear copper(II) complexes. Comparative analysis of these complexes helps us to study the effect of electron withdrawing group present in the carboxylate moiety on the structural features. The bonding parameters of the present complex are in good agreement with the prediction and this is very vital for developing better understanding of structure-property relationships. Further research will be carried out to explore the magnetic exchange coupling of this complex.

#### Acknowledgement

The author gratefully acknowledges Department of Chemistry, Jadavpur University, India for infrastructural support.

#### References

- [1] Tudor, V., Kravtsov, V.Ch., Julve, M., Lloret, F., Simonov, Y.A., Averkiev, B.B. and Andruh, M., "A new ferromagnetically coupled  $\mu$ -alkoxo- $\mu$ -acetato copper(II) trinuclear complex:  $\text{Cu}_3(\text{H}_2\text{tea})(\text{Htea})(\text{CH}_3\text{COO})_2(\text{ClO}_4)$  ( $\text{H}_3\text{tea}$ =triethanolamine)", *Inorg. Chim. Acta*, vol. 358, pp. 2066-2072, 2005.
- [2] Song, Y., Gamez, P., Roubau, O., Lutz, M., Spek, A.L. and Reedijk, J., "Structural and Magnetic Characterization of a Linear Trinuclear Copper Complex Formed through Ligand Sharing", *Eur. J. Inorg. Chem.*, pp. 2924-2928, 2003.
- [3] Liu, X., Miranda, M.P.de, McInnes, E.J.L., Kilner, C.A. and Halcrow, M.A., "Antisymmetric exchange in two tricopper(II) complexes containing a  $[\text{Cu}_3(\mu_3\text{-OMe})]^{5+}$  core", *Dalton Trans.*, pp. 59-64, 2004.
- [4] Bian, H.-D., Xu, J.-Y., Gu, W., Yan, S.-P., Cheng, P., Liao, D.-Z. and Jiang, Z.-H., "Synthesis, X-ray structure and magnetic properties of trinuclear copper(II) tridentate Schiff base complexes containing a partial cubane  $\text{Cu}_3\text{O}_4$  core", *Polyhedron*, vol. 22, pp. 2927-2932, 2003.

- [5] Sakai, K., Yamada, Y., Tsubomura, T., Yabuki, M. and Yamaguchi, M., "Synthesis, Crystal Structure, and Solution Properties of a Hexacopper(II) Complex with Bridging Hydroxides, Pyrazolates, and Nitrates", *Inorg. Chem.*, vol. 35, pp. 542-544, 1996.
- [6] Spira-Solomon, D.J., Allendorf, M. and Solomon, E.I., "Proton inventory of the second step of ribonuclease catalysis", *J. Am. Chem. Soc.*, vol. 108, pp. 5316-5318, 1986.
- [7] Messerschmidt, A., Leucke, H. and Huber, R., "X-ray Structures and Mechanistic Implications of Three Functional Derivatives of Ascorbate Oxidase from Zucchini: Reduced, Peroxide and Azide Forms", *J. Mol. Biol.*, vol. 230, pp. 997-1014, 1993.
- [8] Datta, A., Choudhury, C.R., Talukder, P., Mitra, S., Dahlenburg, L. and Matsushita, T., "A novel doubly phenoxo-bridged Cu(II) trimer: synthesis, crystal structure and low-temperature magnetic behavior", *J. Chem. Res. (S)*, vol 10, pp. 642-644, 2003.
- [9] Thakurta, S., Chakraborty, J., Rosair, G., Tercero, J., Fallah, M.S.El, Garribba, E. and Mitra, S., "Synthesis of Two New Linear Trinuclear Cu<sup>II</sup> Complexes: Mechanism of Magnetic Coupling through Hybrid B3LYP Functional and CShM Studies", *Inorg. Chem.*, vol. 47, pp. 6227-6235, 2008.
- [10] Sheldrick, G. M., SHELXTL, Program for the Solution and Refinement of Crystal Structures, version 5.1; Bruker AXS, Inc.: Madison, WI, 1999.
- [11] Sheldrick, G. M., SADABS, Programs for Area Detector Adsorption Correction; Institute for Inorganic Chemistry, University of Göttingen: Göttingen, Germany.
- [12] Addison, A.W., Rao, T.N., Reedijk, J., Van Rijn, J. and Verschoor, G.C., "Synthesis, structure, and spectroscopic properties of copper(II) compounds containing nitrogen-sulphur donor ligands; the crystal and molecular structure of aqua[1,7-bis(N-methylbenzimidazol-2'-yl)-2,6-dithiaheptane]copper(II) perchlorate", *J. Chem. Soc., Dalton Trans.*, pp. 1349-1356, 1984.
- [13] Rahaman, S.H., Ghosh, R., Lu, T.-H. and Ghosh, B.K., "Chelating N,N'-(bis(pyridin-2-yl)alkylidene)propane-1,3-diamine pseudohalide copper(II) and cadmium(II) coordination compounds: Synthesis, structure and luminescence properties of [M(bpap)(X)]ClO<sub>4</sub> and [M(bpap)(X)<sub>2</sub>] [M=Cu, Cd; X=N<sup>3-</sup>, NCS<sup>-</sup>]", *Polyhedron*, vol. 24, pp. 1525-1532, 2005.
- [14] Tarafder, M.T.H., Kasbollah, A., Crouse, K.A., Ali, A.M., Yamin, B.M. and Fun, H.-K., "Synthesis and characterization of Zn(II) and Cd(II) complexes of S-benzyl-β-N-(2-pyridyl)methylenedithiocarbamate (HNNS): bioactivity of the HNNS Schiff base and its Zn(II), Cu(II) and Cd(II) complexes and the X-ray structure of the [Zn(NNS)<sub>2</sub>] complex", *Polyhedron*, vol. 20, pp. 2363-2370, 2001.
- [15] Lever, A.B.P., *Inorganic Electronic Spectroscopy*, 2nd Edn., Elsevier, Amsterdam 1984.
- [16] Dapporto, P., Formica, M., Fusi, V., Giorgi, L., Micheloni, M., Paoli, P., Pontellini, R. and Rossi, P., "Addition of Small Molecules by Zn(II) and Cu(II) Dinuclear Complexes Obtained by an Amino-Phenolic Ligand. Crystal Structures of the Dinuclear Zinc Complex Assembling Butanolate and Azide Anions", *Inorg. Chem.*, vol. 40, pp. 6186-6192, 2001.