



# Synthesis, Characterisation and Antimicrobial studies of Dinuclear copper(II) complexes derived from Pentadentate Schiff base ligand

Kannappan Geetha<sup>1\*</sup> and Sundaramurthy Santha Lakshmi<sup>2</sup>

<sup>1\*</sup>PG & Research Department of Chemistry, Muthuramangal Govt. Arts College (Autonomous), Vellore-632 002, INDIA

<sup>2</sup>PG & Research Department of Chemistry, D.K.M. College for Women (Autonomous), Vellore-632 001, INDIA

Available online at: [www.isca.in](http://www.isca.in), [www.isca.me](http://www.isca.me)

Received 30<sup>th</sup> January 2014, revised 12<sup>th</sup> February 2014, accepted 15<sup>th</sup> March 2014

## Abstract

Four dinuclear Schiff base copper(II) complexes  $[Cu_2L(O_2CC_6H_4-p-X)]$  (1-4) [where  $X = OH(1), NH_2(2), OCH_3(3), NO_2(4)$ ], where  $H_3L$  is a trianionic pentadentate Schiff base ligand 1,3-bis(5-chlorosalicylideneamino) propan-2-ol were synthesised without isolating Schiff base ligand. The synthesised complexes were characterised by molar conductance, C, H and N analyses, UV-Vis., FTIR, EPR spectroscopic techniques and CV. The synthesised complexes have been screened for *in vitro* antibacterial activity against three Gram-positive bacteria *Bacillus subtilis*, *Staphylococcus aureus*, and *Streptococcus pyogenes* as well as three Gram-negative bacteria *Enterobacter aerogenes*, *Escherichia coli* and *Klebsiella pneumonia*, and anti fungal activity against *C. albicans*, *C. glabrata* and *C. tropicalis*.

**Keywords:** Dinuclear Schiff base, spectroscopic techniques, *in vitro* antibacterial and antifungal activity.

## Introduction

The chemistry of binuclear copper(II) complexes are great interest among the researchers as models for investigating intramolecular magnetic exchange interactions between two metal centres in different structural motifs, viz. the *paddle-wheel* dicopper(II) tetracarboxylates, symmetrically bridged hydroxo or alkoxo species, and asymmetrically dibridged complexes with a ( $\mu$ -hydroxo/alkoxo) ( $\mu$ -carboxylato) dicopper (II) core. Some of the ligands used for bridging are hydroxo<sup>1</sup>, halides<sup>2</sup>, carboxylates<sup>3</sup>, azide and thiocyanate<sup>4</sup> and purine bases<sup>5</sup>.

Multidentate Schiff base ligands have generally been used to stabilise the asymmetrically dibridged dicopper(II) core. Literature shows that many researchers have reported carboxylate<sup>6, 7</sup> and pyrazolate<sup>8</sup> bridged dinuclear complexes based on the synthesis of pentadentate Schiff base ligands reported by Nishida and Kida<sup>9</sup>. In the present series we have used *p*-substituted benzoates as a bridging ligand for the synthesis of dinuclear copper(II) complexes derived from the Schiff base ligand 1,3-bis(5-chlorosalicylideneamino)propan-2-ol.

## Material and Methods

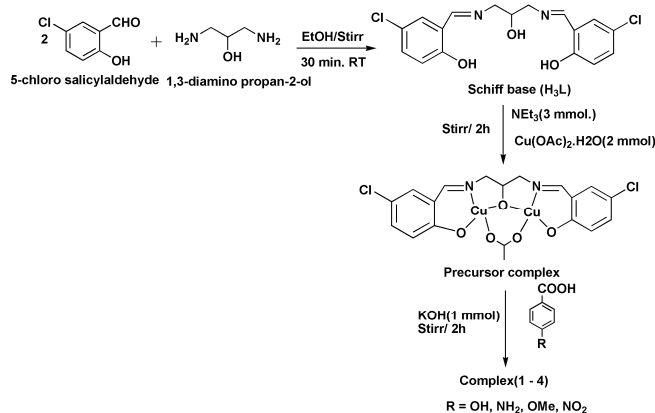
All the reagents and chemicals were procured from commercial sources and were used without any further purification. Molar conductance of the complexes were measured in DMF ( $10^{-3}$  M) solutions using a Guna digital conductivity meter. Infrared spectra of solids using KBr pellets were recorded in the region of 4000 - 400  $cm^{-1}$  on Shimadzu FTIR spectrophotometer. Electronic absorption spectra were recorded in the region 200 -

800 nm using a Systronics double beam UV-Vis spectrophotometer-2202 in DMF. The X band EPR spectra of the complexes in solid state was recorded using Bruker EMX-10/2.7 EPR spectrometer at LNT using DPPH as g marker. Elemental analyses were conducted using Flash 2000 organic elemental analyzer. Magnetic moment of the complexes was determined using VSM Lake Shore-7404 at room temperature.

**Synthesis of Cu(II) complexes:** A trianionic pentadentate Schiff base ligand 1,3-bis(5-chlorosalicylideneamino) propan-2-ol ( $H_3L$ ) was synthesised by the reaction of 1,3-diamino-2-hydroxypropane (1 mmol) with 5-chloro salicylaldehyde (2 mmol) in ethanolic solution (25 mL) under stirring condition for 30 min at room temperature. The pale yellow coloured solution was then treated with triethylamine (3 mmol) followed by addition of an ethanolic solution of  $Cu(CH_3COO)_2 \cdot H_2O$  (2 mmol). The solution was stirred for two hour. Then an ethanolic solution of stirred mixture of appropriate para substituted sodium benzoate (1 mmol) was added in drops and stirred for additional 2 h. The resultant green coloured product was filtered washed with ethanol and dried. The schematic diagram of preparation of dinuclear copper(II) complexes(1-4) is represented in scheme 1.

**Pharmacology: Antimicrobial activity (*in vitro*):** All the synthesised copper(II) complexes were tested *in vitro* for their antimicrobial activity against a variety of pathogenic microorganisms. Antibacterial activity of the complexes were investigated against *Bacillus subtilis* (MTCC-121), *Staphylococcus aureus* (MTCC-3160), *Streptococcus pyogenes* (MTCC-1924), *Escherichia coli* (MTCC-1195), *Klebsiella pneumonia* (MTCC-3384), *Enterobacter aerogenes* (MTCC-3159) and antifungal activity was investigated against three

strains of fungi viz., *Candida albicans* (MTCC-1637), *Candida glabrata* (MTCC-3019) and *Candida tropicalis* (MTCC-1000). The *in vitro* antimicrobial activity was studied by using the current NCCLS guidelines by Well diffusion method, using Mueller-Hinton agar medium for bacteria and Sabouraud dextrose agar medium for *Candida*<sup>10</sup>. DMSO was used as a negative control while, tetracycline and ketoconazole were used as a positive control for bacteria and fungi respectively.



Scheme-1

The agar media (20 mL) was poured into each petri plate and plates were swabbed with 100  $\mu$ L inocula of the test microorganisms and kept for 15 min for adsorption. Using sterile cork borer of 8 mm diameter, wells were bored into the seeded agar plates and these were loaded with a 100  $\mu$ L solution of each compound in dimethylsulphoxide (DMSO) with concentration of 4.0 mg/mL. Inhibition was recorded by measuring the diameter of the inhibition zone at the end of 24 h. This procedure was performed in three replicate plates for each organism<sup>11</sup>.

**Minimum Inhibitory Concentration (MIC):** MIC is the lowest concentration of antimicrobial compound, which inhibit the visible growth of a microorganism after overnight incubation. MIC of all the synthesised copper(II) complexes was tested against bacterial strains through a macro dilution tube method as recommended by NCCLS. In this method, the

various test concentrations of synthesised compounds were made from 100 to 0.25  $\mu$ g/mL in sterile tubes. A 100  $\mu$ L sterile Muller Hinton Broth (MHB) was poured in each sterile tube followed by addition of 200  $\mu$ L test compound in tube 1. Two fold serial dilutions were carried out from all the tubes and excess broth (100  $\mu$ L) was discarded from the last tube. To each tube, 100  $\mu$ L of standard inoculums ( $1.5 \times 10^8$  cfu/mL) was added. Turbidity was observed after incubating the inoculated tubes at 37  $^{\circ}$ C for 24 h<sup>12</sup>.

## Results and Discussion

All the copper(II) complexes are green coloured, non-hygroscopic solids. They are found to be stable at room temperature and soluble in DMF, DMSO and partially soluble in acetonitrile. The analytical data of the copper(II) complexes are given in table 1. The data suggests that all the complexes are dinuclear in nature. Based on the analytical data the molecular formula has been assigned to the complexes. The data is consistent with the earlier reports support the proposed formulation of the binuclear complexes<sup>13</sup>.

The molar conductance of the all the dinuclear copper(II) complexes (table 2) in DMF exhibited a lower molar conductivity value of 11-16  $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$  in DMF, indicates a non-electrolytic nature of the complex<sup>14</sup>.

The experimentally determined room temperature magnetic moments ( $\mu_{\text{eff}}$ ) values of all the copper(II) complexes (table 2) in this series lie below the spin only value of 1.73 BM and found to be in the range of 0.65-1.44 BM. These values correspond to one unpaired electron in a square planar environment<sup>15</sup>. Each  $\text{Cu}^{2+}$  ion has a  $d^9$  electronic configuration, and so should have one unpaired electron. If there were a covalent bond between the copper ions, the electrons would pair up and the compound would be diamagnetic. Instead, there is an exchange interaction in which the spins of the unpaired electrons become partially aligned to each other. In fact two states are created, one with spins parallel and the other with spins opposed.

Table-1  
Analytical data of dinuclear Schiff base copper(II) complexes

Complex	Molecular formula	Formula Weight	Elemental analyses Calculated (Found) %		
			C	H	N
[Cu <sub>2</sub> L(O <sub>2</sub> CC <sub>6</sub> H <sub>4</sub> -p-OH)] (1)	C <sub>24</sub> H <sub>18</sub> Cl <sub>2</sub> Cu <sub>2</sub> N <sub>2</sub> O <sub>6</sub>	628.41	45.87 (45.89)	2.89 (2.86)	4.46 (4.49)
[Cu <sub>2</sub> L(O <sub>2</sub> CC <sub>6</sub> H <sub>4</sub> -p-NH <sub>2</sub> )] (2)	C <sub>24</sub> H <sub>19</sub> Cl <sub>2</sub> Cu <sub>2</sub> N <sub>3</sub> O <sub>5</sub>	627.42	45.94 (45.91)	3.05 (3.08)	6.70 (6.73)
[Cu <sub>2</sub> L(O <sub>2</sub> CC <sub>6</sub> H <sub>4</sub> -p-OMe)] (3)	C <sub>25</sub> H <sub>20</sub> Cl <sub>2</sub> Cu <sub>2</sub> N <sub>2</sub> O <sub>6</sub>	642.43	46.74 (46.73)	3.14 (3.16)	4.36 (4.40)
[Cu <sub>2</sub> L(O <sub>2</sub> CC <sub>6</sub> H <sub>4</sub> -p-NO <sub>2</sub> )] (4)	C <sub>24</sub> H <sub>17</sub> Cl <sub>2</sub> Cu <sub>2</sub> N <sub>3</sub> O <sub>7</sub>	657.4	43.85 (43.80)	2.61 (2.64)	6.39 (6.38)

In the present series such a decrease in the magnetic moment values for the copper(II) complexes indicate a marked magnetic interaction between  $\text{Cu}^{2+}$ , which confirms the presence of antiferromagnetic coupling. The complexes have low  $\mu_{\text{eff}}$  values similar to the values reported earlier for antiferromagnetic dinuclear complexes, where carboxylate group acts as a bridge between two metal ions and possessing spin-spin interactions<sup>16</sup>. According to the report of Tadashi Tokii and Yoneichiro Muto<sup>17</sup> such an interaction takes place through bridging carboxylate groups of Cu-O-C-O-Cu linkages rather than in terms of direct metal-metal interaction.

**Table-2**

**Molar conductance, melting point and magnetic moment of the copper(II) complexes**

Complex	$\Lambda_M$ $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$	M.P. °C	* $\mu_{\text{eff}}$ BM
(1)	15	190	1.44
(2)	11	200	0.93
(3)	16	206	1.45
(4)	13	240	0.65

\*Magnetic moment value per copper atom in the complex.

**UV-Vis., spectra:** The significant bands appeared in UV-Vis spectral data of the copper(II) complexes in DMF are depicted in table 3. The electronic spectra shows peak at 274-277 nm for the copper(II) complexes is associated with  $\pi \rightarrow \pi^*$  transition of benzene ring<sup>18</sup>. All the complexes exhibited an absorption band around 350 nm are attributed to  $n \rightarrow \pi^*$  transition originating from electrons present on the nitrogen atom of the azomethine moiety<sup>19</sup> present in Schiff base ligand. Appearance of band around 400 nm corresponds to the charge transfer spectra caused by ligand to the metal ions<sup>20</sup>. The broad band observed around 620–630 nm of all the complexes corresponds to d-d transition of Cu(II) ion.

**Table-3**

**Electronic spectral assignments for copper(II) complexes**

Complex	$\pi \rightarrow \pi^*$	$n \rightarrow \pi^*$	L→M CT	d-d
(1)	274	352	402	630
(2)	275	350	400	623
(3)	274	351	404	626
(4)	277	351	411	620

**FTIR spectra:** Selected vibrational bands of the complexes, useful for determining the coordination modes of donor atoms are given in Table 4. In the present series appearance of strong bands at 1626–1633 $\text{cm}^{-1}$  related to conjugated C=N stretching of Schiff base moiety<sup>21, 22</sup>. According to the literature, medium to strong bands appeared in the range of 1225  $\text{cm}^{-1}$  corresponds to  $\nu(\text{O}-\text{C})$ , suggesting the coordination of phenolic oxygen atom to copper(II) ion<sup>23</sup>. Further, the medium band observed in the range of 1120  $\text{cm}^{-1}$  corresponds to the stretching frequency of

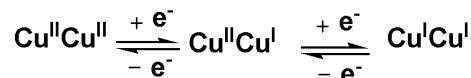
alcoholic O-C group<sup>24</sup>, confirmed the coordination of alcoholic oxygen atom present in the Schiff base ligand to the metal atom.

IR spectra is an important tool for the determination of coordination mode of carboxylate group to the metal atom. According to Deacon and Phillips<sup>25</sup> for unidentate coordination, the value of  $\Delta\nu [\nu_{\text{as}}(\text{COO}^-) - \nu_{\text{s}}(\text{COO}^-)]$  is more than that of free carboxylate anion value, where as for bidentate bridging or chelating carboxylate group, the separation value is less than the free carboxylate. For the current series of binuclear complexes the lower value of  $\Delta\nu$  which in the range of 169 - 174  $\text{cm}^{-1}$  suggests bridging coordination mode<sup>26, 27</sup>. Further, the bands observed in the far IR region of 570 for (1) 568 for (2), 564 for (3) and 574  $\text{cm}^{-1}$  for (4) can be attributed to Cu-N linkage. Similarly the  $\nu(\text{Cu}-\text{O})$  bands are observed at 459 for (1), 461 for (2), 470 for (3) and 464 for (4) respectively<sup>28</sup>.

Hence the FTIR spectra of the complexes indicates that the Schiff base ligand is coordinated to the copper(II) ions through imino nitrogen, phenolic oxygen, alcoholic oxygen. The oxygen atoms of carboxylate group of *p*-substituted aryl carboxylates acts as a bridging group between the two Cu(II) ions.

**Cyclic voltammetry:** The electrochemical properties of the complexes were studied by cyclic voltammetry. Cyclic voltammetric studies of the copper(II) complexes were investigated in DMF ( $10^{-3}$  M) at a scan rate of 0.1 V/s in the potential range +2 to -2 V. The representative cyclic voltammogram of the copper(II) complex(4) is shown in figure 1 and the electrochemical data of all the dinuclear copper(II) complexes are summarised in table 5.

All the dinuclear Cu(II) complexes undergo two one-electron reduction and oxidation at different potentials. Cyclic voltammograms for all the complexes are similar and the cathodic ( $I_{\text{p,c}}$ ) and anodic ( $I_{\text{p,a}}$ ) peak currents were not equal. This indicates the quasi-reversible nature of the electron transfer process<sup>29</sup>. Even though in all the complexes both the metal ions have the same geometry and same environment, two reduction waves are obtained in the cathodic region corresponding to stepwise one-electron reductions through a  $\text{Cu}^{\text{II}}\text{Cu}^{\text{I}}$  intermediate to give a dinuclear  $\text{Cu}^{\text{I}}\text{Cu}^{\text{I}}$  species. In spite of the ligands being symmetrical, their dicopper(II) complexes show two quasi-reversible reduction waves<sup>30</sup>. The two redox processes are represented as follows:



The reason for the observation of two reduction waves may be due to electronic exchange between the metal ions, after the first one-electron reduction some of the electron density is transferred from the reduced metal ion to the other metal ion and hence the second reduction appears at a high negative potential.

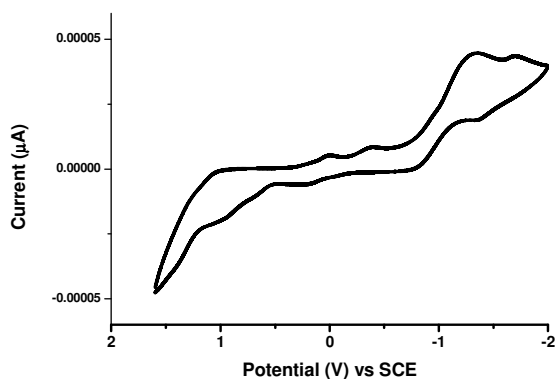
**Table-4**  
**Infrared spectral data of the copper(II) complexes (cm<sup>-1</sup>)**

Complex	C=N	COO <sup>-</sup>			Phenolic C-O	Alcoholic C-O	Cu-N	Cu-O
		$\nu_{as}$	$\nu_s$	$\Delta\nu$				
(1)	1630	1555	1381	174	1229	1170	570	459
(2)	1626	1533	1368	165	1220	1179	568	461
(3)	1633	1572	1402	170	1219	1177	565	470
(4)	1629	1573	1388	185	1225	1174	574	464

**Table-5**  
**Redox potentials for copper(II) complexes in DMF at 298 K.**

Complex	E <sub>pc</sub> (V)	E <sub>pa</sub> (V)	ΔE <sub>p</sub> (V)	E <sub>1/2</sub> (V)	I <sub>pc</sub> (μA)	I <sub>pa</sub> (μA)	I <sub>pc</sub> /I <sub>pa</sub>
(1)	0.124	0.163	0.039	0.144	6.915	5.16	1.34
	0.974	-1.236	-2.21	-0.131	0.221	0.418	0.53
(2)	0.2146	0.3609	0.1463	0.2876	7.4734	6.1629	1.21
	1.0567	-1.233	-2.2897	-0.0882	0.20076	0.4816	0.42
(3)	0.1710	0.08167	-0.0893	0.1263	7.5443	5.0649	1.48
	0.7102	-1.3563	-2.0665	-0.3231	0.1427	0.4707	0.30
(4)	0.2250	0.08654	-0.1385	0.1558	6.269	5.0649	1.24
	0.9433	-1.3154	-2.2587	-0.1861	0.1973	0.4455	0.44

E<sub>pc</sub> = anodic peak potential; E<sub>pa</sub> = cathodic peak potential; I<sub>pc</sub> = anodic peak current; I<sub>pa</sub> = cathodic peak current; I<sub>pc</sub>/I<sub>pa</sub> = number of electrons; ΔE<sub>p</sub> = E<sub>pa</sub> – E<sub>pc</sub>; scan rate 0.1 V/s



**Figure-1**

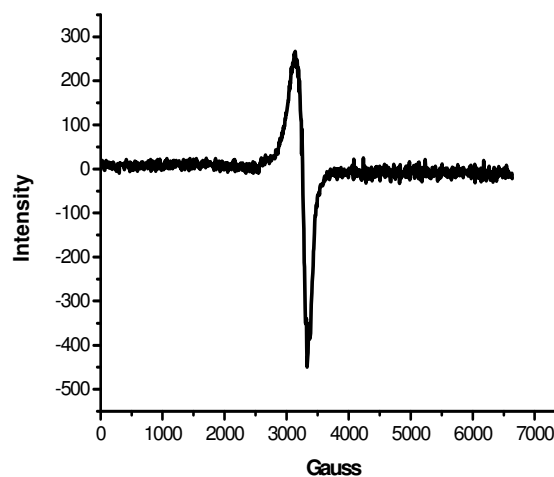
**Cyclic voltammogram of dinuclear copper(II) complex(4)**

**ESR spectra:** The solid state ESR spectra (figure 2) of the complexes in the polycrystalline state at 77K was recorded in the X band region, using 100 KHz field modulation and the g factors were quoted relative to the standard marker DPPH (g = 2.0036). The g values of the complexes are listed in table 6.

Except complex(4) ESR spectra of all the complexes displayed an isotropic spectra with the g<sub>iso</sub> values 2-2.01, indicating an axial symmetry with all the principal axes aligned parallel<sup>31</sup>. Such a spectrum is expected in complexes with elongated tetragonal-octahedral, square planar, or square based pyramidal stereo chemistries. However, complex(4) is ESR inactive due to strong antiferromagnetic spin coupling between the two spin-half copper(II) ions<sup>32</sup>.

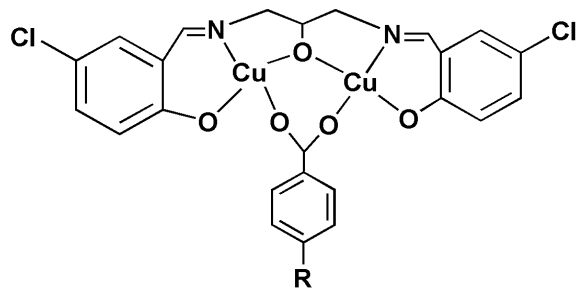
**Table-6**  
**ESR data of the copper(II) complexes**

Complex	(1)	(2)	(3)	(4)
g <sub>iso</sub>	2.01	2.01	2.00	-



**Figure-2**  
**ESR spectra of complex(2)**

Single crystals of the complexes could not be isolated from any solutions, thus no definite structure may be described. However, based on the literature and the analytical, spectroscopic and magnetic data enable us to predict the possible structure of the complexes. The proposed structure of the complexes is shown in figure 3.



Where R = OH, NH<sub>2</sub>, OCH<sub>3</sub>, NO<sub>2</sub>

Figure-3

Proposed structure of the complexes

**Antimicrobial activity:** The study of activities of the synthesised compounds towards the biological systems is an important feature of current research. In the present work, the susceptibility of dinuclear copper(II) was assessed on the basis

of diameter of zone of inhibition against some Gram-positive and Gram-negative bacteria as well as fungi. The results of diameter of zone of inhibition in mm (figures 4 and 5) against the strains of bacteria and fungi are given in table 7 and 8 respectively. Tables 9 and 10 summarise the minimum inhibitory concentration (MIC) values of the complexes under investigation.

In the *in vitro* antimicrobial studies of the present series, complex(3) with *p*-methoxy substituent in the aryl carboxylate exhibits comparatively good antibacterial activity against Gram-negative bacteria under investigation. Complex(4) with nitro substituent exhibits good activity against *B.subtilis* and *K. pneumoniae*. Complex(1) exhibits higher zone of inhibition against *C.candida* and *C.glabrata* than other complexes and complex(2) inhibits *C.tropicalis* with higher zone of inhibition.

Table-7  
Antibacterial activity of the copper(II) complexes

Complex	Diameter of zone of inhibition (mm)					
	Gram-positive bacteria			Gram-negative bacteria		
	<i>B. subtilis</i>	<i>S. aureus</i>	<i>S. pyogenes</i>	<i>E. aerogenes</i>	<i>E. coli</i>	<i>K. pneumonia</i>
(1)	14±0.24	10±0.23	11±2.9	15.5±1.33	13.4±2.4	15.4±1.5
(2)	11±0.11	17±1.1	16.2±2.5	12±0.16	12±2.4	16±1.32
(3)	16±2.9	11±1.64	15±0.3	17.5±1.3	17.1±1.32	17±0.16
(4)	17±1.32	12±0.56	14.5±4.03	10.3±1.7	11±0.32	17.1±1.2
Tetracycline (Control)	20±1.32	20±1.20	19±1.74	18±0.23	19.5±1.03	21±0.03

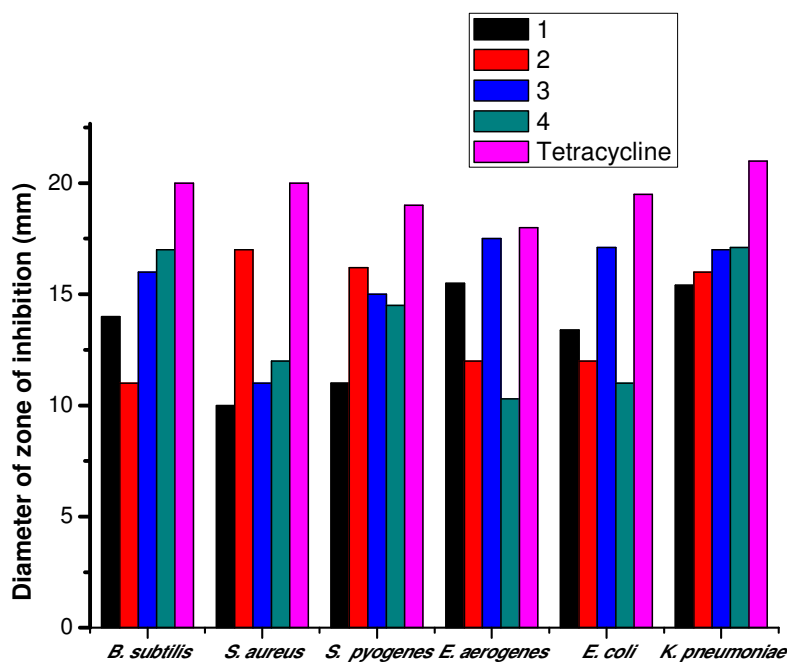


Figure-4  
Antibacterial activity of dinuclear copper(II) complexes

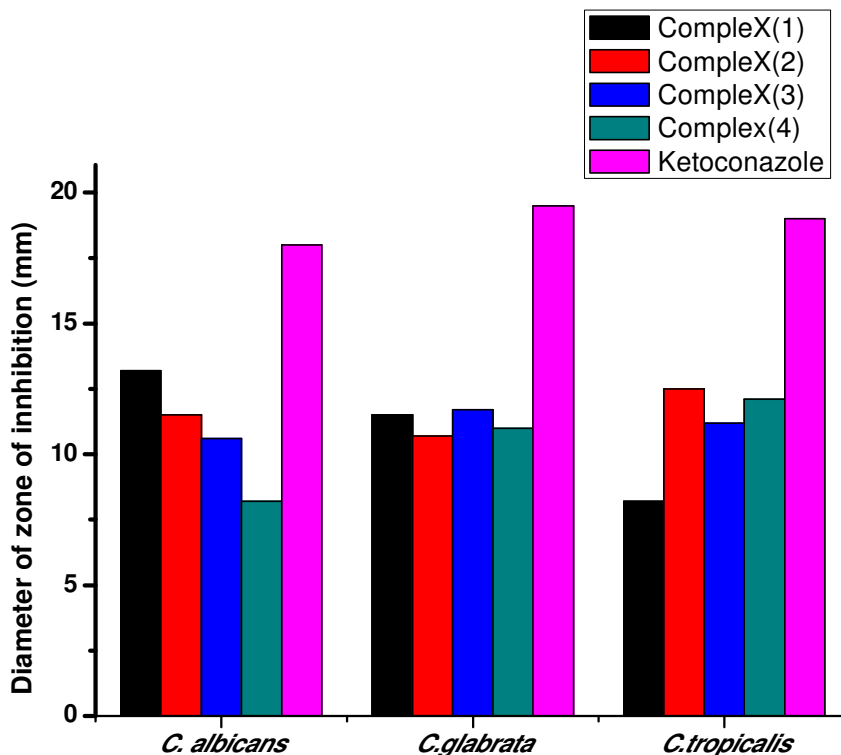


Figure-5  
Antifungal activity of dinuclear copper(II) complexes

Table-8  
Antifungal activity of the copper(II) complexes

Complex	Diameter of zone of inhibition (mm)		
	<i>C. albicans</i>	<i>C. glabrata</i>	<i>C. tropicalis</i>
(1)	13.2±0.7	15.9±0.21	8±0.59
(2)	11.5±0.35	10.7±0.11	12.5±0.6
(3)	10.6±0.63	11.7±0.2	11.2±0.8
(4)	8.2±0.37	11±0.5	12.1±0.6
Ketoconazole (Control)	18±0.23	19.5±1.03	19±1.74

Table-7  
MIC (µg/mL) of copper(II) complexes against bacteria

Complex	Gram-positive bacteria			Gram-negative bacteria		
	<i>B. subtilis</i>	<i>S. aureus</i>	<i>S. pyogenes</i>	<i>E. aerogenes</i>	<i>E. coli</i>	<i>K. pneumoniae</i>
(1)	7.5±0.24	8.5±0.23	6.4±2.9	6.8±1.33	8±2.4	9.1±3.0
(2)	8.1±0.11	7.6±3.1	8±2.5	6.3±0.16	8.7±2.4	6.9±1.32
(3)	7.1±2.9	8.3±1.64	7.5±0.3	8.9±1.03	7.9±1.32	6.3±0.16
(4)	6±1.32	7±0.56	6.2±4.03	8.7±3.7	8.8±32	6.5±3.2

Table-9  
MIC (µg/mL) of copper(II) complexes against fungi

Complex	<i>C. albicans</i>	<i>C. glabrata</i>	<i>C. tropicalis</i>
(1)	6.4±0.42	5.3±0.32	7.2±0.5
(2)	8.2±0.1	7.4±1.43	6.2±0.24
(3)	7.6±1.3	6.5±0.42	7.9±0.43
(4)	9.8±0.52	7.4±0.63	8.1±1.3

The MIC is the lowest concentration of the test compound, which can restrain the apparent growth after 18 h incubation at 37 °C. The MIC was determined visually after incubation for 18 h, at 37 °C. The fungicidal screening shows that *C. albicans* and *C. glabrata* was inhibited by complex(1) with MIC values 6.4 and 5.3 µg/mL respectively. *C. tropicalis* was inhibited by complex(2) with the MIC value of 6.2 µg/mL.

## Conclusion

In the present work four dinuclear copper(II) complexes were synthesised and characterised by various analytical techniques like elemental analyses, molar conductance, VSM-RT, UV-Vis., FTIR, EPR and cyclic voltammetry. The lower molar conductance values suggested the non-electrolytic nature of the complexes. The structure of the complexes were proposed with the help of elemental analyses and FTIR spectra. The cyclic voltammogram of all the complexes confirmed the redox property. The *in vitro* antibacterial and antifungal studies of the complexes suggested that the dinuclear Cu(II) complexes shows a significant antimicrobial activity.

## References

1. Crawford V.H., Richardson H.W., Wasson J.R., Hodgson D.J. and Hatfield W. E., Relation between the singlet-triplet splitting and the copper-oxygen-copper bridge angle in hydroxo-bridged copper dimers, *Inorg. Chem.*, **15(9)**, 2107-2110 (1976)
2. Romero M.A., Salas J.M., Quirós M., Sánchez M.P., Romero J. and Martín D., Structural and Magnetic studies on a Bromine-Bridged Copper(II) Dimer with 5,7-Dimethyl[1,2,4]triazolo[1,5-a] pyrimidine, *Inorg. Chem.*, **33(24)**, 5477-5481 (1994)
3. Colacio E., Ghazi M., Kivekäs R. and Moreno J.M., Helical-Chain Copper(II) Complexes and a Cyclic Tetranuclear Copper(II) Complex with Single Syn–Anti Carboxylate Bridges and Ferromagnetic Exchange Interactions, *Inorg. Chem.*, **39(13)**, 2882-2890 (2000)
4. Navarro J.A.R., Romero M.A., Salas J.M., Quirós M. and Tiekink E.R.T., First Example of Equatorial–Equatorial Disposition of End-to-End Thiocyanate Bridges in a Polynuclear Copper(II) Complex and Its Relation to the Very Efficient Transmission of the Magnetic Interaction, *Inorg. Chem.*, **36(22)**, 4988-4991 (1997)
5. Sonnenfroh D. and Kreilick R.W., Exchange coupling in copper dimers with purine ligands, *Inorg. Chem.*, **19(5)**, 1259-1262 (1980)
6. Chih-Yu, Jian-Wei L and Ho-Hsiang W., Crystal Structures, Magnetic Properties and Catecholase-Like Activities of  $\mu$ -Alkoxo- $\mu$ -Carboxylato Double Bridged Dinuclear and Tetranuclear Copper(II) Complexes, *J. Chin. Chem. Soc.*, **56(1)**, 89-97 (2009)
7. Chin-Jhan L., Sung-Chung C., Hsin-Huang L and Ho-Hsiang W., Ferromagnetic exchange in  $\mu$ -alkoxo- $\mu$ -dicarboxylato double bridged tetranuclear copper(II) complexes:  $[\text{Cu}_4(\text{L-X})_2(\mu\text{-C}_4\text{H}_4\text{O}_4)(\text{dmf})_2]$  (L = 1,3-bis(5-X-salicylideneamino)-2-propanol, X = Br, Cl), *Inorg. Chem. Commun.*, **8(3)**, 235-238 (2005)
8. (a) Kara H., Elerman Y. and Prout K., Antiferromagnetic Coupling in a (m)-Hydroxo(m)-pyrazolato)dicopper(II) Complex. Synthesis, Crystal Structure, Magnetic Properties, and Theoretical Studies, *Z. Naturforsch B.*, **56(8)**, 719-727 (2001) (b) Kara H., Elerman Y. and Prout K., Synthesis, Crystal Structure and Magnetic Properties of a (m-Hydroxo)(m-Pyrazolato) Dicopper(II) Complex, *Z. Naturforsch B.*, **55(9)**, 796-802 (2000)
9. Nishida Y. and Kida S., Crystal structures and magnetism of binuclear copper(II) complexes with alkoxide bridges. Importance of orbital complementarity in spin coupling through two different bridging groups, *J. Chem. Soc. Dalton Trans.*, 2633-2640 (1986)
10. Manjula B., Arul Antony S. and Arul Antony S., Studies on DNA Cleavage and Antimicrobial screening of Transition Metal complexes of 4-aminoantipyrene Schiff base, *Res. J. Chem. Sci.*, **3(12)**, 22-28, (2013)
11. NCCLS, Method for dilution antimicrobial susceptibility test for bacteria that grow aerobically. Approved Standards, 5<sup>th</sup> Ed., National Committee for Clinical Standards, Villanova, PA. (2000)
12. Andrews J.M., Determination of minimum inhibitory concentrations, *J. Antimicrob. Chemother.*, **48**, 5-16 (2001)
13. Veronica D., Hernan B., Claudia P., Sergiu S., Jean-Pierre T. and Sandra S., Synthesis, characterisation and catalase-like activity of dimanganese(III) complexes of 1,5-bis(5-X-salicylideneamino)pentan-3-ol (X = nitro and chloro), *J. Inorg. Biochem.*, **98(11)**, 1806-1817 (2004)
14. Geary W.J., The use of conductivity measurements in organic solvents for the characterisation of coordination compounds, *Coord. Chem. Rev.*, **7**, 81-122 (1971)
15. Hathaway B.J., Bradley J. N. and Gillard R.D.,(Eds) *Essays in Chemistry*, Academic press, New York (1971)
16. Melník and Krátsmár-Šmogrovič, Copper(II) complexes with organic ligands. XV. Magnetic properties of copper(II) benzoate complexes of heterocyclic N-oxides, *Chem. Zvesti.*, **27(5)**, 594-599 (1973)
17. Tadashi Tokii and Yoneichiro Muto, Preparative and Magnetic Studies of Several Binuclear Copper(II) Alkanoate Complexes with Salicylideneamines, *Bull. Chem. Soc. Jpn.*, **49(7)**, 1849-1854 (1976)
18. Hussein S. Seleem, Mostafa M., Saif M. and Amin A., Copper(II)-Complexes of an Isatinic Quinolyl

- Hydrazone-Anion effect, *Res.J.Chem. Sci.*, **3(1)**, 86-91, (2013)
19. Edward Szlyk, Andrzej Surdykowski, Magdalena Barwiolek and Erik Larsen, Spectroscopy and stereochemistry of the optically active copper(II), cobalt(II) and nickel(II) complexes with Schiff bases N, N'-(1R, 2R)-(-)-1,2-cyclohexylenebis(3-methylbenzylideneiminato) and N, N'-(1R, 2R)-(-)-1,2-cyclohexylenebis (5-methylbenzylideneiminato), *Polyhedron*, **21(27-28)**, 2711-2717 (2002)
20. João Costa Pessoa, Maria J. Calhorda, Isabel Cavaco, Paulo J. Costa, Isabel Correia, Dina Costa, Luís F. Vilas-Boas, Vítor Félix, Robert D. Gillard, Rui T. Henriques and Robert Wiggins, N-Salicylideneamino acidato complexes of oxovanadium(IV). The cysteine and penicillamine complexes, *Dalton. Trans.*, **18**, 2855-2866 (2004)
21. Davar M., Boghaei and Mehrnaz Gharagozlou, Spectral characterization of novel ternary zinc(II) complexes containing 1,10-phenanthroline and Schiff bases derived from amino acids and salicylaldehyde-5-sulfonates, *Spectrochimica Acta Part A: Mol. Biomol. Spec.*, **67(3-4)**, 944-949 (2007)
22. Tantry Rajesh N., Jathi Keshavayya, Prasanna S.M., Angadi Shoukat Ali R. and Chinnagiri Keerthi Kumar T., Synthesis and Characterization of Tetraformamido [2-amino-5-(phenyl) thiazole] substituted metal Phthalocyanines, *Res. J. Chem. Sci.*, **4(1)**, 1-8, (2014)
23. Offiong E. Offiong, Emmanuel Nfor and Ayi A. Ayi, Synthesis, spectral and cytotoxicity studies of palladium(II) and platinum(II) amino acid Schiff base complexes, *Trans. Met. Chem.*, **25(4)**, 369-373 (2000)
24. Silverstein R. M., Clayton Bassier G. and Terence C. Morrill, *Spectrometric Identification of Organic Compounds.*, 5<sup>th</sup> ed., John Wiley and Sons, New York (1991)
25. Deacon G.B. and Phillips R.J., Relationships between the carbon-oxygen stretching frequencies of carboxylato complexes and the type of carboxylate coordination, *Coord. Chem. Rev.*, **33**, 227-250 (1980)
26. Ki-Young Choi, Synthesis and Crystal Structure of One-Dimensional Carboxylate-Bridged Copper(II) Complex with 2-Pyridylmethylamino-3-butyric acid, *J. Chem. Crystallogr.*, **38(1)**, 53-56 (2008)
27. Sabah M. Mohamed, Synthesis and Characterization of Co<sup>+2</sup>, Ni<sup>+2</sup>, Cu<sup>+2</sup>, Zn<sup>+2</sup> and Hg<sup>+2</sup> Complexes with 1,1,2,2-tetrakis (Sodium Thioproponate) ethylene, *Res. J. Chem. Sci.*, **3(7)**, 9-14, (2013)
28. Ferraro J R., *Low frequency vibrations of inorganic and coordination compounds*, Plenum press, NewYork (1971)
29. Prabu R., Vijayaraj A., Suresh R., Jagadish L., Kaviyaran V. and Narayanan V., New Unsymmetric Dinuclear Copper(II) Complexes of Trans-disubstituted Cyclam Derivatives: Spectral, Electrochemical, Magnetic, Catalytic, Antimicrobial, DNA Binding and Cleavage Studies, *Bull. Korean Chem. Soc.*, **32(5)**, 1669-1678 (2011)
30. Tandon S.S., Thompson L.K. and Bridson, J.N., Dinuclear copper(II) and mixed-valence copper(II)-copper(I) complexes of 34-membered macrocyclic ligands (H<sub>2</sub>M<sub>1</sub>, H<sub>2</sub>M<sub>2</sub>) capable of forming endogeneous phenolate and pyridazino bridges. X-ray crystal structures of the dinuclear copper(II) complexes [Cu<sub>2</sub>M<sub>1</sub>][BF<sub>4</sub>]<sub>2</sub>.H<sub>2</sub>O and [Cu<sub>2</sub>M<sub>2</sub>][BF<sub>4</sub>]<sub>2</sub>.CH<sub>3</sub>OH, which exhibit a remarkable ligand twist, *Inorg. Chem.*, **32(1)**, 32-39 (1993)
31. Leese C.L. and Rydon H.N., Polyazanaphthalenes. Part I. Some derivatives of 1:4:5-triazanaphthalene and quinoxaline, *J. Chem. Soc.*, 303-308 (1955)
32. Jnan Prakash Naskar, Chiranjan Biswas, Bhargab Guhathakurta, Núria Aliaga-Alcalde, Liping Lu, Miaoli Zhu, Oximate bridged copper(II) dimers: Synthesis, crystal structure, magnetic, thermal and electrochemical properties, *Polyhedron.*, **30**, 2310-2319 (2011)