



## Synthesis, Characterization and Antimicrobial Properties of $[\text{Cu}_2(\mu\text{-O}_2\text{CC}_9\text{H}_{19})_4(4\text{-CNpy})_2]$

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Reports on the isolation and crystallographic characterization of metal carboxylates having long alkyl chains are relatively rare. Herein, a dinuclear copper(II) tetracaprate (*i.e.* tetradecanoate) complex,  $[\text{Cu}_2(\mu\text{-O}_2\text{CC}_9\text{H}_{19})_4(4\text{-CNpy})_2]$  (**I**), where 4-CNpy = 4-cyanopyridine is reported. The complex has been synthesized by a facile method and characterized by various physico-chemical techniques such as IR and UV-vis spectroscopy, magnetic susceptibility measurement and single crystal X-ray diffraction. The structure is dimeric with the familiar paddle-wheel geometry, which was originally observed in the structure of copper(II) acetate monohydrate. In the dimeric structure, both copper(II) centres display distorted square pyramidal geometry. The substituted pyridine ligands occupy the apical positions through the pyridyl nitrogen atoms. Complex **I** has been tested for antimicrobial behaviour against a few bacterial strains. Owing to the redox-active nature of copper, complex **I** shows considerable promise as an antimicrobial agent.

**Keywords:** Dicopper(II) tetracaprate, 4-Cyanopyridine, Antimicrobial activity, *Rhizobium leguminosarum*, *Staphylococcus aureus*.

### INTRODUCTION

Copper(II) carboxylates constitute an important class of coordination compounds owing to their wide range of applications [1-3]. A large number of dimeric 'paddle-wheel' type copper(II) carboxylate adducts,  $[\text{Cu}_2(\text{OOCR})_4\text{L}_2]$ , have been reported, where L is an apical ligand which is commonly coordinated *via* a nitrogen or an oxygen atom [4-8]. These complexes have been studied extensively to identify the factors influencing the intramolecular magnetic exchange interactions that occur between the  $\text{Cu}^{2+}$  ions in the paddle-wheel unit [9,10] and also to investigate their catalytic properties, *etc.* [11]. More recently, these complexes have been shown to be useful as secondary building units (SBUs) to form metal organic framework compounds (MOFs) [12].

Such dicopper(II) tetracarboxylates with higher aliphatic carboxylic acids, for example, those with long-chain alkyl groups, can exhibit thermotropic columnar mesomorphic character [13,14]. On the other hand, Kozlevèar *et al.* [15,16]

reported that dimeric complexes with carboxylic acids of different alkyl chain lengths (*e.g.*, caprylic acid and capric acid) are especially interesting owing to their biological activity as in preserving woods from the wood destroying fungi *Trametes versicolor* and *Antrodia vaillantii*. Copper(II) caprylate (*i.e.*, decanoate) complexes with nicotinamide [15], *N,N*-diethyl-nicotinamide [16] and pyridine ligands [17] containing one metal center are also known. A mononuclear copper(II) decanoate complex with ammonia and water as ligands was also reported [18]. To the best of our knowledge, there is just one structurally characterized dimeric copper(II) decanoate with urea ligand known in the literature [19].

From the literature available on this class of copper complexes, it appeared to be a challenge to synthesize and crystallize dinuclear copper(II) complexes bearing the decanoato ligand. In particular, it would be interesting to analyze crystal structure of such a complex containing a substituted pyridine like 4-cyanopyridine, with which the dicopper(II) acetate [8] as well as the benzoate [3] was reported earlier from this laboratory.

In addition to other factors, their solid-state structures are likely to be influenced by significant non-covalent interactions involving the alkyl chains present in the complexes. Moreover, copper is well known to act as a Fenton-like catalyst under intracellular environment and bring about Reactive Oxygen Species (ROS) associated damage to cellular components [20,21]. Copper(II), under the influence of intracellular reductants like glutathione, acts as a catalyst to generate ROS by utilizing cellular  $H_2O_2$  and cause cell death. Also, presence of fatty acid ligands like caprate is expected to enhance lipophilicity of the complex and thereby augment the cellular uptake property of such a metal complex [22,23]. So, it would be worth evaluating the antimicrobial activity of the synthesized copper(II) caprate complex. We have recently reported dicopper(II) tetracaprate complex of 4-methylpyridine ligand [24].

Herein, we describe the synthesis, characterization, crystal structure analysis and antimicrobial properties of a dicopper(II) tetracaprate,  $[Cu_2(\mu-O_2CC_9H_{19})_4(4-CNpy)_2]$  (**I**) (Fig. 1), where 4-CNpy = 4-cyanopyridine. A facile synthetic methodology was adopted to obtain pure samples of dinuclear metal complex. The results of the antimicrobial behaviour of compound **I** against a few clinically relevant pathogenic microbes are also described.

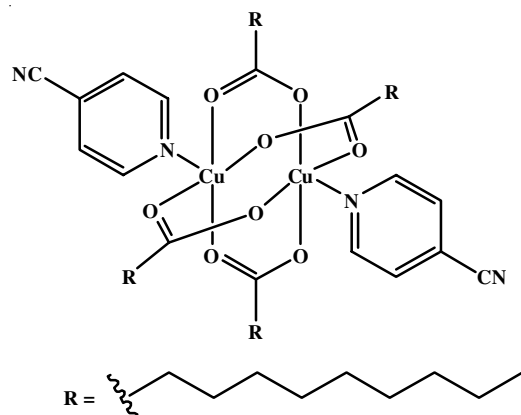


Fig. 1. Schematic representation of complex **I**

## EXPERIMENTAL

The reagents and solvents used in this work were obtained from commercial sources and employed without further purification. Solution phase UV-vis spectra have been recorded using a Shimadzu UV-1800 spectrophotometer. Diffuse reflectance UV-vis-NIR spectra (DRS) have been obtained by using a Hitachi U-4100 spectrophotometer.  $BaSO_4$  powder was used as reference (100% reflectance). From the reflectance data using the Kubelka-Munk function ( $a/S = (1-R)^2/2R$  where  $a$  is the absorption coefficient,  $R$  the reflectance and  $S$  the scattering coefficient), absorption data were calculated from the reflectance data. IR spectra were recorded in an IR Affinity Shimadzu spectrophotometer for KBr pellets. The magnetic susceptibility measurements were carried out at 298 K on a Sherwood Mark 1 magnetic susceptibility balance by Evans Method using  $Hg[Co(NCS)_4]$  as the reference. The susceptibilities were corrected for diamagnetism using Pascal's constants.

**Synthesis of complex  $[Cu_2(\mu-O_2CC_9H_{19})_4(4-CNpy)_2]$  (**I**):** A methanolic solution of  $CuSO_4 \cdot 5H_2O$  (0.499 g, 2 mmol), sodium decanoate (0.777 g, 4 mmol) and 4-cyanopyridine (0.206 g, 2 mmol) was stirred at room temperature for 2 h. This resulted in the formation of a greenish blue product, which was filtered off under suction, washed with small volumes of methanol and dried overnight in a vacuum desiccator over fused  $CaCl_2$ . Yield: 80%. IR (KBr disc,  $cm^{-1}$ ): 3444 (s, br), 3084 (sh), 2924 (s), 2835 (s), 2341(s), 2237(s), 1603 (s), 1423 (s), 1311 (w), 1257 (w), 1222 (w), 1174 (w), 803 (w), 771 (w), 669 (m), 543(sh). UV-vis in acetonitrile ( $\lambda_{max}$ , nm;  $\epsilon$ ,  $mol^{-1} L cm^{-1}$ ): 276 (4000), 380 (40), 667 (120). Effective magnetic moment,  $\mu_{eff} = 1.61$  BM.

The product isolated as above was dissolved in acetonitrile to get greenish homogeneous solution that upon slow evaporation at room temperature gave single crystals suitable for X-ray diffraction after 24 h.

The single crystal X-ray diffraction data of the complexes were recorded using a Bruker Smart Apex II X-ray diffractometer. Suitable crystals were picked up for X-ray crystallographic work by microscopic examination. The intensity data were collected and prepared for crystal structure solution and refinement by standard techniques. The structures were solved by direct methods (SHELXS-97) and standard Fourier techniques, refined on  $F^2$  using full matrix least squares procedures (SHELXL-97) with SHELX-97 [25] incorporated into WinGX [26]. Structural illustrations were drawn using ORTEP-3 for Windows [27] and Mercury [28]. The hydrogen atoms were placed at calculated positions and were included in structure factor calculation using standard procedures for all the structures. The residuals in the crystal structure refinement are relatively high because of thermal disorder. Crystallographic and structure refinement details for the complex **I** are listed in Table-1.

**Antimicrobial activity:** Antimicrobial studies were performed in petri-plates. Bacteria for use were cultured and incubated at 37 °C for 24 h. The sterilized material was kept at a constant laminar air flow (Sensocin/S2000-25MM) [29]. The cultured bacteria were poured on the top of solidified nutrient material and spread over with an L spreader. The test samples of different concentration in DMSO solvent were added to each petri-plate on small filter paper disk. The petri-plates carrying test samples were then finally incubated at 37 °C for 24 h. On completion of incubation period, zone of inhibition diameters were measured by slide calipers in millimeter scale [30,31]. Ofloxacin was used as the standard antibacterial agent.

## RESULTS AND DISCUSSION

The compound,  $[Cu_2(\mu-O_2CC_9H_{19})_4(4-CNpy)_2]$  (**I**) was synthesized in good yield at room temperature by stirring a mixture of  $CuSO_4 \cdot 5H_2O$ , sodium decanoate (caprate) and 4-cyanopyridine in the 1:2:1 molar ratio in 25 mL methanol. The present method for obtaining complex **I** is straightforward and it leads to excellent product purity as judged from a comparison of the infrared spectra of reaction (powder) product and the single crystalline sample. The greenish blue product is insoluble in water but appreciably soluble in organic solvents such as dichloromethane, acetonitrile and dimethyl sulfoxide.

TABLE-1  
CRYSTAL AND STRUCTURE REFINEMENT  
DATA FOR  $[\text{Cu}_2(\mu\text{-O}_2\text{CC}_9\text{H}_{19})_4(4\text{-CNpy})_2]$  (I)

Details	$[\text{Cu}_2(\mu\text{-O}_2\text{CC}_9\text{H}_{19})_4(4\text{-CNpy})_2]$
Empirical formula	$\text{C}_{48}\text{H}_{84}\text{N}_4\text{O}_8\text{Cu}_2$
Formula weight	972.29
Crystal system, space group	Triclinic, P1
Wavelength	0.71073 Å
Unit cell dimensions	$a = 8.8051(7)$ Å, $b = 18.1311(14)$ Å, $c = 19.4007(14)$ , $\alpha = 68.862(4)^\circ$ , $\beta = 78.940(4)^\circ$ , $\gamma = 84.006(4)^\circ$
Volume	$2833.09(11)$ Å <sup>3</sup>
Z, Calculated density	4, 2.05 g/cm <sup>3</sup>
Absorption coefficient	$1.577$ mm <sup>-1</sup>
F(000)	1723.60
Theta range for data collection	$1.10^\circ$ to $30.10^\circ$
Index ranges	$-12 \leq h \leq 12$ , $-25 \leq k \leq 25$ , $-27 \leq l \leq 27$
Reflections collected/unique	60278/16455 [ $R(\text{int}) = 0.1609$ ]
Refinement method	Full-matrix least-squares on $F^2$
Data/restraints/parameters	16455/0/284
Final R indices [ $I > 2\sigma(I)$ ]	$R1 = 0.096$ , $wR2 = 0.268$
R indices (all data)	$R1 = 0.289$ , $wR2 = 0.397$
Goodness-of-fit* on $F^2$	0.876
(Shift/esd) <sub>max</sub>	0.000
$^a \text{Goof} = \sum \{ \sum [w(F_o^2 - F_c^2)^2] / (n-p) \}^{1/2}$ , $^b wR2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_c^2)^2] \}^{1/2}$ , $R1 = \sum  F_o  -  F_c  / \sum F_o$	

We are not aware about previous examples of copper(II) caprates of the type  $[\text{Cu}_2(\mu\text{-O}_2\text{CC}_9\text{H}_{19})_4\text{L}_2]$ , which has been crystallographically characterized. The isolation of the species  $[\text{Cu}_2(\mu\text{-O}_2\text{CC}_9\text{H}_{19})_4(\text{py})_2]$  using a two-step method was reported [17], but it was stated to be unstable due to the loss of pyridine in air at room temperature and only limited physicochemical data on the compound was reported. However, the presently prepared decanoate complex (I) is quite stable in air. Earlier Petriè *et al.* [18] also reported monomeric decanoate complex of copper(II) with ammonia,  $\text{Cu}(\text{O}_2\text{CC}_9\text{H}_{19})_2(\text{NH}_3)_2(\text{H}_2\text{O})$  having the caprate anions as monodentate ligands.

Complex I has been characterized using infrared spectroscopy for KBr pellets in the mid-IR region (4000-450  $\text{cm}^{-1}$ ). The IR spectrum (Fig. 2) is characteristic of the complex under study. The  $\nu_{\text{asym}}(\text{COO}^-)$  stretching vibration appears at 1603  $\text{cm}^{-1}$ , while the  $\nu_{\text{sym}}(\text{COO}^-)$  stretching vibration is seen at 1423  $\text{cm}^{-1}$ . The  $\Delta\nu$  value of 180  $\text{cm}^{-1}$  for these two absorptions indicates symmetrical bridging bidentate coordination mode of

the carboxylato ligand giving rise to a dimeric structure. The  $-\text{C}\equiv\text{N}$  stretching vibration of nitrile group present in 4-CNpy is indicated by a sharp but weak peak at 2237  $\text{cm}^{-1}$  observed for the compound. While this vibration was observed for  $[\text{Cu}_2(\mu\text{-O}_2\text{CC}_6\text{H}_5)_4(4\text{-CNpy})_2]$  at 2238  $\text{cm}^{-1}$ , for  $[\text{Cu}_2(\mu\text{-O}_2\text{C-CH}_3)_4(4\text{-CNpy})_2]$  the same is observed at 2249  $\text{cm}^{-1}$  making it appear as though the nature of the R group in  $[\text{Cu}_2(\mu\text{-O}_2\text{CR})_4(4\text{-CNpy})_2]$  cannot be easily correlated with the energy of  $-\text{C}\equiv\text{N}$  stretching vibration of the nitrile group present at the 4-position in 4-CNpy but in the present instance also the absorption due to the  $-\text{C}\equiv\text{N}$  group suggests that the nitrile group is not coordinated to the metal ion. For free 4-CNpy, this vibration appears at 2237  $\text{cm}^{-1}$ . The structure suggested by the IR data matches well with the X-ray structure for the complex.

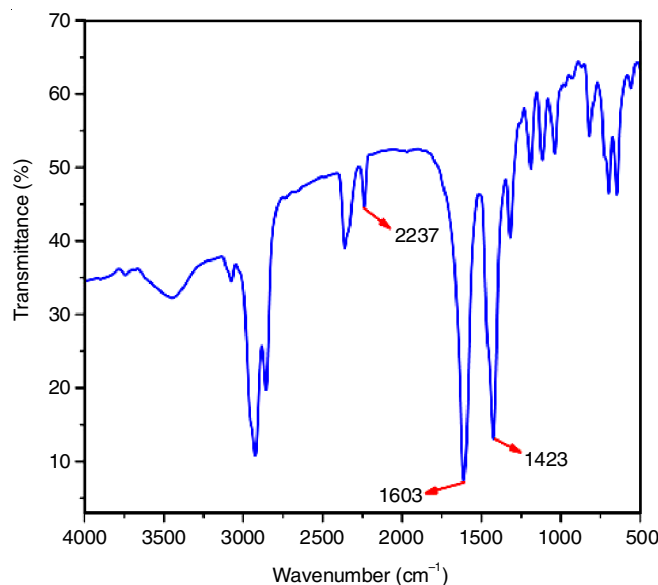


Fig. 2. IR spectrum of complex I

In the UV-visible spectrum for the complex in acetonitrile (Fig. 3b), an expected band due to the ligand field  $d_{x^2-y^2} \rightarrow d_{xz}$ ,  $d_{yz}$  transition occurs at 667 nm gives the characteristic greenish blue colour to the complex [32]. A band at 380 nm signifies the dimeric nature of the complex [33]. The higher energy band at 276 nm is due to the  $\pi \rightarrow \pi^*$  transition of the pyridyl ligand present in the complex. These band positions are nearly the same with those observed in the diffuse reflectance

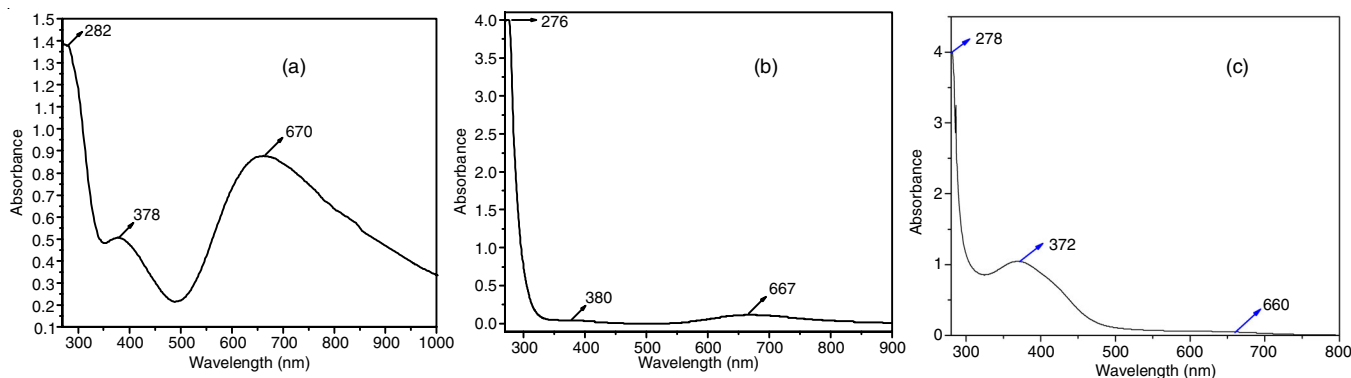


Fig. 3. Electronic absorption spectra of complex I in (a) solid state, (b) acetonitrile and (c) DMSO

spectrum of the complex recorded in the solid state, but the band shapes and intensities in the solid (Fig. 3a) and solution phases show significant differences in the spectra recorded in the two phases. Band intensities are also significantly different in the spectrum recorded in DMSO medium (Fig. 3c). These results suggest that solvents influence the local structure of the Cu(II) coordination spheres of dimeric complex significantly in the solution phase.

The room temperature magnetic moment ( $\mu_{\text{eff}}$ ) of complex **I** is 1.61 BM. The  $\mu_{\text{eff}}$  value is less than the expected spin-only value of 1.70-2.20 BM for the  $d^9$ -Cu<sup>2+</sup> system. This may be due to the presence of antiferromagnetic coupling which is typical for paddle-wheel type dicopper(II) carboxylate complexes [34,35]. The  $\mu_{\text{eff}}$  value of complex **I** compares well with the corresponding reported [3] value of 1.68 BM for the complex [Cu<sub>2</sub>( $\mu$ -O<sub>2</sub>CC<sub>6</sub>H<sub>5</sub>)<sub>4</sub>(4-CNpy)<sub>2</sub>] which differs from complex **I** only in terms of the carboxylate ligands. The small difference may be due to the alkyl and aryl groups present in bridging carboxylate ligands in two complexes.

The crystal structure of the title compound, [Cu<sub>2</sub>( $\mu$ -O<sub>2</sub>C-C<sub>9</sub>H<sub>19</sub>)<sub>4</sub>(4-CNpy)<sub>2</sub>] (**I**) has been determined by the single crystal X-ray diffraction technique. An ORTEP view of the molecular structure of complex **I** is shown in Fig. 4. While the crystallographic and structure refinement data are presented in Table-1, selected bond distances and angles for the molecule are given in Table-2. The species has the familiar dinuclear ‘paddle-wheel’ structure wherein the two Cu centres are bridged by four decanoate ligands with the two apical positions occupied by the two 4-cyanopyridine ligands being very similar to that observed in acetate [8] and benzoate [3] species having 4-CNpy as the apical ligand. The centre of symmetry is the midpoint of the Cu...Cu axis through which the two copper atoms are related. The Cu...Cu separation of 2.598(3) Å in complex **I** is very close to the corresponding distance of 2.600(1) Å in [Cu<sub>2</sub>( $\mu$ -O<sub>2</sub>CCH<sub>3</sub>)<sub>4</sub>(4-CNpy)<sub>2</sub>] [8], but is considerably shorter than the Cu...Cu distance of 2.6461(6) Å in [Cu<sub>2</sub>( $\mu$ -O<sub>2</sub>C-C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>(4-CNpy)<sub>2</sub>] [3]. The +I effect of the alkyl groups on the bridging carboxylate ligands makes more electrons available

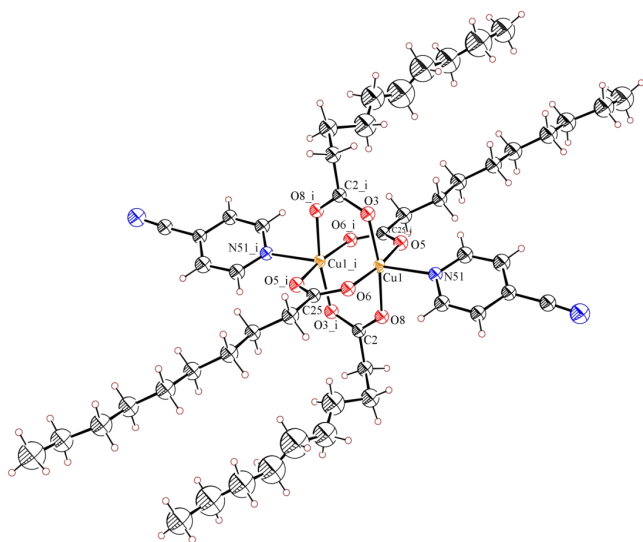


Fig. 4. An ORTEP representation of complex **I**

TABLE-2  
SELECTED BOND LENGTHS (Å) AND  
ANGLES (°) FOR [Cu<sub>2</sub>( $\mu$ -O<sub>2</sub>C-C<sub>9</sub>H<sub>19</sub>)<sub>4</sub>(4-CNpy)<sub>2</sub>] (**I**)

Distances (Å)			
Cu(1)-O(3)	1.957(9)	Cu(2)-O(4)	1.954(10)
Cu(1)-O(6)	1.961(9)	Cu(2)-O(8)	1.963(10)
Cu(1)-O(8)	1.965(9)	Cu(2)-O(7)	1.967(9)
Cu(1)-O(5)	1.964(10)	Cu(2)-O(1)	1.977(10)
Cu(1)-N(51)	2.187(12)	Cu(2)-N(50)	2.176(10)
Cu(1)-Cu(1)#1	2.598(3)		
Angles (°)			
O(5)-Cu(1)-O(3)	88.8(4)	O(4)-Cu(2)-O(8)	91.9(4)
O(5)-Cu(1)-O(6)	168.7(4)	O(4)-Cu(2)-O(7)	87.3(4)
O(3)-Cu(1)-O(6)	89.8(4)	O(8)-Cu(2)-O(7)	168.6(4)
O(5)-Cu(1)-O(8)	90.8(4)	O(4)-Cu(2)-O(1)	169.2(4)
O(3)-Cu(1)-O(8)	169.3(4)	O(8)-Cu(2)-O(1)	87.9(4)
O(6)-Cu(1)-O(8)	88.5(4)	O(7)-Cu(2)-O(1)	90.7(4)
O(5)-Cu(1)-N(51)	92.4(4)	O(4)-Cu(2)-N(50)	93.2(4)
O(3)-Cu(1)-N(51)	99.7(4)	O(8)-Cu(2)-N(50)	91.7(4)
O(6)-Cu(1)-N(51)	98.8(4)	O(7)-Cu(2)-N(50)	99.7(4)
O(8)-Cu(1)-N(51)	91.0(4)	O(1)-Cu(2)-N(50)	97.6(4)
#1, -x+1,-y+1,-z			

in overlapping orbitals on Cu<sup>2+</sup> ions to bring the metal ions closer to one another.

Copper(II) carboxylates with fatty acids having long-chain alkyl groups displaying dimeric structures of paddle-wheel geometry are rare and indeed, only structures with pyridine [36], nicotinamide [15], *N,N*-diethylnicotinamide [16] and urea [19] as apically positioned ligands have been reported so far. A fascinating feature of the present crystal structure is the disposition of the fatty acid ligands about one another. Although one pair of the bridging carboxylates is oriented perpendicular to the other pair, the alkyl chains of all four ligands however lie parallel to one another.

**Antimicrobial activity:** Microbial strains are increasingly acquiring resistance to many existing drugs and therefore, it has become an urgent need to look for newer alternatives [37]. Metal-based antibiotics, owing to their redox-active nature, flexible coordination geometry and maneuverability, could prove to be attractive therapeutic options [38,39]. Antimicrobial property of copper(II) complexes have long been known in the history of mankind [40]. A number of copper complexes have previously been studied for their potential antimicrobial properties [40]. The complex [Cu<sub>2</sub>( $\mu$ -O<sub>2</sub>CC<sub>9</sub>H<sub>19</sub>)<sub>4</sub>(4-CNpy)<sub>2</sub>] (**I**) synthesized herein is a dinuclear species that can act synergistically towards causing efficient cell death. Moreover, it holds fatty acid ligands for enhanced cellular penetration and planar aromatic 4-CNpy ligands for better interaction to DNA and proteins. So, complex **I** was evaluated for its antimicrobial activity.

The synthesized copper(II) complex was tested for antibacterial activity against Gram-positive bacteria (*Rhizobium leguminosarum*, MTCC-99 and *Staphylococcus aureus*, MTCC-3160) as well as Gram-negative bacteria (*Escherichia Coli*, MTCC-448) using disk diffusion method at four different concentrations in DMSO solvent [28,29,41]. The antibacterial activity of the complex measured at different concentrations were compared with the standard antibacterial agent ofloxacin

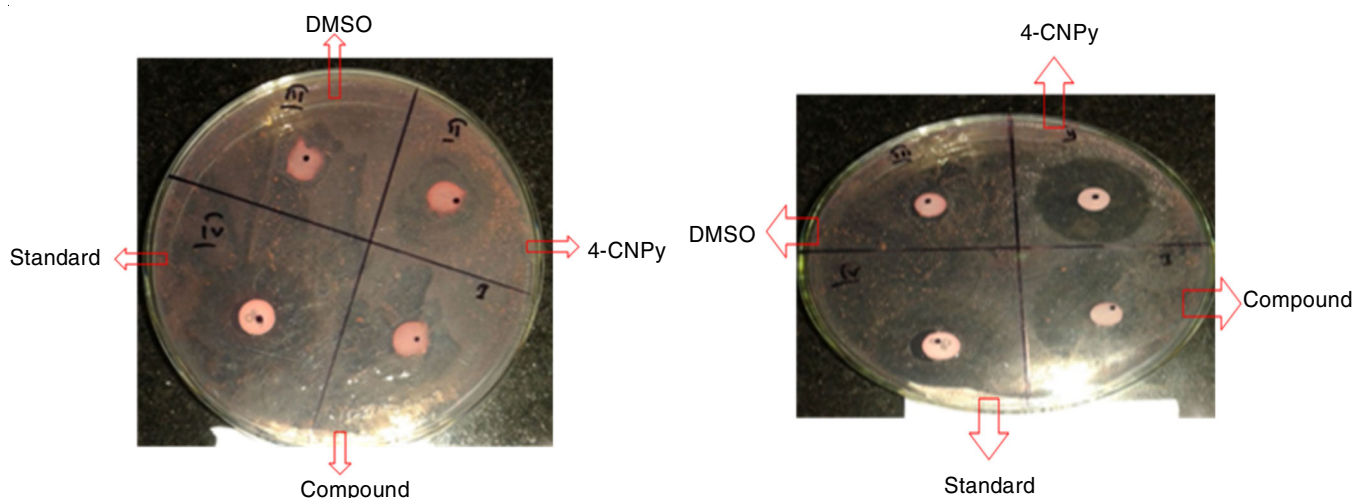


Fig. 5. Antimicrobial activity of complex I on (a) *Staphylococcus aureus* MTCC-3160 and (b) *Rhizobium leguminosarum* MTCC-99

(Fig. 5). A maximum growth inhibition of 12 mm was observed at a concentration of 550  $\mu\text{g/mL}$  (Fig. 6). The results were compared with standard antibacterial ofloxacin and % activity index were calculated. The result (Table-3) showed that the complex is moderately active for Gram-positive bacteria at higher concentration but inactive in case of Gram-negative bacteria. The corresponding percentage activity indices of the complex I for MTCC-3160 and MTCC-99 are 58.33 and 66.66, respectively. This could be because of differential interaction of the complexes to the lipopolysaccharides on the bacterial capsule. Contrary to our expectation, the moderate activity of the complex could be attributed to its structural rigidity. Also, the dinuclear structure and presence of long-chain fatty acid ligands might have restricted the access of the metal centers by the incoming oxidants and reductants inside cells. These effects in combination might have limited the potential of complex I as an antimicrobial agent. Nonetheless, the complex was found to have higher activity than the 4-cyanopyridine ligand alone implying that there is indeed an enhancement in efficacy upon complexation. A comparison of the antimicrobial activities of complex I, 4-cyanopyridine ligand and the standard is shown in Table-4. The carboxylic acid ligand was not used in this study since fatty acids are present in abundance in biological systems and usually non-toxic.

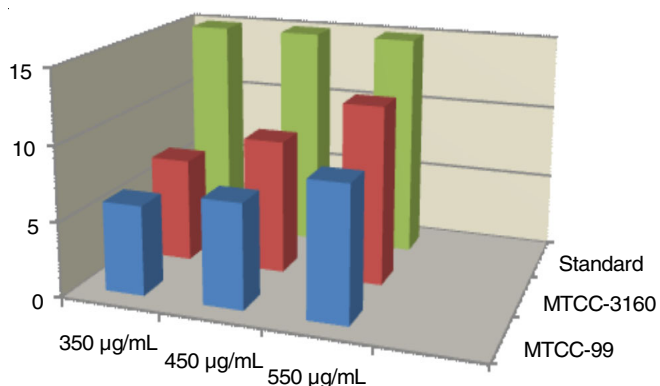


Fig. 6. Comparison of the antibacterial activities of complex I on MTCC-99 and MTCC-3160 with standard ofloxacin at MIC

TABLE-3  
PERCENTAGE ACTIVITY INDEX AT THE DIFFERENT CONCENTRATIONS FOR COMPLEX I

Organism	% Inhibition Index
MTCC-3160	$[7/12] \times 100\% = 58.33\%$
MTCC-99	$[6/9] \times 100\% = 66.66\%$

TABLE-4  
MEASUREMENTS (mm) OF THE INHIBITION ZONES USING VARIOUS TEST ARTICLES

Compound	Conc. ( $\mu\text{g/mL}$ )	MTCC-3160	MTCC-99	MTCC-448
DMSO	250	7	7	7
	350	7	7	7
	450	7	7	7
	550	7	7	7
2. 4-CNPpy	250	6	6	6
	350	7	7	7
	450	8	8	8
	550	9	9	9
Standard (Ofloxacin)	250	15	15	15
	350	15	15	15
	450	15	15	15
	550	15	15	15
Complex I	250	5	5	< 5
	350	7	6	< 5
	450	9	7	< 5
	550	12	9	< 5

## Conclusion

In summary, the present investigation has made it possible to develop a facile method to prepare a dimeric copper(II) complex,  $[\text{Cu}_2(\mu\text{-O}_2\text{CC}_9\text{H}_{19})_4(4\text{-CNpy})_2]$  (I), of a long-chain fatty acid ligand having the paddle wheel geometry. In spite of the presence of long-chain alkyl group, it has been made possible to crystallize the complex and determine its molecular structure unequivocally. The antimicrobial property of the complex has been evaluated and it has been found to be active against both Gram-positive and Gram-negative bacteria. In particular, the ease of synthesis, stability and solubility behaviour makes complex I an ideal candidate for biological applications. This

study opens up new avenues towards the design and optimization of such complexes as potent antimicrobials.

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### CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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