

# Synthesis, characterisation and microbial studies of [bis(1,10-phenanthroline) (ethylenediamine) copper(II)] diperchlorate and its bromide analogue

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## ABSTRACT

Two new tris-chelate-complexes have been synthesized and characterized with elemental and spectroscopic methods. IR and thermal studies correlate with the structures of the complex in the solid state. The structure of  $[\text{Cu}(\text{en})(\text{phen})_2] \cdot 2\text{ClO}_4^-$  was determined with X-ray data using single crystal X-ray diffractometer while the molecular structure of  $[\text{Cu}(\text{en})(\text{phen})_2] \cdot 2\text{Br}^- \cdot 2\text{Phen} \cdot 8\text{H}_2\text{O}$  was deduced from the used characterization methods.  $[\text{Cu}(\text{en})(\text{phen})_2] \cdot \text{ClO}_4^-$  crystallizes as orthorhombic with space group Pbcn. Both complexes have distorted octahedral geometry. Microbial activities of these complexes against *Staphylococcus aureus*, *Escherichia coli*, *Pseudomonas aeruginosa*, *Streptococcus pyogenes*, *Candida albicans*, and *Aspergillus niger* were also reported.

**Keywords:** Tris-Chelate Complexes; X-Ray Data; Electronic Spectra; Microbial Studies

## 1. INTRODUCTION

Copper(II) ions and its metal complexes have continued to attract attention of coordination chemists due to its various interesting structural features, its usefulness as models of the active centers of various metallo-enzymes, magnetic, electronic, catalytic and biological properties [1-3].

In recent times, Copper(II) complexes from various ligand systems such as 1,10-phenanthroline and 1,2-diaminoethane have been synthesized and characterized with the aim of gaining a better understanding of the chemistry of copper and the various ligands in different environments.

We have previously described [4] the synthesis and spectral studied of tris chelate of mixed-ligand complexes of copper(II) ion of nitrate and that of chloride with 1,2-diaminoethane and 1,10-phenanthroline in which

the H-bonded network of lattice water molecules and the anions in both compounds are quite different from one another. The  $\text{NO}_3^-$ ,  $\text{H}_2\text{O}$ , H-bonded network has a 1D chain structure while  $\text{Cl}^-$ ,  $\text{H}_2\text{O}$  network has a 3D structure. The change in the structure is due to the change in the size of anions as  $\text{Cl}^-$  ions allow very close H-bonding because of its smaller size compare to  $\text{NO}_3^-$ . We are considering the effect of  $\text{ClO}_4^-$  ion upon these supra-molecular structures. The activities of these two complexes on micro-organisms such as *Staphylococcus aureus*, *Escherichia coli*, *Pseudomonas aeruginosa*, *Streptococcus pyogenes*, *Candida albicans*, and *Aspergillus niger* being the micro-organisms that affect man and plants were also carried out.

In this paper, we therefore report the synthesis, characterization, structure, and microbial studies of  $[\text{Cu}(\text{en})(\text{phen})_2](\text{ClO}_4)_2$  (1) and  $[\text{Cu}(\text{en})(\text{phen})_2]2\text{Br} \cdot 2\text{Phen} \cdot 8\text{H}_2\text{O}$  (2).

## 2. EXPERIMENTAL

All the chemicals used, were analytical reagent from commercial sample. They were procured from Fluka and Merck. The reagents were used without further purification.

### 2.1. Synthesis of $[\text{Cu}(\text{en})(\text{phen})_2](\text{ClO}_4)_2$ (1)

$\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  (0.370 g, 1 mmol) and 1,2-diaminoethane (0.20 mL, 2.92 mmol) were dissolved in 25 mL water and heated to  $80^\circ\text{C}$  for 10 mins with stirring. To this, 5 mL ethanolic solution of 1,10-phenanthroline (0.198 g, 1.00 mmol) was added and stirred for another 5 mins and the solution was filtered. There was blue precipitate. The precipitate was recrystallized with methanol. Greenish blue block shaped X-ray type crystals were obtained after four days. Yield: 0.3576 g (52.35%). Anal. calcd. for  $\text{C}_{26}\text{H}_{24}\text{CuN}_6\text{Cl}_2\text{O}_8$ :

C 45.73, H, 3.54; N, 12.31, Found: C 45.72; H, 3.50; N, 12.27.

IR (KBr disk,  $\text{cm}^{-1}$ ): 3393, 3312, 2953, 2853, 1622,

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1585, 1507, 1094, 843, 728, 422.

## 2.2. Synthesis of

### [Cu(en)(phen)<sub>2</sub>]·2Br<sup>-</sup>·2(phen)·8H<sub>2</sub>O (2)

The procedure was similar to that of 1, except for the use of CuBr<sub>2</sub>, (0.223 g, 1 mmole). Blue crystals in the form of hexagonal shaped were obtained from the filtrate after four days. Similar crystals were obtained when the synthesis was carried out with the reagent in ratio 1:1:4 of Cu:en:phen in order to maximize the yield. Yield: 0.1857 g (64.68%). Anal. calcd. for C<sub>50</sub>H<sub>56</sub>Br<sub>2</sub>CuN<sub>10</sub>O<sub>8</sub>: C, 52.29; H, 4.91; N, 12.19 Found: C, 52.19; H, 4.88; N, 12.14.

IR (KBr disk, cm<sup>-1</sup>): 3403, 3226, 3093, 1623, 1585, 1506, 1420, 846, 727, 420.

## 2.3. Physical Measurements

IR spectra were recorded using KBr discs on a Perkin Elmer, GX-FTIR spectrometer in the range 4000 - 400 cm<sup>-1</sup>. Elemental analysis for C, H and N was performed on a Perkin-Elmer, Series II, 2400. Electronic spectra measurements were obtained using a Shimadzu UV-3101 PC spectrophotometer. Thermogravimetric analysis was done using Mettler Toledo.

## 2.4. X-Ray Crystallography

X-ray data were collected on a Bruker SMART APEX CCD X-ray diffractometer, using graphite-monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) at 298 K. Data were reduced using SAINTPLUS [5] and a multi-scan absorption correction using SADABS [6] was performed. The structures were solved by direct method using SHELXS-97 and full-matrix least-square refinement was carried out using SHELXL-97. [7] All ring hydrogen atoms were assigned on the basis of geometrical considerations and were allowed to ride upon the respective carbon atoms. Drawings were made using Mercury [8].

## 2.5. Antimicrobial Screening

The antimicrobial screening was performed by paper diffusion method. The activities were expressed in terms of millimeter (mm) by diameter of zone of inhibition. Ampicilline, Chloramphenicol, Ciprofloxacin and Norfloxacin were used as standard drugs for bacteria. Greseofulvin and Nystatin were used for fungi.

### 2.5.1. Microorganisms Used

The following common standard strains were used for screening of antibacterial and antifungal activities. The strains, listed below, were procured from Institute of Microbial Technology, Chandigarh India. The bacteria used are 1) *Staphylococcus aureus* MTCC 96; 2) *Es-*

*cherichia coli* MTCC 443; 3) *Pseudomonas aeruginosa* MTCC 1688; and 4) *Streptococcus pyogenes* MTCC 442, while fungi used are 5) *Candida albicans* MTCC 227; and 6) *Aspergillus niger* MTCC 282.

### 2.5.2. Culture Media

Nutrient agar medium was prepared by dissolving 7.0 g of agar powder in 250 mL of distilled water in a conical flask (for bacteria). Potato dextrose agar medium was prepared by dissolving 9.75 g of potato dextrose agar powder in 250 mL of distilled water in a conical flask (for fungi). The conical flask was capped with cotton wool and aluminium foil and then sterilized in an autoclave for 15 minutes at 121°C.

Using an inoculate wire loop, the micro organisms were collected from slant cultures of all the different micro-organisms and were inoculated separately into fresh sterile nutrient broths for bacteria and the resulting cultures were incubated at 37°C for 18 hrs and at room temperature to obtain new cultures of bacteria respectively.

### 2.5.3. Zone of Inhibition

The zone of inhibition of the complexes was carried out by dipping sterile paper disc into a range of metal complexes solutions using sterile forceps. These were then carefully and aseptically laid on the media flooded with cultures of test organisms. The concentrations used were 250, 100, 50, 25 and 5  $\mu\text{g/mL}$  and finally, the Petri plates were incubated for 26 - 30 hrs, at 28°C  $\pm$  2°C. The zone of inhibition was measured in millimetre. The results are shown in **Table 3** for bacteria and **Table 4** for the fungi.

## 3. RESULTS AND DISCUSSION

### 3.1. Synthesis

The two complexes were prepared by a similar method of synthesis using the reagents in molar ratio of 1:3:1 of Cu<sup>2+</sup>:en:phen. For the complex 2 it was resynthesized in ratio 1:1:4 to improve its yield. Greenish blue good crystals were isolated from the precipitate of 1 after re-crystallization from methanol while navy blue crystals can be isolated directly from the filtrate of 2 but its structure could not be refined. The complexes are non hygroscopic and thermally stable. They were obtained in fairly good yield and the C, H and N analysis calculated agrees with the experimental value for the two complexes. The anions of the complexes are different in that there are no free phenanthroline and lattice water in 1 as found in 2. This may be due to dissolution of the free phenanthroline and water during recrystallisation of precipitate of 1. The complexes are soluble in methanol, ethanol, DMF, DMSO, acetonitrile and water.

### 3.2. Infrared Spectra

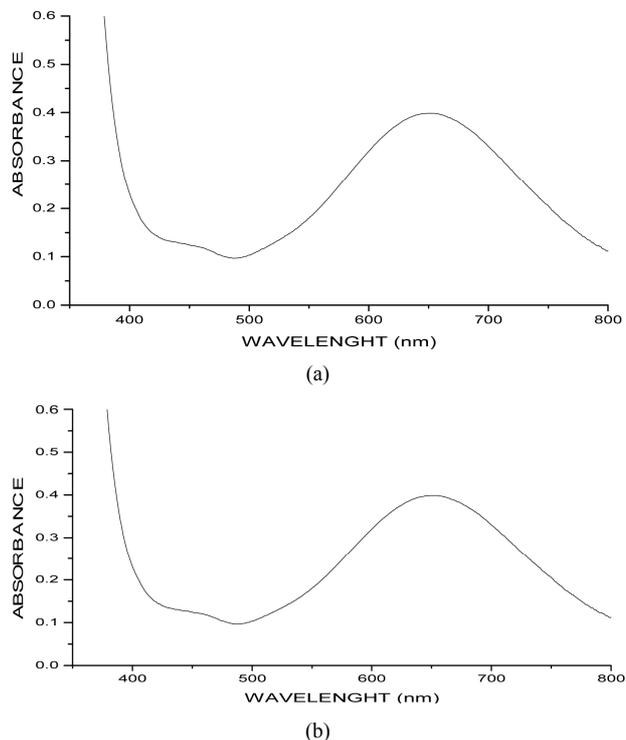
The two complexes have almost similar IR absorption bands. Broad bands for  $\nu$  ( $\text{NH}_2$ ) stretching vibration in 1,2-diaminoethane appeared at  $3393\text{ cm}^{-1}$ ,  $3312\text{ cm}^{-1}$  for complex 1. Both asymmetric and symmetric  $\nu$  (C-H) bands in 1,2-diaminoethane could be seen at  $2953\text{ cm}^{-1}$  and  $2853\text{ cm}^{-1}$ .  $\text{NH}_2$  deformation bands appeared at  $1585\text{ cm}^{-1}$ , while aromatic ring stretching vibration for phenanthroline occurs at  $1507\text{ cm}^{-1}$ .  $\text{ClO}_4$  band is observed at  $1094\text{ cm}^{-1}$ . Complex 2 also has similar bands as found in 1,  $\nu$  (O-H), from uncoordinated water and  $\nu$  ( $\text{NH}_2$ ) stretching band from 1,2-diaminoethane could be seen at  $3403\text{ cm}^{-1}$  and  $3226\text{ cm}^{-1}$  respectively while  $\nu$  (C-H) aromatic stretching vibrational band could be seen at  $3093\text{ cm}^{-1}$ , aromatic ring stretching occurred at  $1506\text{ cm}^{-1}$  for the coordinated and at  $1623\text{ cm}^{-1}$  for the uncoordinated phenanthroline rings.  $\text{NH}_2$  deformation band is found at  $1585\text{ cm}^{-1}$  [9]. The IR result shows that the two complexes coordinated via the N atoms from the 1,2-diaminoethane and from the N atoms of the aromatic rings. Molecules of water also present in complex 2 with free phenanthroline molecules. This is also confirmed from the C, H, N analysis. Cu-N band could not be observed for phenanthroline as its absorb at relatively low frequency [9]. The  $\nu$  (Cu-N) from 1,2-diaminoethane for complexes 1 and 2 are  $422$  and  $420\text{ cm}^{-1}$  respectively.

### 3.3. Electronic Spectra

The electronic absorption spectra of both complexes were measured in methanol solution.  $[\text{Cu}(\text{en})(\text{phen})_2](\text{ClO}_4)_2$  absorb at  $15.3 \times 10^3\text{ cm}^{-1}$  ( $652\text{ nm}$ ), while  $[\text{Cu}(\text{en})(\text{phen})_2]\text{Br}_2 \cdot 2\text{phen} \cdot 8\text{H}_2\text{O}$  absorb at  $15.3 \times 10^3\text{ cm}^{-1}$  ( $646\text{ nm}$ ). (Figures 1(a) and (b)). All the four d-d transitions of the rhombic distorted octahedral copper(II) chromophore may be placed within the broad envelop of the observed band. The energy band in this position for the two complexes is typically expected for a rhombic distorted octahedral configuration and may be assigned to  ${}^2\text{E}_g \rightarrow {}^2\text{T}_{2g}$  transition [10].

### 3.4. Thermal Gravimetric Analysis

Thermal gravimetric studies and differential thermal analysis were carried out on the complexes in the temperature range of  $50^\circ\text{C}$  to  $800^\circ\text{C}$  at a heating rate of  $10^\circ\text{C}/\text{min}$ . The measurements were done primarily to determine the composition of materials and to predict their thermal stability and also to determine extent of weight loss or gain due to decomposition, oxidation or dehydration. The thermal analysis shows that there are two broad endothermic peaks in the differential thermal analysis curve of the bromide analogue which is typical of dehydration reaction [11], whereas the perchlorate analogue showed three sharp endothermic peaks which shows changes in the crystalline or fusion process in the complex. The two



**Figure 1.** (a) UV-Visible spectra of  $[\text{Cu}(\text{en})(\text{phen})_2]_2\text{phen} \cdot 2\text{Br} \cdot 8\text{H}_2\text{O}$ ; (b) UV-Visible spectra of  $[\text{Cu}(\text{en})(\text{phen})_2] \cdot 2\text{ClO}_4^-$ .

complexes showed no weight loss up to  $170^\circ\text{C}$  indicating the absence of uncoordinated water molecules in the complexes. The bromo complex decomposes in two endothermic peaks the first step occurs from  $55^\circ\text{C} - 300^\circ\text{C}$  and this corresponds to the loss of the eight  $\text{H}_2\text{O}$  molecules and second from  $300^\circ\text{C} - 500^\circ\text{C}$  represent the decomposition of the organic part. The perchlorate decomposes with two peaks the first from  $150^\circ\text{C} - 250^\circ\text{C}$  then to  $350^\circ\text{C}$ . The remaining organic part decomposes with the peak occurring from  $350^\circ\text{C} - 650^\circ\text{C}$ .

### 3.5. Structure of $[\text{Cu}(\text{en})(\text{phen})_2](\text{ClO}_4^-)_2$ (1)

The molecular structure of complex 1 was established by single crystal X-ray study. The crystal system in 1 is orthorhombic with space group Pbcn (Table 1). The coordination sphere of copper consists of one 1,2-diaminoethane and two phenanthroline molecules with distorted octahedral geometry. The equatorial plane of hexa coordinated copper consists of both nitrogen atoms of 1,2-diaminoethane molecule and nitrogen from the two phenanthroline molecules (Figure 2(a)). Two perchlorate anions also present in the lattice, there are no water molecules. The equatorial distances are Cu1-N1:  $2.370(2)$ , Cu1-N2:  $2.036(2)\text{ \AA}$  and Cu1-N4:  $2.367(2)\text{ \AA}$  and Cu1-N5:  $2.036(2)\text{ \AA}$ , while the axial distances are Cu1-N3:  $2.054(2)\text{ \AA}$  and Cu1-N6:  $2.042(2)\text{ \AA}$  compared to the bond distances of its nitrate and chloride ions analogy

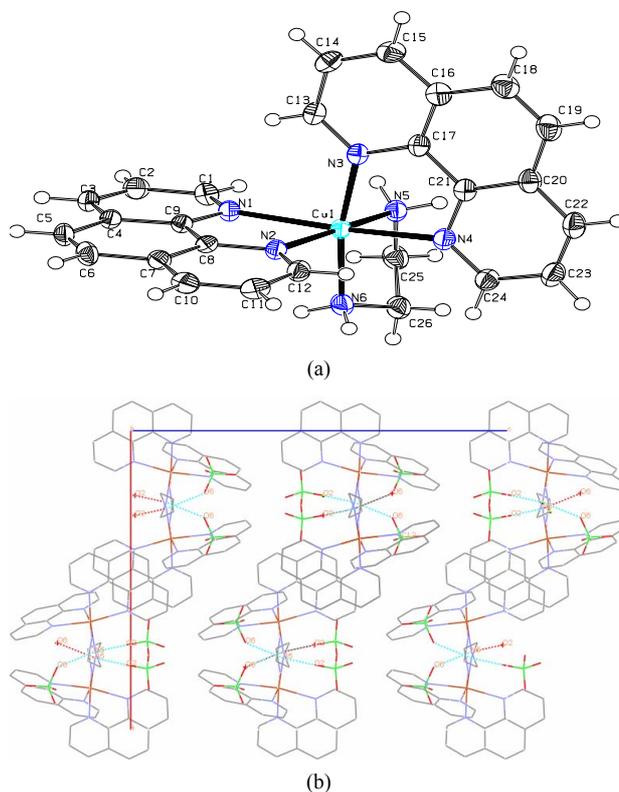
**Table 1.** Crystallographic data for  $[\text{Cu}(\text{en})(\text{phen})_2] \cdot (\text{ClO}_4)_2$  (1).

1	
Formula	$\text{C}_{26}\text{H}_{24}\text{CuN}_6\text{Cl}_2\text{O}_8$
Formula weight	682.95
Colour	Blue
Crystal system	Orthorhombic
$a$ (Å)	18.4895 (12)
$b$ (Å)	13.2926 (9)
$c$ (Å)	22.9599 (15)
$\alpha$ (°)	90.00
$\beta$ (°)	90.00
$\gamma$ (°)	90.00
$V$ (Å <sup>3</sup> )	5642.9 (6)
$Z$	8
Space group	Pbcn
$T$ (°C)	110 (2)
$\lambda$ (Å)	0.71073
$D_{\text{calcd}}$ (g·cm <sup>-3</sup> )	1.608
$\mu$ (mm <sup>-1</sup> )	1.025
$F(000)$	2792
Crystal size (mm)	0.45 × 0.35 × 0.25
$\theta$ range for data collection (°)	1.80 - 28.29
$h/k/l$	-23, 24/-17, 17/-30, 13
Reflections collected/unique [ $R_{\text{int}}$ ]	32270/5695/0.0459
Completeness to $2\theta = 25.00$ (%)	99.7
Refinement method	Full-matrix least-squares on $F^2$
Data/restraints/parameters	5695/0/388
Goodness of fit on $F^2$	1.049
Final $R$ indices [ $I > 2\sigma(I)$ ]	
$R1$	0.0459
$wR2$	0.1200
$R$ indices (all data)	
$R1$	0.0548
$wR2$	0.1269

[4], which have Cu-N<sub>1</sub>: 2.390 (2), Cu-N<sub>2</sub> 2.0608 (17), Cu-N<sub>3</sub>: 2.0210 (18) Å and 2.406 (3), 2.071 (3), 2.028 (3) Å respectively. Selected geometrical parameters are presented in **Table 2**. The packing diagram for 1 showing hydrogen bonding interactions as viewed along the  $b$ -axis is shown in **Figure 2(b)**. There is H-bonding interaction between the hydrogen of N5 from 1,2-diaminoethane and from O<sub>2</sub> and O<sub>6</sub> from perchlorate ions [N-H-O<sub>2</sub> = 2.936 Å, N-H-O<sub>6</sub>: 3.064] Å.

### 3.6. Biological Activities

The antibacterial and antifungi activities of the com-



**Figure 2.** (a) ORTEP diagram depicting the cationic part of the copper complex with atom numbering scheme (50% probability factor for the thermal ellipsoids); (b) Packing structure of complex 1 showing the H-bonding between diaminoethane-H and O from perchlorate as viewed along the  $b$ -axis.

**Table 2.** Bond lengths and bond angles for  $[\text{Cu}(\text{en})(\text{phen})_2] (\text{ClO}_4)_2$ .

Bond Lengths (Å)		Bond Angles (°)	
Cu1-N1 2.370 (2)	N2-Cu1-N5 173.02 (8)	C25 N5 Cu1 109.74 (16)	
Cu1-N2 2.036 (2)	N2 Cu1 N6 92.92 (8)	C25 N5 H5A 109.7 (16)	
Cu1-N3 2.054 (2)	N5 Cu1 N6 83.65 (9)	Cu1 N5 H5A 109.7 (16)	
Cu1-N4 2.367 (2)	N2 Cu1 N3 92.33 (8)	C25 N5 H5B 109.7 (16)	
Cu1-N5 2.036 (2)	N5 Cu1 N3 92.00 (8)	Cu1 N5 H5B 109.7 (16)	
Cu1-N6 2.042 (2)	N6-Cu1-N3 169.91 (8)	H5A N5 H5B 108.2 (16)	
O1-Cl1 1.428 (2)	N2 Cu1 N4 96.53 (8)	C26 N6 Cu1 107.89 (16)	
O2-Cl1 1.4388 (19)	N5 Cu1 N4 89.82 (8)	C26 N6 H6A 110.1 (16)	
O3-Cl1 1.434 (2)	N6-Cu1-N4 94.60 (8)	Cu1 N6 H6A 110.1 (16)	
O4-Cl1 1.412 (2)	N3 Cu1 N4 76.23 (8)	C26 N6 H6B 110.1 (16)	
O5-Cl2 1.429 (3)	N2 Cu1 N1 75.96 (7)	H6A N6 H6B 108.4 (16)	
O6-Cl2 1.449 (3)	N5 Cu1 N1 98.08 (8)	N1 C1 C2 123.6 (2)	
O7-Cl2 1.409 (3)	N6 Cu1 N1 92.84 (8)	N1 C1 H1 118.2 (2)	
O8-Cl2 1.422 (2)	N3 Cu1 N1 96.79 (8)	C2 C1 H1 118.2 (2)	
	N4 Cu1 N1 169.69 (7)	C3 C2 C1 118.6 (2)	

plexes can easily be observed from **Tables 3** and **4** and from the bar chart as seen in **Figures 3-8**. The data were obtained for the bacteria and fungi which cause diseases in man and plants with that of the standard drugs nor-

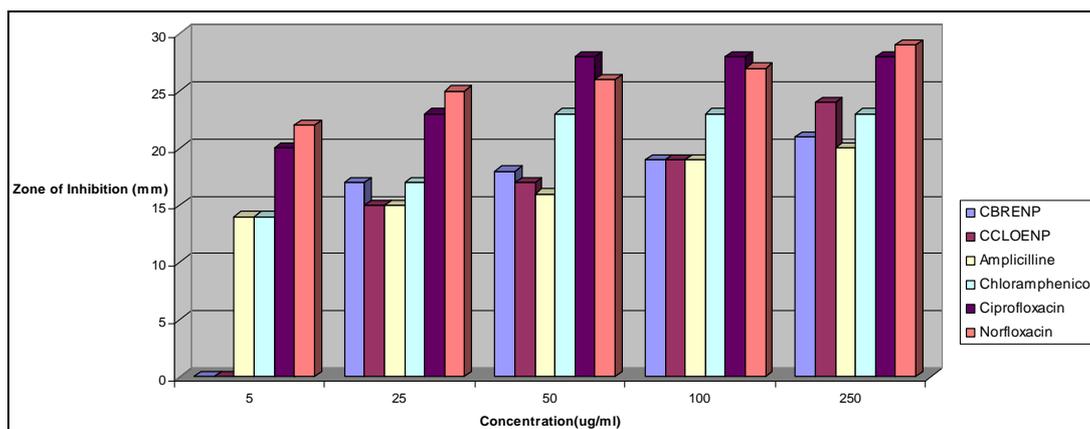
mally used for these micro-organisms. From the results it can be observed that at higher concentrations the perchlorate analog have higher zone of inhibitions than their bromide counterpart when tested against the following bacteria: *E. coli*, *P. aeruginosa*, *S. aureus* and *P. pyogenes* compared to the zone of inhibitions observed with known antibiotics like Ampicillin and Chloralphenicol (Figures 3-6). The zones of inhibition are however lower when the values are compared to other antibiotics like Ciproflaxin and Norflaxacin. In general the results indicate that the complexes have potential and promising

activity. Further investigations may however be required to illustrate the mechanisms by which the complexes exhibit its antibacterial effect [12].

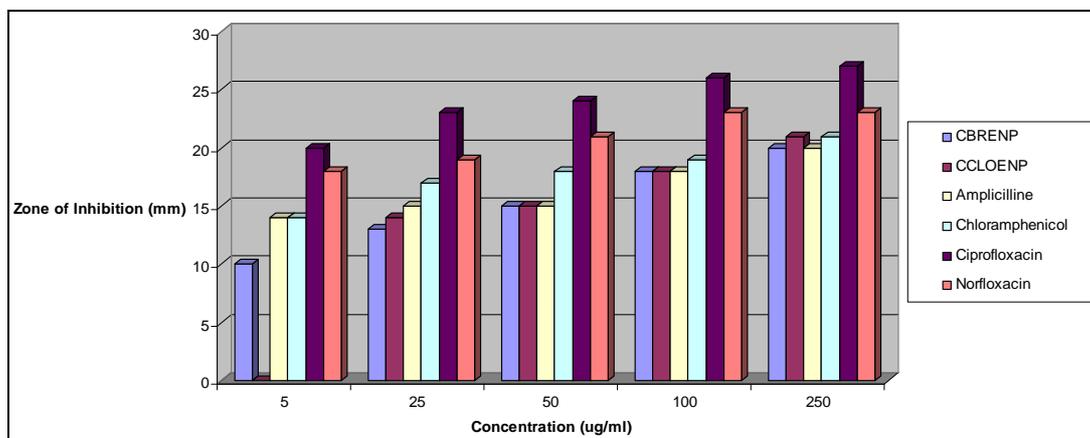
Similarly, the perchlorate complex was more potent than the bromide complex as shown by the results of the zone of inhibition observed when tested with *A. niger* and *C. albicans* (Figures 7 and 8). Though the zones of inhibitions observed for standard antifungal drugs like Greseofulvin and Nystatin are higher than the ones observed for the complexes they are significant enough to indicate some antifungal properties inherent in the complexes.

**Table 3.** Zone of inhibition of complexes and the standard drugs against the bacteria (mm).

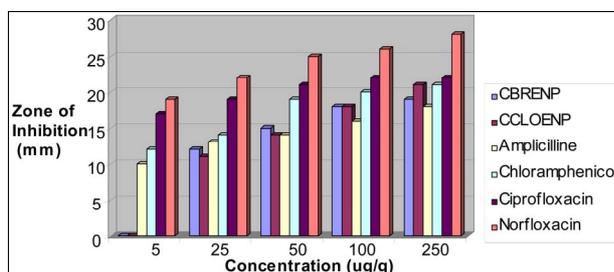
Bacteria species	<i>E. coli</i> MTCC 443					<i>P. aeruginosa</i> MTCC 1688					<i>S. aureus</i> MTCC 96					<i>S. pyogenes</i> MTCC 442				
Concn $\mu\text{g/ml}$	5	25	50	100	250	5	25	50	100	250	5	25	50	100	250	5	25	50	100	250
CCLOENP	-	15	17	19	24	-	14	15	18	21	-	11	14	18	21	-	13	15	17	18
CBRENP	-	17	18	19	21	10	13	15	18	20	-	12	15	18	19	-	12	14	16	18
Ampicilline	14	15	16	19	20	14	15	15	18	20	10	13	14	16	18	11	14	16	18	19
Chloramphenicol	14	17	23	23	23	14	17	18	19	21	12	14	19	20	21	10	13	19	20	20
Ciproflaxacin	20	23	28	28	28	20	23	24	26	27	17	19	21	22	22	16	19	21	21	22
Norflaxacin	22	25	26	27	29	18	19	21	23	23	19	22	25	26	28	18	19	20	21	21



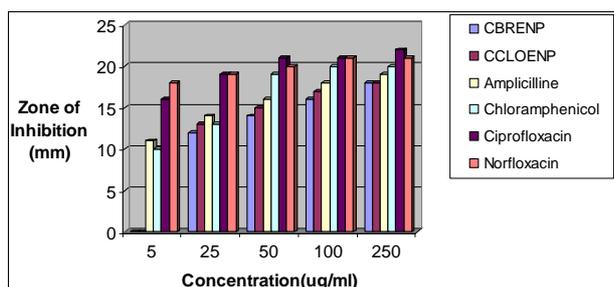
**Figure 3.** Zone of inhibition of *E. coli* against the concentration of the standard drugs and the complexes.



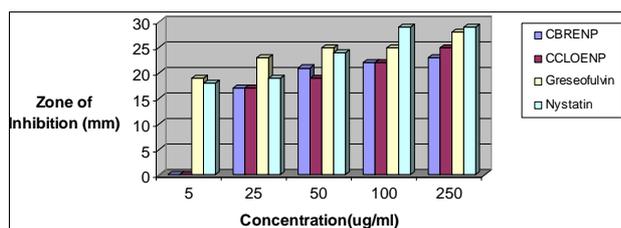
**Figure 4.** Zone of inhibition of *P. aeruginosa* against the concentration of the standard drugs and the complexes.



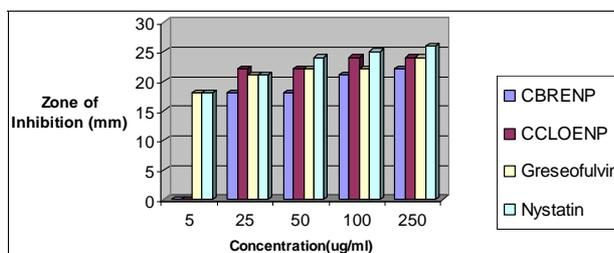
**Figure 5.** Zone of inhibition of *S. aureus* against the concentration of the standard drugs and the complexes.



**Figure 6.** Zone of inhibition of *S. ptogenes* against the concentration of the standard drugs and the complexes.



**Figure 7.** Zone of inhibition of *A. niger* against the standard drugs and the complexes.



**Figure 8.** Zone of inhibition of *C. albican* against the concentration of the standard drugs and the complexes.

**Table 4.** Zone of inhibition of the complexes and the standard against the fungi (mm).

Fungi species	<i>A. niger</i> MTCC 282					<i>C. albicans</i> MTCC 227				
Concn $\mu\text{g/ml}$	5	25	50	100	250	5	25	50	100	250
CCLOENP	-	11	14	18	21	-	13	15	17	18
CBRENp	-	12	15	18	19	-	12	14	16	18
Greseofulvin	19	23	25	25	28	18	21	22	22	24
Nystatin	18	19	24	29	29	18	21	24	25	26

## 4. CONCLUSION

Two new mixed ligand complexes of copper(II) with two chelating ligands have been synthesized and characterized. Both complexes 1 and 2 have the same  $[\text{Cu}(\text{en})(\text{phen})_2]^{2+}$  cation, but differ in anionic part, though complex 1 has no water molecule, hydrogen bonding exists between the H in 1,2-diaminoethane and O from chlorate ion which form network within the lattice. The two complexes exhibit antimicrobial activities which are comparable to the known standard drugs used for some of the micro-organisms considered.

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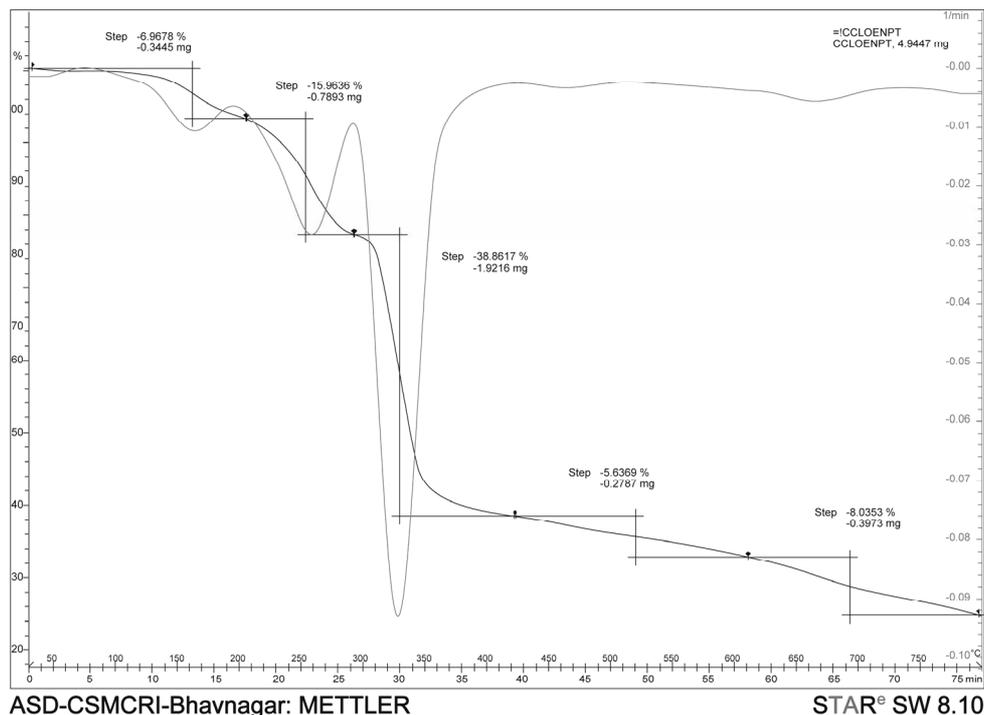
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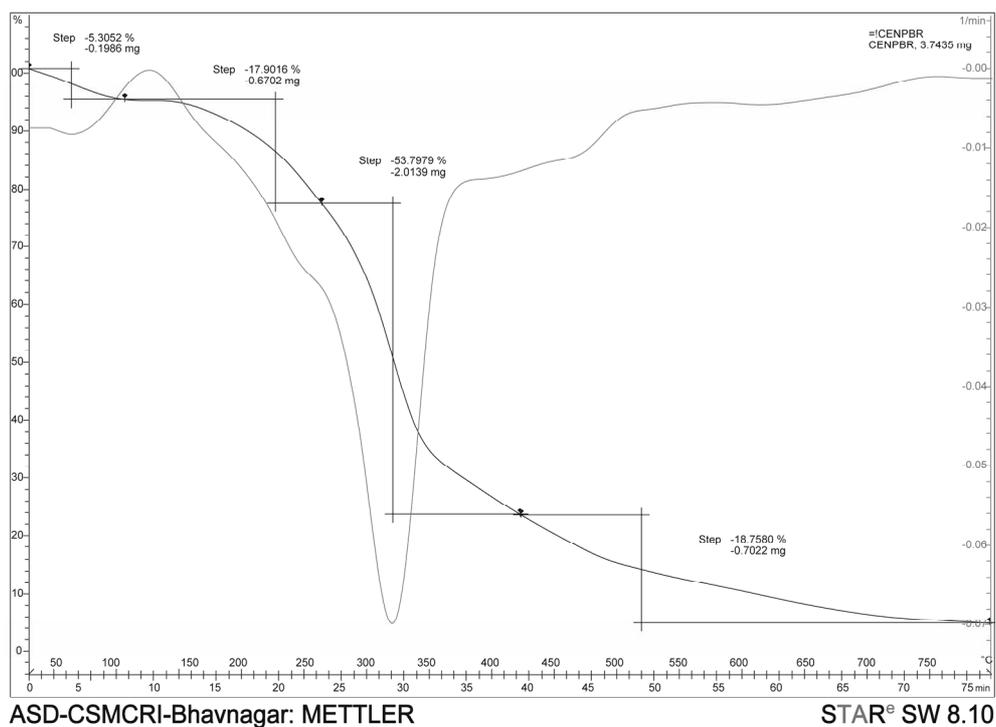
## APPENDIX

CCDC 870713 contain the supplementary crystallographic data for compound 1. These data can be obtained free of charge via

<http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk).



Thermogravimetric analysis of  $[\text{Cu}(\text{en})(\text{phen})_2](\text{ClO}_4)_2$ .



Thermogravimetric analysis of  $[\text{Cu}(\text{en})(\text{phen})_2]\text{Br}_2 \cdot 2\text{phen} \cdot 8\text{H}_2\text{O}$ .