Computational, crystal structure and antimicrobial studies of directly synthesized dichloroethylenediaminecopper (II) complex

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Abstract: The computational calculations of [CuCl$_2$(en)] complex in the gaseous phase has been carried out using MM3 and PM5 methods. First time, crystallographic structure determination of directly synthesized dichloroethylenediamminecopper (II) complex from copper metal has been reported here. A comparison of the crystallographic structure in the solid state and gaseous state with optimized molecular geometry has been also presented. An agreement has been found in the computational analysis and the experimental observations. The theoretical calculations of HOMO-LUMO energies have revealed that the charge transfer occur within the complex. Crystallographically determined structure having dimensions: a = 6.795 (5) Å, b = 5.760 (5) Å, c = 8.223 (5) Å, β = 93. 841 (5)° with monoclinic crystal system and P2$_1$/m space group. The structure was refined by Fourier and full matrix least squares methods. The antimicrobial property of the present complex has also been screened against four bacterial strains.

Supporting information: X-Ray, IR, Uv-vis, HOMO-LUMO diagram.

Keywords: *Computational calculations, Direct synthesis, Crystal structure, Copper, HOMO-LUMO, Antimicrobial activity.*

Figure 1. ORTEP diagram of the complex with atom labelling scheme.

1. INTRODUCTION

In transition metal complexes, Cu(II) ions are well known for their importance in biological systems and also for their pharmacological values. Metal complexation can changes or increases the biological activity of organic ligands after coordination [1]. Cu(II) complexes are important because they offer various potential advantages as antimicrobial, antiviral, antii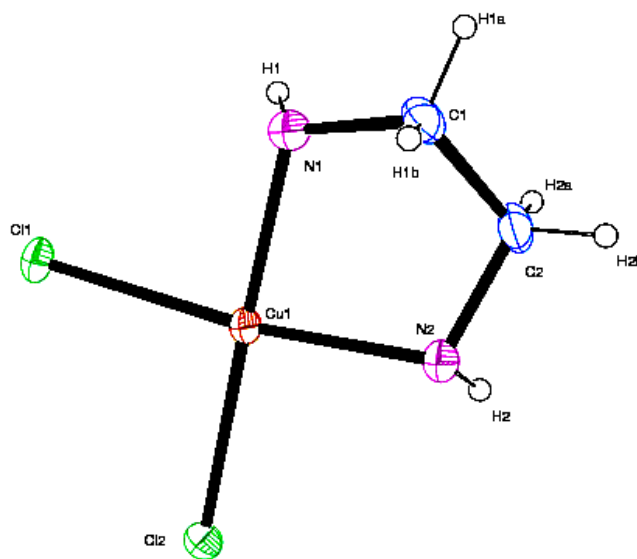nflammatory, antitumor agents, enzyme inhibitor, chemical nucleases [2,3], anticancer activity [4] and they also proved to be beneficial against several diseases like copper rheumatoid and gastric ulcers. The treatment with copper complexes produced remarkable pharmacological effects, which are not observed when the parent ligand or inorganic forms of copper is used. Many of copper complexes have been reported earlier which are effective to inhibit bacterial growth, fungal, yeast, algal, mycoplasma and viral growth as well as to cause the death of these organisms [5-13]. Copper complexes with aliphatic and heterocyclic amines are also known to catalyze the autooxidation of substituted phenols. Cu(II) complexes with a series of ethylenediamine bearing N-alkyl substituents used to determine the effect of the number and type of alkyl groups on the activity of complexes in catalyzing the oxidation of phenols as well as the

nature of product formed [14]. Copper complexes with imidazole derivative ligands have been found to be effective against gram positive and negative bacteria. Copper(II) complexes of pyridine derivatives, 2-benzoylpyridine N(4)-cyclohexyl and 2,9-dimethyl derivative phenanthrolines also possess antimicrobial activities. Antimicrobial effects of copper(II) salicylideneglycinate complexes on various strains of bacteria, yeasts and filamentous fungi have been tested and found to be efficient and effective. The antimicrobial activity of [Cu (L-orn)$_2$(H$_2$O)](PIC)$_2$ complex was also screened against *Serratia marcescens, Sphingobium japonicum, Stenotrophomonas maltophilia, Staphylococus aureus* bacterial strains using the microbroth dilution method [14].

Many copper complexes with amino acids are studied for their antibacterial activity on different bacterial strains like *E. coli, B. cereus* and *M. luteus*. Cu(II) complexes have been tested for antimicrobial activity on *Staphyccccus, Faecal coliform, E. Coli, Proteus vulgaris* and *Pseudomonas sp.* [15]. Now a days anticancer drugs like cisplatin, carboplatin, oxaliplatin, tetraplatin based on platinum are widely used and this inspires synthetic chemists to search for new metal complexes like copper which has particularly attracted the researchers.

Transition metal ions form a number of complexes with chelate diamine ligands. Diamine complexes Pt(en)Cl$_2$, like *cis*-Pt (NH$_3$)$_2$Cl$_2$ have attracted the attention because of their antitumor, biological as well as catalytic activity whereas Cu(II) complex with ethylenediamine ligand have also been reported [16]. During the last few decades mixed transition metal complexes have been studied and dark brown colored oligomeric chlorocuprates have been characterized crystallographically [17]. Copper complexes related to ethyelediammine were reported in the literature viz. [Cu(en)$_2$][CuCl$_2$]$_2$ [18], [Cu(en)$_2$](NO$_3$)$_2$[19], [CuCl(H$_2$O)(en)$_2$]Cl [20], [Cu(en)$_2$](BF$_4$)$_2$ [21]. Complexes of type [CuCl$_2$(en)] [16] are generally prepared by treating anhydrous CuCl$_2$ and ethylenediamine in tetrahydrofuran and complex [22] from CuCl$_2$.2H$_2$O and ethylenediamine. But metal complexes prepared from the elemental metal having zero oxidation state is an active area of research both from scientific and technological point of view [23]. In the present study, we have investigated the similar structure by the reaction of 1:2 ratio of elemental copper (having zero oxidation state) and ethylenediaminedihydrogenchloride in aqueous solution at room temperature. Coordination compounds prepared from direct method possess several advantages over conventional ligand displacement reactions. Recently, we have synthesized bis(D,L-aminobutyric)copper(II) complex from direct metal [24]. From the present study, it was found that coordination complexes can be prepared from the direct metal than their salts. The experiments in computer-aided chemistry use mathematical models derived from computational chemistry to calculate molecular properties and geometries [25]. According to best of our knowledge the reported crystal structure are essentially the same as the structure described by us but previously reported crystal structure showed more positional disorder for the carbon atoms. Here in crystal structure presented in the paper (R = 0.0181) is

the smallest value in our case as comparison to the structure described earlier from the copper salts and in these studies the R values were .0490 [22] , (.0213 and .0212) at 123K and 173K in which complex undergoes a phase transition [26], and 0.0460 for the complex[Cu(en)$_2$Cl$_4$]n [16]. We have also reported a comparison of experimental data with theoretically optimized structure.

2. EXPERIMENTAL

2.1 Material and instrumentation

All chemicals and solvents used were commercially available and used as received. The IR spectra was performed using PERKIN Elemer FT-IR RX I spectrophotometer in the 400-4000 cm^{-1} range at room temperature. Pathogenic bacteria *Serratia marcescens, Sphingobium japonicum, Stenotrophomonas maltophilia* and *Staphylococcus aureus* were procured from MTCC Chandigarh. All the glasswares and materials to be used for antimicrobial activity were sterilized in an autoclave for 2h to prevent contamination. Deionized water was obtained from ELIX 3 Millipore.

2.2 Synthesis

The small blue colour crystals of dichloroethylenediamminecopper(II) were obtained in large amount by slow diffusion of aqueous solution of ethylenediamminedihydrogenchloride and copper metal. Copper metal sheets were purified with the help of sonicator to remove the impurities and then washed with acetone before carrying out the reaction. The complex dichloroethylenediamminecopper(II) was prepared by reaction of 1:2 molar ratio of copper metal and ethylenediamminedihydrogenchloride in an aqueous medium at 70-80 °C for 1-2 hour and then left at room temperature. The product obtained was in the form of square shape blue crystals and it was observed that there was a complete solubility of copper metal sheet in the ligand solution. The crystals were separated from solution by filtration and washed with deionized water and methanol. IR (KBr) cm^{-1}: 3299 (ν_{as} (N-H)), 3232 (ν_s (N-H)), 2966 (ν_{as} (C-H), 2937 (ν_s(C-H)), 1570 vs (δ (N-H), 1455 (CH$_2$ Scissor), 1385 (CH$_2$ wag), 1128 (s(NH$_2$ wag)), 1043 (vs(ring stretch)), 975 (s (NH$_2$ twist)), 681 (vs(NH$_2$ rock)), 530 (vs (ring def.)), (476 (m (ring def.)).

2.3 X-ray crystallography

X- ray crystallographic data was collected on "Bruker APEX2 CCD" area detector diffractometer by using graphite-monochromatized MoKα radiation (λ = 0.71069) at room temperatura. The structure solution was determined by Patterson method using XS program of SHELX – PC [27]. All the hydrogen atoms with carbon atoms were attached geometrically where as on the nitrogen atoms were firstly calculated and then fixed. The crystallographic data for the complex is summarized in the Table 1.

Table 1: Crystallographic data for [CuCl$_2$(en)]n complex

Compound	[CuCl$_2$(en)]$_n$
Empirical formula	C$_2$H$_8$Cl$_2$Cu$_1$N$_2$
Formula weight	194.54
Crystal system	Monoclinic
Crystal size	0.35 x 0.25 x 0.20 mm
Color	Blue
Shape	plate
Space group	P2$_1$/m
Unit cell dimensions (Å), (°)	a = 6.795(5) α = 90.000 (5) b = 5.760(5) β = 93.841(5) c = 8.223 (5) γ = 90.000 (5)
Volume (Å^3), Z	321.1(4), 2
ρ calc. g cm^{-3}	2.012
μ (cm^{-1})	4.113
F$_{(000)}$	194.0
Range of data collection (°)	2.48 – 27.50
Limiting frequency	-7 < h < 8 -5 < k < 7 -10 < l < 10
Reflections collected / unique	4453 / 804 [R(int) = 0.0312]
Refinement method	Full matrix least squares on F^2
Goodness of fit on F^2	1.093
Final R indices [I>2 (I)]	R1 = 0.0181, wR2 = 0.0477
R indices (all data)	R1 = 0.0206, wR2 = 0.0492
Largest diff. peak & hole (e Å^3)	0.26 and -0.32

2.4 Theoretical calculations

The geometry of the complex has been optimized using MM3 level of theory which was used to determine the infrared and UV-visible spectra of the complex. The HOMO – LUMO energies are also calculated that shows the maximum wavelength and it also shows the charge transferred occur within the molecule. The computations were performed with the Scigress Explorer 7.7 at the MM3 and PM5 level [28].

2.5 Antibacterial activity

The antibacterial activity of synthesized complex was tested on different bacterial strains on Gram negative (*Serratia marcescens, Sphingobium japonicum, Stenotrophomonas maltophilia*) and Gram positive (*Staphylococcus aureus*) bacterial strains using the broth microdilution method. The antimicrobial activities of metal complex was evaluated as minimum inhibitory concentration where no viability of bacteria was observed after incubation of 48 h.

3. RESULTS AND DISCUSSION

3.1 Synthesis

The copper metal complex was synthesized by a reaction of ethylenediaminedihydrogenchloride and copper metal in a 1:2 molar ratio in deionized water, giving the square planar Cu(II) complex, [CuCl$_2$(en)]n.

3.2 Description of the crystal structure

Atomic coordinates and equivalent isotropic displacement parameters for the present complex and bond lengths as well as bond angles are given in Table S1, 2 & 3. The crystal structure of the square planar complex dichloroethylenediamminecopper (II) was determined by single –crystal x-ray diffraction (Fig. 1). The copper atom was located by Patterson method and all the other non –hydrogen atoms found from electron density peaks. The carbon atoms are disordered over two positions, which are related by a mirror plane (m) of symmetry. Number of crystal structures were described for the same complex at room temperature.

Table 2: Comparison of selected bond lengths from X- ray and computational (MM3 and PM5) method

Bond Distance	Experimental	Theoretical MM3	Deviation	Theoretical. PM5	Deviation
Cu(1)-N(1)	2.017(2)	1.936	.081	1.985	.031
Cu(1)-N(2)	2.017(2)	1.935	.082	1.958	.059
Cu(1)-Cl(1)	2.309(15)	2.164	.145	2.215	.094
Cu(1)-Cl(2)	2.289(13)	2.164	.125	2.254	.035
N(1)-C(1)	1.500(4)	1.525	-.024	1.516	-.016
N(2)-C(2)	1.486(4)	1.525	-.038	1.513	-.027

Table 3: Selected bond angles from X –ray and computational (MM3 and PM5) methods

Bond Angles	Experimental	Theoretical		Deviation	
		MM3	PM5	MM3	PM5
N2-Cu-Cl2	94.32	91.88	91.35	2.44	2.97
Cl2-Cu-Cl1	92.91	87.22	88.16	5.69	4.75
N2-Cu-N1	84.12	89.13	89.15	-5.01	-5.03
N1-Cu-Cl1	88.65	91.78	91.34	-3.13	-2.69
Cu-N2-C2	109.06	106.23	106.19	2.83	2.87
N2-C2-C1	107.5	104.91	104.77	2.59	2.73
N1-C1-C2	106.6	105.17	104.82	1.43	1.78
Cu-N1-C1	107.9	106.64	106.26	1.26	1.64
N1-Cu-Cl2	178.44(6)	181.01	180.5	-2.56	-2.06
N2-Cu-Cl1	172.77(6)	180.91	180.49	-8.13	-7.72

The geometry of the present complex is also similar to the geometry of the Pt and Pd atoms in dichloro(ethylenediamine) metal (II) (metal = Platinum or Palladium) [29]. The molecular structure of the copper complex was drawn with the help of ORTEP program [30] shown in Fig. 1 and unit cell packing diagram of the complex is shown in Fig. 2. All the non hydrogen atoms were refined anisotropically using full –matrix least square's technique. The average bond lengths of Cu – N is 2.017 (2) Å and 2.017 (3) Å for the ethylenediamine unit. The bond length for the chlorine atoms for the Cu–Cl entities are 2.309 (15) Å and 2.2891(13) Å. These distances are observed here in well agreement with the previous results [31,22]. The Crystal packing diagram of the complex shows that in a given molecule each chlorine atom is hydrogen bonded to a nitrogen atom of the ethylenediamine ligand above and below. However, confirmation disorder has been noticed in crystal structure of Cu(en)Cl2 because there are two five - membered chelate rings having disordered on carbon atoms. A molecular mechanics analysis showed that chelate rings are puckered and as a result crystal structure having conformational disorder but refined geometry corresponding to an average of two puckered confirmations. In addition to that present Cu (II) complex found to be in octahedral environment, two nitrogen atoms of the (en) ring and two chlorine atoms occupy the equatorial positions whereas
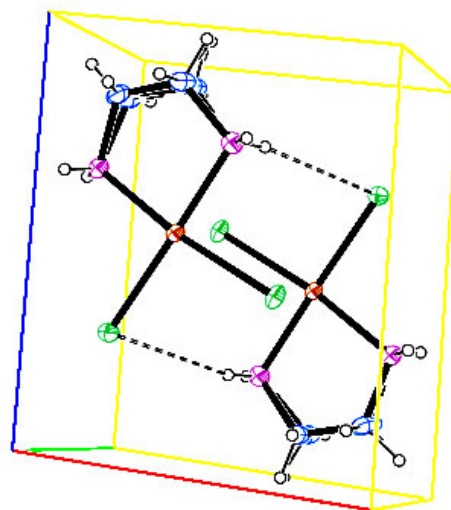
Figure 2: Unit cell packing diagram of the complex. Hydrogen bonds are shown by dotted lines. Orientation is shown for the ethylenediamine ring give rise to the extra carbon and hydrogen atoms.

two of the axial positions are occupied by two chlorine atoms with longer Cu-Cl distances. In packing diagram of the complex weak inter chain N-H..Cl hydrogen bonds characterize the crystal structure. Some of the same crystal structural views are also studied earlier by many authors [32].
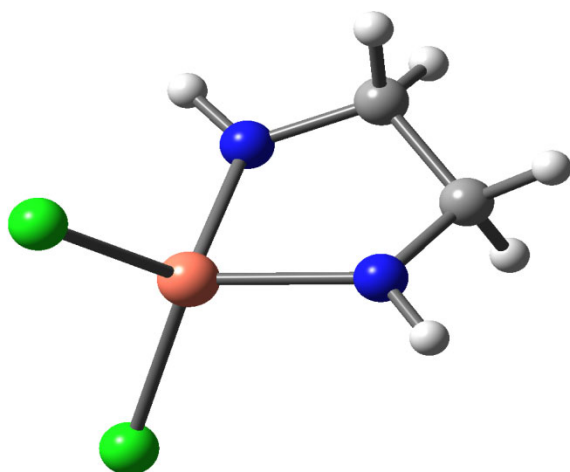
Figure 3: Optimized geometry of the complex [CuCl$_2$(en)]$_n$

Table 4: Comparison of simulated and experimental IR Spectra

Assignments	Experimental (cm^{-1})	Theoretical (cm^{-1})
(ν_{as} (N-H))	3299	3308
(ν_s (N-H))	3232	-
(ν_{as} (C-H)	2966	2987
(ν_s (C-H))	2937	2917
vs (δ (N-H)	1570	1586
(CH$_2$ Scissor)	1455	-
(CH$_2$ wag)	1385	1348
(s (NH$_2$ wag)	1128	1183
vs (ring stretch)	1043	1055
(s (NH$_2$ twist)	975	962
vs (NH$_2$ rock)	681	-
vs (ring def.)	530	-
m (ring def.)	476	491

m- medium, s-strong, vs- very strong

3. 3 Computational details

3.3.1 Optimized geometry

The ground state structure of the studied complex has been carefully optimized with Scigress Explorer using the MM3 level of theory. The optimized structure (Fig. 3) of the complex generally agrees very well with the X- ray crystalline structure obtained from X- ray diffraction data. Table 3 presents some theoretical selected structural parameters of the complex along with the experimental values.

3.3.2 Infrared Spectra

IR spectra of the complex contain an absorption band in the 3300-2800 cm^{-1} due to NH$_2$ and CH$_2$ stretching vibrations, bending vibrations is observed at 1570 cm^{-1} which is commonly observed for (δ (N-H) and the ring stretching mode is obserbed at 1043 cm^{-1}. The theoretical calculated vibrational spectra of complex are in reasonable agreement with the experimental data (Table 4 & Fig S1). The absorption band at 3520 cm^{-1} and 3385 cm^{-1} belonging to the asymmetric and symmetric stretching vibrations that suggest the presence of NH$_2$ group. The vibrations at 2988 and 2908 cm^{-1} show asymmetric and symmetric stretching vibrations indicates the presence of (C-H) methylene group.

3.3.3 Electronic spectra

UV-vis spectrum of the prepared complex has been investigated by theoretical calculation. In order to understand the electronic transition of compound, calculation of electronic absorption spectra was carried out. The visible absorption maxima of this molecule from calculations of the molecular orbital geometry corresponds to the electron transition between frontier orbital such as translation from HOMO to LUMO. The calculated absorption maximum value is found to be 134.21nm (Fig. 2 S2).

3.3.4 HOMO –LUMO analysis

The HOMO and LUMO are very important parameters for chemical reaction. HOMO is the orbital that primarily acts as an electron donor and LUMO is the orbital that largely acts as the electron acceptor and the gap between the HOMO and LUMO characterizes the molecular chemical stability.

Lower value in the HOMO and LUMO energy gap explains the eventual charge transfer interactions taking place within the molecule. The HOMO-LUMO energy gap could be regarded as the quantitative index in evaluating the impact sensitivity of energetic complexes with similar geometric structure.
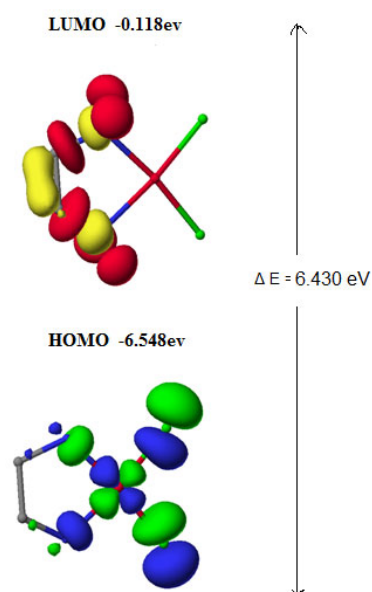

Figure 4: HOMO-LUMO diagram corresponding to maximum wavelength.

Table 5: Minimium inhibitory concentrations for the complex (µg/ml) on bacterial strains by microbroth dilution method.

Complex	*Serratia marcescens*	*Sphingobium japonicum*	*Stenotrophomonas maltophilia*	*Staphylococus aureus*
$[CuCl_2(en)]_n$	6.2	3.2	25	12.5
$[Cu(THEEN)(H_2O)]$ $(PIC)_2$	6.2	6.2	6.2	50
$[Cu(THPEN)](PIC)_2 . C_3H_8O$	12.5	6.2	3.2	25
$[Cu(TEAH_3)(PIC)](PIC). H_2O$	6.2	12.5	3.2	6.2
$[Ag(THEEN)]_2(PIC)_2$	3.2	6.2	12.5	6.2
$[Ag(THPEN)]_2(PIC)_2$	0.7	6.2	1.5	6.2
$[Ag(TEAH_3)_2](PIC)$	12.5	3.2	3.2	50
Ciprofloxacin	3.2	1.5	6.2	3.2

The less the energy gap is, the more sensitive the energetic complex listed the energies of HOMO and LUMO and their gaps [33, 34]. This is in good agreement with the fact that the metallic complex can be used as initiator due to its high sensitivity. The energy values of HOMO-LUMO are -6.548 and -0.118eV where as the energy gap is 6.430eV (Fig 4). In case of present complex charge transfer transition takes place in which an electron moves from an orbital (HOMO) that is mainly ligand in character to one that is mainly metal in character that is LUMO (ligand-to –metal charge transfer), LMCT).

3.4 Antibacterial study

Many microorganisms, which cause damage to human health, exhibit drug resistance due to inadequate use of antibiotics. Thus, there is a need for the discovery of new substances to control. In the current study, the synthesized complex has been tested against pathogenic clinically isolated strains *Serratia marcescens, Sphingobium japonicum, Stenotrophomonas maltophilia, Staphylococus aureus* compared with a standard antiobiotic ciprofloxacin . For the tested bacteria, the complex shows a good inhibitory effect, and its inhibitory activity is shown in the Table 5.

We postulate that effectiveness of the copper complex could either be due to the directly used elemental copper for the synthesis of complex. This study suggest that such type of complexes can further be explored as specific antibacterial drugs, antiflammatory, antiulcer and even for antitumoral due to their decent activity against above mentioned bacterial strains.

Recently, we have reported both experimental and theoretical study of Cu(II) and Ag(II) metal picrate complexes [35]. The antimicrobial activity of these complexes has also been studied on same pathogenic bacteria *Serratia marcescens, Sphingobium japonicum, Stenotrophomonas maltophilia* and *Staphylococcus aureus* and have been found to be effective antimicrobial agents and possess antimicrobial character (Table 5).

4. CONCLUSION

In the present paper an attempt has been made to prepare the coordination complex from the zero valent metal having zero oxidation state. Crystal structure of the compound $[CuCl_2(en)]n$ has been determined by single crystal X- ray diffraction. Theoretical study on the complex has been studied in which molecular parameters and frequency assignments for the complex have been studied. HOMO – LUMO energies are also calculated and it shows that charge transfer occurs within the molecule. The theoretical calculations show well agreement with the experimental data. The antibacterial activity of this complex has shown good results against *Serratia marcescens, Sphingobium japonicum, Stenotrophomonas maltophilia* and *Staphylococus aureus*.

List of Abbreviations

(en) : ethylenediamine

HOMO : Highest occupied molecular orbital

LUMO : lowest unoccupied molecular orbital

IR : infrared

UV : Ultra violet

Supplementary data

Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as the supplementary publication no. CCDC 896932.

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