



Synthesis, Characterization and Antibacterial Studies on Copper(II) Binuclear Complexes with Substituted Piperidin-4-ones

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ABSTRACT

Copper(II) Chloride binuclear complexes with variously substituted 2,6-diphenyl piperidin-4-ones $[\text{Cu}_2\text{LCl}_4(\text{H}_2\text{O})_3]$ have been synthesized and characterized by elemental analysis, molar conductance, magnetic susceptibility measurements, thermal and spectral studies. Molar conductance data show that these complexes are non-electrolytes. The presence of three coordinated water molecules is confirmed by thermal and infrared spectral studies. IR spectral data indicate that the piperidin-4-ones are monodentate and coordinate only through ring nitrogen. The electronic spectral and magnetic studies suggest distorted square-pyramidal environment for Cu(II) complexes. Antibacterial activities of the ligands and their complexes have been tested against bacterial culture by disc diffusion method. It has been found that all the complexes have higher activity than the free ligands.

Key words: Piperidin-4-ones, Copper(II) binuclear complexes, Thermal studies, Antibacterial Activities.

INTRODUCTION

There has been considerable interest in the coordination chemistry of 4- or 5-coordinate copper(II) compounds that mimic the aspects of the properties of copper in protein¹. The binuclear copper active centers are important functional units in metalloproteins. Current research work concerning the structural and magnetic properties of polynuclear transition metal compounds is aimed at understanding the structural and chemical features governing electronic exchange coupling through multi-atom bridging ligands². It also explores the possibilities for magnetic interaction

between the two metal ions, leading to the design of molecular magnetic materials³. The research on the coordination chemistry of transition metal complexes with piperidin-4-one ligands has rapidly progressed in recent years. The copper complexes with piperidin-4-ones have received much attention because of their biological applications. Molecules with hetero atomic rings are widely distributed in nature. Five and six membered heterocycles with nitrogen or oxygen as a heteroatom are gaining importance as they are found in a variety of biological activities^{4,6}. The earlier reports showed that piperidin-4-ones possess analgesics, anti-inflammatory, central nervous system (CNS), local

anesthetic, anticancer and antimicrobial activity. They are also used as corrosion inhibitors. The reports ⁷ indicated that the biological activities of piperidin-4-ones were associated with the substituents at 2,3 and 6 positions. The biological activity was found to be significant in compounds possessing aromatic substituents in 2 and 6 positions. The presence of methyl substitution at 2 or 3 positions was also attributing to biological activities. The piperidin-4-ones have been reported ⁸ to act as bidentate ligands, coordinating through the ring nitrogen and carbonyl group. This would lead to severe steric strain as the piperidin-4-one ring should adopt a boat conformation during simultaneous complexation through these sites. Ramalingam *et.al.*,⁹ have prepared dithiocarbamate complexes involving 2-aryldecahydroquinolin-4-ones as ligands which are similar to piperidin-4-ones and confirmed the participation of only the ring nitrogen and not the carbonyl group. However, it has been unambiguously confirmed that only ring nitrogen of piperidin-4-ones is coordinated to lanthanide(III) ions ¹⁰⁻¹³. Herein we report the synthesis, characterization and antibacterial studies on copper(II) binuclear complexes with substituted piperidin-4-ones as ligands.

MATERIALS AND METHOD

Materials

Commercially available chemicals of Analar or equivalent grade were used without further purification. Organic solvents such as alcohol, chloroform, dichloromethane were distilled and used for preparations and analysis.

Measurements

Elemental analysis (C, H and N) were determined by using a Carlo-Erba 1106 microanalytical instrument. Molar conductance of the Cu(II) complexes were determined in DMF at room temperature using CM – 82 Elico conductivity bridge with a dip type conductivity cell fitted with platinum electrode (cell constant – 1.0 cm⁻¹). The magnetic measurements were carried out by the Gouy method at room temperature. Infrared spectra were obtained using KBr disc (4000–400 cm⁻¹) on a Shimadzu 830 FT-IR spectrophotometer. The electronic spectra in the 300–1100 nm range were recorded on a Shimadzu 160 spectrophotometer.

The thermal analysis studies were performed on Universal V 4.3 model thermal analyzer. The simultaneous TG-DTA measurements were carried out in air using 3-5 mg samples at a heating rate of 10 °C min⁻¹ in a temperature range from ambient to 800 °C using a platinum cup as the sample holder.

Preparation of the Ligands

The variously substituted piperidones (L¹)–(L⁶) were prepared by the following reported procedure¹³⁻¹⁴. The mixture of dry ammonium acetate (50 mmols), aldehyde (100 mmols) and ketone (50 mmol) in 95% ethanol was just heated to boil and allowed to stand over night at room temperature. Then concentrated HCl (13 mL) was added to the mixture. The precipitated hydrochloride was collected and washed with ethanol-ether (1:5) and crystallized from ethanol yielded the pure hydrochloride.

A suspension of the hydrochloride in acetone was treated with ammonia (1:1) and the free base was obtained by diluting with larger amount of water. The product was filtered off and recrystallized from ethanol.

2,6-di(p-methoxy phenyl)-3-methyl piperidin-4-one (L¹)

Compound L¹ was obtained from p-methoxy benzaldehyde (12.2 mL, 100 mmols) with ethyl methyl ketone (4.5 mL, 50 mmols) and ammonium acetate (3.9 g, 50 mmols). IR spectrum, ν , cm⁻¹: 1705(C=O), 3321(NH). ¹H NMR spectrum(CDCl₃), δ , ppm: 2.12(s, NH); 3.65(d, 2-H); 3.78(d, 3-H); 2.70-2.89(5-H); 4.16(dd, 6-H); 6.68-7.29(Aromatic protons); 0.93(d, 3C-CH₃); 3.70, 3.71(Ar-OCH₃). Melting point 136 °C. Yield 75%. C₂₀H₂₃NO₃. Calculated, %: C 73.82; H 7.12; N 4.30; O 14.75.

2,6-di(p-methoxy phenyl)-3,5-dimethyl piperidin-4-one(L²)

Compound L² was obtained from p-methoxy benzaldehyde (12.2 mL, 100 mmols) with 3-pentanone (5.3 mL, 50 mmols) and ammonium acetate (3.9 g, 50 mmols). IR spectrum, ν , cm⁻¹: 1709(C=O), 3317(NH). ¹H NMR spectrum(CDCl₃), δ , ppm: 2.00(s, NH); 3.54(d, 2-H); 2.71(dd, 3-H and 5-H); 3.54(6-H); 6.86-7.35(Aromatic protons); 0.82(d, 3C and 5C-CH₃); 3.79(s, Ar-OCH₃). Melting point

128 °C. Yield 84%. $C_{21}H_{25}NO_3$. Calculated, %: C 74.30; H 7.42; N 4.12; O 14.14.

$C_{19}H_{19}NOCl_2$. Calculated, %: C 65.52; H 5.49; N 4.02; O 4.59; Cl 20.35.

2,6-di(p-tolyl)-3-methyl piperidin-4-one (L³)

Compound L³ was obtained from p-tolunealdehyde (11.2 mL, 100 mmols) with ethyl methyl ketone (4.5 mL, 50 mmols) and ammonium acetate (3.9 g, 50 mmols). IR spectrum, ν , cm^{-1} : 1697(C=O), 3319(NH). ¹H NMR spectrum(CDCl₃), δ , ppm: 1.98(s, NH); 3.68(d, 2-H); 3.80(d, 3-H); 2.71-2.89(5-H); 4.16(dd, 6-H); 6.91-7.39(Aromatic protons); 0.97(d, 3C-CH₃); 2.22, 2.25(Ar-CH₃). Melting point 98 °C. Yield 70%. $C_{20}H_{23}NO$. Calculated, %: C 81.87; H 7.90; N 4.77; O 5.45.

2,6-di(p-tolyl)-3,5-dimethyl piperidin-4-one (L⁴)

Compound L⁴ was obtained from p-tolunealdehyde 11.2 mL, 100 mmols) with 3-pentanone (5.3 mL, 50 mmols) and ammonium acetate (3.9 g, 50 mmols). IR spectrum, ν , cm^{-1} : 1703(C=O), 3313(NH). ¹H NMR spectrum(CDCl₃), δ , ppm: 1.89(s, NH); 3.82(d, 2-H and 4-H); 2.76(dd, 3-H and 5-H); 6.88-7.55(Aromatic protons); 0.89(d, 3C and 5C-CH₃); 2.63(s, Ar-CH₃). Melting point 90 °C. Yield 68%. $C_{21}H_{25}NO$. Calculated, %: C 82.04; H 8.19; N 4.55; O 5.20.

2,6-di(p-chlorophenyl)-3-methyl piperidin-4-one (L⁵)

Compound L⁵ was obtained from p-chloro benzaldehyde (14 g, 100 mmols) with ethyl methyl ketone (4.5 mL, 50 mmols) and ammonium acetate (3.9 g, 50 mmols). IR spectrum, ν , cm^{-1} : 1709(C=O), 3326(NH). ¹H NMR spectrum(CDCl₃), δ , ppm: 2.24(s, NH); 3.62(d, 2-H); 3.76(d, 3-H); 2.71-2.84(5-H); 4.17(dd, 6-H); 6.88-7.99(Aromatic protons); 0.91(d, 3C-CH₃). Melting point 92 °C. Yield 68%. $C_{18}H_{17}NOCl_2$. Calculated, %: C 64.68; H 5.12; N 4.19; O 4.78; Cl 21.21.

2,6-di(p-chlorophenyl)-3,5-dimethyl piperidin-4-one (L⁶)

Compound L⁶ was obtained from p-chloro benzaldehyde (14 g, 100 mmols) with 3-pentanone (5.3 mL, 50 mmols) and ammonium acetate (3.9 g, 50 mmols). IR spectrum, ν , cm^{-1} : 1710(C=O), 3315(NH). ¹H NMR spectrum(CDCl₃), δ , ppm: 2.11(s, NH); 3.82(d, 2-H and 6-H); 3.52(d, 3-H and 5-H); 6.75-7.21(Aromatic protons); 1.09(d, 3C and 5C-CH₃). Melting point 140 °C. Yield 80%.

Preparation of the complexes

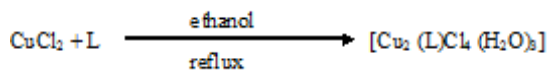
A solution of copper(II) chloride (5 mmol) in ethanol (30 mL) was added to a solution of piperidin-4-one (10 mmol) in ethanol (30 mL) and the mixture was refluxed on a water bath for 3-4 hours. The solvent was then removed by vacuum distillation and the residue was thoroughly washed with hot ethanol, acetone and diethyl ether to remove the unreacted piperidin-4-one. The complex obtained was dried over phosphorous(V) oxide in vacuum. The complexes are stable in air and insoluble in almost all organic solvents and water.

Antibacterial activity determination

The test of antibacterial activity adopts a method by agar diffusion¹⁶ using DMSO as the solvent. The antibacterial activity of the ligands and their binuclear copper(II) complexes was studied under two different concentrations. The culture medium (antibiotic medium) consisted of beef extract, albumins and agars. The culture medium, glass plates and filter paper disc of 5 mm diameters were sterilized for 1 hour at 120 °C; the culture medium was transferred to glass plates and frozen at about 37 °C. After that the bacterial strains were inoculated to the solid culture medium surface, the filter paper disc with 10 μ L samples were placed on the surface. They were allowed to incubate at 37 °C for 18 hours. The inhibition zone around the disc was calculated as zone diameter in millimeters. Blank tests showed that DMSO solvent does not affect the antibacterial activity of the complexes¹⁷.

RESULTS AND DISCUSSION

The binuclear copper complexes were synthesized resulting in a moderate yield by mixing the molar ratio of 1:2 $CuCl_2 \cdot 2H_2O$ and the ligand (L) in the ethanolic solution as shown in the following equation.



The elemental analyses and analytical data for all the complexes are given in Table 1. The ligands are soluble in common organic solvents,

while the complexes are insoluble in water and common organic solvents and soluble only in DMF and DMSO

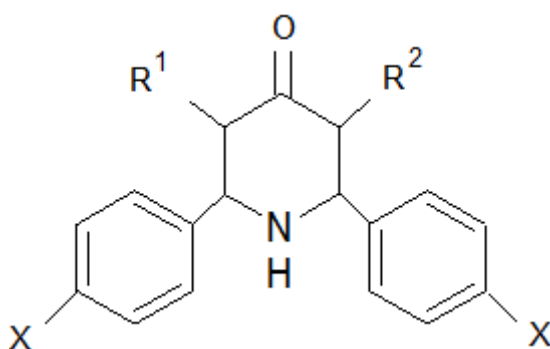
Magnetic Properties and Molar conductance

The effective magnetic moments of copper(II) complexes are found between 0.1–1.16BM, thus suggesting a strong antiferromagnetic exchange interaction between two copper(II) centres in binuclear complexes¹⁸. The magnetic moment of the all the complexes are abnormally small and consistent with a dimeric structure at room temperature.

The molar conductance of the solution of all the complexes in DMF are in the range of 0.86–1.02 $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$. These observation suggest that all the complexes are non-electrolytes¹⁹ in DMF at room temperature.

IR Spectra

The IR spectral data of the ligands and their complexes are shown in Table 2. Infrared spectroscopy has proved to be a valuable tool in the study of the stereochemistry of heterocyclic compounds²⁰, mainly on the basis of a series of bands in the region 2800-2600 cm^{-1} called Bohlmann bands²¹. The piperidin-4-ones also exhibit these bands in the region 3000-2800 cm^{-1} .



Ligand	R ¹	R ²	X
L ¹	CH ₃	H	OCH ₃
L ²	CH ₃	CH ₃	OCH ₃
L ³	CH ₃	H	CH ₃
L ⁴	CH ₃	CH ₃	CH ₃
L ⁵	CH ₃	H	Cl
L ⁶	CH ₃	CH ₃	Cl

Fig. 1: The structure of Ligand.

The sharp band at 3321 cm^{-1} is due to N-H stretching frequency for the piperidin-4-ones. The C=O stretching frequency of the piperidin-4-ones lie around 1701 cm^{-1} . The absorption band around 1600 cm^{-1} is due to the aromatic C-H stretching frequency.

The IR spectra of the complexes revealed that a sharp band around 3300 cm^{-1} is due to N-H stretching as the ligand has been shifted to higher frequency and is broadened²² in the corresponding complexes. The Bohlmann bands which occur in the region 3000-2800 cm^{-1} in the IR spectra of the ligands are found to be missing in the spectra of the corresponding complexes. The absence of these bands reveals that there may be a conformational change of piperidin-4-one ring due to its complexation with the metal ion through the lone pair of electrons in the ring nitrogen. The carbonyl stretching frequency of the ligands appears at 1700 cm^{-1} . This absorption is shifted to higher frequency at about 20-31 cm^{-1} in the corresponding complexes. The higher frequency shift may be due to conformational changes that occur as a result of coordination of the ring nitrogen and also reveals that carbonyl group is not involved in complexation⁸. The presence of water molecules in the complexes is shown by a broad absorption band in the region 3600-3200 cm^{-1} (merged with the energy absorption) is due to O-H stretching vibration and a short medium peak around 1602-1595 cm^{-1} due to H-O-H bending vibration²³. The sharp peaks in the region 900-800 cm^{-1} in all the complexes are due to rocking mode of coordinating water molecules²⁴. Two new bands observed in the region 520-500 cm^{-1} and 426-415 cm^{-1} are attributed to M-N and M-O bonding respectively²⁵. Generally, if the chloride

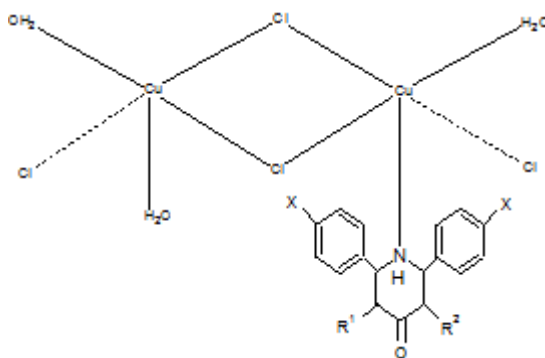
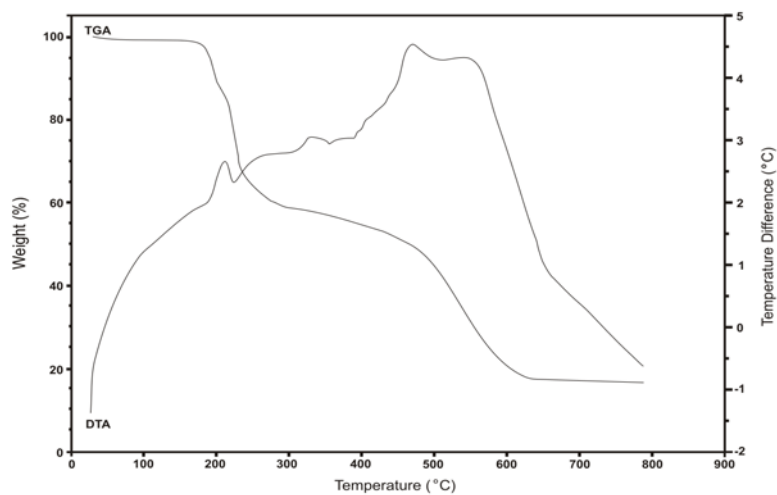
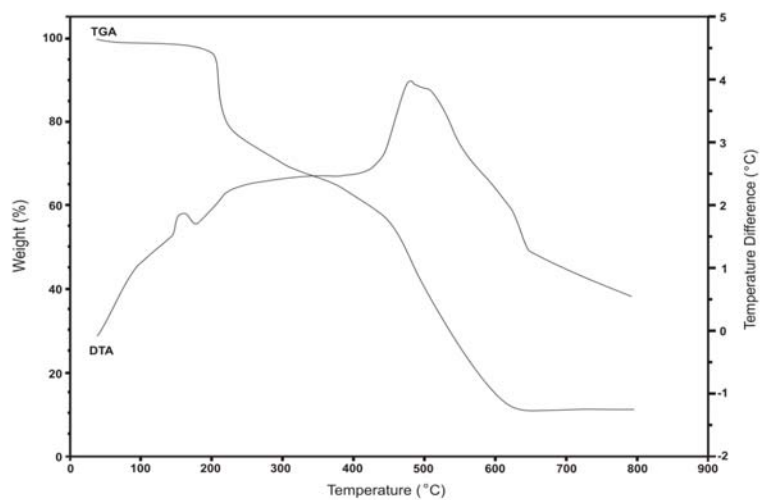
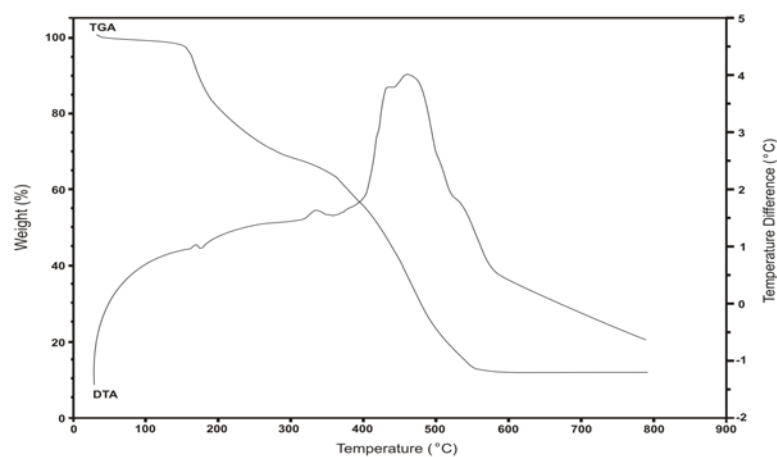


Fig. 2: The structure of the complex

**Fig. 4: TG-DTA Curve of complex 4****Fig. 5: TG-DTA Curve of complex 5****Fig. 3: TG-DTA Curve of complex 1**

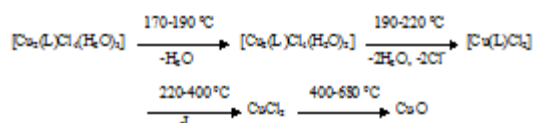
ion act as a monodentate ligand, the absorption is due to M–Cl bond²⁶ would be observed around 300 cm⁻¹ and if it act as a bidentate ligand bridging two ions absorption band would be shifted to lower frequency²⁷. The study, exhibit absorption around 260 cm⁻¹, thereby revealing the presence of bridged Cu–Cl–Cu system in these complexes²⁸.

Electronic Spectra

Electronic spectra of the complexes were recorded in DMSO solution. The complexes exhibit absorption at 836 and 372 nm. The band at 372 nm can be attributed to the distorted square-pyramidal geometry around the Cu(II) ion²⁹. On the other hand, the low intensity band at 836 nm consists with a d-d transition of square-pyramidal Cu(II) complexes³⁰.

Thermal Studies

The TG–DTA measurements of copper(II) complexes were carried out in air and their thermal data are given in Table 3. The thermal curves of a few complexes are shown in Fig. 2 to Fig. 4. The TG–DTA curves of all the complexes are similar. Generally, the thermal decomposition takes place in four stages. The thermal decomposition sequences of copper(II) complexes are given in the following equations.



The thermal curves of all the complexes show an exothermic peak in the temperature range of 170–190 °C. The mass loss at this temperature

Table 1: Elemental analysis data and Physical properties of the complexes

No.	Complex Formula	Molecular Weight	Decomposition Temperature(°C)	Yield (%)	Element, Found (Calc.) (%)				Conductance Ohm ⁻¹ cm ² mol ⁻¹
					C	H	N	M	
1	[Cu ₂ (L ¹)Cl ₄ (H ₂ O) ₃]	648.35	168 – 170	75	37.36 (37.05)	3.67 (3.58)	2.32 (2.16)	20.12 (19.60)	1.02
2	[Cu ₂ (L ²)Cl ₄ (H ₂ O) ₃]	662.38	192 – 194	80	38.62 (38.08)	3.52 (3.80)	2.42 (2.11)	20.23 (19.18)	0.96
3	[Cu ₂ (L ³)Cl ₄ (H ₂ O) ₃]	616.36	180 - 182	70	40.25 (38.97)	3.95 (3.76)	2.72 (2.27)	20.76 (20.61)	0.94
4	[Cu ₂ (L ⁴)Cl ₄ (H ₂ O) ₃]	630.38	220 – 221	73	39.78 (40.04)	3.76 (3.99)	2.66 (2.22)	20.89 (20.16)	0.94
5	[Cu ₂ (L ⁵)Cl ₄ (H ₂ O) ₃]	657.19	190 – 192	72	33.06 (32.89)	2.73 (2.61)	2.65 (2.13)	19.89 (19.33)	0.86
6	[Cu ₂ (L ⁶)Cl ₄ (H ₂ O) ₃]	671.22	240 - 242	70	34.21 (33.99)	2.68 (2.85)	2.43 (2.09)	19.05 (18.93)	0.92

Table 2: Important IR absorption bands (cm⁻¹) of the ligands and its copper (II) complexes

S.No.	Complex Formula	$\nu(\text{C}=\text{O})^a$	$\nu(\text{C}=\text{O})^b$	$\nu(\text{N}-\text{H})^a$	$\nu(\text{N}-\text{H})^b$	$\nu(\text{O}-\text{H})$	$\delta(\text{H}-\text{O}-\text{H})$
1	[Cu ₂ (L ¹)Cl ₄ (H ₂ O) ₃]	1705s	1722s	3321s	3348s	3200–3600b	1612m
2	[Cu ₂ (L ²)Cl ₄ (H ₂ O) ₃]	1709s	1720s	3317s	3344s	3200–3600b	1614m
3	[Cu ₂ (L ³)Cl ₄ (H ₂ O) ₃]	1697s	1720s	3319s	3344s	3200–3600b	1612m
4	[Cu ₂ (L ⁴)Cl ₄ (H ₂ O) ₃]	1703s	1735s	3313s	3346s	3200–3600b	1618m
5	[Cu ₂ (L ⁵)Cl ₄ (H ₂ O) ₃]	1709s	1718s	3326s	3357s	3200–3600b	1595m
6	[Cu ₂ (L ⁶)Cl ₄ (H ₂ O) ₃]	1710s	1714s	3315s	3344s	3200–3600b	1596m

Here, ^a For ligand, ^b For complex, s: strong; b: broad; m: medium

Table 3: Thermal analysis data of the complexes

No.	Complex Formula	DTA Peak (°C)	Thermogravimetry		Decomposition product
			TG Temp. Range(°C)	Weight loss Found (Calc.) %	
1	[Cu ₂ (L ¹)Cl ₄ (H ₂ O) ₃]	170-	150-180	2.68 (2.77)	[Cu ₂ (L ¹)Cl ₄ (H ₂ O) ₂]
		220+	180 -250	15.92 (16.49)	[Cu ₂ (L ¹)Cl ₂]
		443-	250- 450	49.93 (50.18)	CuCl ₂
		531-	450-580	12.34 (12.26)	CuO
2	[Cu ₂ (L ²)Cl ₄ (H ₂ O) ₃]	180-	170-190	2.66 (2.72)	[Cu ₂ (L ²)Cl ₄ (H ₂ O) ₂]
		206-	190 -220	15.81 (16.14)	[Cu ₂ (L ²)Cl ₂]
		450-	220- 460	52.23 (51.30)	CuCl ₂
		580-	460-600	11.88 (12.00)	CuO
3	[Cu ₂ (L ³)Cl ₄ (H ₂ O) ₃]	174-	150-180	2.74 (2.92)	[Cu ₂ (L ³)Cl ₄ (H ₂ O) ₂]
		212+	180 -220	17.77 (17.34)	[Cu ₂ (L ³)Cl ₂]
		420-	220- 430	46.56 (47.60)	CuCl ₂
		593-	430-620	12.49 (12.90)	CuO
4	[Cu ₂ (L ⁴)Cl ₄ (H ₂ O) ₃]	186-	160-190	1.35 (2.85)	[Cu ₂ (L ⁴)Cl ₄ (H ₂ O) ₂]
		225-	190-230	15.00 (16.96)	[Cu ₂ (L ⁴)Cl ₂]
		446-	230-460	48.15 (48.76)	CuCl ₂
		663-	460-680	13.45 (12.61)	CuO
[Cu ₂ (L ⁵)Cl ₄ (H ₂ O) ₃]	[Cu ₂ (L ⁵)Cl ₄ (H ₂ O) ₃]	163-	150-190	3.34 (2.74)	[Cu ₂ (L ⁵)Cl ₄ (H ₂ O) ₂]
		215+	190-220	21.29 (16.27)	[Cu ₂ (L ⁵)Cl ₂]
		474-	220-480	51.54 (50.85)	CuCl ₂
		615-	480-650	12.02 (12.10)	CuO
6	[Cu ₂ (L ⁶)Cl ₄ (H ₂ O) ₃]	168-	150-170	2.96 (2.68)	[Cu ₂ (L ⁶)Cl ₄ (H ₂ O) ₂]
		218-	170 -220	16.08 (15.93)	[Cu ₂ (L ⁶)Cl ₂]
		480-	220- 500	50.69 (51.88)	CuCl ₂
		630-	500-650	11.94 (11.85)	CuO

Here, (-) exothermic, (+) endothermic

Table 4: Antibacterial Activities of the ligands (diameter zone of inhibition in mm)

Ligand	Bacterial cultures							
	<i>Staphylococcus Aureus</i>		<i>Bacillus</i>		<i>Klebsiella Pneumoniae</i>		<i>Pseudomonas Aeruginosa</i>	
	cl	c2	cl	c2	cl	c2	cl	c2
L ¹	6	9	6	7	6	-	6	6
L ²	7	7	5	6	6	7	6	8
L ³	6	7	6	6	7	9	6	7
L ⁴	6	8	7	8	6	6	5	6
L ⁵	5	7	6	8	5	7	-	-
L ⁶	6	7	5	6	6	7	-	-

Here, c1: 500ppm; c2: 800ppm

corresponds to the dehydration of one water molecule. The second stage decomposition takes place between 175-215 °C temperature range leads to loss of two water molecules and two chloride ions. The loss of water molecules in this temperature range confirms that they are coordinated with the copper(II) ion³¹. This is followed by an exothermic decomposition in the temperature range of 215–450 °C and the mass loss corresponds to one organic ligand molecule. The final decomposition takes place in an exothermic manner between 450–680 °C resulting in the formation of CuO as residue

Antibacterial Studies

The bacterial cultures used for screening antibacterial activity of the ligands and its

complexes are *Staphylococcus Aureus*, *Bacillus Klebsiella Pneumoniae* and *Pseudomonas Aeruginosa*. The results of present investigation reveal that all the complexes shows good activity against tested bacterial culture. It has been observed from the results that the metal complexes have higher activity than that of the free ligands. This is probably due to greater lipophilic nature of the complexes. Such increased activity of the metal complexes can be explained on the basis of Overtone's concept and coordination theory¹⁶. According to Overtone's concept of cell permeability, the lipid membrane that surrounds the cell favours the passage of only lipid soluble materials. Due to this liposolubility becomes an important factor that controls the antimicrobial activity. On coordination, the polarity of the metal

Table 5: Antibacterial Activities of the complexes (diameter zone of inhibition in mm)

Complex Formula	Bacterial cultures							
	<i>Staphylococcus Aureus</i>		<i>Bacillus</i>		<i>Klebsiella Pneumoniae</i>		<i>Pseudomonas Aeruginosa</i>	
	c1	c2	c1	c2	c1	c2	c1	c2
[Cu ₂ (L ¹)Cl ₄ (H ₂ O) ₃]	8	11	6	8	6	9	-	-
[Cu ₂ (L ²)Cl ₄ (H ₂ O) ₃]	9	11	10	12	6	7	7	8
[Cu ₂ (L ³)Cl ₄ (H ₂ O) ₃]	8	10	9	11	8	9	7	8
[Cu ₂ (L ⁴)Cl ₄ (H ₂ O) ₃]	9	10	8	11	8	10	6	7
[Cu ₂ (L ⁵)Cl ₄ (H ₂ O) ₃]	9	11	9	11	8	9	6	7
[Cu ₂ (L ⁶)Cl ₄ (H ₂ O) ₃]	8	10	6	8	7	9	-	-

Here, c1: 500ppm; c2: 800ppm

ion will be reduced to a greater extent due to the overlap of the ligand orbital and partial sharing of positive charge of metal ion with donor groups. This increased lipophilicity enhances the penetration of the complexes into lipid membrane and blocks the metal binding sites on enzymes of microorganisms. The diameter zones of inhibition of the ligands and its binuclear copper(II) complexes are shown in the Table 4-5.

CONCLUSION

The formula assigned for binuclear copper(II) chloride complexes namely [Cu₂(L)Cl₄·(H₂O)₃] is in accordance with the

elemental analysis, conductance and thermal data. In these complexes each copper(II) atom is located in the centre of a distorted square pyramidal configuration of five coordinating atoms. The IR spectral data suggested that the coordinating site of piperidin-4-one is ring nitrogen and not the carbonyl group. The thermal curves of these complexes show that the water molecules coordinate with copper(II) ion. The antibacterial data reveal that the complexes are superior than the free ligand. This factor increases the lipophilic character of the metal complex and favours its permeation through the lipid layer of the bacterial membranes. The proposed structure for the binuclear copper(II) chloride complexes is shown in Fig. 2.

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