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ANTI MICROBIAL AND SPECTROSCOPIC CHARACTERIZATION OF TWO NEW PYRIDINE BASED 16-MEMBERED N-HEXADENTATE LIGANDS THEIR Cu II METAL COMPLEXES

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Abstract

3d Transtion metal i.e. Copper (II) Complexes of the general composition $[CuL]X_2$ (where X = NO_3^-, ½SO_4^{-2} and L_1=2,8,14.20.25,26,27,28] octaaza Pentacyclo[19.3.$1^{1,21}$.$1^{3,7}$.$1^{9,13}$.$1^{15,19}$] octacosa[1(25),2,7,9(27),10,12,14,19,21,23] decaene, L_2 = 2,6,12,16,21,22 hexaaza tricyclo [15.3.$1^{1,17}$.$1^{11,7}$] docosa 1,6,11,16 teraene) have been prepared. On the basis of IR, electronic, EPR, thermal studies all the complexes were found to have six coordinate tetragonal geometry. Macrocyclic ligand and its complexes have also been screened against pathogenic bacteria and fungi in vitro as growth inhibiting agent.

Keywords: Copper (II) macrocyclic complexes, biological activities, cyclic voltammetry.

INTRODUCTION

During the past 20 years the metal ion chemistry of macrocyclic ligands has become a major subdivision of inorganic chemistry. In the early stage of growth of macrocyclic field, the main goal was the analogy between synthetic macrocyclic compounds and many natural product systems. But more recently, the emphases of reported research have been ranged over the whole spectrum of chemistry. The preparation and characterization of metal complexes with macrocyclic ligands is the goal of much research in recent years [1]. Synthetic macrocycles are a growing class of compounds with varying chemistry with a wide range of different molecular topologies and sets of donor atoms [2]. Transition metal complexes have received much attention as catalyst in oxidation and epoxidation processes [3]. Macrocyclic complexes containing copper center has been prepared to study biological activity [4]. Transition metal ion complexes with macrocyclic ligands are also significant for the development of new methodologies in separation science [6]. Macrocyclic transition metal complexes are important because of their biological relevance, the stable structure and different spectral

characteristics [7]. Schiff base macrocyclic ligands display very important and interesting biological properties such as anti-tumor, anti-bacterial [8], anti-fungal activities. The macrocyclic ligands involving pyridine rings are a progressing and important class of ligands [9]. In this paper we report an efficient route for the synthesis of new series of copper (II) macrocyclic complexes by template condensation. The aim of antibacterial and antifungal activities was to contribute to a better understanding of the antibacterial and antifungal activities of copper complexes.

PHYSICAL MEASUREMENTS

IR spectra were recorded on a Perkin Elmer 137 instrument as Nujol mulls/KBr pellets. Microanalyses (C, H and N) of these complexes were carried out on a Carlo-Erba 1106 elemental analyzer. Electronic spectra were recorded in DMSO solution on a Shimadzu UV mini – 1240 spectrophotometer. The molar conductance was measured on an Elico conductivity bridge (type CM82T). Magnetic moment measurements (Gouy balance) were made at room temperature using $CuSO_4$ $5H_2O$ as a callibrant. Electron impact mass spectra were recorded on JEOL, JMS, DX-303 mass spectrometer. EPR spectra of the complexes were recorded as polycrystalline sample For Cu(II) complexes EPR spectra were recorded using DPPH as g-marker at room temperature on E_4-EPR spectrometer. Thermogravimetric analysis measurements were carried out by a Metter Toledo thermal analysis system. The experiments were done in nitrogen atmosphere using alumina powder as reference material. The weight of sample taken was 8-10mg and heating rate was 10^oC/min. The antifungal activity of the ligands and their complexes with divalent copper has been done on agar medium having the composition, glucose 20 g, starch 20 g, agar–agar 20 g and distill water 1000 ml. Solutions of the test compound in dimethylformamide at 50, 100 and 200 ppm concentrations were prepared. The medium was then poured into the petriplates and the spores of fungi were placed on the medium with the help of an inoculum needle. These petriplates were wrapped in the polythene bags containing a few drops of alcohol and were placed in an incubator at 30 ± 1 °C. The controls were also run and three replicates were used in each case. The linear growth of the fungus was obtained by measuring the fungal colony diameter after four days. The organisms used in these investigations included *Aspergillus niger* and *Aspergillus glaucus*. The nutrient agar medium having the composition peptone 5 g, beef extract 5 g, NaCl 5 g, agar–agar 20 g and distill water 1000 ml was pipetted into the petridish. 5 ml of warm seeded agar was applied, on solidification. The seeded agar was prepared by cooling the molten agar to 40 °C and then added the amount of bacterial suspension. The compounds were dissolved in dimethylformamide in 500 and 1000 ppm concentrations. Paper discs of Whatman No. 1 filter paper measuring diameter of 5 mm were soaked in these solutions of varied concentrations. Organism was placed on dried discs on the medium in petriplates at suitable distance. For 24h the petriplates were stored in an incubator at 28 ± 2 °C. The zone of inhibition thus formed around each disc containing the test compounds was measured accurately in mm. The organisms used in these investigations included *Sarcina lutea* (Gram positive) and *Escherchia coli* (Gram negative).

EXPERIMENTAL

Preparation of the ligand L_1 and L_2

{2,8,14.20.25,26,27,28octaazapentacyclo[19.3.$1^{1,21}$.$1^{3,7}$.$1^{9,13}$.$1^{15,19}$]octacosa[1(25),2,7,9(27),10,12,14, 19,21,23] decaene and 2,6,12,16,21,22hexaazatricyclo[15.3.$1^{1,17}$.$1^{11,7}$] docosa 1,6,11,16 teraene.

Hot ethanolic solution (20mL) of glutarimide (5 mmol, 5.65 g) and a hot ethanolic solution (20mL) of L_1; 2, 6 diaminopyridine (5 mmol, 5.45 g), L_2; 1, 3, diaminopropane (5 mmol, 3.7 g) were mixed slowly with constant stirring. This mixture was refluxed at ~ 76^oC for 8h in presence of few drops of concentrated hydrochloric acid. On cooling dark brown (L_1) and cream colored (L_2) compounds separated out, which were filtered, washed with cold ethanol and dried under vacuum over P_4O_{10}. (Yield - 18%, 20%). Since the ligands yield are very poor all complexes were prepared by the template method.

Preparation of Cu (II) complexes of L_1 and L_2 (Template Method)

A mixture of an ethanolic solution (20mL) of glutarimide (5 mmol, 5.65 g), L_1 ; 2,6 diaminopyridine (5 mmol, 5.45 g), L_2; 1,3,diaminopropane (5 mmol, 3.7 g) and an ethanolic solution (20 mL) of appropriate metal salt (2.5mmol) (except for metal sulphate where aqueous solution was used) was refluxed for 5-6h at 70°C. On cooling the solution for 10h at 0°C, the colored complexes that separated out were washed with ethanol and dried over silica gel. The purity of the complexes was checked by TLC in DMF using pet ether as eluents**.**

RESULTS AND DISCUSSIONS

The complexes were stable in atmosphere and were polycrystalline. All the complexes have high melting point (>250°C). The results of elemental analysis [Table 3] support the proposed macrocyclic structure. The molar conductance values of all the complexes in DMSO solution suggest that the complexes are 1:2 electrolytes [10]. Magnetic moments of the complexes under study at room temperature lie in the range of 1.90 to 1.97 B.M. corresponding to one unpaired electron. I.R Spectra of the ligands shows the absence of absorption around 3400cm^{-1} and 1700cm^{-1} indicates that there is no free amino or C=O group. It also supports the macrocyclic structure and complete condensation. Presence of absorption band at 1680-1685 cm^{-1} attribute to the imine ν (C=N) [10] group. Further in L_1 two extra medium bands at 1593-1591cm^{-1} and 1499-1497 cm^{-1} are expected for the two highest energy pyridine ring vibrations. Mass spectra of L_1 shows a peak 371 amu corresponding to molecular ion (M^{+}+ 1) and different peaks corresponding various fragments [Fig 1]. Mass spectra of L_2 shows a peak 301 amu corresponding to molecular ion (M^{+}+ 1) and different peaks corresponding various fragments [Fig.2].

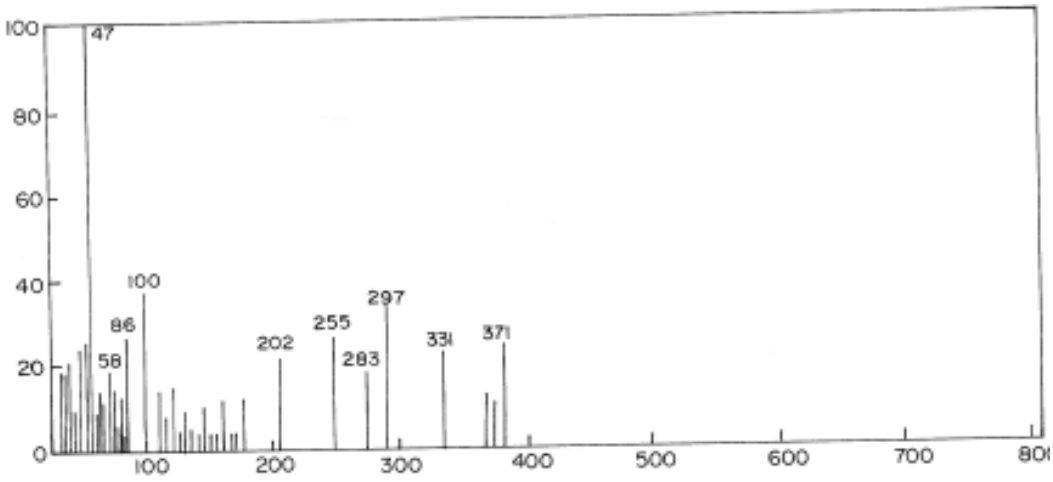

Fig. 1: Mass Spectra of Ligand 1

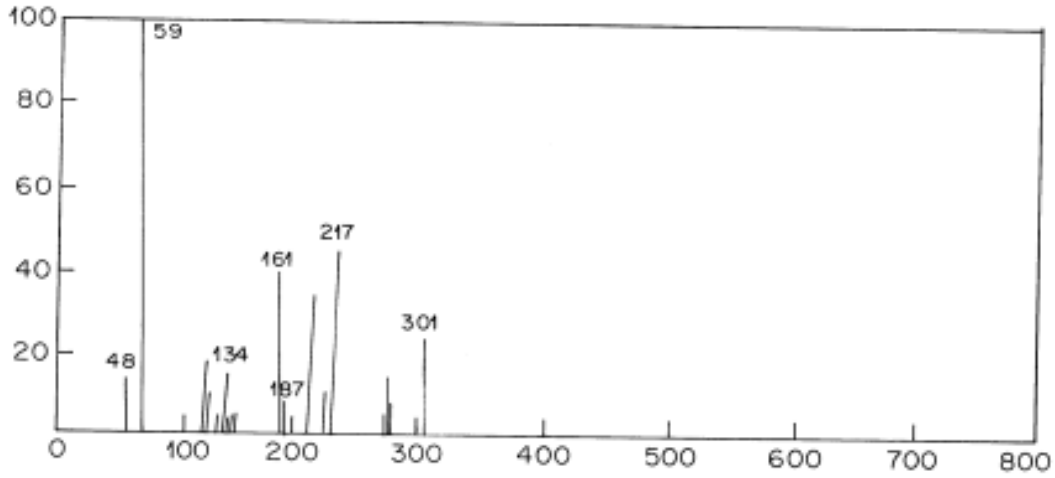

Fig. 2: Mass Spectra of Ligand 2

I.R spectra of copper complexes of the type $[CuL_1]X_2$ presence of absorption at 1593-1591 cm^{-1} and 1499-1497 cm^{-1} shows that pyridine nitrogen does not take part in the coordination. On comparing with the ligands, the complexes $[CuL_1]X_2$ and $[CuL_1]X_2$ shows the slight negative shift in the ν (N-H) and ν (C=N) band which appeared in the region 3210-3233 cm^{-1} and 1650-1655 cm^{-1} was noticed. It is ascribed to the coordinated N-H and C=N stretching vibrations. This is further substantiated by the fact that all the complexes show a medium intensity band in the region 429-433 cm^{-1} which is attributed to Cu-N stretching vibrations [10]. I.R spectra of nitrato complexes display one absorption band at 1380-1386 cm^{-1} suggests that both the nitrate ions are uncoordinated to metal ion [10]. I.R spectra of sulphato complexes show a single broad sharp band near 1099-1100 cm^{-1} indicating that the sulphate ion is uncoordinated to metal ion in the complexes [10].

The electronic spectra of complexes reported here show characteristic bands at 13400–13470 and 18500–18700 cm^{-1} [Table 5]. These may be assigned to the $^2B_{1g} \rightarrow {}^2A_{1g}$ and $^2B_{1g} \rightarrow {}^2E_g$ transitions respectively [11]. Complexes under study showed anisotropic EPR spectra characteristic of tetragonal Cu^{2+}. g–Values (Table 6). **The TGA** of $[CuL_1]X_2$ and $[CuL_1]X_2$ have been recorded under nitrogen atmosphere at a heating rate of 10°C / min over the temperature range of 25 – 600.0°C and their decomposition started in this temperature range and were completed at 500.0°C No weight loss up to 100°C indicates the absence of lattice water molecules in all complexes. The first thermal degradation in all the complexes occurred in the range 150 – 200°C corresponding to the loss of uncoordinated anions. In the subsequent steps weight loss is due to organic molecule. Since thermograms were obtained in nitrogen atmosphere, only metal was left in the end [Table 4]. **Antimicrobial assays:** The results of the biological activity have been compared with the conventional fungicide Bavistin and the conventional bactericide Streptomycin used as standards. The results achieved out of these studies have been enlisted in [Table 1 and Table 2].

Table 1: Fungicidal screening data of the ligands and their copper (II) complexes

Compound	Aspergillus niger			Aspergillus glaucus		
	50 ppm	**100 ppm**	**200 ppm**	**50 ppm**	**100 ppm**	**200 ppm**
Bavistin	70	100	110	75	100	120
L^1	32	49	65	29	51	71
L^2	35	44	51	34	–	60
$[CuL_1](NO_3)_2$	64	76	86	74	81	85
$[CuL_1]SO_4$	64	72	82	60	69	82
$[CuL_2]Cl_2$	39	58	83	36	55	–
$[CuL_2]SO_4$	63	80	94	67	87	100

Table 2: Bactericidal screening data of the ligands and their Cu (II) complexes

Compound	Sarcina lutea(+)		Escherchia coli(-)	
Streptomycin	10	15	12	20
L^1	6	8	5	8
L^2	6	9	5	7
$[CuL_1](NO_3)_2$	8	11	7	12
$[CuL_1]SO_4$	6	10	8	10
$[CuL_2](NO_3)_2$	8	12	9	12

CONCLUSION

On the basis of spectral analysis (IR, EPR, U.V-VISIBLE, and MASS) and magnetic **studies** it is clear that the ligands are acting as hexadentate chelating agents having six coordination sites. All the copper (II) complexes have tetragonal geometry. From antimicrobial Assays studies it can be seen that variation in the ligand and anion imposes an influence on the bacterial and fungal activities. Single crystals of the complexes could not be isolated from any solutions, thus no definitive structure may be described. However, the analytical, spectroscopic, magnetic data and thermal investigation enable us to predict the possible structures as shown in Fig. 4 and 5

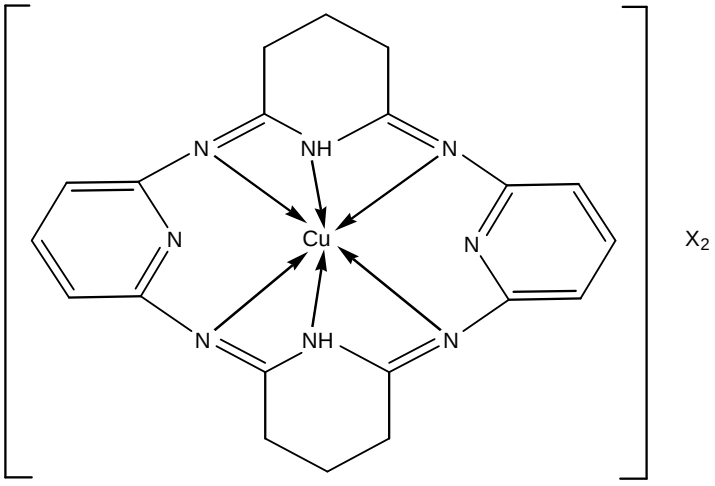

Fig. 4: Structure of $[CuL_1]X_2$ (where $X = NO_3^-, ½SO_4^{-2}$)

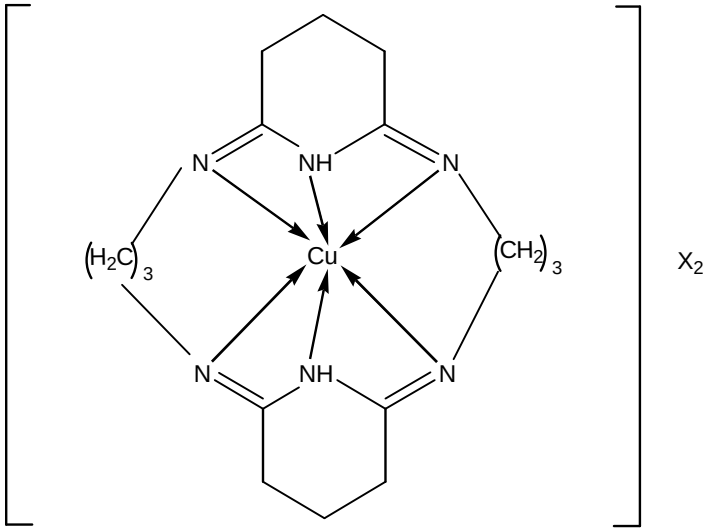

Fig. 5: Structure of $[CuL_1]$ X2 (where X = NO_3^-, $½SO_4^{-2}$)

Table 3: Analytical and Physical data of the Complexes

Complexes Molecular Formula	**Molecular Wt. found(Calc.)**	**Colour**	**M.Pt ^{0}C**	**Molar cond. $\Omega^{-1}cm^2mol^{-1}$**	**Yield %**	**Found(Calc.%)**			
						M	**C**	**H**	**N**
$[Cu(L_1)]SO_4$ ($C_{20}CuH_{20}N_8O_4S$)	531.54 (530)	Dark Brown	254	249	68	11.95 (11.97)	45.15 (45.17)	3.76 (3.77)	21.07 (21.08)
$[Cu(L_1)](NO_3)_2$ ($C_{20}CuH_{20}N_{10}O_6$)	559.54 (558)	Earthy brown	270	262	62	11.35 (11.36)	42.89 (42.90)	3.57 (3.58)	20.01 (20.03)
$[Cu(L_2)]SO_4$ ($C_{16}CuH_{26}N_6O_4S$)	461.54 (460)	Dark blue	265	217	73	13.76 (13.77)	42.46 (42.48)	5.63 (5.64)	18.19 (18.20)
$[Cu(L_2)](NO_3)_2$ ($C_{16}CuH_{26}N_8O_6$	489.54 (488)	Dark blue	260	233	70	12.97 (12.99)	40.03 (40.05)	5.31 (5.33)	17.15 (17.16)

Table 4: TGA data of the complexes [weight loss %, found (calculated)].

Complexes	First step (°C)	Second step (°C)	Third step (°C)	Residue (%) Found (Calc.)
$[Cu(L_1)]SO_4$	160.0-195.0 19.01(18.06)	195.0-300.0 27.96(28.97)	300.0-500.0 41.05(41.01)	11.98(11.96) 88.02(88.04)[a]
$[Cu(L_1)](NO_3)_2$	160.0-200.0 22.19(22.16)	200.0-300.0 26.45(27.52)	300.0-500.0 37.95(38.96)	13.41 (11.36) 88.64(86.59)[a]
$[Cu(L_2)]SO_4$	160.0-185.0 21.71(20.79)	185.0-300.0 29.88(30.33)	300.0-500.0 35.10(35.09)	13.31(13.79 86.69(86.21)[a]
$[Cu(L_2)](NO_3)_2$	160.0-190.0 26.31(25.32)	190.0-300.0 28.59(28.59)	300.0-500.0 34.12(33.09)	12.11(13.00) 87.99(87.00)[a]

Table 5: Electronic and ESR Spectral bands of Cu (II) complexes

Complexes	Electronic spectral bands (cm^{-1})	μ_{eff} (B.M.)	$g_{\|\|}$ or g_3	G_2	$g_\perp$ or g_1	G
$[Cu(L_1)]SO_4$	13425, 18504	1.92	2.22	2.21	2.0710	5.43
$[Cu(L_1)](NO_3)_2$	13489, 18507	1.97	2.26	2.23	2.0627	5.41
$[Cu(L_2)]SO_4$	13572, 18572	1.94	2.29	2.17	2.0619	4.82
$[Cu(L_2)](NO_3)_2$	13589, 18699	1.99	2.27	2.13	2.04	4.79

$g_\perp = (3g_{iso} - g_{\|\|}) / 2$, $A_\perp = (3A_{iso} - A_{\|\|}) / 2$

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