

SYNTHESIS, SPECTRAL AND ANTIFUNGAL STUDIES OF COPPER(II) TETRA AZA MACROCYCLIC COMPLEXES

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A novel family of Tetra aza macrocyclic Cu(II) complexes $[CuLx_2]$ where L = N₄ donor macrocyclic ligand and X = Cl⁻, NO₃⁻ and (CH₃COO⁻) have been synthesized and characterized by elemental analysis, magnetic moment, IR, EPR, electronic spectra. The molar conductance measurements of crown ether complexes of ligand LF and LG show that complexes are in 1:2 electrolytes in nature and may be formulated as $[Cu(L)]X_2$ where L=LF & LG. The biological against different plant pathogenic fungi has been evaluated. The EPR studies suggest the tetragonal geometry for all the chloride, nitrate and acetate complexes with all the seven ligand.

KEYWORD : A.macrocyclic complex, IR, magnetic moment, antifungal activity

INTRODUCTION

Copper is the third most abundant metallic element in the human body, following iron and zinc. Though trace amount of copper is essential for life, larger amounts become toxic. Copper containing enzymes[1]and proteins are widely distributed in both *fauna and flora* kingdoms. The accumulation of copper in the liver, kidneys and brain leads to *Wilson's disease* that is hereditary shortage of ceruloplasmin. It can be treated by giving EDTA that form a complex with copper and then is excreted [2]. a great deal of study of copper complexes has been driven by the hope of modeling biological molecules that contain copper [3-5]. Plastocyanin occurs in the chloroplasts of green plants and contains one copper atom. It is used in photosynthesis as an electron carrier [6-7]. They have attracted much attention because in addition to have antimicrobial and antiviral properties, they have also used in the treatment of a number of tumors, including Hodgkin's disease [8-9].

EXPERIMENTAL

SYNTHESIS OF LIGANDS

Ligand LA

Hot ethanolic solution (50 mL) of diethyloxalate (7.30 g, 0.05 mol) and a hot ethanolic solution (50 mL) of 1,3-diaminopropane (3.70 g, 0.05 mol) were mixed slowly with constant stirring. This mixture was refluxed at 80°C (+5°C) for 6h in the presence of few drops of concentrated hydrochloric acid. On cooling, white coloured precipitate was formed. It was filtered, washed with cold EtOH, and dried under vacuum over P4O10. Yield 78%, m.p. 240°C.

Ligand LB

Hot ethanolic solution (50 mL) of diethyloxalate (7.30 g, 0.05 mol) and a hot ethanolic solution (50 mL) of 2,6-diaminopyridine (5.46 g, 0.05 mol) were mixed slowly with constant stirring. This mixture was refluxed at 75°C (+30°C) for 9h in the presence of few drops of concentrate dihydrochloric acid. On cooling, dull white coloured precipitate was formed. It was filtered, washed with cold EtOH, and dried under vacuum over P4O10- Yield 75%, m.p. 269°C.

Ligand LC

Hot ethanolic solution (50 mL) of ethylcinnamate (8.80 g, 0.05 mol) and a hot ethanolic solution (50 mL) of 1,3-diaminopropane (3.70 g, 0.05 mol) were mixed slowly with constant stirring. This mixture was refluxed at 72°C for 6h in the presence of few drops of concentrated hydrochloric acid. On cooling, cream coloured precipitate was formed. It was filtered, washed with cold EtOH, and dried under vacuum over P4O10. Yield 80%, m.p. 271°C.

Ligand LD

Hot ethanolic solution (50 mL) of ethylcinnamate (8.80 g, 0.05 mol) and a hot ethanolic solution (50 mL) of thiourea (3.80 g, 0.05 mol) were mixed slowly with constant stirring. This mixture was refluxed at 78°C for 7h in the presence of few drops of concentrated hydrochloric acid. On cooling, white coloured precipitate was formed. It was filtered, washed with cold EtOH, and dried under vacuum over P4O10. Yield 77%, m.p. 281°C.

Ligand LE

Hot ethanolic solution (30 mL) of thiodiglycolic acid (7.50 g, 0.05 mol) and a hot ethanolic solution (30 mL) of thiourea (3.80 g, 0.05 mol) were mixed slowly with constant stirring. This mixture was refluxed at 68°C for 6h in the presence of few drops of concentrated hydrochloric acid. On cooling, pale white coloured precipitate was formed. It was filtered, washed with cold EtOH, and dried under vacuum over P4O10. Yield 69%, m.p. 267°C.

Ligand LF and LG (Crown ether)

Ligand LF and LG purchased from Sigma Eldrich and used as such without any further purification.

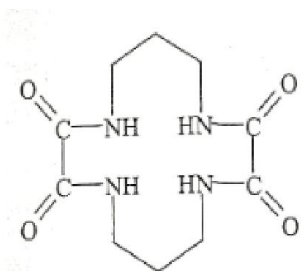


Fig. 1 : Ligand LA

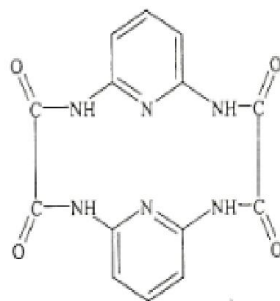


Fig. 2 : Ligand LB

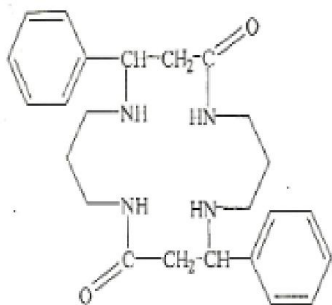


Fig. 3 : Ligand LC

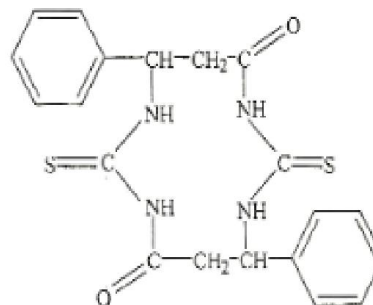


Fig. 4 : Ligand LD

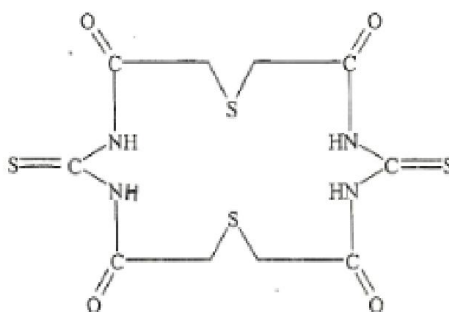


Fig. 5 : Ligand LE

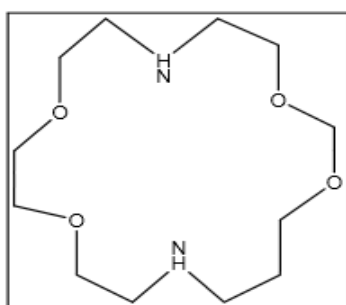


Fig. 6 : Ligand LF

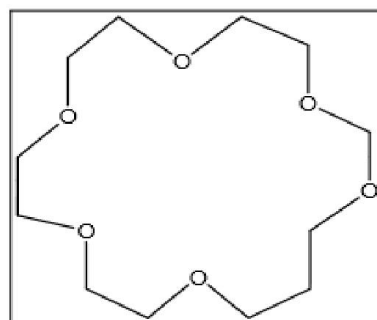


Fig. 7 : Ligand LG

SYNTHESIS OF COMPLEXES

A hot ethanolic solution (20 mL) of the ligand L (0.002 mol; L = LA: 0.512g; LB:0.652g; LC: 0.816g; LD: 0.824g and LE: 0.760g) and hot ethanolic solution (20 mL) of corresponding Cu(II) salt (0.001 mol) ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$), $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$) were mixed together with constant stirring. The mixture was refluxed for 4-9h at 65-80°C. On cooling, coloured complex was precipitated out. It was filtered, washed with cold EtOH and dried under vacuum over P4O10, recrystallized and purity was

checked by TLC method, yield 55-71%. Hot aqueous solution (10mL) of ligand (0.002 mol; LF:0.052g; LG:0.052g) and corresponding Cu(II) salt (0.001 mol) were mixed with constant stirring. The mixture was refluxed for 10h at 40°C. On cooling, coloured complex was precipitated out, which was filtered, washed with cold EtOH and dried under vacuum over P4O10.

RESULTS AND DISCUSSION

On the basis of elemental analysis the complexes were found to possess the general compositions $CuLX_2$ (where L = LA, LB, LC, LD and LE, X = Cl^- , NO_3^- and CH_3COO^-). The room temperature molar conductance measurement indicates that all the complexes are non-electrolyte in nature. Thus these complexes may be formulated as $[Cu(L)X_2]$ (where L = LA, LB, LC, LD and LE, X = Cl^- , NO_3^- and CH_3COO^-) [Table 1]. Where as molar conductance measurements of crown ether complexes of ligand LF and LG shows that complexes are 1:2 electrolyte in nature and may be formulated as $[Cu(L)]X_2$ (where L=LF, LG).

Table 1: Molar conductance and elemental analysis of the complexes

Complexes	M.W. amu	Molar Cond. $\Omega^{-1}cm^2 mol^{-1}$	Colour	Yield %	M.P. (°C)	Elemental analyses % Found (Calculated%)			
						Cu	C	H	N
$[Cu(LA)Cl_2]$ $Cu C_{11}H_{12}N_2O_4Cl_2$	391	09	New satin blue	68	286	16.30 (16.37)	30.58 (30.69)	4.00 (4.09)	14.41 (14.32)
$[Cu(LA)(NO_3)_2]$ $Cu C_{11}H_{12}N_4O_{10}$	444	08	Opaline green	62	282	14.49 (14.41)	27.11 (27.03)	3.67 (3.60)	18.98 (18.92)
$[Cu(LA)(CH_3COO)_2]$ $Cu C_{14}H_{22}N_2O_6S_2$	438	05	Oxford blue	65	277	14.70 (14.61)	38.43 (38.36)	4.97 (5.02)	12.70 (12.79)
$[Cu(LB)Cl_2]$ $Cu C_{11}H_{12}N_2O_4Cl_2$	461	06	Phirozi	61	284	13.95 (13.88)	36.32 (36.44)	2.11 (2.17)	18.14 (18.22)
$[Cu(LB)(NO_3)_2]$ $Cu C_{11}H_{12}N_4O_{10}$	514	07	Shiny purple	60	289	12.51 (12.45)	32.60 (32.68)	1.99 (1.95)	21.70 (21.79)
$[Cu(LB)(CH_3COO)_2]$ $Cu C_{14}H_{22}N_2O_6S_2$	508	05	Nile blue	61	>300	12.68 (12.60)	42.44 (42.52)	3.21 (3.15)	16.46 (16.54)
$[Cu(LC)Cl_2]$ $Cu C_{12}H_{12}N_2O_4Cl_2$	543	10	Shiny blue	68	290	11.70 (11.79)	52.96 (53.04)	5.95 (5.89)	10.25 (10.31)
$[Cu(LC)(NO_3)_2]$ $Cu C_{12}H_{12}N_4O_{10}$	596	08	Aqua marine	60	>300	10.72 (10.74)	48.41 (48.32)	5.30 (5.37)	14.00 (14.09)
$[Cu(LC)(CH_3COO)_2]$ $Cu C_{15}H_{12}N_2O_6S_2$	590	03	Sea green	58	277	10.93 (10.85)	57.02 (56.95)	6.52 (6.44)	9.40 (9.49)
$[Cu(LDCl_2)]$ $Cu C_{10}H_{12}N_2O_4S_2Cl_2$	547	04	Nilgiri blue	70	>300	11.61 (11.70)	43.80 (43.88)	3.73 (3.66)	10.17 (10.24)

Magnetic Moment

Magnetic moments of all the complexes at room temperature lie in the range 1.93 to 2.04B.M, [Table2], corresponding to one unpaired electron. There should be some correlation between the magnitude of orbital contribution and the coordination geometry but in practice it is not observed, presumably because of distortion and other variables like covalent character. Some of these complexes may be considered to have tetragonal geometries with planar

coordination of the ligand around Cu^{2+} ion and the anions occupying the axial positions and six coordinate octahedral geometry.

Table 2 : Electronic spectra of the complexes

Complexes	$\lambda_{\text{max}}(\text{cm}^{-1})$
[Cu(LA)Cl ₂]	10526,15986,26247
[Cu(LA)(NO ₃) ₂]	10542,17212,28736
[Cu(LA)(CH ₃ COO) ₂]	10672,16318,24038
[Cu(LB)Cl ₂]	10430,16000,23255
[Cu(LA)(NO ₃) ₂]	10460,22988
[Cu(LB)(CH ₃ COO) ₂]	10668,16667,26398
[Cu(LC)Cl ₂]	10183,17322,24376
[Cu(LC)(NO ₃) ₂]	10885,15432,24358
[Cu(LC)(CH ₃ COO) ₂]	11210,13889,25562
[Cu(LD)Cl ₂]	10718, 18622, 27119
[Cu(LD)(NO ₃) ₂]	15432,20120
[Cu(LD)(CH ₃ COO) ₂]	10905,16110,27933
[Cu(LE)Cl ₂]	10648, 16000
[Cu(LE)(NO ₃) ₂]	15972,17183
[Cu(LE)(CH ₃ COO) ₂]	11792,18622,27397

Infra red Spectra

A comparative study of the spectra of the ligand and their complexes show that all the ligand behave as octahedral [10-14] coordinating through nitrogen atom of the -NH groups.

IR Spectral Bands Due to Anions

IR spectra of nitrate complexes

The IR spectra of nitrate complexes of the ligands LA, LB, LC, LD, and LE show absorption bands in the region of 1423-1438 (ν_5) $\nu_a(\text{NO}_2)$, 1307-1347(ν_1) $\nu_s(\text{NO}_2)$ and 811-830 cm^{-1} (ν_2) $\nu(\text{NO})$. This indicates that both the nitrate groups are coordinated to the centrally located copper(II) metal ion in an unidentate fashion [15-19]. In case of the nitrate complex of ligand LG shows bands at 1382 cm^{-1} indicates that nitrate complex is uncoordinated where as appearance of band at 510 cm^{-1} strengthens the fact that metal and oxygen lie in the same environment.

IR spectra of chloride complexes

Infra red spectra of of Cu (II) chloride complexes of crown ether, with ligand LF display bands at 3448 cm^{-1} , 3000 cm^{-1} , 986 cm^{-1} of $\nu(\text{N-H})$, $\nu(\text{C-H})$ aliphatic and alkyl ether respectively and in complex of ligand LG bands appear at 3319 cm^{-1} , 988 cm^{-1} of $\nu(\text{C-H})$ aliphatic and alkyl ether respectively. Shifting of bands gives strong support to the formation of complexes.

However, an IR spectrum of ligand LF shows a band at 411cm^{-1} supports that metal is coordinated with nitrogen. There is not any band is found at $307\text{ }321\text{cm}^{-1}$ indicates that chloride is uncoordinated. Where as in ligand LG appearance of band at 257 cm^{-1} gives sturdy fact that metal is coordinated metal in the same environment.

Table-3: Magnetic moment of the complexes

Complexes	μ_{eff} (B.M.)
[Cu(LA)Cl ₂]	1.95
[Cu(LA)(NO ₃) ₂]	1.99
[Cu(LA)(CH ₃ COO) ₂]	2.00
[Cu(LB)Cl ₂]	2.01
[Cu(LB)(NO ₃) ₂]	1.93
[Cu(LB)(CH ₃ COO) ₂]	1.95
[Cu(LC)Cl ₂]	2.00
[Cu(LC)(NO ₃) ₂]	1.97
[Cu(LC)(CH ₃ COO) ₂]	1.94
[Cu(LD)Cl ₂]	2.04
[Cu(LD)(NO ₃) ₂]	1.96
[Cu(LD)(CH ₃ COO) ₂]	2.04
[Cu(LE)Cl ₂]	2.01
[Cu(LE)(NO ₃) ₂]	1.98
[Cu(LE)(CH ₃ COO) ₂]	2.02
[Cu(LF)Cl ₂]	1.94
[Cu(LG)Cl ₂]	1.98
[Cu(LG)(NO ₃) ₂]	1.95

IR spectra of acetate complexes

According to Nakamoto [20] the IR spectral bands corresponding to $\nu_a(\text{COO}^-)$ and $\nu_s(\text{COO}^-)$ are present at 1560 cm^{-1} and 1416 cm^{-1} for free acetate ion. The separation between them is 144 cm^{-1} . In the unidentate complex, $\nu(\text{C}=\text{O})$ is higher than $\nu_a(\text{COO}^-)$ and $\nu(\text{C}^-\text{O})$ is lower than $\nu_s(\text{COO}^-)$. Thus separation between the two $\nu(\text{C}^-\text{O})$ is much larger ($\sim 150\text{-}250\text{cm}^{-1}$) in unidentate complexes than in the free ion *i.e.* 144 cm^{-1} . But in bidentate complexes the separation between the two $\nu(\text{C}^-\text{O})$ is smaller ($< 50\text{ cm}^{-1}$) than that of the free ion. The IR spectra of acetate complexes under study, of ligands LA, LB, LC, LD and LE show bands in the region $1560\text{-}1590\text{ cm}^{-1}$, $\nu(\text{C}=\text{O})$, $1385\text{-}1405\text{ cm}^{-1}$, $\nu(\text{C}^-\text{O})$. The difference between these two bands $A = 158\text{-}241\text{cm}^{-1}$, which suggests that the acetate group is, coordinated to the copper ion, in unidentate manner. [21-23].

Electronic Spectra

The electronic spectra of six-coordinate Cu(II) complexes have either D_{4h} or C_{4v} symmetry. The ground state in an octahedral field is the 2E_g. According Hathaway[24], very few regular octahedral Cu(II) complexes exist. In an octahedral field if the E_g and T_{2g} separation varies from 13000 to 18000 cm^{-1} results distortions. Because of Jahn-Teller effect

operating on the $2E_g$ ground term of an octahedron, distortions will occur. It is useful to define a tetragonality factor T (where $T = \text{in-plane Cu-L distance} / \text{mean out-of-plane Cu-L distance}$). In general T may be less than one or greater than one. Thus due to distortions a several absorption bands may be expected in these regions. The E_g and T_{2g} levels of the 2D free ion term will split into B_{1g} , A_{1g} , B_{2g} and E_g levels respectively. Thus three spin-allowed transitions are expected in the visible and near IR region in Cu(II) complexes. The energy level sequence will depend on the amount of tetragonal distortion due to ligand- field and the Jahn-Teller effect [25-26]. The electronic spectra of tetragonal complexes show bands in range of 13,400-13,800 and 18,500-18,900 cm^{-1} which can be assigned to $2B_{1g} \rightarrow 2A_{1g}$ and $2B_{1g} \rightarrow E_g$ transitions respectively. $2B_{1g} \rightarrow 2B_{2g}$ is usually not observed as a separate band in the tetragonal field [27]. The splitting of the E_g state is a measure of the planar and axial field.

Table-4: EPR spectra of the complexes

Complexes	a_{\perp}	\bar{g}_{\parallel}	\bar{g}_{iso}	G
[Cu(LA)Cl ₂]	2.1760	2.0519	2.0932	3.3911
[Cu(LA)(NO ₃) ₂]	2.2402	2.1345	2.1697	1.7859
[Cu(LA)(CH ₃ COO) ₂]	2.2191	2.1248	2.1562	1.7556
[Cu(LB)Cl ₂]	2.1156	2.0430	2.0672	2.6883
[Cu(LB)(NO ₃) ₂]	2.1687	2.0686	2.1020	2.4592
[Cu(LB)(CH ₃ COO) ₂]	2.1480	2.0596	2.0891	2.4832
[Cu(LC)Cl ₂]	2.1492	2.0563	2.0873	2.6500
[Cu(LC)(NO ₃) ₂]	2.1142	2.0522	2.0729	2.1877
[Cu(LC)(CH ₃ COO) ₂]	2.1913	2.0496	2.0968	3.8568
[Cu(LD)Cl ₂]	2.1220	2.0530	2.0760	2.3019
[Cu(LD)(NO ₃) ₂]	2.0998	2.0499	2.0665	2.0000
[Cu(LD)(CH ₃ COO) ₂]	2.1810	2.0580	2.0990	3.1206
[Cu(LE)Cl ₂]	2.1722	2.0776	2.1091	2.2190
[Cu(LE)(NO ₃) ₂]	2.2086	2.0882	2.1283	2.3650
[Cu(LE)(CH ₃ COO) ₂]	2.1634	2.0638	2.0970	2.5611
[Cu(LF)Cl ₂]	-	-	1.819	-
[Cu(LG)Cl ₂]	-	-	1.843	-
[Cu(LG)(NO ₃) ₂]	-	-	1.845	-

Electronic spectra of chloride, nitrate and acetate Cu(II) complexes

The electronic spectra of the chloride and acetate complexes with all the five ligands LA, LB, LC, LD and LE and with LA, LB and LC ligands complexes show three bands in range of

10183-11792 cm^{-1} , 13889-18622 cm^{-1} and 22988-28736 cm^{-1} corresponds to tetragonal geometry, which can be assigned to $2B1g \rightarrow 2A1g$, $2B1g \rightarrow 2B2g$ and $2B1g \rightarrow 2Eg$ transitions, respectively. In all cases the transition $2B1g \rightarrow 2B2g$ is usually not observed as a separate band in the tetragonal field [28]. The bands above $25,000\text{cm}^{-1}$ in some cases, may be due to charge transfer bands [Table2] which could arise from the transfer of an electron from an orbital largely belonging to a central atom. The splitting of the $2Eg$ state is a measure of the planar and axial field. Since the planar field as well as axial field is constant in all the present complexes, the difference in the position of the bands may be due to axial field only (lower symmetry). In the copper(II) complexes $2B2g \rightarrow 2A1g$ transition is shifted to higher energies in the order: $\text{Cl}^- < \text{NO}_3^- < \text{CH}_3\text{COO}^-$ [29].

Table-5: Bonding coefficient parameters of the complexes

Complexes	K_{\perp}	K_{\parallel}	α	β
[Cu(LA)Cl ₂]	0.7261	0.6494	0.6494	1.1181
[Cu(LA)(NO ₃) ₂]	1.2404	0.7886	0.7886	1.5729
[Cu(LA)(CH ₃ COO) ₂]	1.0920	0.7330	0.7330	1.4898
[Cu(LB)Cl ₂]	0.6191	0.5247	0.5247	1.1799
[Cu(LB)(NO ₃) ₂]	0.7857	-	-	-
[Cu(LB)(CH ₃ COO) ₂]	0.7827	0.6073	0.6073	1.2888
[Cu(LC)Cl ₂]	0.7302	0.6217	0.6217	1.1745
[Cu(LC)(NO ₃) ₂]	0.7016	0.5121	0.5121	1.3700
[Cu(LC)(CH ₃ COO) ₂]	0.6998	0.6314	0.6314	1.1083
[Cu(LD)Cl ₂]	0.7462	0.5819	0.5819	1.2823
[Cu(LD)(NO ₃) ₂]	0.8057	-	-	-
[Cu(LD)(CH ₃ COO) ₂]	0.7938	0.6612	0.6612	1.2005
[Cu(LE)Cl ₂]	-	0.6426	0.6426	-
[Cu(LE)(NO ₃) ₂]	1.0878	-	-	-
[Cu(LE)(CH ₃ COO) ₂]	0.8261	0.6750	0.6750	1.2238

Antifungal screening

The antifungal [30-35] activity of Cu(II) complexes was checked, by the agar plate technique [36] for the *Aspergillus-niger* and *Aspergillus-glaucus* fungi. The compounds were directly mixed to the medium in different concentrations. The fungus was placed in the medium with the help of an inoculum needle. The petri-dishes were wrapped in polythene sheets, containing some drops of EtOH and kept in incubator at $35 \pm 2^\circ\text{C}$ for 66-75 h. The growth of fungus was measured by the recording the diameter of fungal colony. The following relation was used to calculate the fungal growth inhibition. Fungal growth inhibition % = $(A - B) \times 100/A$ Where: A = diameter of fungal colony in control plate. B = diameter of fungal colony in test plate. The Cu(II) complexes show fungal growth inhibition in the order: $\text{LA} < \text{LB} < \text{LC} < \text{LE} < \text{LD}$, The results of antifungal activity are shown in Table-6 100% growth of

fungus which is represented as *, 50% growth by- **, less than 50% growth by-*** and noble inhibition by-****.

Table-6: Antifungal activity of the Cu(II) complexes

Complexes	Fungal growth inhibition in %	
	<i>A. niger</i>	<i>A. glaucus</i>
[Cu(LA)Cl ₂]	***	*
[Cu(LA)(NO ₃) ₂]	**	***
[Cu(LB)Cl ₂]	***	***
[Cu(LB)(NO ₃) ₂]	***	***
[Cu(LC)Cl ₂]	***	***
[Cu(LC)(NO ₃) ₂]	***	****
[Cu(LD)Cl ₂]	****	***
[Cu(LD)(NO ₃) ₂]	***	****
[Cu(LE)Cl ₂]	****	***
[Cu(LE)(NO ₃) ₂]	***	***

CONCLUSION

On the basis of elemental analysis, molar conductance measurements, magnetic susceptibility, IR, electronic and EPR spectral studies and the subsequent discussion given above the following structures [Figs. 9-14] has been assigned for the copper(II) complexes. X = Cl⁻, NO₃ and CH₃COO

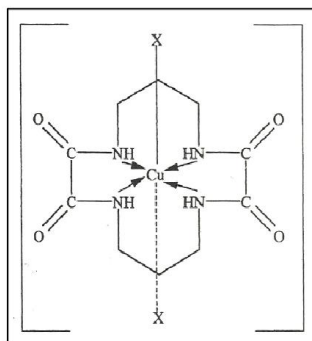


Fig. 9. Complexes with ligand LA

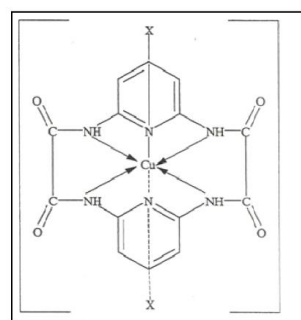


Fig. 10. Complexes with ligand LB

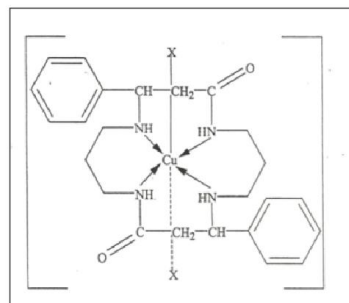


Fig. 11. Complexes with ligand LC

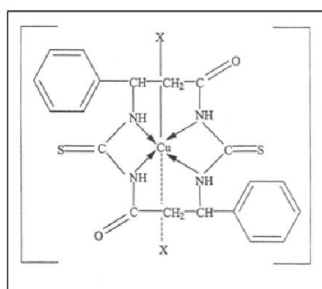


Fig. 12. Complexes with ligand LD

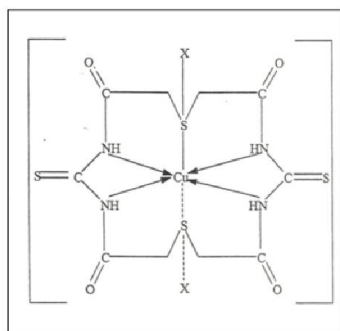


Fig. 12. Complexes with ligand LE

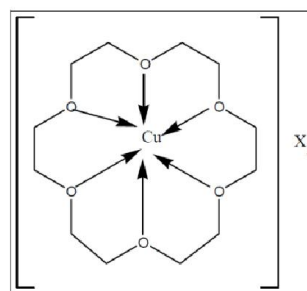


Fig. 13. Complexes with ligand LF

REFERENCES

1. Cotton, F.A., Wilkinson, G., Murillo, C.A. and Bochman, M., "Advanced Inorganic Chemistry", Sixth Edition, John Wiley and Sons, Inc. (1999).
2. Xavier, A. V., Frontiers in Bioinorganic Chemistry, VCH Eds. (1985).
3. Li, M. F. and Palmer, G., *Biochemistry*, **1867**, 40 (2001).
4. Pozdnyakova, I. and Stafshede, P. W., *Biochemistry*, **13728**, 40 (2001).
5. Kuehn, U., Warzeska, S., Pritzkow, H. and Kiaemer, R., *J. Am. Chem. Soc.*, **6125**, 123(33), (2001).
6. Adam, E.T. and Harrison, Eds. P.M., *Metalloproteins*, Verlag Chemie, 1985.
7. A.G. Maiik, R.A. Scott and H.B. Gray, *J. Am. Chem. Soc.*, **4360**, 102 (1980).
8. Hecht, S.H., Bleomycin, Eds., *Chemical Biochemical and Biological Aspects*, Springer-Verlag, New-York (1979).
9. Satia, G.B., "Fundamental of Nuclear Pharmacy", Springer, New-York (1984).
10. Karciovglu, Z.A. and Sarper, R.M. (eds.); *Zinc and Copper in Medicine*, C.C. Thomas, Springfield, IL (1980).
11. Sarkar, B., "Metal Ions in Biological Systems" edited by H. Sigel, Vol. **12**, pp. 233-281 (1980).
12. Owen, C.A. (Jr.), "Copper Deficiency and Toxicity", Noyes Publication, New Jersey (1981).
13. Druce, P.M., Kingston, B.M., Lappert, M.F. and Srivastava, R.C., *J. Chem. Soc. A*, 2106 (1969).
14. Druce, P.M., Kingston, B.M., Lappert, M.F., Srivastava, R.C. and Frazer, M. J. and Newton, W.E., *J. Chem. Soc. A*, 2814 (1969).
15. Raines, R.J., Nyhoim, R.S. and Stiddard, M.H.B., *J. Chem. Soc. A*, 1606 (1966).
16. Gerioch, M. and Mason, R., *J. Chem. Soc.*, 296 (1965).
17. Tebbe, F.N. and Parshall, G.W., *J. Am. Chem. Soc.*, **3793**, 93 (1971).
18. Fritz, H.P. and Paulus, E.F., *Naturforsch. Z., J. Chem. Phys.*, **435**, 18b (1963).
19. Paiker, D.J., *J. Chem. Soc. A*, 1382 (1970).
20. Hyams, I. J., Bailey, R.T. and Lippincott, E.R., *Spectrochim Acta*, **273**, 23 A (1967).
21. Nakamoto, K., Udovich, C., Ferraro, J.R. and Quattrochi, A., *Appl. Spectrosc.*, **606**, 24 (1970).
22. Schafer, L., Brunvoli, J. and Cyvin, S.J., *J. Mol. Struct.*, **549**, 11 (1972).
23. Adams, D.M. and Fernado, W.S., *J. Chem. Soc. Dalton Trans.*, 2507 (1972).

24. Chandra, S., Sangeetika and Rathi, A., *J. Saudi Chem. Soc.*, **175**, 5 (2001).
25. Kantouri, M.L. and Hartophylles, M., *Polyhedron*, **789**, 11(7) (1992).
26. Chandra, S. and Sharma, K.K., *Acta. Chim. Acad. Sci. Hung.*, **111(1)**, 5-12 (1982).
27. Hathaway, B.J., Dufey, R.J. and Nichollas, P., *J. Chem. Soc.*, 1845 (1968).
28. Hathaway, B.J., *Essays in Chemistry* (Ed. J.N. Bardley and R.D. Gillard), Academic Press, New York, 61 (1971).
29. El-Sharnly, M.F., El-Dissowky, A., Salem, T. and Osman, M., *Inorg. Chim. Acta*, **40 (1)** (1980).
30. Singh, B., Yadav, B.P. and Aggarwal, R.C., *Ind. J. Chem.*, **23A**, 441 1984

