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Spectral Studies of Cu(II) Complexes of Substituted Schiff Bases

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Schiff base ligands (L) were synthesized using 2-hydroxy-1-napthaldehyde and various primary amines like anthranilic acid, *o*-toluidene, *p*-toluidene and aniline. Copper complexes of the Schiff base were synthesized having metal : ligand stoichiometry 1 : 1 or 1 : 2. The ligands and respective copper complexes were diagnosed for their analytical parameters and various spectral features. The structures of copper complexes were proposed on the basis of electronic absorption, IR spectra and ESR spectral data

INTRODUCTION

The literature survey reveals that Schiff base ligand is an excellent coordinating ligand and can exhibit variety in the structure of their metal complexes. Schiff bases and their copper complexes are known for their biological importance as fungicides[1, 2] and bactericides[3]. Some of the copper complexes are known to possess antiinflammatory[3] and anticancer[4] properties. Schiff bases can also be used as analytical reagents for transition metal analysis and as catalysts for epoxydation of olefins[5–7]. It becomes important and worth investigating the behaviour of various substituted Schiff bases with transition metals. Copper can provide best example for such structrual investigations.

For the purpose of systematic diagnosis few Schiff bases were selected and their copper complexes were synthesized and characterized for various spectral features. The Schiff's base ligands derived from 2-hydroxy-1-napthaldehyde and primary amines like anthranilic acid, *o*-toluidene, *p*-toluidene and aniline were used for this purpose.

EXPERIMENTAL

All the chemicals used for the synthesis and characterization were of synthetic grade. The ligand Schiff base was prepared by condensing stoichiometric amount of 2-hydroxy-1-napthaldehyde with different primary amines. The solution was refluxed on a water bath for 5 h. The ligand was separated from the mixture on cooling. The isolated product was filtered, dried and recrystallised using suitable solvent. The recrystallised product was characterized with its analytical parameters.

Copper complexes of the above Schiff bases were synthesized by mixing aqueous solution of copper acetate (1 mg/cm^3) with excess of methanolic solution of ligand. The mixture was refluxed on a water bath for 2 h. On cooling copper complexes of the Schiff base were precipitated. The crystalline product was filtered, washed and dried at 60°C. All the copper complexes were recrystallised from their methanolic solution prior to characterization.

The ligand and the respective copper complexes were tested for its antimicrobial activity using paper disc method. Four different types of indicator cultures were used to evaluate activity of ligand and copper complexes.

Each recrystallised copper complex was characterised for various physico-chemical parameters and analytical properties. Various spectral techniques were used to characterize these complexes. Electronic absorption spectra were recorded on UV spectrophotometer supplied by M/S Shimadzu, Japan. Similarly IR spectra were recorded on FTIR 4200 supplied by M/S Shimadzu, Japan. ESR spectra were recorded on an instrument from RSIC, IIT Powai. The results of all the above spectral investigations are summarized in Tables 1–3 and are discussed in the light of proposed structural configuration.

TABLE-1
ANALYTICAL CHARACTERISTICS OF LIGANDS AND COPPER COMPLEXES

Complex (Colour)	m.w.	m.p. (°C)	Molar cond. mho cm^2 mole^{-1}	Elemental analysis % Found (Calcd.)			
				C	H	N	Cu
$C_{17}H_{13}NO$	247.10	84	9.40	81.75	5.99	5.12	—
L_1 (yellow)				(82.56)	(5.30)	(5.67)	
$Cu(C_{17}H_{12}NO)_2$	553.72	—	47.29	72.11	4.75	4.94	10.97
$Cu(L_1)_2$ (green)				(73.68)	(4.00)	(5.06)	(11.47)
$C_{18}H_{15}NO$	261.12	127	11.55	82.81	5.46	5.06	—
L_2 (yellow)				(82.72)	(5.79)	(5.36)	
$Cu(C_{18}H_{13}NO)_2$	581.75	—	15.38	71.71	4.39	4.78	10.63
$Cu(L_2)_2$ (brown)				(74.26)	(4.51)	(4.51)	(10.92)
$C_{18}H_{15}NO$	261.12	134	16.96	83.27	5.49	5.08	—
L_3 (yellow)				(82.72)	(5.79)	(5.36)	
$Cu(C_{18}H_{13}NO)_2$	581.75	—	20.19	73.85	4.97	4.83	10.04
$Cu(L_3)_2$ (brown)				(74.26)	(4.51)	(4.81)	(10.92)
$C_{18}H_{13}NO_3$	291.10	231	24.22	73.04	4.09	4.09	—
L_4 (orange)				(74.20)	(4.50)	(4.81)	
$Cu(C_{18}H_{12}NO_3)$	352.53	—	47.29	59.99	3.38	4.86	17.37
$Cu(L_4)$ (green)				(61.25)	(3.14)	(3.91)	(18.02)

TABLE-2
UV VISIBLE AND IR SPECTRAL PROPERTIES OF LIGANDS AND COPPER COMPLEXES

Complex	Electrical Absorbance (cm^{-1})		IR Bands (cm^{-1})			
	UV Visible	Reflectance	ν(C—O)	ν(C=N)	ν(Cu—N)	ν(Cu—O)
L_1	21786 22779	—	1345	1620	—	—
$Cu(L_1)_2$	21739 24937 13793	22222 38095	1360	1600	560	465
L_2	21645 22675	—	1325	1620	—	—
$Cu(L_2)_2$	22727 25348	24509 41237	1360	1600	520	460
L_3	21645 22650	—	1320	1620	—	—
$Cu(L_3)_2$	22650 25773	23501 42283	1360	1600	560	460
L_4	21621 22522	—	1365	1610	—	—
$Cu(L_4)$	23068 30769	46296 23809	1380	1580	510	420

TABLE-3
ESR SPECTRAL STUDIES OF COPPER COMPLEXES

Complex	$g_{\parallel}$	$g_{\perp}$	g_{avg}	μ_{eff} (B.M.) from ESR	μ_{eff} (B.M.) Gouy's method
$Cu(L_1)_2$	1.8946	1.9463	1.9290	1.67	1.99
$Cu(L_2)_2$	1.9644	1.9874	1.9797	1.71	1.92
$Cu(L_3)_2$	1.9040	1.9557	1.9384	1.68	1.82
$Cu(L_4)$	1.8991	1.9797	1.9258	1.69	1.88

RESULTS AND DISCUSSION

All the ligands and copper complexes were crystalline in nature. The elemental analysis of these compounds agrees very well with theoretically calculated values. Copper complexes derived from ligands L_1–L_3 have metal: ligand stiochiometry 1:2 while copper complex of ligand L_4 has metal: ligand stoichiometry 1:1. All the complexes are anhydrous in nature and show appreciable stability at room temperature. The complexes are insoluble in various solvents but sufficiently soluble in ethanol, DMSO, chloroform, nitrobenzene, etc.

The 10^{-3} M solutions of complexes in nitrobenzene were used to measure the molar conductance. The low molar conductance values (15–47 mhos cm^2 $mole^{-1}$) of these complexes indicate non-electrolytic behavior.

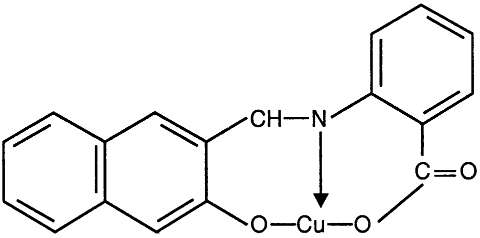
The salient features of IR absorption frequencies of ligands and their copper complexes are summarised in Table-2. The spectra of free Schiff base ligand exhibit a characteristic stretching frequency for hydroxyl group pointed in the region 3400 cm^{-1}, while $\nu(C{=}N)$ stretching vibrations for these ligands appear in the range 1620–1610 cm^{-1} as strong absorption bands. The absence of absorption bands in the region greater than 3400 cm^{-1} in the spectra of copper complexes suggests that oxygen atom of hydroxyl group is involved in coordination with metal ion after deprotonation. Similarly, the azomethine stretching vibration is shifted towards lower frequency in the corresponding spectra of copper complexes, indicating involvement of azomethine-N in coordination. The additional bands pointed in the spectra of copper complexes in the far IR region 560–510 cm^{-1} and 465–420 cm^{-1} are assignable to the stretching vibrations of (Cu—N) and (Cu—O) respectively.

Copper complexes were characterised with respect to various electronic transitions associated with it in the UV-visible spectral region. All the copper complexes are either green or brown in colour. The UV-visible spectra of the copper complexes exhibit broad adsorption bands around 24000 cm^{-1} which is assignable to charge-transfer transitions. Similarly absorption bands appearing in the range 21379–23068 cm^{-1} may be assigned to d-d transitions for these copper complexes. The diffused reflectance spectra of these copper complexes also exhibit d-d transitions for the ground state level $2B_g^1 \rightarrow 2B_g^2$. Ganorkar *et al.*[10] have also reported copper complexes to exhibit charge transfer and d-d transitions in the similar range. Many researchers have reported that copper complexes which exhibit such d-d transitions may be assigned square-planar geometry.

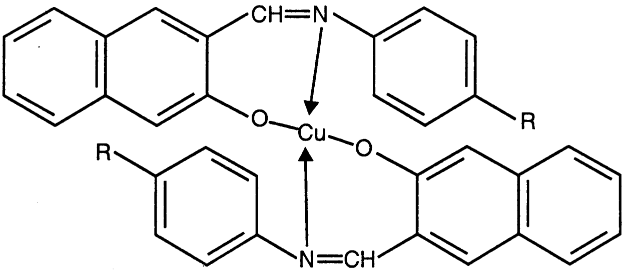
The copper complexes were also characterised for magnetic properties to ascertain the number of unpaired electrons associated with copper metal after complexation. The Gouy's balance method indicates that μ_{eff} values of copper complexes are in the range 1.82–1.99 B.M. which corresponds to one unpaired electron. The little abnormal value at room temperature is probably due to influence of various substituents on the ligand moiety. Ganorkar *et. al.*[10] have also reported copper complexes with μ_{eff} values in the similar range. Magnetic behaviour of copper complexes was further evaluated by recording their ESR spectra. From the ESR spectra of each copper complex $g_{\|}$, $g_{\perp}$ and g_{avg} values were calculated and are summarised in Table-3. The average g value ranges from 1.9290–1.9797. The table also reveals that $g_{\|} < g_{\perp} < 2.0023$ indicating the covalent character of copper complexes[11]. The μ_{eff} values of these complexes were further calculated using g_{avg} values. The close agreement between μ_{eff} values provides better authenticity to our interpretations on magnetic properties of copper complexes.

All the Schiff base ligands and copper complexes were used to characterise antimicrobial activity *in vitro* against gram negative (*Escherichia coli* and *Salmonella typhi*) and gram-positive (*Staphylococcus aureus* and *Bacillus subtilis*) by the paper disc method. Their study suggests that copper chelates of these ligands do not possess appreciable antimicrobial activity. Hence, unlike other reported copper chelates we do not recommend copper complexes of these ligands for any antimicrobial application.

Conclusively, from the various analytical and spectral investigations it is suggested that copper complexes of these ligands have well defined strutural configuration having square-planar geometry. The copper complexes may be used as analytical reagents in the laboratory. Complexes may be assigned structures as given below.



1 : 1



1 : 2
R = o-CH_3, p-CH_3, H

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