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

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Some novel complexes of Cu(II) with substituted Schiff bases as ligands are reported. The complexes invariably conform to the stoichiometry CuL_2 and CuL. The ligands behave as bidentate one and the electronic absorption spectra, magnetic moment values and infrared spectral data in KBr disc indicate coordination number six to the Cu^{2+} ion. The low molar conductance values of all complexes show non-electrolytic nature of compexes. The overall stereochemistry has been assigned as octahedral or distorted octahedral.

INTRODUCTION

Schiff bases are known for their biological importance as fungicides. The Schiff bases can also be used as anaytical reagents for the analysis of transition metals. Literature[1–3] also reveals that transition metal complexes of Schiff bases have been found to be effective catalysts for epoxydation of various olefins. The biological utility, catalytic activity and analytical applications can be correlated to the structure of Schiff base and substituent groups of Schiff bases.

Amongst transition metal complexes of Schiff bases, Cu(II) complexes of Schiff bases have aroused great interest because such complexes can be used as a starting material for synthesis of many other compounds. The coordination ability of differently substituted Schiff bases derived from salicylaldehyde are extensively studied for their analytical applications.[4, 5] In view of the above facts, it is worthwhile to synthesise few Schiff base complexes of Cu(II) and diagnose various structural aspects of such complexes.

The pre-investigation deals with synthesis and characterising of Cu(II) complexes of Schiff bases. The Schiff base chelate was derived by condensation of 5-nitrosalicylaldehyde with various primary amines like aniline, *o*-toluidine, *p*-toluidine and anthranilic acid.

EXPERIMENTAL

The chemicals used in this investigation were all of the highest purity available. The Schiff base ligands were prepared by coupling the corresponding primary amines with 5-nitrosalicylaldehyde in ethanolic media under reflux. The components of aldehyde and amines were mixed in stoichiometric proportions. The resulting precipitates were recrystallised from appropriate solvents.

The Cu(II) complexes were obtained by refluxing a mixture of an ethanolic solution of Cu(II) acetate (1 mg/cm^3) with 1% w/v ethanolic solution of Schiff base for 2 h on a boiling water bath. The resulting complexes were washed with water and ethanol and dried at 60°C. The per cent yield of the product ranges between 60–80%. Each complex was stored in a desiccator.

The elemental analyses of complexes were carried out using the reported methods[6]. Complexes were tested for solubility in several polar and non-polar solvents. The molar conductance for each one of these complexes was recorded on a Toshniwal conductivity bridge using nitrobenzene as solvent at room temperature. The electronic absorption spectra in UV-visible region as well as diffused reflectance pattern were recorded on UV-visible spectrophotometer, which was supplied by M/s Shimadzu Corp. The diffused reflectance spectrum was recorded using $BaSO_4$ as a diluent. The IR spectrum of ligand as well as of complexes were recorded on FTIR 4200 manufactured by M/s Shiamadzu Corp., using KBr pellet technique. The magnetic susceptibilities at room temperature were measured using Gouy balance method.

TABLE-1
ANALYTICAL AND PHYSICO-CHEMICAL CHARACTERISTICS OF LIGAND AND COPPER COMPLEXES

Complex (m.w.)	Colour	m.p. (°C)	Molar conductivity (c = 5 × 10^{-3} M) (mho cm^2 mol^{-1})	Analysis %, found (calcd.)			
				C	H	N	Cu
$L_1(C_{13}H_{10}O_3N_2)$ (243)	Yellow	133	4.6	63.48 (64.18)	4.69 (4.14)	10.36 (11.52)	—
$Cu(L_1)_2(Cu_{26}H_{18}O_6N_4Cu)$ (550)	Green	—	31.3	57.10 (56.77)	3.61 (2.93)	9.92 (10.68)	11.90 (11.59)
$L_2(C_{14}H_{12}O_3N_2)$ (256)	Yellow	125	4.8	67.34 (65.62)	5.96 (4.48)	10.76 (10.93)	—
$Cu(L_2)_2(C_{28}H_{22}O_6N_4Cu)$ (576)	Green	—	39.2	59.29 (58.37)	3.09 (2.93)	8.17 (9.72)	11.90 (11.03)
$L_3(C_{14}H_{12}O_3N_2)$ (256)	Yellow	160	4.8	64.84 (65.62)	5.33 (4.48)	11.33 (10.93)	—
$Cu(L_3)_2(C_{28}H_{22}O_6N_4Cu)$ (576)	Green	—	38.6	58.70 (58.37)	4.22 (3.85)	9.34 (9.72)	11.20 (11.03)
$L_4(C_{14}H_{10}O_5N_2)$ (286)	Orange	265	6.6	57.34 (57.84)	4.18 (3.49)	9.68 (9.79)	—
$Cu(L_4)(C_{14}H_9O_5N_2Cu)$ (348)	Green	—	20.4	43.95 (48.20)	3.17 (2.58)	8.95 (8.03)	19.10 (18.20)

TABLE-2
KEY ELECTRONIC ABSORPTION AND IR/VISIBLE BANDS OF LIGANDS AND THEIR COPPER COMPLEXES

Complexes	μ_{eff} at room temp. in B.M	Electrical absorption spectral data in cm^{-1}		IR bands (cm^{-1})			
		UV-visible	Reflectance	ν(C=O)	ν(C=N)	ν(Cu—N)	ν(Cu—O)
L_1	Diamagnetic	—	—	1590(s)	1620(s)	—	—
$Cu(L_1)_2$	1.33	26110	27233 19610	1615(s)	1600(s)	510(s)	450(s)
L_2	Diamagnetic	—	—	1600(s)	1600(s)	—	—
$Cu(L_2)_2$	1.71	26490	25031 14706	1620(s)	1590(s)	550(s)	460(s)
L_3	Diamagnetic	—	—	1600(s)	1620(s)	—	—
$Cu(L_3)_2$	1.92	26774	26882 16393	1620(sh)	1600(s)	535(m)	460(m)
L_4	Diamagnetic	—	—	1710(s)	1640(s)	—	—
$Cu(L_4)$	1.65	23694 16666	24390	1640(s)	1605(s)	520(s)	480(s)

TABLE-3
ESR MAGNETIC AND BONDING PARAMETERS

Complex	$g_{\parallel}$	$g_{\perp}$	g^*	H_2
$Cu(L_1)_2$	1.9618	2.0456	2.0149	3170
$Cu(L_2)_2$	1.9432	2.0641	2.0218	3140
$Cu(L_3)_2$	1.9586	2.0479	2.0161	3165
$Cu(L_4)$	1.9494	2.0576	2.0195	3150

RESULTS AND DISCUSSION

The analytical data suggest metal-ligand stoichiometry as 1 : 2 for ligands L_1, L_2, L_3 while it forms 1 : 1 complex with L_4. The complexes are insoluble in common organic solvents but as fairly soluble in DMF, DMSO, nitrobenzene etc. The molar conductance values as seen in nitrobenzene at 0.005 M solution for these complexes were in the range 20.4 to 39.2 mho cm^2 mol^{-1}. Such low value of molar conductance suggests a non-electrolytic behaviour of these complexes.

In the Cu(II) complexes with $3d^9$configuration, the predicted μ_{eff} values at room temperature for Cu(II) complexes were found to be in the range of 1.33 to 1.92 B.M. These values correspond to one unpaired electron.[7] However, no definite conclusion regarding the stereochemistry could be drawn merely on the basis of magnetic moment data.

The electronic absorption spectra of Cu(II) complexes show a strong band in the region 23694 cm^{-1} to 26774 cm^{-1}. These absorption bands can be assigned to the charge transfer transitions. A diffused reflectance spectra suggests appearance of this band in a similar range. The other weak band appearing in the range 14706 cm^{-1} to 19610 cm^{-1}can be assigned to the d-d transitions responsible for $^2E_g \rightarrow {}^2T_{2g}$. Many authors[8–10] have reported appearance of this transition in a similar range and suggested distorted octahedral configuration for Cu(II) complexes. Sharma and Sharma[11] have reported the absorption band at 13400 cm^{-1} for Cu(II) complexes having distorted octahedral geometry. Similar conclusion was drawn by Agamber and Orrel[12] where they concluded that tthe band appearing in the region 14000 to 16000 cm^{-1}assignable to $^2E_g \rightarrow {}^2T_{2g}$ transition is due to distorted octahedral geometry around Cu ions having D_{4h} symmetry.

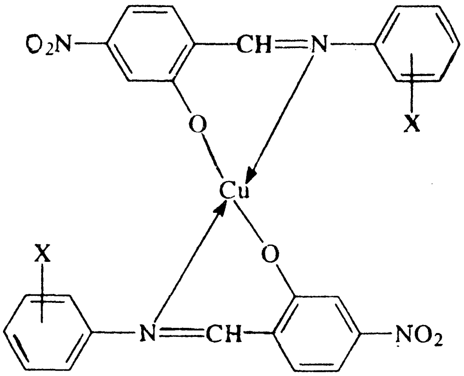
Thus the magnetic susceptibility data, electronic absorption spectral data and green colour of the Cu complexes are in favour of distorted octahedral geometry for Cu(II) complexes under investigation.

The ligand Schiff base gives four characteristic vibrational bands in the range of 3400–3300 cm^{-1}, 1650 cm^{-1}, 1600 cm^{-1} and 1100 cm^{-1}. These bands can be assigned to the ν(OH) of the N—O—H, ν(C=O), ν(C=N) and ν(N—O) stretching vibrations. Few more bands also appear in finger print region which are assignable to the ν(C—H) and ν(phenyl) of the ligand groups. In the spectra of Cu(II) complexes, ν(OH) band disappears showing the protonation of the —OH group and participation of O in the coordination. The position of C=O sharp band is lowered in intensity and stretching frequency from 1650 cm^{-1} to 1600 cm^{-1} indicates the participation of carbonyl O in complex formation. The ν(C=N) band at 1620 cm^{-1} decreasesd to 1600 cm^{-1} value. Such a red shift of IR band suggests involvement of azomethine N in coordination. An asymmetric stretching vibration band due to $—NO_2$ group appears at 1100 cm^{-1}. This is of equal intensity and is unaffected by complexation. This band is assignable to the ν(N—O) stretching vibration.

The inference regarding the bonding of Cu with O and N is well supported by the additional bands appearing in the far IR region. In the far IR region spectra, weak intensity bands in all the complexes show two additional bands. These bands can be assigned to the stretching frequency of ν(Cu—O) and ν(Cu—N) in the range of 480 to 450 $cm^{-1}$and 590 to 510 cm^{-1}respectively. These bands confirm that Schiff base ligand is coordinated to the Cu ion as a bidentate ligand.

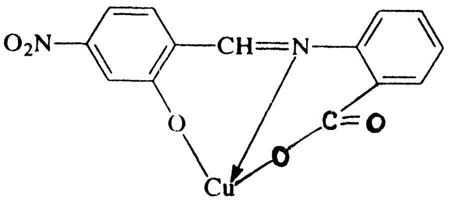
The ESR parameters calculated for Cu(II) chelates given in Table-3. The values indicate that $g_{\parallel} < g_{\perp} < g_0$ indicating the presence of unpaired electron in d_{xy} or b_{2g}^* orbital. Such trends for Cu complexes are consistent with the occupation of unpaired electron in d_{xy} orbital, as reported by Goodman and Raynor[13]. The σ bonding parameter indicates a significant amount of orbital overlap. However, for complexes, the trend is reverse. It means $g_{\parallel} > g_{\perp} > g_0$ is consistent with the occupation of unpaired electron in the $d_{x^2-y^2}$ orbital resulting in Z-out tetragonal distortion. The μ_{eff} values evaluated by using g values are in agreement with those obtained by bulk magnetic susceptibility measurements. The $g < 2.3$ indicates covalent nature of metal-ligand bond[14] and this is further supported by the G value[15] which is > 4. The spin order coupling constant for the complex (λ-value) is < that of free metal ion (λ_0 value) suggesting considerable mixing of ground and excited levels. The distorted octahedral nature of Cu(II) complexes is further confirmed from g values obtained from ESR data where $g_{\parallel} > g$.

All the above discussions suggest that the Cu complexes of Schiff bases under investigation have structure as shown in Fig. 1.



(a)

$Cu(L_1)_2$, $Cu(L_2)_2$ and $Cu(L_3)_2$; X = H, *o*-CH_3, *p*-CH_3



(b)

$Cu(L_4)$

·Fig. 1

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