

Preparation and characterization of Cu(II) transition metal mixed ligand complexes

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Abstract

A new mixed ligand complex has been prepared by reaction of chloride salts of Cu(II) with Schiff base 2-((E)-4-(E)-phenal-diazenyl) phenol [PDIMP=(HL₁)] and (Z)-2-((P-Tolylimino) methyl) phenol [TIMP=(HL₂)]. Both the ligand/complexes were characterized on the basis of microanalysis, melting point, conductivity, solubility, determining of the metal content M%, IR, and UV/VIS spectral studies. The Schiff bases act as monobasic bidentate ligands, coordinating through deprotonated phenolic oxygen and azomethine nitrogen atoms. The complexes are non-electrolytic in DMSO. From the analytical and spectral data the stoichiometry of these complexes has been found to be [M(L₁)(L₂)(H₂O)₂]. Where M=Cu(II). The electronic absorption spectra and magnetic susceptibility measurements suggest the square planar geometry for the copper (II) ion. The *in vitro* antibacterial activities of the complex were tested using number of bacteria species such as Escherichia coli, Salmonella typhi, Pseudomonas aeruginosa, Streptococcus pyogenes, and Bacillus subtilis. The Schiff bases act as monobasic bidentate ligands, coordinated phenolic oxygen and azomethine nitrogen atoms.

Key words: Synthesis, characterization, Cu(II), preparation, Schiff base, mixed ligand complex,

Introduction

The synthesis of Schiff base ligand and their metal complex has been extensively studied because of their interesting biological activities¹⁻⁴. The condensation product of an

amine and a ketone or aldehyde with general formula of R₂C=NR are well known Schiff base compounds. They have been reported to be useful in medicine, catalyst, as antibiotics, antifungal and have applications in various fields⁷⁻¹⁰.

In the present work, the author has prepared two Schiff base compounds, (PDIMP) and (TIMP). The structure of this compound was studied by elemental analysis, IR, and UV-Vis spectra. Then, their Cu(II) mixed ligand complex was prepared and the spectral, magnetic and molar conductance properties of these complexes were studied.

Experimental section

All the chemicals and solvents used were of analytical (AR) grade and were used without further purification. They are 4-aminoazobenzene was prepared as reported procedure. Melting point of compound was determined using Griffin melting point apparatus.

Preparation of Schiff base ligand:

[A] Preparation of Schiff base ligand(HL₁):

The Schiff base ligand (HL) was prepared as described by Raman *et al.*¹⁵ 2004. This was done by the hot solution (50°C) of salicylaldehyde (2.442g, 20mmol) was mixed with hot solution (50°C) of p-aminoazobenzene (3.944g, 20mmol) in (200ml) ethanol and two drops of glacial acetic acid. The mixture was then refluxed for 1 hour. The product obtained was filtered, washed in distilled water, dried, and preserved in a desiccator containing CaCl₂.

[B] Preparation of Schiff base ligand(HL₂):

An ethanolic 100ml warm solution (40°C) of salicylaldehyde (4.2884g, 40mmol) and warm solution (40°C) p-toluidine (4.286g, 40mmol) was added drop wise to 100ml of the metal(II) salts. The reaction mixture was

refluxed for 1 hour and formed shiny yellow crystals. The product was separated by filtration, purified by recrystallization from hot ethanol, and then dried in a vacuum over CaCl₂.

Preparation of mixed ligand complex:

The mixed ligand complex was prepared by adding the appropriate amount of the metal salt (1mmol), name CuCl₂.2H₂O dissolved in (4ml) of distilled water slowly with constant stirring to a solution of (0.3013g, 1mmol). From 2-((E)-4-(E)-phenyl-di azenyl) phenylimino) methyl phenol(HL₁) and (0.02113g, 1mmol) from (Z)-2-((p-tolylimino)methyl) phenol (HL₂) in (50ml) ethanol. The resulting mixture was refluxed for 1 hour. The metal complex thus formed were filtered out, washed with (1:3) aqueous alcohol mixture followed by recrystallization from hot ethanol, and dried over anhydrous CaCl₂.

Results and Discussion

The analytical data along with some physical properties are summarized in Table 1. The Schiff base ligands (PDIMP) and (TIMP) were red and shiny yellow crystals respectively, but the complexes of these ligands vary in colour depending on the metal ion. All the complexes are stable and have sharp melting points (118-119°C) except the ligands (L) which melted above 300°C). Elemental analysis gave satisfactory agreement between observed and calculated values for Carbon, hydrogen, nitrogen and metal ions compositions in the complexes. The results show that the compounds formed in a ratio (1:1:1) of M(II) ion to (PDIMP) to (TIMP), corresponding to the molecular formula proposed for all mixed ligand complexes.

Table 1. Physical characteristics and analytical data for the Schiff base ligand and the metal (II) complex

Compound	Molecular formula	Colour	Melting Point (°C)	Yield(%)
[Cu(L ₁)(L ₂)]	C ₃₃ H ₂₆ N ₄ O ₂ Cu	Deep red	119	72

Table 2. The microanalysis and metal estimation data of the Schiff base ligands and their metal complexes

Compound	Molecular Formula	Microanalysis, % found (calc)			
		C	H	N	M
[Cu(L ₁)(L ₂)]	C ₃₃ H ₂₆ N ₄ O ₂ Cu	43.17 (43.41)	3.75 (4.68)	8.85 (8.97)	9.08 (10.59)

Microanalysis: The microanalysis of the ligands and their metal (II) complexes are presented in Table 2. The data revealed that the % C,H and N are in good agreement with the proposed structures.

IR spectra: The selected vibrational frequencies exhibited by the (PDIMP) and (TIMP) Schiff base ligands and the mixed ligand complexes are presented in Table 3. The infra red spectra of the free ligands (HL₁) and (HL₂) show a broad weak intensity band centered at around 3424 and 3402cm⁻¹ respectively, due to the intra molecular hydrogen bond O---H---N=C. This band disappeared in the spectra of the complex indicating probably the coordinating through phenolic oxygen moiety. A very weak intensity bands had been observed at 3020-3082 and 2980-2914cm⁻¹ in the spectra of both Schiff bases and metal complex are due to N(C-N) aromatic and aliphatic respectively. Another strong bands appeared at 1620-1618cm⁻¹ in the spectra of (HL₁) and (HL₂) ligands respectively, due to (C=N) group. IR spectra of free azo-azomethine ligand (PDIMP) shows a medium absorption

band at 1480cm⁻¹ due to $\nu(-N=N-)$ group. The new bands at 543-501cm⁻¹ and 461-426 cm⁻¹ have been assigned to $\nu(M-O)$ and $\nu(M-N)$, respectively.

Electronic spectra: UV-VIS spectra of the Cu(II) complex were recorded 10000-50000cm⁻¹ using ethanol as a solvent. The values of band position (cm⁻¹) together with the magnetic moment values are listed in Table 4. The UV-VIS spectra of both two ligands showed bands at 40000, 27027 and 31348, 29586cm⁻¹ assigned to $\pi \rightarrow \pi^*$ and $n \rightarrow n^*$ transitions within the molecule, these inner ligand transitions are common due to the presence of (C=N), (N=N) and (C=C) groups in the ligands structures. The visible spectrum of the mixed ligand complex of Cu(II) exhibit one broad band at 20408cm⁻¹ which may be assigned to the ${}^2B_{1g} \rightarrow {}^2A_{1g}$ and ${}^2B_{1g} \rightarrow {}^2E_g$ transitions respectively, corresponding to a square planar geometry around the Cu(II) ion. The magnetic moment value (1.66BM) observed for this metal complex is comparable with the assignment of square planar stereochemistry.

Molar conductance studies: The

conductance of the complexes in DMSO(10^3 M) at room temperature are shown in Table 4. The molar conductance values lying in the range (14.35-16.88) $\text{s cm}^2\text{mol}^{-1}$ confirmed the monionic behavior of all the complexes.

Table 3. Characteristic IR frequencies(in cm^{-1}) of Schiff bases and their mixed ligand complexes

Compound	$\nu(\text{O-H})$	$\nu(\text{C-H})_{\text{Ar}}$	$\nu(\text{C-H})_{\text{Alph}}$	$\nu(\text{C=N})$	$\nu(\text{N=N})$	$\nu(\text{M-N})$	$\nu(\text{M-N})$
$[\text{Cu}(\text{L}_1)(\text{L}_2)]$	3261m	3082w	2914w	1597s	1482w	531w	448w

Table 4. Electronic spectra, conductivity and magnetic moment of mixed ligand complexes

Metal complexes	Absorption bands(cm^{-1})	Transition	Conductivity $\text{S.cm}^2.\text{mol}^{-1}$	μ_{eff} (B.M)
$[\text{Cu}(\text{L}_1)(\text{L}_2)]$	20408	${}^2\text{B}_{1g} \rightarrow {}^2\text{A}_{1g}$ ${}^2\text{B}_{1g} \rightarrow {}^2\text{E}_g$	14.35	1.66

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