

Preparation and Characterization of Mn(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 Mn(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=Mn(II). The electronic absorption spectra and magnetic susceptibility measurements suggest the square planar geometry for the Mn(II) ion. The *in vitro* antibacterial activities of the complex were tested using number of bacterial 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, Mn(II), preparation, Schiff base, mixed ligand complex, Antimicrobial studies.

INTRODUCTION:

The synthesis of Schiff base ligand and their metal complex has been extensively studied because of their interesting biological activities [1-4]. 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 fields (7-10).

In the present work, we have prepared two Schiff base compounds, (PDIMP) and (TIMP). The structure of these compounds was studied by elemental analysis, IR, and UV-Vis spectra. Then, their Mn(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. 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. 2004(15). This was done by the hot solution (50⁰C) of salisaldehyde (2.442g, 20mmol) was mixed with hot solution (50⁰c) 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, filtered, washed in distilled water, dried, and preserved in a desiccator contained CaCl₂.

[B] Preparation of Schiff base ligand(HL₂): An ethanolic 100ml warm solution (40⁰C) of salisaldehyde (4.2884g, 40mmol) and warm solution (40⁰C) 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 shine yellow crystals product was separated by filtered, purified by recrystallized 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 MnCl₂.4H₂O dissolved in (4ml) of distilled water slowly with constant stirring to a solution of (0.3013g, 1mmol) from 2-((E)-4-(E)-phenyl-diazanyl)phenylimino)methyl phenol (HL₁) and (0.02113g, 1mmol) from (Z)-2-((p-tolyliminio)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 recrystallized 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 bases ligands (PDIMP) and (TIMP) were red and shine yellow crystals respectively, but the complex of these ligands vary in colour depended of metal ion. All the complexes are stable and have sharp melting points (118-119⁰C) except the ligands (L) which melted above 300⁰C. 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 ratio (1:1:1) of M(II) ion to (PDIMP) to (TIMP), corresponding to the molecular formula proposed for the 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(%)
[Mn(L ₁)(L ₂)(H ₂ O) ₂]	C ₃₃ H ₃₀ N ₄ O ₄ Mn	red	297	70

Table2: 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
[Mn(L ₁)(L ₂)(H ₂ O) ₂]	C ₃₃ H ₃₀ N ₄ O ₄ Mn	59.67 (65.61)	4.15 (4.26)	7.61 (8.52)	6.71 (7.93)

MICROANALYSIS:

The microanalysis of the ligands and their metal(II) complexes are presented in Table2. The revealed that the % C, H and N are in good agreement with the proposed structures. From the data obtained, it appears that the compound analyzed as [Mn(L₁)(L₂)(H₂O)₂] indicating a 1:2 mole ratio (M:L).

IR spectra: The selected vibration frequencies exhibited by the (PDIMP) and (TIMP) Schiff base ligands and their mixed ligand complexes are presented in Table3. The infra red spectra of the free ligands (HL₁) and (HL₂) show a broad weak intensity band centered at around 3424 and 3402 cm⁻¹ respectively, due to the intra molecular hydrogen bond O---H---N=C⁽²¹⁾. 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 2980-2914 cm⁻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 1620-1618 cm⁻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 1480 cm⁻¹ due to ν(-N=N-) group. The new bands at 543-501 cm⁻¹ and 461-426 cm⁻¹ have been assigned to ν(M-O) and ν(M-N), respectively. A broad medium intensity band at 3444 cm⁻¹ suggests the presence of coordinated water in Mn(II).

Electronic spectra: UV-VIS spectra of the Mn(II) complex were recorded 10000-50000 cm⁻¹ using ethanol as a solvent. The values of band position (cm⁻¹) together with the magnetic moment values are listed in Table4. The electronic spectrum of the Mn(II) complex shows two absorption bands at 16695 and 25316 cm⁻¹ which are ascribed to the transitions ⁶A_{1g} → ⁴T_{1g}(P) and ⁶A_{1g} → ⁴T_{1g}(G) respectively. The transition are characteristics to the octahedral environment around Mn(II) ion. The magnetic moment (5.95 BM) is an additional evidence for an octahedral structure.

Molar conductance studies: The conductance of the complexes in DMSO (10⁻³ M) at room temperature are shown in Table4. The molar conductance values lying in the range (14.35-16.88) Ω cm² mol⁻¹ confirmed the monionic behavior of the complex.

CONCLUSION:

The spectral, molar conductance and magnetic studies of the prepared mixed ligands complex of (PDIMP) and (TIMP) Schiff base ligands reveals that Mn(II) metal complex is having octahedral geometry.

Table3: Characteristic IR frequencies(in cm-1) of Schiff bases and their mixed ligand complexes:

Compound	v(O-H)	v(C-H) Ar	v(C-H) Alph	v(C=N)	v(N=N)	v(M-O)	V(M-N)
[Mn(L ₁)(L ₂)(H ₂ O) ₂]	3444w	3035w	2922w	1597s	1481w	501w	433w

Table4:Electronic spectra conductivity and magnetic moment of mixed ligand complexes:

Metal complexes	Absorption bands(cm ⁻¹)	Transition	Conductivity S.cm ² .mol ⁻¹	μ _{eff} (B.M)
[Mn(L ₁)(L ₂)(H ₂ O) ₂]	16695 25316	⁶ A _{1g} (F)→ ⁴ T _{1g} (P) ⁶ A _{1g} (F)→ ⁴ T _{1g} (G)	16.32	5.95

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