



**SYNTHESIS AND CHARACTERIZATION OF MANGANESE (II),
COBALT (II), NICKEL (II), COPPER (II) AND ZINC (II) MIXED LIGAND
COMPLEXES WITH [(1-PHENYL-3-METHYL-5-HYDROXOPYRAZOL-4-
YL) PHENYLIMINO]2',3' DIMETHYLANILINE AND
2-HYDROXY-1-NAPHTHALDEHYDE**

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ABSTRACT

Mixed ligand complexes of the type $[MLL']$ where $M = Mn(II), Co(II), Ni(II), Cu(II), Zn(II)$ $HL = [(1\text{-phenyl-3-methyl-5-hydroxypyrazol-4-yl)phenylimino}]_{2,3}\text{-dimethylaniline; (HPMPZP)dma. } HL' = 2\text{-hydroxy-1-naphthaldehyde; (HNA)}$, have been synthesized and characterized on the basis of elemental analysis, conductivity measurements, magnetic, electronic and infra red spectral studies. The complexes confirm to 1:1:1 stoichiometry and are non electrolytes. The schiff base HL act as a monovalent bidentate ligand co-ordinating through azomethine nitrogen and phenolic oxygen. On the basis of electronic spectra, IR spectra and magnetic moment measurements; six coordinated octahedral structures have been proposed for the complexes. Thermal studies revealed the presence of two co-ordinated water molecules. The schiff base and mixed ligand complexes have been tested for their antibacterial activity against the *Escherichia coli*, *Bacillus subtilis*, *staphylococcus aureus*.

Key words: Mixed ligand complexes, Elemental analysis, Non electrolyte.

INTRODUCTION

1-Phenyl-3-methyl-5-pyrazolone (PMP) has different biological effects as antipyrene metabolic and is a good biologically active molecule¹⁻³. In recent years, several pyrazolone derivatives have been synthesized such as 4-acyl-pyrazolones⁴. It has been observed from literature survey that these 4-substituted pyrazolone derivatives mainly exhibit bidentate co-ordinate behaviour, in which keto-enol tautomerism plays an important role in the chelate formation with numerous metal ions. The acyl pyrazolones in turn are utilized in the synthesis of schiff base pyrazolone⁵⁻⁷, which act as either tridentate or tetradentate ligands.

In view of growing interest in the biological properties of schiff base complexes, the present study is carried out with the synthesis, characterization and biological study of mixed ligand complexes of general formula $[MLL']$. where $M = Mn(II), Co(II), Ni(II), Cu(II), Zn(II)$ $HL = [(1\text{-phenyl-3-methyl-5-hydroxypyrazol-4-yl)phenylimino}]_{2,3}\text{-dimethylaniline; (HPMPZP)dma. } HL' = 2\text{-hydroxy-1-naphthaldehyde; (HNA)}$.

EXPERIMENTAL

All the reagents used were of analytical grade. Solvents were purified and dried according to standard procedures.

Synthesis of Schiff base (HPMPZP) dma

1-Phenyl-3-methyl-4-benzoyl-5-pyrazolone was synthesized by reported method⁸ and recrystallized from ethyl alcohol.

The pure crystals of 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone and 2,3-dimethylaniline were taken in round bottom flask in 1:1 stoichiometric proportion. The mixture was dissolved in about 20-25 mL of alcohol. The resulting solution was refluxed in presence of 2 mL of concentrated hydrochloric acid for 4-5 hrs. On cooling the crystals of schiff base i.e. (HPMPZP) dma separated out, which were filtered under suction.

Synthesis of mixed ligand complexes

An appropriate quantity of the schiff base (HPMPZP)dma was weighed and mixed with an equimolar quantity of ligand (HNA). The mixture of schiff base and ligand was dissolved in minimum quantity of alcohol. An equimolar quantity of bivalent transition metal chloride was dissolved in minimum quantity of water. Alcoholic solution of ligands was added to an aqueous solution of metal chloride with constant stirring. The pH of the solution was raised to 7.5-8.0 by adding 0.1 N sodium hydroxide. The resulting reaction mixture was stirred on a magnetic stirrer for 1-1.5 hrs. The solid complex was separated out, filtered, washed with water and air dried. This is the general method of synthesis of ternary complex of (HPMPZP)dma and (HNA) with bivalent transition metal chlorides. The metal to schiff base to ligand ratio is 1:1:1, i.e Schiff base, metal and ligand are in 1:1:1 stoichiometric proportion.

Elemental analysis was carried out in micro analytical laboratory of IIT (Powai). The metal contents in the complexes were determined by standard complexometric titrations⁹. IR spectra of the Schiff base and the complexes were recorded on Perkin-Elmer spectrophotometer. UV-visible spectra of the complexes were recorded on Shimadzu UV-160 spectrophotometer. Magnetic moments were measured by Gouy method using $\text{Hg}[\text{Co}(\text{SCN})_4]$ as a calibrant. Conductivity measurements were made Elico CM-180 conductometer using DMSO as a solvent. Thermogravimetric analysis of complexes was carried out in Mettler TA40000 system. The ESR spectra of copper complex at room temperature was recorded on Varian-E line ESR spectrophotometer at IIT (Powai) using TCNE as the 'g' marker.

RESULTS AND DISCUSSION

Analytical data presented in (Table 1) indicate that Metal : Ligand : Schiff base stoichiometry is (1:1:1) i.e the probable general formulae of the complexes is $[(\text{MLL})(\text{H}_2\text{O})_2]$. All the complexes decompose in the 200-270°C temperature range. The complexes are insoluble in water and poorly soluble in common organic solvents, but fairly soluble in DMSO and DMF. The molar conductance values lie in the range of 10.30-15.0 $\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$. Low molar conductance values of 10^{-3} M solutions in DMSO showed them to be non electrolytes. Insufficient solubility of these complexes in suitable solvent precluded the determination of molecular weights.

IR Spectra

The IR spectra of uncomplexed ligand i.e. the Schiff base shows the broad band at 3448 cm^{-1} (HL),

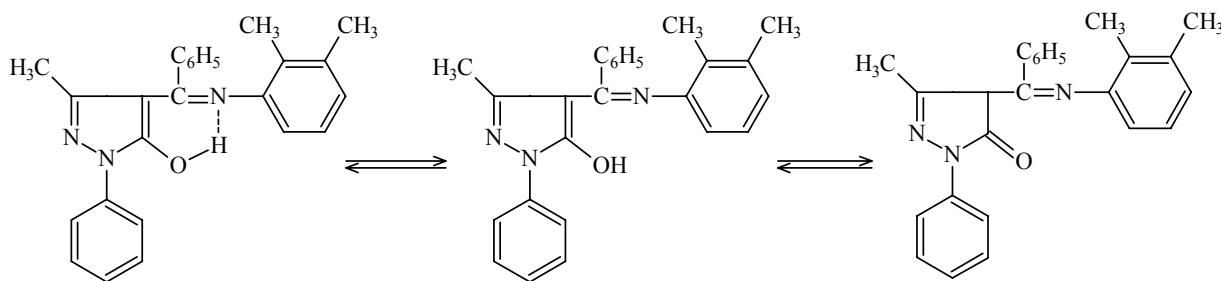
which can be assigned to symmetric and antisymmetric vibrations ν_{OH} . The free ν_{OH} is generally observed between 3500 and 3600 cm^{-1} . The observed low value is due to intermolecular or intramolecular hydrogen bonding⁷. At 1260 cm^{-1} , a medium sharp peak is obtained which is due to δ_{OH} . It also shows a weak band at 1365 cm^{-1} , which can be assigned to $\nu_{\text{C-O}}$ phenolic. The spectra also show the sharp bands at 1587 cm^{-1} and 1627 cm^{-1} due to $\nu_{\text{C=N}}$ of pyrazolone nucleus and $\nu_{\text{C=N}}$ of azomethine group, respectively. The ligand HL' shows a band at 1246 cm^{-1} due to $\delta_{\text{O-H}}$. The spectra also show the sharp band at 1367 cm^{-1} and 1646 cm^{-1} , which can be assigned to $\nu_{\text{C-O}}$ phenolic and $\nu_{\text{C=O}}$ carbonyl group, respectively. All the complexes exhibit an identical pattern suggesting them to be isostructural. Metal complexes show bands in the region 3390 cm^{-1} – 3500 cm^{-1} . The bands are rather diffused and broadened. Broadening may be caused by the participation of oxygen from OH group in complexation, and appearance of $\nu_{\text{O-H}}$ of co-ordinated water molecules. A new band appears in the spectra of all complexes in the range 830 cm^{-1} – 890 cm^{-1} , which is characteristic of $\delta_{\text{O-H}}$ of co-ordinated water molecules¹⁰.

In all the complexes a sharp and strong band appears in the range of 1610 cm^{-1} – 1615 cm^{-1} and 1587 cm^{-1} – 1589 cm^{-1} , which are characteristic of $\nu_{\text{C=N}}$ azomethine group and $\nu_{\text{C=N}}$ pyrazolone nucleus, respectively. The shift in $\nu_{\text{C=N}}$ azomethine by 12-17 cm^{-1} indicates that co-ordination of schiff base with metal ion takes place through nitrogen¹¹. It is expected that co-ordination of the nitrogen atom of the ligand to the metal ion would reduce the electron density from ligand to metal ions, which in turn reduce the electron density in the azomethine link, thereby reducing the $\nu_{\text{C=N}}$ frequency. The $\nu_{\text{C=N}}$ of pyrazolone nucleus has not shifted appreciably suggesting the non involvement of nitrogen of pyrazolone nucleus in the co ordination to metal ion. The frequency $\nu_{\text{C-O}}$ phenolic in the complexes is shifted to higher frequency and is in the range of 1367-1395 cm^{-1} .

This indicates that the other co-ordination of Schiff base is through phenolic oxygen in all the complexes¹². The lower frequency region of spectra also confirm the participation of nitrogen of azomethine group and oxygen of phenolic group in the in co-ordination to metal ion by showing the weak bands in the region 400-650 cm^{-1} and 450-510 cm^{-1} , respectively.

In both ligands the sharp and strong bands, characteristic of $\delta_{\text{O-H}}$ vibration are observed (HL = 1260 cm^{-1} , HL' = 1246 cm^{-1}). In the spectra of complexes, band from HL becomes a very band at a slightly lower frequency and from ligand HL' it disappears indicating the deprotonation of the phenolic protons prior to co-ordination. The shift is also observed for the strong band due to $\nu_{\text{C=O}}$ (carbonyl) from ligand HL' by 8-10 cm^{-1} suggesting the involvement of oxygen from aldehyde group in the complex formation.

The Schiff base is expected to exist in tautomeric forms as depicted below. These structures show keto-enol tautomers along with hydrogen bond.



Electronic spectra and magnetic moments

The UV spectra of schiff base (HPMPZP)dma show the bands at 28,571 cm^{-1} and 34,013 cm^{-1} the ligand (HNA) show two bands at 34,483 cm^{-1} and 25,974 cm^{-1} . These bands are attributed to intra ligand transitions. In the complexes the bands show the blue shift in their positions. Mn (II) complex has magnetic moment value of 5.58 B.M. suggesting octahedral environment. The electronic spectra of Mn (II) complex registers weak bands at 22,075 cm^{-1} and 17,860 cm^{-1} , which can be assigned to ${}^6A_{1g} \rightarrow {}^4T_{2g}(G)$ and ${}^6A_{1g} \rightarrow {}^4T_{1g}(G)$ transitions of Mn(II) ion in a spin free d^5 configuration confirming to octahedral arrangement.

The Co(II) complex registers an intense band at 20,000 cm^{-1} and a weak one at 10,101 cm^{-1} . These bands may be assigned to ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ (ν_3) and ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ (ν_2) transitions; characteristic of an octahedrally co-ordinated Co (II) ion. The magnetic moment of 5.19 B. M supports octahedral environment around Co(II) ion. The other parameters for Co(II) ion are $Dq = 1120 \text{ cm}^{-1}$, $B' = 746 \beta = 0.768$ $\beta' = 23.14 \%$ suggesting the appreciable covalent character in the complex. The ν_3/ν_1 ratio (1.98) is in accordance with expected (1.92-2.95) value for an octahedral Co(II) complex.

The Ni (II) complex registers an intense band at 24,500 cm^{-1} , broad one at 16,700 cm^{-1} and a weak one at 9,900 cm^{-1} . These bands may be assigned respectively to ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ (ν_3), ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ (ν_2), ${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ (ν_1). The ν_2/ν_1 equals to 1.68, $Dq = 990$, $B' = 767$, $\beta = 0.725$, $\beta' = 27.4\%$. For Ni(II) complex the magnetic moment is 3.9 B.M. suggesting distorted octahedral geometry. The μ_{eff} value higher than expected for $2e^-$ may be due to ferromagnetic nature Ni(II) complex or due to incomplete quenching of orbital angular momentum by ligands^{13,14}. The high value can also be due to mixing of multiplet excited state in which spin orbit coupling is appreciable¹⁵. The visible spectra of Cu complex show a broad band spanning at 13,333 cm^{-1} . This band appears due to ${}^2E_g \rightarrow {}^2T_g$ transition in an octahedral field. The copper complex has magnetic moment of 1.86 B.M., which is usually observed for octahedral Cu (II) complex. The ESR spectra exhibit a single broad signal resulting from the interaction of unpaired electron. The analysis gave $g_{\parallel} = 2.19$, $g_{\perp} = 2.11$. The observed value g_{\parallel} for the Cu complex is less than 2.3 in agreement with the covalent character of the metal ligand bond. The trend $g_{\parallel} > g_{\perp} > 2.003$ observed for the complex indicate that the unpaired electron is localized in $d_{x^2-y^2}$ orbital of the Cu(II) ion and the spectral features are characteristic of axial symmetry. Tetragonally elongated structure may be assumed for Cu(II) complex. The zinc complex is found to be diamagnetic in nature.

TGA Studies

The existence of co-ordinated water molecules in the complexes is confirmed by TGA studies. The representative complex $[\text{Ni}(\text{LL})(\text{H}_2\text{O})_2]$ is stable upto the temperature of 130°C and there after it registers a mass loss of 5.5% (calculated 5.57%) which corresponds loss of two water molecules. The above mentioned mass loss takes place in temperature range of 135°C-195°C. After 200°C the anhydrous complex starts decomposing. Total mass loss upto 580°C is found to be 89%, which corresponds to the loss of two ligands. Finally the residue left is 5.2% hence from TGA, it is clear that the complexes under study contain two water molecules co-ordinated to metal ion¹⁶⁻¹⁸.

Antimicrobial activity

The schiff base, ligand along with the mixed ligand complexes were tested for their anti-microbial activity Gram positive (*Staphylococcus aureus* and *Bacillus subtilis*) and Gram negative (*Escherichia Coli* and *Salmonella typhi*) by paper disc diffusion method.

Streptomycin was used as a standard. The ligand and schiff base show moderate activity against all organisms except *S-typhi*. Mn(II), Co(II), Ni(II) complexes show moderate activity with *E-Coli*, *S-aureus*

and *B. subtilis*. Copper and Zinc complexes do not possess any activity. It has been observed from these results that some metal complexes exhibit slightly higher activity than free ligands against the same microorganism and under the identical conditions. The mode of action of the complexes may involve the formation of hydrogen bonds involving the azomethine group with microbes or ribosomes of microbial cells resulting in interference with normal cell processes.

On the basis of above discussion the mixed ligand complexes $[M(LL')(H_2O)_2]$ may be assigned the following structure –

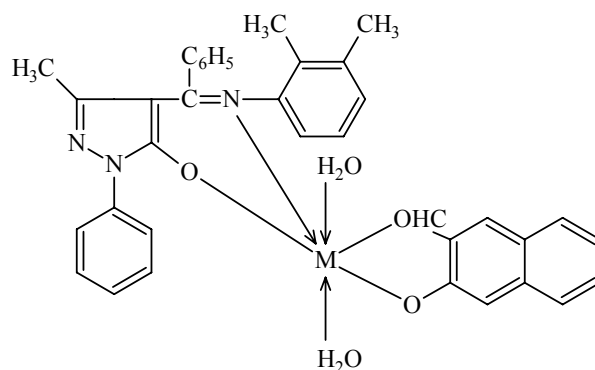


Table 1: Physical properties of ligands and their mixed ligand complexes

S. No.	Compound	Molecular formula (formula wt.)	Colour	M.P. (°C)	μ_{eff} B.M	Λ_M $\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$
1	HL = (HPMPZP)dma	$\text{C}_{25}\text{H}_{23}\text{N}_3\text{O}$ (381)	Whitish yellow	140	-----	-----
2	HL' = (HNA)	$\text{C}_{11}\text{H}_8\text{O}_2$ (172)	Yellow		-----	-----
3	$[\text{Mn}(\text{LL}')(\text{H}_2\text{O})_2]$	$\text{C}_{36}\text{H}_{33}\text{N}_3\text{O}_5\text{Mn}$ (642)	Light green	270	5.58	10.3
4	$[\text{Co}(\text{LL}')(\text{H}_2\text{O})_2]$	$\text{C}_{36}\text{H}_{33}\text{N}_3\text{O}_5\text{Co}$ (645.9)	Yellowish green	210	5.19	12.0
5	$[\text{Ni}(\text{LL}')(\text{H}_2\text{O})_2]$	$\text{C}_{36}\text{H}_{33}\text{N}_3\text{O}_5\text{Ni}$ (645.8)	Greenish yellow	200	3.9	13.5
6	$[\text{Cu}(\text{LL}')(\text{H}_2\text{O})_2]$	$\text{C}_{36}\text{H}_{33}\text{N}_3\text{O}_5\text{Cu}$ (650.3)	Green	260	1.86	14.2
7	$[\text{Zn}(\text{LL}')(\text{H}_2\text{O})_2]$	$\text{C}_{36}\text{H}_{33}\text{N}_3\text{O}_5\text{Zn}$ (652.5)	Light green	230	Diamagnetic	14.9

Table 2: Elemental analysis of ligands and mixed ligand complexes

S. No.	Compound	Elemental analysis			
		% C Cal (Found)	% H Cal (Found)	% N Cal (Found)	% M Cal (Found)
1	HL = (HPMPZP)dma	78.74 (78.45)	6.036 (6.15)	11.02 (10.89)	
2	HL' = (HNA)	76.75	4.65	----	
3	$[\text{Mn}(\text{LL}')(\text{H}_2\text{O})_2]$	67.29 (66.98)	5.14 (4.99)	6.54 (6.73)	8.57 (8.25)
4	$[\text{Co}(\text{LL}')(\text{H}_2\text{O})_2]$	66.8 (66.3)	5.109 (4.99)	6.502 (6.61)	9.12 (8.99)
5	$[\text{Ni}(\text{LL}')(\text{H}_2\text{O})_2]$	66.9 (66.25)	5.109 (5.24)	6.5 (6.46)	9.1 (8.98)
6	$[\text{Cu}(\text{LL}')(\text{H}_2\text{O})_2]$	66.4 (66.7)	5.07 (4.85)	6.45 (6.50)	9.7 (9.15)
7	$[\text{Zn}(\text{LL}')(\text{H}_2\text{O})_2]$	66.2 (65.9)	5.05 (4.65)	6.436 (6.51)	10.038 (9.57)

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