

Synthesis, Characterization and Biological Studies of Cu(II), Ni(II), Co(II) Complexes Containing Mixed Ligand

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The mixed ligand metal complexes were prepared by using 4,7-dimethyl-1,10-phenanthroline (phen.), 2-hydroxybenzalidine anthranilic acid (HBAA) and $M(\text{CH}_3\text{COO})_2$ [$M = \text{Cu(II)}, \text{Ni(II)}, \text{Co(II)}$]. The prepared mixed ligand metal complexes have been characterized on the basis of elemental analysis, infrared spectra, electronic spectra, magnetic susceptibilities and molar conductivity measurements. The microbial activities of mixed ligand metal complexes were tested against *Aspergillus flavus*, *Aspergillus fumigatus*, *Aspergillus niger*, *Escherichia coli* and *Staphylococcus aureus*.

Key Words: Cu(II), Ni(II), Co(II), Complexes, 4,7-Dimethyl-1,10-phenanthroline, 2-Hydroxybenzalidine anthranilic acid.

INTRODUCTION

The stability constant of the mixed ligand metal complexes are much greater and they are finding larger analytical and biological applications. Heterocyclic 4,7-dimethyl-1,10-phenanthroline (phen.) containing two heteroatoms and HBAA containing azomethine group possess various applications. They are great of importance due to their synthetic flexibility, selectivity and sensitivity towards the metal ions. The hetero donor atoms containing mixed ligand metal complexes possess greater importance due to antibacterial, antifungal, antiviral, anticancer and also as spray agents in chromatography¹⁻⁵. The present work concerned on the synthesis and structural studies of the mixed ligand metal complexes of Cu(II), Ni(II) and Co(II) with their antimicrobial screening.

EXPERIMENTAL

All chemicals were of AR grade^{6,7} for the synthesis of ligand and their mixed ligand metal complexes.

Ligand (L^1) 4,7-dimethyl-1,10-phenanthroline(phen.): It was commercially available and used without further purification.

Synthesis of ligand (L^2) 2-hydroxybenzalidine anthranilic acid (HBAA): The solution obtained by dissolving 0.05 mol of anthranilic acid in minimum volume of ethanol was mixed with 25 mL of ethanolic solution of 0.05 mol of salicylaldehyde.

The resulting solution was refluxed on a water bath for 1 h and then allowed to stand over night. Orange-red crystals so obtained, filtered and washed with cold water and finally with ethanol. The precipitate was dried and finally recrystallized from ethanol.

Synthesis of complexes M(phen.)HBAA [M = Cu(II), Ni(II), Co(II)]: Equimolar solutions of 4,7-dimethyl 1,10-phenanthroline (0.4164 g, 2×10^{-3} M) in acetone and HBAA (0.4820 g, 2×10^{-3} M) in alcohol and in this equimolar amount of metal(II) acetate in alcohol mixed with constant stirring. The pH of the solution was adjusted between 5 and 6. The precipitate obtained was digested on a water bath, filtered and washed with water, alcohol, acetone and finally with ether. The washed precipitate was dried in vacuum desiccator over P_4O_{10} .

Microbial activities: All the mixed ligand metal complexes were screened against *staphylococcus aureus* (gram positive) and *Escherichia coli* (gram negative) bacteria and fungi like *Aspergillus flavus*, *Aspergillus niger*, *Aspergillus fumigatus* by using agar diffusion method or serial dilution method. A nutrient agar at 40 °C was poured in two different and well cleaned petri-dishes and allowed to solidify. The desired fungi or bacteria were inoculated by the loop of platinum wire in the petri-dishes. Filter paper disc were dipped into complex solution (10^{-3} M). Petri-dishes were then kept in BOD incubator observed inhibition of growth of bacteria and fungi after 2 and 7 days, respectively. The petri-dishes with lowest concentration of ligand/metal chelate were selected in which fungi/bacteria was not detectable. Elemental analysis were obtained from the microanalytical laboratory of CDRI, Lucknow. A Perkin-Elmer spectrophotometer (model 521) at instrumentation centre of IIT, New Delhi was used to make infrared spectral studies in range of 4000-200 cm^{-1} at room temperature. Magnetic susceptibilities of mixed ligand metal complexes were measured by Gouy's technique in magnetic field of 5 and 10 kg at room temperature using AR $CuSO_4 \cdot 5H_2O$ ($g = 5.8472 \times 10^{-5}$ CGS units at 20 °C) as calibrant. Molar conductance was measured in DMF (10^{-3} M) solution by using a Toshniwal digital conductivity meter with a dip type cell. Bausch and Lomb electronic 20 and Backman DU-6 spectrophotometer were use to record the electronic data at room temperature. Reference used is pure solvent DMF.

RESULTS AND DISCUSSION

The analytical data of mixed ligand metal complexes and their physical properties are given in Table-1. The elemental analysis agree with stoichiometry and chemical formula of the mixed ligand complexes (ML^1L^2). The purity of the ligand was checked by their elemental analysis and TLC. The molar conductance values for all the mixed ligand metal complexes in DMF solutions recorded in the range of 6.30-15.14 $ohm^{-1} cm^2 mol^{-1}$, indicating non electrolytic nature of mixed ligand metal complexes. In the IR spectra of free ligand HBAA, the stretching bending vibration of -OH (phenolic) group are indicated by 3450 cm^{-1} and another band at 1365 cm^{-1}

due to intramolecular hydrogen bonded -OH. In the IR spectra of mixed ligand metal complexes the broad band disappear indicating metal to ligand coordination has take place *via* deprotonation of phenolic -OH group. -OH deformation (acid) show a band at 920 cm^{-1} . A broad band in the region of 3580-3410 cm^{-1} in phen-metal complexes of HBAA is observed. It may be attributed to the stretching frequency of O-H of coordinated water. In these complexes a moderate band in the region 850-810 and 690-680 cm^{-1} is also seen rocking and bending vibrations⁸ of -O-H. The $\nu(\text{C}=\text{N})$ vibration of azomethine group in HBAA is indicated by sharp spectral band at 1640 cm^{-1} , when the metal (phen) HBAA complexes are formed, this frequency is lowered by 22-25 cm^{-1} . This lowering of frequency may be attributed to coordination of ligand to metal through nitrogen of azomethine group⁹⁻¹².

TABLE-1
ELEMENTAL ANALYSIS, PHYSICAL PROPERTIES AND MAGNETIC
SUSCEPTIBILITIES OF SYNTHESIZED MIXED LIGAND METAL COMPLEXES

Compound	m.f.	Elemental analysis			Decomp. temp. (°C)	Colour	μ_{eff} BM	Molar conductance (ohm ⁻¹ cm ² mol ⁻¹)
		C	H	N				
HBAA	C ₁₄ H ₁₁ NO ₃	69.48 (69.70)	4.34 (4.56)	5.65 (5.80)	–	Orange red	–	–
Cu(phen.) HBAA·H ₂ O	Cu(C ₂₈ H ₂₃ N ₃ O ₄)	63.51 (63.53)	4.25 (4.39)	8.04 (7.96)	292	Dark brown	2.13	15.14
Ni(phen.) HBAA·H ₂ O	Ni(C ₂₈ H ₂₃ N ₃ O ₄)	64.27 (64.18)	4.60 (4.44)	8.14 (8.04)	242	Dark brown	2.90	6.30
Co(phen.) HBAA·H ₂ O	Co(C ₂₈ H ₂₃ N ₃ O ₄)	64.00 (64.09)	4.48 (4.43)	8.12 (8.03)	311	Light yellow	4.20	6.67

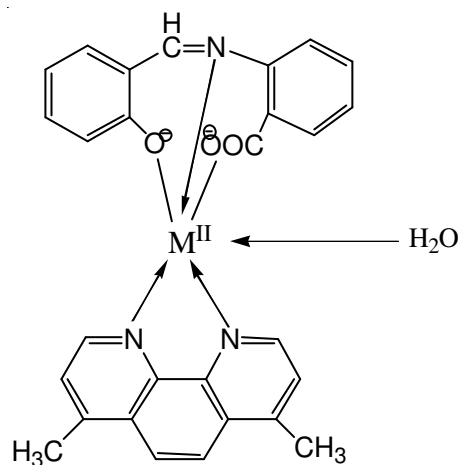
For free phen. a moderate band appears at 1600 cm^{-1} . This frequency is lowered by 20-80 cm^{-1} in mixed ligand metal complexes suggest pyridine nitrogen in coordination¹³. The presence of bands for out of plane C-H bending and deformation (850-620 cm^{-1}) and the ring system (1150-1000 cm^{-1}) has been observed¹⁴ and the aromatic C=C stretching vibration at 1600 cm^{-1} . The electronic spectra of mixed ligand metal complex of Cu(II) ion in DMF shows band at 14395 cm^{-1} , assigned spectral band due to transition ${}^2E_g \rightarrow {}^2T_{2g}$ and complex is octahedral. Mixed ligand metal complex of Ni(II) ion exhibits three bands in the range at 12710, 20924 and 27594 cm^{-1} corresponding to transitions ${}^3A_{2g} \rightarrow {}^3T_{2g}(v_1)$, ${}^3A_{2g} \rightarrow {}^3T_{1g}(v_2)$ and ${}^3A_{2g} \rightarrow {}^3T_{1g}(P)(v_3)$. The β % value reduced 64.40 % due to partial covalent character in metal-ligand bond^{15,16}. In Ni(phen.) HBAA·H₂O complex, lower value of v_2/v_1 (1.60) suggest some distortion in octahedral symmetry. In the mixed ligand metal complex of Co(II), three types of spectral bands at 8795, 15060 and 20410 cm^{-1} corresponding to transitions ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)(v_1)$, ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)(v_2)$ and ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)(v_3)$. The β % value reduced 54.68 %, lower value of v_2/v_1 (1.7) for the complex assume

their distortion octahedral configuration¹⁷. In all the metal complexes values of effective magnetic moment (μ_{eff}) higher than the normal value, indicating the monomeric nature of complexes. Complexes of type M(phen.) HBAA·H₂O are paramagnetic in nature due to presence of unpaired electrons. The antimicrobial activities of ligands and their mixed ligand metal complexes are given in Table-2. The biocidal activities of the mixed ligand metal complexes are more than metal or ligand alone. With increase in the ligands concentration in a complex, the inhibition of growth of rate of fungi and bacteria also increases.

TABLE-2
ANTIFUNGAL AND ANTIBACTERIAL ACTIVITIES OF LIGANDS
AND THEIR MIXED LIGAND METAL COMPLEXES

Ligand/complexes	Fungal growth after 7 days			Bacterial growth after 2 days	
	<i>A. flavus</i>	<i>A. fumigatus</i>	<i>A. niger</i>	<i>S. aureus</i>	<i>E. coli</i>
phen.	-	-	-	++	+
HBAA	++	++++	+++	+++	++
Cu(phen.) HBAA·H ₂ O	-	+	+	-	-
Ni(phen.) HBAA·H ₂ O	+	-	+	-	-
Co(phen.) HBAA·H ₂ O	-	-	-	+	+

++++ = Very high growth. +++ = High growth. ++ = Moderate growth. + = Poor growth. - = No growth.



M(II) = Cu(II), Ni(II), Co(II)

Structure of mixed ligand M(phen.) HBAA·H₂O complex

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