

FINAL REPORT

PROJECT TITLE: “Mixed – ligand complexes: Synthetic , thermal and spectral aspects and Biocidal activities.”

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FINAL REPORT OF THE WORK DONE

INTRODUCTION

Many mixed ligand complexes of Schiff's bases are known to show significant biocidal activity even at low concentration of about 5×10^{-4} gm/ml. Several researchers have done antimicrobial activity on species like *Pseudomonas crusiviae* and *Pseudomonas fluorescens*. The mixed ligand complexes of Schiff's bases offer excellent academic interest as well as tremendous industrial potential. This is attributed to their suitable thermal, chemical and biocidal properties. An ample amount of work is already done in this field. However, a more focused work depending upon their applications is still in significant demand. Moderate solubility of these complexes in polar organic solvents makes them suitable for application in paints, textile, insecticide and agro industries. A niche combination of transition metal and ligand can certainly lead to a complex with exact properties as desired for the application. The extensive conjugation in the ligand may also impart interesting electronic properties to the complexes. Moreover, the presence of the auxochromes in the ligand may also impart interesting photochemical properties to the complexes.

BRIEF OBJECTIVE OF THE PROJECT

One of the main objective of the proposed work is to arrive at a complex with biocidal properties that is suitable for applications in the paint industries. The extensive study carried out on a large number of complexes will also provide a good database for further research intended with similar potential applications.

WORK DONE

EXPERIMENTAL

PREPARATION OF SCHIFF'S BASES OF SALICYLDEHYDE WITH P- NITROANILINE/

P-CHLOROANILINE:

An ethanolic solution of p-nitroaniline and salicylaldehyde in equimolar ratio was mixed with constant stirring. Refluxing was carried out for an hour and was cooled at room temperature. The obtained crystals were collected and dried in air. The yield was 80%.

Similarly the preparation of Schiff's bases of Salicyldehyde with p-chloroaniline was carried out in the similar manner.

The schiff's bases obtained were abbreviated as:

SB₁ = p- nitroaniline Salicyldehyde

SB₂ = p-chloroaniline Salicyldehyde

SYNTHESIS OF DIAQUO COMPLEXES OF TYPE [M(SB₁).2H₂O] & [M(SB₂).2H₂O]

Prepare 0.1 nickel chloride hexahydrate in alcohol- water mixture (1:1) and 0.2 M SB₁ in alcohol water mixture. Mix the two solutions and adjust the pH of the solution to neutral by adding sufficient amount of caustic soda. Reflux the solution for an hour. Allow to cool. Pale green and thick precipitates settle at the bottom. They are filtered, washed with ethanol and dried in air. Yield was 85%.

The diaquo complexes of M = Mn(II), Fe(II), Co(II), Ni(II), Cu(II) and Zn(II) were prepared by similar procedure.

Similarly diaquo complexes of [M(SB₂).2H₂O] were prepared in the similar manner.

SYNTHESIS OF MIXED LIGAND COMPLEXES OF TYPE [M(SB₁).BIPY.AMINE]. H₂O & M(SB₂). BIPY.AMINE]. H₂O [M = Mn(II), Fe(II), Co(II), Ni(II), Cu (II) and Zn(II)]

Mixed ligand complexes of [M(SB₁).2H₂O] & [M(SB₂).2H₂O] was prepared using 2,2' dipyridyl amine. The preparation of [Ni (p-Cl.Anil.Sal)₂.Bipy.amine]. H₂O was carried out by refluxing an ethanolic solution 50 ml) [Ni (p – Cl. Anil. Sal)₂]. 2H₂O (0.02 M, 1.112 gm) with 2,2' dipyridyl amine(0.02 M, 0.342 gm) for an hour. The solution was then concentrated to 20 ml, scratched and cooled in a refrigerator overnight. The formed crystals were collected and recrystallis crystals were dried in air. The complexes of Mn(II), Fe(II), Co(II), Cu (II) and Zn(II) were prepared in the similar manner. The mixed ligand complexes of [M (p-NO₂. Anil. Sal)₂.Bipy.amine]. H₂O [M = Mn(II), Fe(II), Co(II), Ni(II), Cu(II) and Zn(II)] were also prepared by similar procedure.

ANALYSIS AND INSTRUMENTATION.

The carbon, hydrogen and nitrogen contents were analysed using Perkin – Elmer C, H, N, S – O analyser model 2400 Series II. The FTIR spectra was recorded on Perkin Elmer – Spectrum GXFT IR spectrophotometer employing KBr pellets of the compounds. The UV visible spectra were recorded on Shimadzu UV visible recording spectrophotometer model UV – 160 A. thermograms were recorded on Perkin Elmer thermogravimetric analyser TGA -1. The magnetic susceptibility was obtained using Guoy balance.

The complexes were analyzed for the metal contents by the EDTA titration technique.

RESULTS AND DISCUSSION

IR Spectra

The Infrared spectra of complexes register the sharp bands in the range of 1525-1535 cm⁻¹ and 750-780 cm⁻¹ due to aromatic $\nu(\text{C}=\text{C})$ and $\nu(\text{Bipy.amine})$. The frequencies in the range of 1600–1640 cm⁻¹ and 1170 -1180 cm⁻¹ attribute to $\nu(\text{C}=\text{N})$ and $\nu(\text{C}-\text{N})$ stretching indicating the involvement of pyridyl nitrogen in coordination. This has been further substantiated by observation of $\nu(\text{M}-\text{O})$ band around 430 cm⁻¹ and the $\nu(\text{M}-\text{N})$ band in the range of 510-520 cm⁻¹ respectively.

MAGNETIC MOMENTS AND ELECTRONIC SPECTRA

The magnetic moment values of $[\text{Mn}(\text{p-Cl.Anil.Sal})_2 \cdot \text{Bipy.amine}] \cdot \text{H}_2\text{O}$ and $[\text{Mn}(\text{p-NO}_2\text{.Anil.Sal})_2 \text{Bipy.amine}] \cdot \text{H}_2\text{O}$ are observed at 6.1 and 5.9 B.M respectively due to high spin d^5 system with an octahedral geometry. The electronic spectra exhibits three d-d transition bands ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{1g} ({}^4\text{G})(\cong 15,000 \text{ cm}^{-1})$, ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{2g} ({}^4\text{G})(\cong 19,500 \text{ cm}^{-1})$ and ${}^6\text{A}_{1g} \rightarrow {}^4\text{E}_g, {}^4\text{A}_{1g} ({}^4\text{G})(\cong 25,000 \text{ cm}^{-1})$ considering octahedral geometry.

The magnetic moments of Fe(II) complexes lies between 5.1- 5.5 B.M suggesting high spin Complexes in octahedral geometry. The electronic spectra exhibits bands at $\cong 11,200 \text{ cm}^{-1}$ assigned to ${}^5\text{T}_{2g} \rightarrow {}^5\text{E}_g$ transition. A strong charge transfer band is observed at $\cong 26,000 \text{ cm}^{-1}$ suggesting octahedral geometry. The magnetic values (4.7 and 8.9 B.M) and intense transfer band at $\cong 25,000 \text{ cm}^{-1}$ also suggest octahedral geometry for Co(II) complexes. The magnetic moment value (2.9 – 3.5 B.M) are in the usual range expected for similar hexa- coordinated Ni (II) ions. The electronic spectra shows three d-d transition bands at ${}^3\text{A}_{2g} (\text{F}) \rightarrow {}^3\text{T}_{2g} (\text{F})(\cong 10,500 \text{ cm}^{-1})$, ${}^3\text{A}_{2g} (\text{F}) \rightarrow {}^3\text{T}_{1g} (\text{F})(\cong 17,500 \text{ cm}^{-1})$ and ${}^3\text{A}_{2g} (\text{F}) \rightarrow {}^3\text{T}_{1g} (\text{P})(\cong 23,800 \text{ cm}^{-1})$. The magnetic moments of Cu(II) complexes lies between 2.06- 1.9 B.M suggesting octahedral geometry and exhibiting a band at $\cong 15,500 \text{ cm}^{-1}$ assigned to ${}^2\text{E}_g (\text{F}) \rightarrow {}^2\text{T}_{2g}$ Zn(II) complexes show diamagnetism and exhibit electronic bands at 40,000; 32,895 and 31,000 cm^{-1} due to $n \rightarrow \pi^*$ transitions.

THERMOGRAVIMETRIC ANALYSIS

There are remarkable features in the TGA curves. First, the melting points (or decomposition temperatures) of the complexes are higher than those of ligands, indicating that the complexes are more stable than the ligands. The loss in weight between 50-100°C corresponds to one water molecule for all the complexes. Because of low temperatures, this water molecule could be considered as water of crystallization. In the range between 100-300°C the loss in weight corresponds to evaporation of 2,2'-bipyridylamine. In the temperature range of 300-450°C the remaining organic ligand molecules are lost. In all the cases the final products are metal oxides. These results are in good accordance with the composition of the complexes.

ANTIMICROBIAL ACTIVITY

The bacterial activities of the complexes have been screened against *Bacillus Subtilis* and *E. Coli* using Agar diffusion method.

All the compounds have significant antimicrobial activity at $5 \times 10^{-4} \text{ g. ml}^{-1}$ against bacteria. It was observed that the compounds $[\text{M}(\text{SB}_1) \cdot \text{Bipy.Amine}] \cdot \text{H}_2\text{O}$ are more active as compared to the compounds $\text{M}(\text{SB}_2) \cdot \text{Bipy.Amine} \cdot \text{H}_2\text{O}$ [$\text{M} = \text{Mn(II), Fe(II), Co(II), Ni(II), Cu (II) and Zn(II)}$] against both bacterial species. All compounds screened are more active against *Bacillus Subtilis* than *E. Coli*.