

MINOR RESEARCH PROJECT

PRINCIPLE INVESTIGATOR: Dr Ketulkumar Narendrabhai Patel

DATE OF IMPLIMENTATION: 18-03-2008

APPROVAL NO: F. No. 47-063/07 (WRO)

TITLE OF THE PROJECT: SYNTHESIS, CHARACTERIZATION AND BIOCIDAL ACTIVITIES OF SOME MIXED-LIGAND COMPLEXES.

FINAL REPORT OF THE WORK DONE

INTRODUCTION

In the recent years, the inorganic constituents of biological systems have been receiving an increasing attention. 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. The mixed ligand complexes of Schiff's bases play a vital role in chemical industry and life itself. 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. Mixed-ligand complexes are widely used as catalyst in chemical and petrochemical industries, thermal stabilizer, semiconductive materials, moisture and water repellent, polymer additive, fungicides etc. It is a well known fact that the reactive group of Schiff bases is an azomethine and its biological importance has been studied in the fungicidal and insecticidal fields. Also the intermediate of the azomethine group shows biological importance in a larger number of enzymatic reactions. Chelation therapy may be the only acceptable treatment for metal poisoning. The extensive conjugation in the ligand may also impart interesting electronic properties to the complexes.

BRIEF OBJECTIVE OF THE PROJECT

One of the main objectives 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

Synthesis of N,N'-bis[2-hydroxyacetophenone]ethylenediamine (OAcPh-en):

The ligand OAcPh-en was synthesized by refluxing an ethanolic solution of 2-hydroxyacetophenone (OAcPh) and ethylenediamine (en) (2:1 molar ratio) for one hour. The reaction mixture was cooled and a bright yellow crystalline solid of N,N'-bis[2-hydroxyacetophenone]ethylenediamine (OAcPh-en) separated [10,11]. The solid was filtered off and recrystallized from ethanol to give bright yellow crystals.

Synthesis of bis[benzylidene]ethylenediamine (Ben-en):

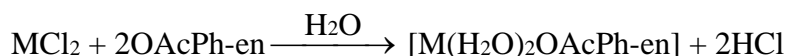
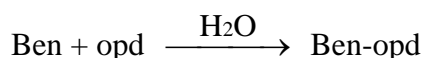
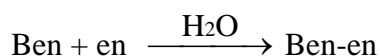
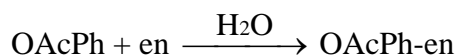
The ligand Ben-en was synthesized by refluxing an ethanoic solution of benzaldehyde (Ben) and ethylenediamine (en) (2:1 molar ratio) for one hour. The reaction mixture was cooled and a bright yellow crystalline solid of bis[benzylidene]ethylenediamine (Ben-en) separated. The solid was filtered off and recrystallized from ethanol to give light yellow crystals.

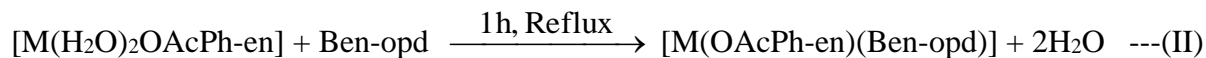
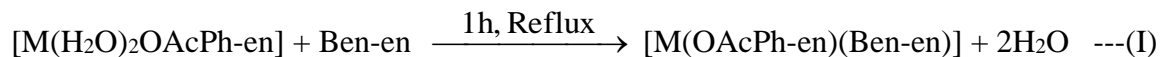
Synthesis of bis[benzylidene]o-phenylenediamine (Ben-opd):

The ligand Ben-opd was synthesized by refluxing an ethanoic solution of benzaldehyde (Ben) and o-phenylenediamine (opd) (2:1 molar ratio) for one hour. The reaction mixture was cooled and a bright yellow crystalline solid of bis[benzylidene]o-phenylenediamine (Ben-opd) separated. The solid was filtered off and recrystallized from ethanol to give yellow crystals.

Preparation of the complexes:

The preparation of [Ni(OAcPh-en)(Ben-en)]H₂O was carried out by refluxing an ethanoic solution (250ml) of Nickel diaquo complex (0.01M) with Neutral bi dentate ligand bis[benzylidene]ethylenediamine (Ben-en) (0.01M) for one hour. The solution was then concentrated and cooled in air to overnight. The formed crystals were collected and recrystallized, dry in air. The metal complexes of Cu(II), Co(II), Fe(II), Mn(II), and Zn(II) were prepared similarly. The mixed ligand complexes of [M(OAcPh-en)(Ben-opd)]H₂O [M = Ni(II), Cu(II), Co(II), Fe(II), Mn(II) and Zn(II)] were also prepared similarly. The formation of the complexes may be represented by the following equations.





Analytical procedures:

The complexes were analyzed for the metal contents by the EDTA-titration technique after decomposing the organic matter first with a mixture of perchloric, sulphuric and nitric acid (1:1.5:2.5). The infrared spectra were recorded on spectrum GX FT-IR (Perkin Elmer, USA). The magnetic susceptibility of the chelates was determined by the Gouy method at room temperature. The uv-visible spectra were recorded on Lambda 19 (Perkin Elmer, USA). The thermo gravimetric analyses were recorded on Thermo gravimetric Analyzer (Perkin Elmer, USA). Elemental analyses were performed on a C, H, N analyzer (Perkin Elmer, USA). All melting points were recorded in open capillaries in a capillary melting point apparatus.

Results and Discussion:

Magnetic Measurements:

The magnetic moment of the Cu(II) complex (1.80-1.85 B.M.) is very close to the spin-only value (1.73 B.M.) expected for the one unpaired electron which offers the possibility of an octahedral geometry. The magnetic moment value for Fe(II) complex is 5.25-5.24 B.M. at room temperature and this value is characteristic of high spin octahedral geometry for this complex. The magnetic moment values for Co(II) complexes are 4.00-4.10 B.M. corresponding to three unpaired electrons which suggests an octahedral geometry. The magnetic moment of the nickel complex at room temperature was observed 2.71-2.69 B.M. These values are in tune with a high spin configuration and show the presence of an octahedral environment around the Ni(II) ion in the complex. The Mn(II) complex show magnetic moments is 5.74-5.75 B.M. at room temperature corresponding to five unpaired electrons which suggest octahedral geometry. Zn(II) complex is show diamagnetic nature and is found to be octahedral geometry.

IR Spectra:

The infrared spectra of the complexes have been studied to characterize their structures. The IR spectra of the complexes register $\nu(C-O)$ at about 1324-1340 cm^{-1} . The IR spectra of Schiff base shows a sharp band near 1610 cm^{-1} which may be due to azomethine linkage and shows lowering

in frequency in metal complex indicating the coordination of metal ion through azomethine linkage. The sharp bend in the range $750\text{-}780\text{ cm}^{-1}$ and $1525\text{-}1535\text{ cm}^{-1}$ are due to aromatic $\nu(\text{C-H})$ and $\nu(\text{C}=\text{C})$ respectively. The frequencies in the range $1145\text{-}1165\text{ cm}^{-1}$ attributed to $\nu(\text{C-N})$ stretching. Conclusive evidence of the bonding is also shown by the observation that new bands in the spectra of the metal complexes appears at $455\text{-}460\text{ cm}^{-1}$ and $514\text{-}525\text{ cm}^{-1}$ these are assigned to $\nu(\text{M-O})$ and $\nu(\text{M-N})$ stretching vibrations and are not observed in the spectra of the ligand. The presence of sharp band corresponding to the remaining hydroxyl group at 3400 cm^{-1} but it is obscured by the presence of water molecules bands. This was appeared for the most complexes and a very broad band at about $3100\text{-}3500\text{ cm}^{-1}$ region, which was associated with coordinated or solvent water molecules.

Electronic spectra:

Electronic spectrum of Co(II) complex exhibits absorption bands at $12,920$, $16,260$, and $23,450\text{ cm}^{-1}$, which may be assigned to ${}^4\text{T}_1(\text{F}) \rightarrow {}^4\text{T}_2(\text{F})$, ${}^4\text{T}_1(\text{F}) \rightarrow {}^4\text{A}_2(\text{F})$ and ${}^4\text{T}_1(\text{F}) \rightarrow {}^4\text{T}_1(\text{P})$ transitions respectively which are in support of octahedral arrangement of binding centers around the metal ion. The electronic spectra of Mn(II) complexes show the absorption bands in the range $16970\text{-}19540$, $22280\text{-}24390$ and $26109\text{-}27624\text{ cm}^{-1}$. These absorption bands may be assigned to the ${}^6\text{A}_{1g} \rightarrow {}^4\text{A}_{1g} ({}^4\text{G})$, ${}^6\text{A}_{1g} \rightarrow {}^4\text{A}_{2g} ({}^4\text{G})$, and ${}^6\text{A}_{1g} \rightarrow {}^4\text{E}_g, {}^4\text{A}_{1g} ({}^4\text{G})$ transitions, respectively. These bands suggest that the complexes possess an octahedral geometry. Bands at the regions 675 nm (14815 cm^{-1}) and 535 nm (18690 cm^{-1}) for Cu(II) complex were assigned to the ${}^2\text{B}_{1g} \rightarrow {}^2\text{B}_{2g}$ and ${}^2\text{B}_{2g} \rightarrow {}^2\text{E}_g$ transitions respectively, found for octahedral Cu(II) complexes. The electronic spectrum of the Fe(II) complex exhibit a band at $11,200\text{ cm}^{-1}$, assigned to the ${}^5\text{T}_{2g} \rightarrow {}^5\text{E}_g$ transition. A strong charge transfer band is observed at $26,000\text{ cm}^{-1}$. These data suggest an octahedral geometry. The electronic spectra of the Ni(II) complex showed d-d bands in the region 10115 and $26280\text{-}26410\text{ cm}^{-1}$ ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{2g}(\text{F})$ and ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{2g}(\text{P})$ respectively, consistent with their well-defined octahedral configuration. The Zn(II) complex has not shown any d-d absorptions.

Thermo gravimetric Analysis:

The analysis of the thermal curve of the complexes clearly indicated that the weight loss between $35\text{-}105^\circ\text{C}$ corresponds to one water molecule for all complexes. Because of the low temperatures, this molecule may be consider as crystal water. The curves in the range between $105\text{-}385^\circ\text{C}$ suggested that loss in weight for all complexes correspond to evaporation of bis[benzylidene]ethylenediamine (Ben-en) and bis[benzylidene]o-phenylenediamine (Ben-opd). The range above 385°C loss in weight correspond to remaining organic ligand molecules. In all

cases, final products are metal oxides. These results are in good accordance with the composition of the complexes.

Antimicrobial activity:

The antimicrobial activity of the complexes against Gram positive bacteria *Bacillus Substlis* and Gram negative bacteria *E.Coli* have been done using the “Agar diffusion method”. The diameter of inhibition zone of the various compounds is recorded. All the compounds have significant antibacterial activity at $1.0 \times 10^4 \mu\text{gml}^{-1}$ against bacteria. The compounds $[\text{M}(\text{OAcPh-en})(\text{Ben-en})] \cdot \text{H}_2\text{O}$, $[\text{M} = \text{Ni(II)}, \text{Cu(II)}, \text{Co(II)}, \text{Fe(II)}, \text{Mn(II)}$ and $\text{Zn(II)}]$ are more active as compared to the compounds $[\text{M}(\text{OAcPh-en})(\text{Ben-opd})] \cdot \text{H}_2\text{O}$, $[\text{M} = \text{Ni(II)}, \text{Cu(II)}, \text{Co(II)}, \text{Fe(II)}, \text{Mn(II)}$ and $\text{Zn(II)}]$ against bacteria. All the compounds screened are more active against gram positive bacteria *Bacillus Substlis* then gram negative bacteria *E.Coli*.

ACKNOWLEDGEMENTS

I am thankful to University Grants Commission, Pune for providing financial assistance for the present study. Authors also thank SICART, V V Nagar for providing analytical services.