



Research Article

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Charge Transfer and Photoluminescence Properties of Hetero- and Homo-Bimetallic Complexes of Ni(II) and Cu(II)-4,5-bis(benzimidazol-2-yl)imidazole

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Abstract

A number of hetero-bimetallic and homo-bimetallic complexes of Ni(II) and Cu(II) of composition $[M(\text{imbz})_2\text{CuCl}_2]$ and $[(M(\text{imbz})_2\text{NiCl}_2(\text{bipy}))]$ [$M = \text{Ni}^{\text{II}}$ or Cu^{II} , $\text{Himbz} = 4,5\text{-bis}(\text{benzimidazol-2-yl})\text{imidazole}$ and $\text{bipy} = 2,2\text{-bipyridine}$] have been prepared and characterized. The absorption spectra, magnetic susceptibility, redox behavior and photoluminescence properties of the complexes have been examined thoroughly. Electronic absorption band positions and magnetic moment values of complexes are consistent with octahedral structure of metal ions.

Key words: Photoluminescence and metal ligand charge transfer, bimetallic 4,5-bis (benzimidazol-2-yl) imidazole complexes.

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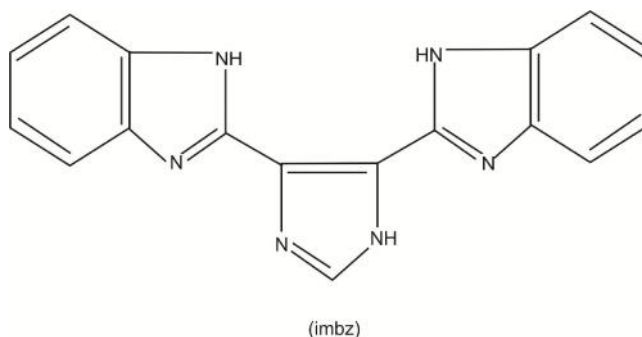
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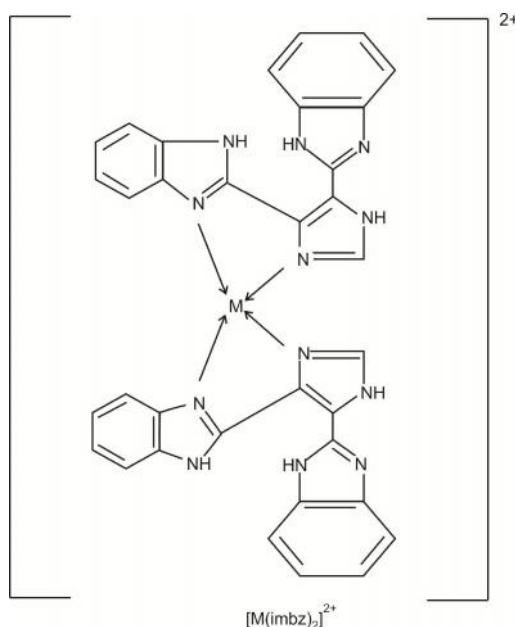
1. Introduction

Among all heterocyclic compounds the chemistry of benzimidazole and benzothiazole derivatives are most widely studied organic molecules due to their wide spectrum of application in various field of physiological significance, agricultural utility and industrial applications. Multidimensional bio chemical and physiological activity of benzimidazole and benzothiazole derivatives and their metal complexes enhanced the interest of chemists during last few decades to look extensively for biological utility and complexing behavior with metal ions of their new derivatives. The importance of benzimidazole and benzothiazole derivatives further arises because they are found in many biologically active compounds [1-5]. In addition, the benzimidazole moiety is found in various synthetic pharmaceuticals displaying a broad spectrum of biological activity including anti-ulcer, anti-tumor and anti-viral effects [6-10].

Bis (benzimidazol-2-yl) imidazole (imbz) is a polydentate coordinating molecule and can form bonds with benzimidazole tertiary nitrogen and imidazole rings nitrogens as well.



The ligand Himbz can form bis chelate with bivalent metal ions $[M(\text{imbz})_2]^{2+}$ in which one benzimidazole ring and imidazole ring NH nitrogen of each Himbz still remains available for further bond formation



The bivalent metallic complexes of Cu (II) Ni (II) of (Himbz) has been isolated and characterized by physicochemical methods.

2. Materials and Methods

The ligand Himbz was obtained from Flucka Germany & metal salts used were obtained from E- Merck and BDH. The magnetic susceptibility of complexes was determined at room temperature by Gouy method. Electronic absorption spectra and i r spectra were determined at IIT Patna. The results of CHN were obtained from BIT, Mesra Ranchi

Experimental

Preparation of complexes: $[M(\text{imbz})_2\text{CuCl}_2]$ $[(M=\text{Ni}^{2+}$ or Cu^{2+} , Himbz= 4,5- bis (benzimidazol-2-yl)imidazole] About 0.01 mol of metal chloride was dissolved in 30 ml dry ethanol and treated with 0.02 mol of ligand dissolved in minimum volume of ethanol and refluxed on water bath when desired product separated. The coloured complexes separated were collected on a filter paper and dried over CaCl_2 . The complexes were analyzed and found to correspond with composition ML_2Cl_2 ($M=\text{Cu}^{2+}$ or Ni^{2+}). About 0.005 mol of complex was suspended in 30 ml dry ethanol and treated with molar proportion of CuCl_2 dissolved in dry ethanol. On refluxing the whole content went into solution and from which fine crystalline precipitate separated on cooling the refluxate. The product were collected on a filter and dried over CaCl_2 in a desiccators. On analysis the analytical results correspond to composition $[M(\text{imbz})_2\text{CuCl}_2]$.

Preparation of complexes: $[M(\text{imbz})_2\text{NiCl}_2(\text{bipy})]$ $[(M=\text{Ni}^{2+}$ or Cu^{2+} , Himbz= 4,5- bis (benzimidazol-2-yl)imidazole and bipy=2,2'-bipyridine]- About 0.005mol of bis chelate $M(\text{imbz})_2$ was suspended in 25 ml ethanol and treated with molar proportion of NiCl_2 and bipyridine dissolved in Ethanol. The resulting solutions were refluxed for 1 hr when clear solution was obtained from which fine crystalline complexes separated on cooling. The

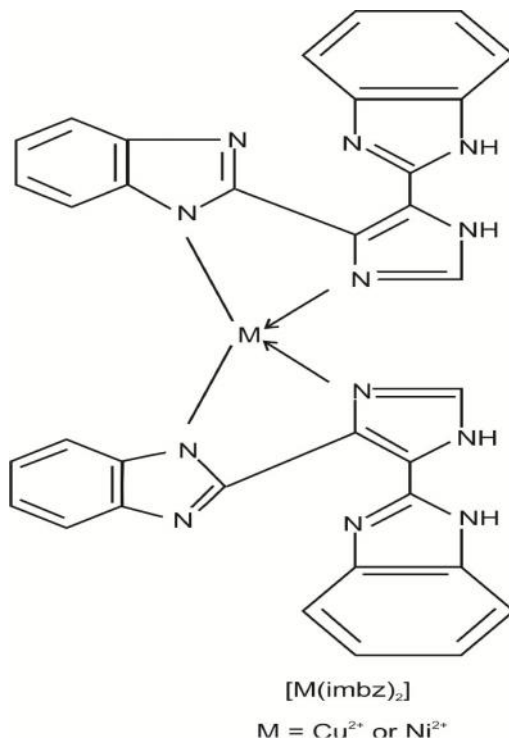
product was collected on a filter dried over CaCl_2 and analyzed for metal carbon hydrogen and nitrogen. The analytical results correspond to composition $[\text{M}(\text{imbz})_2 \text{NiCl}_2(\text{bipy})]$

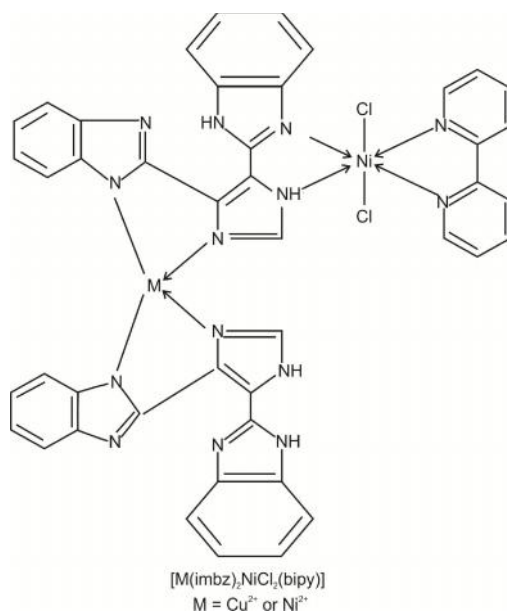
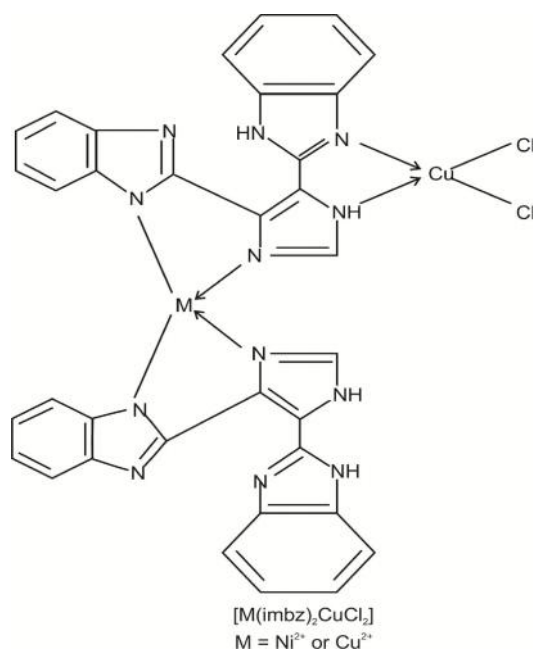
3. Results and Discussion

The analytical results of complexes correspond to compositions $[\text{M}(\text{imbz})_2 \text{CuCl}_2]$ ($\text{M}=\text{Cu}^{2+}$ or Ni^{2+}) and $[\text{M}(\text{imbz})_2 \text{NiCl}_2(\text{bipy})]$. The complexes are stable and dissolve appreciably in DMF or dioxane. The complexes are quite stable to heat and do not decompose or dissociate below 250-280°C. The complexes melts between 240-250 °C and decomposes on heating at 280-300°C. The complexes are paramagnetic and magnetic moment value of complexes $[\text{Cu}(\text{imbz})_2 \text{CuCl}_2]$ and $[\text{Ni}(\text{imbz})_2 \text{NiCl}_2(\text{bipy})]$ are similar to high spin octahedral environment of ligand around metal ions. The electrical conductance values of complexes were evaluated in DMF solution at room temperature. The complexes show negligible electrical conductance value supporting their non ionic nature.

The electronic absorption spectra of complexes were determined in ethanol in the range 350-850nm. The copper (II) complexes $[\text{Cu}(\text{imbz})_2 \text{CuCl}_2]$ display a broad band between 650-680 nm and strong absorption below 420nm. The Nickel (II) complexes $[\text{Ni}(\text{imbz})_2]$ display a medium band at 410nm and a weak band near 560 nm assignable to ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{P})$ and ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{F})$ transitions in octahedral field. The complexes $[\text{M}(\text{imbz})_2 \text{CuCl}_2]$ display strong absorption below 420 nm and the absorption is assigned as charge transfer transition. The intensity of absorption band of complex $[\text{Cu}(\text{imbz})_2 \text{CuCl}_2]$ at 650-680 nm increased on keeping the solution in visible light and reaches maxima within one hour between 600-650 nm of radiation. The color again changes and the intensity of radiation decreases on keeping the solution in dark. Such photoluminescence properties is also displayed by Ni (II) complex $[\text{Ni}(\text{imbz})_2 \text{NiCl}_2(\text{dipy})]$. The charge transfer absorption of complex was observed at 430 nm with ϵ_{max} value 1.56×10^4 per mol. The absorption of complex observed at 560 nm shift to 530-540 nm on radiation of DMF solution of complex at 550-560 nm. A strong violet red absorption around 530-540 nm of Ni (II) complex was attributed to photoluminescence behaviour.

The i.r spectra of complexes were recorded as KBr optics and i.r. spectrum of ligand was compared with i.r. spectra of complexes. The ligand shows (C=N) stretch of imidazole and benzimidazole ring at 1644cm^{-1} which shifts to lower frequency by $30\text{-}40\text{ cm}^{-1}$ in complexes supporting coordination of (C=N) nitrogen to metal atom. The (NH) vibration of imidazole and benzimidazole ring NH group was observed at $3195\text{-}3245\text{ cm}^{-1}$ as medium band. The (NH) stretches of ligand were retained in complexes with slight change in intensity. The retention of NH stretches of ligand and its complexes suggested non coordinated nature of NH nitrogen. The (NH) of ligand located at 3245 and 3195 cm^{-1} were least affected on coordination. From the study of i.r. spectra the bis coordination of ligand was suggested in complexes $[\text{Ni}(\text{imbz})_2]$, $[\text{Cu}(\text{imbz})_2]$ and $[\text{M}(\text{imbz})_2 \text{CuCl}_2]$ as well as $[\text{M}(\text{imbz})_2 \text{NiCl}_2(\text{bipy})]$. On the basis of magnetic susceptibility data, infrared spectral bands and electronic absorption spectral studies the following structure have been suggested for the hetero and homo bimetallic complexes.





4. Conclusion

In low concentration of metal the ligand coordinates as bidentate chelating molecule while in excess of metal the tetra coordination of ligand were observed where both benzimidazole and imidazole ring tertiary nitrogen atoms are involved in coordination and NH of benzimidazole ring is involved in bonding on deprotonation.

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