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Synthesis spectroscopic (IR, UV- visible and E & P) and magnetic studies of mixed ligand complexes

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Abstract

In this paper, the synthesis, reactions and characterisation of some new monochloro complexes of copper (II), which have proved to be useful precursors for the synthesis of new and novel class of hydrocarbon soluble mixed ligand complexes.

Keywords: synthesis spectroscopic, IR, UV- visible, magnetic studies, mixed ligand complexes

Introduction

In Present day in the synthesis and characterisation of transition metal chelates of benzimidazole derivatives. Among these derivatives, 2-(o-hydroxyphenyl)-benzimidazole is remarkable ligand due to its importance in biological, pharmacological, clinical and analytical applications [1-3]. A literature search reveals that work on these complexes are limited only upto bis- and tris-complexes with the corresponding divalent or trivalent metals. Benzimidazole and its related ligands act as a potential ligand for the preparation of various types of transition metal complexes due to their varying strong chelating behaviour towards metal ions. These are well known for their excellent medicinal properties and biological activities [4-6]. A limited attention [7-11] has been paid to the chemistry of monochloro complexes of later '3d' transition metals containing benzimidazole moieties, possibly due to their insoluble non-volatile and polymeric nature.

Materials and Method

All chemicals of A.R. grade were used in the present investigations. Quantitative analysis of copper present in the complexes were carried out by atomic absorption spectroscopy, GBC-932 AA. IR spectra (4000-2000 cm^{-1}) were recorded on Perkin Elmer 1000 FTIR spectrometer in nujol-mull. Electronic spectra of the compounds were recorded in benzene and/or tetrahydrofuran on a Hitachi-220 spectrophotometer. Magnetic susceptibility was measured on a Gouy balance using $\text{Hg}[\text{Co}(\text{CNS})_4]$ as calibrating agent. ESR spectra of copper(II) complexes were recorded at room temperature on a E-112 ESR spectrometer.

Preparation of Ligands: The ligands {2-(o-hydroxyphenyl)-benzimidazole, (HOPBZ) and Schiff base, Salicylidene-2-methyl-1-amino-benzene, (SMAB) have been prepared by established method.

Preparation of Complexes

(A) Monochloro {2-(o-hydroxyphenyl)-benzimidazole-copper(II)}; $[(\mu\text{-Cl})_2, \text{Cu}_2 \{\eta^2\text{-}(\text{OPBZ})_2\}]$ (1).

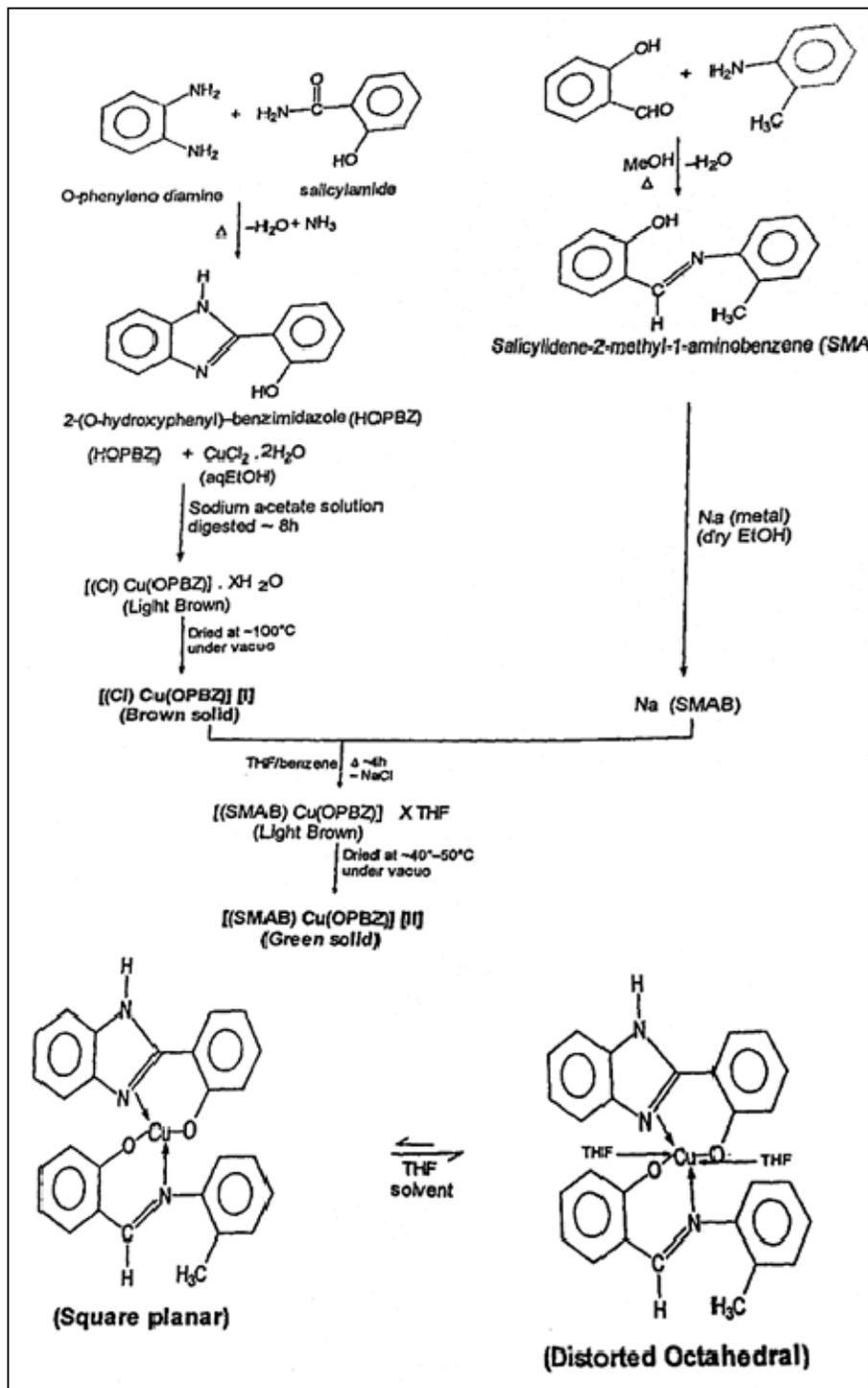
An aqueous ethanolic solution (50% ethanol, $\sim 50 \text{ cm}^3$) of copper (II) chloride (2.433g, 14.3 mmol) was added dropwise to a stirred hot ethanol ($\sim 75 \text{ cm}^3$) solution containing 2-(o-hydroxyphenyl)-benzimidazole (3g, 14.3 mmol), which yielded as a pale yellow coloured precipitate. Further, dropwise addition of dilute solution of sodium acetate with continuous stirring afforded dense light brown coloured precipitate from initial pale yellow colour. After complete precipitation, it was digested on water bath for $\sim 1\text{h}$. The complex so obtained was filtered, washed thrice with aqueous ethanol and dried at 100°C under reduced pressure to obtain $[(\mu\text{-Cl})_2, \text{Cu}_2 \{\eta^2\text{-}(\text{OPBZ})_2\}]$ (1) brown powdered solid. (4.000g 91%). The product on analysis was found to have Cu, 20.10%, Cl, 12.0% and (Cald) for Cu (20.60%), Cl (11.51%).

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(B) Copper (II) complex containing {2-(o-hydroxyphenyl)-benzimidazole and salicylidene-2-methyl-1-aminobenzene moieties [(η^2 -SMAB)Cu(η^2 -OPBZ)] (II).

To a stirred hot brown suspension of monochloro {2-(o-hydroxyphenyl)-benzimidazolato-copper(II)} (0.300g, 0.97mmol) complex in tetrahydrofuran (~30 cm³), was added sodium salt of salicylidene-2-methyl-1-aminobenzene (0.230g, 0.97mmol) in 1:1 stoichiometric ratio. The reaction mixture was allowed to reflux for ~1h,

during which the colour of the solution changed from brown to green. The precipitated NaCl (0.057g, 0.97mmol) was removed by filtration. The solvent was removed from the filtrate under reduced pressure to afford [(η^2 -SMAB) Cu (η^2 -OPAL)] (II) (Scheme-1), which was purified by recrystallization from a benzene/THF mixture to give green powdered solid (0.380g, 81%). Analysis of the title derivative was found to be Cu 12.9% and (Calcd) for Cu (13.17%).



Scheme 1: Synthesis of Copper (II) Complexes (I) and (II)

Results and Discussion

Synthesis and some physical properties of $[(\mu\text{-Cl})_2\text{Cu}_2\{\eta^2\text{-(OPBZ)}\}_2]$ (I):

A hot ethanolic solution of {2-(o-hydroxyphenyl)} benzimidazole; (HOPBZ) added to an aqueous ethanolic solution of copper (II) chloride (hydrated) in equimolar ratio, a pale yellow coloured precipitate was obtained. Further addition of sodium acetate afforded dense brown colour product $[(\mu\text{-Cl})_2\text{Cu}_2\{\eta^2\text{-(OPBZ)}\}_2]$ (I).

The obtained product (I) was digested, filtered, washed with aqueous ethanol, and finally dried at $\sim 100^\circ\text{C}$ under reduced pressure. Attempts have been made to purify the complex using a number of solvents such as benzene, isopropanol, ethanol etc. However, it has been realised that the complex is highly insoluble in most of the common solvents and mixture of solvents. The complex has tendency to form adducts, when treated with THF/pyridine. Due to insolubility in the non-polar solvents, the molecular weight determination could not be made possible either by cryoscopically or by ebullioscopically, though it is expected to be polymeric in nature.

Attempts have been made during the course of present investigation to prepare soluble complex by the interaction of sodium salt of Schiff base; which could throw light on structure of copper (II) complex. The reactions of chloro complex of copper(II) containing benzimidazole moiety with sodium salt of salicylidene-2-methyl-1-aminobenzene, Na(SMAB) in the equimolar ratio, in the presence of mixture of THF/pyridine, which can be represented as follow:

T.H.F./Py.

$[(\text{OPBZ})\text{Cu}(\text{Cl})+\text{Na}(\text{SMAB})]$

slim: LI/reflux

$[(\text{OPBZ})\text{Cu}(\text{SMAB})] + \text{NaCl}$

This mixed ligand complex is coloured solid and found to be soluble in common organic solvents like benzene, n-hexane etc. and has been purified by recrystallization in the mixture of solvents such as THF and benzene.

Infrared spectral studies: The, N-H stretching frequency $\nu_{\text{N-H}}$ observed in the spectra of the ligand 2-(o-hydroxyphenyl)-benzimidazole (HOPBZ) at $\sim 3200\text{ cm}^{-1}$ remain almost unchanged in the complex containing hemimidazole moiety. indicating non-participation of N-H group. The monochloro complex $[(\text{H-Cl})_2\text{Cu}_2\{\eta^2\text{-(OPBZ)}\}_2]$ (1) exhibit characteristic IR frequencies at $280(\text{s})\text{cm}^{-1}$ and has been assigned for $\nu_{\text{Cu-Cl}}$ bridging vibration^[17], suggesting bridging of chlorine between two copper (II) centers.

The IR spectra of the ligands (SMAB and, HOPBZ) showed bands at $1647\text{-}1618\text{ cm}^{-1}$ characteristics for $\nu_{\text{C=N}}$, whereas bands shifted to lower frequency region at $1604\text{-}1595\text{ cm}^{-1}$ in complexes $[(\mu\text{-Cl})_2\text{Cu}_2\{\eta^2\text{-(OPBZ)}\}_2]$ (I) and $[\eta^2\text{-SMAB})\text{Cu}\{\eta^2\text{-(OPBZ)}\}]$ (II) suggesting coordination through hetero nitrogen atom of azomethine group. The IR frequencies of $\nu(\text{C-O})$ (phenolic) in the ligands are generally observed in the region $1256\text{-}1248\text{ cm}^{-1}$, which get shifted towards higher region $1283\text{-}1267\text{ cm}^{-1}$, thereby indicating that bonding takes place through phenolic oxygen (after deprotonation of phenolic OH group of the ligands).

The medium to strong intensity bands in the region $(237(\text{m})\text{-}234(\text{s})\text{ cm}^{-1})$ and $(580(\text{s})\text{-}559(\text{m})\text{ cm}^{-1})$ in complexes have been assigned to $\nu_{\text{Cu-N}}$ and $\nu_{\text{Cu-O}}$ mode respectively.

Electronic spectral studies: The visible spectra of complexes $[(\mu\text{-Cl})_2\text{Cu}_2\{\eta^2\text{-(OPBZ)}\}_2]$ (1) and $[\eta^2\text{-SMAB})\text{Cu}(\eta^2\text{-OPBZ})]$ (II) have been recorded in pyridine/THF mixture which exhibits broad asymmetric band at ~ 14903 and $\sim 15673\text{ cm}^{-1}$

respectively attributed to ${}^2E_g \rightarrow {}^2T_{2g}$ transition, due to Jahn-Teller distortion in d^9 (Cu^{2+}) systems as well as due to the presence of electrogenative 'N' and 'O' donor atoms causes the broadening of the absorption band, suggesting a distorted octahedral geometry (in D_{4h} symmetry) for copper(II) complexes. Besides above bands additional intense bands have been observed at $\sim 26882\text{ cm}^{-1}$ assigned as ligand to metal charge transfer band ($L \rightarrow M$, CT) and at $\sim 33445\text{ cm}^{-1}$ assigned to intraligand charge transfer band.

ESR spectral studies: The ESR spectrum of monochloro {2-(o-hydroxyphenyl)-benzimidazolato}-copper (II) [I] in polycrystalline solid state at room temperature has been measured. ESR spectrum indicates $g_{\parallel} > g_{\perp} > 2.02$ in

$d_{x^2-y^2}$ (or d_{xy}) state, whilst a d_{z^2} ground state term usually gives a spectrum with $g_{\perp} > g_{\parallel} \approx 2.00$. Copper (II) system studied here in, shows a pronounced peak for which $g_{\parallel} \approx 2.32$. in an axial symmetry, the g values are related by the expression $G = (g_{\parallel} - 2)/(g_{\perp} - 2)$, which measures the exchange interaction between copper centres in polycrystalline solid. If $G > 4$, exchange interaction is negligible, values of $G < 4$ indicates considerable exchange interaction in the solid complex. The g_{av} values have been calculated according to the relation $g_{\text{av}} = 1/3(g_{\parallel} + 2g_{\perp})$ and gave values in the range 2.17 ± 0.03 , which are in agreement with an orbitally non-degenerate ground state.

It appears that g value obtained corresponds to molecular g value, which are characteristics of square planar geometry around copper(II), obtained as a result of coordination through nitrogen atom. These have been corroborated by IR and electronic spectral studies.

Magnetic studies: The copper(II) complex of 3d configurations exhibits paramagnetism corresponding to one unpaired spin ($S=1/2$, $\mu_{\text{s.o.}}=1.73\text{BM}$). However, magnetic moment is usually observed to be slightly higher $\sim 2.0\text{BM}$. Copper(II) complexes usually have a distorted octahedral stereochemistry, although a few are known to be square planar approaching towards a tetrahedral stereochemistry. The observed magnetic moment at and room temperature for monochloro-{2-(o-hydroxyphenyl)-benzimidazolato}-copper(II) is 2.36BM which is in agreement with reported values ($1.8\text{-}2.4\text{BM}$) for $\text{Cu}(\text{II})d^9$ system.

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