STUDIES ON MIXED LIGAND COMPLEXES OF COPPER METAL WITH THIOSEMICARBAZONES AS PRIMARY AND NAPHTHOIC ACID AS CO LIGAND

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RECEIVED : 31 March, 2016

The metal complexes of Cu(II) with thiosemicarbazones as primary and naphthoic acid as co-ligand are synthesized and characterized. The structure of newly synthesized complexes and the ligands were estabilished with U.V, I.R, Magnetic moment study and elememtal analysis.The ligand and the complexe were also screened for their fungicidal activity against different fungi viz- Drechlera tetramera, Alterntria alternate and Fusarium oxysporum.

KEYWORDS : Thiosemicarbazones , fungicidal activity & ML.

INTRODUCTION

The compounds formed by the condensation of carbonyl compounds with thiosemicarbazides are called thiosemicarbazones. For the first time Domargk and his co-workers [1] observed tuberculostic activity of thiosemicarbazone and their related compounds. Thiosemicarbazides and their derivatives shows various biological activity [2-5] and they are used in medicine, especially in the cure of tuberculosis. Antimicrobial and antitumor activity have also been shown by some thiosemicarbazones [6, 7]. Some of their derivatives have been tried for application in medicine and remarkable correlation between the coordination properties and antitumor activity of a group of heterocyclic aldehydic thiosemicarbazones in animal system has been noted [8-10]. Thiosemicarbazones has shown activity against viruses, protozoa and smallpox [11-14]. Thiosemicarbazones and their derivatives are also active against influenza, pesticides and fungicides because of their ability to form chelates with trace metals.

The survey of the literature revealed that only a few scattered references [5-9] are available on transition metal complexes of biologically active ligands. However, the survey of literature revealed that no work has been done so far on mixed ligand complexes with thiosemicarbazones as primary and naphthoic acids as co-ligand. So it is worth while to

prepare transition metal complexes of thiosemicarbazone as primary and naphthoic acids as co-ligand and study their structural and biological activity.

The present paper deals with the preparation and characterization of mixed ligand complexes of transition metal complexes formed from Schiff bases derived by the condensation of thiosemicarbazide with o-chloro-acetoacetanilide as primary ligand and 1-hydroxy-2-naphthoic acid as co-ligand. This mixed ligand complex was prepared and characterized by the elemental analysis, I.R. UV and magnetic studies. Ligands and their complexes were also screened for their antifungal activity against different fungi using growth method at different concentrations.

EXPERIMENTAL

All the reagents used were of chemically pure or analytical reagent grade. Solvents used were purified and dried according to standard procedure reported in literature. The analyses of carbon, hydrogen and nitrogen were performed at CDRI Lucknow.

PREPARATION OF PRIMARY LIGAND (SCHIFF BASE):

Schiff base was prepared by refluxing thiosemicarbazides with o-chloroacetoacetanilide in 1:1 molar ratio in alcohol for one hour. After refluxing, it was concentrated on water bath for half its volume. The precipitate obtained after concentration was filtered and dried. The formation of Schiff base was confirmed by elemental analysis and I.R. spectral studies.

PREPARATION OF MIXED LIGAND COMPLEXES:

To a warm ethanolic solution of anhydrous metal (II) chloride, hot ethanolic solution of Schiff base was added drop wise. The reaction mixture was thoroughly stirred and refluxed at 70-80^{o}C for three hours on water bath. Crystalline solid complexes separated out on cooling at room temperature. The newly prepared complexes formed with primary ligand were filtered off washed with ethanol and finally with ether and dried in vacuum over P_4O_{10}.

The desired mixed ligand complexes were prepared by treating the ethanolic solution of binary complexes with the ethanol solution of 1-Hydroxy-2-naphthoic acid. The reaction mixture was refluxed over water bath for about 2 hours. The reaction mixture after refluxing was kept for overnight at room temperature Complexes in the form of precipitate separate out which were filtered washed with acetonitrile and dry ether to remove the excess of unreacted ligand if any. The complexes were recrystallised from ethanol chloroform mixture. The crystalline complexes were dried in vacuum yield 80%.

RESULT AND DISCUSSION

Analytical data of mixed ligand complexes shows 1:1:1 (M: Primary Ligand: Secondary ligand) stoichiometry of isolated mixed ligand complexes. The complexes are stable upto 160^{o}C showing that they are non-hygroscopic. All the complexes are soluble in common organic solvents. The conductance data shows, non-electrolytic nature of the mixed ligand complexes.

I.R. STUDIES:

On comparison of I.R. spectra of free ligands with those of the mixed ligand complexes confirm the coordination of thiosemicarbazones and naphthoic acid to the metals. I.R. spectra of free thiosemicarbazone ligand (Schiff base) show two band at 3445 and 3310 cm^{-1} due to

ν_{as} and ν_{sym} of terminal NH_2 group. In complexes these bands were found unchanged showing the non-involvement of this group in coordination. The absorption due to $\nu_{C=N}$ of the free ligand appear in the region 1610 cm^{-1} undergoes a negative shift by 10-20 cm^{-1} in the spectra of complexes indicating the coordination of azomethine nitrogen to the metal.

The bands of strong intensities in the spectra of the Schiff base around 1640 cm^{-1} are due to $\nu_{C=O}$. In the spectra of complexes, this band is absent and a new band is observed at 1615cm^{-1} which can be attributed to the enolisation and subsequent coordination through the deprotonated oxygen atom of the $–CH_2–C=O$ group. The band due to $\nu_{C=S}$ appearing at 825 cm^{-1} in the free Schiff base disappear on complexation and a new band appears around 740 cm^{-1}. These observations may be attributed to the enolisation of the –NH–C=S group and subsequent coordination through the deprotonated sulphur. From I.R. data it may be concluded that the thiosemicarbazones is potentially dibasic tridentate ligand and the coordination sites are the β-nitrogen and thiolato sulphur and oxygen after deprotonation. The possibility of α-Nitrogen coordination is ruled out because of considerable strain.

The νOH (of COOH group) observed as a broad intense band at 2645 cm^{-1} in napthoic acid has no change in the spectra of the mixed ligand complexes indicating that the carboxylic proton has not been removed in complexation. The symmetrical and asymmetrical stretching vibration of COO of free ligand observed at 1410 and 1630 cm^{-1} respectively has shifted to 10-15 cm^{-1} in the complexes indicating coordination of carboxylate oxygen to metal ion. The band observed at 2960 assigned to phenolic-OH of acid also get shifted indicating that –OH is coordinated to metal. This is also confirmed by the observation of M-O band in the spectra.

Magnetic and Electronic Spectral Studies:

Cu (II) mixed Ligand Complex:The cupric ion has $3d^9$ configuration having one unpaired electron. Its complexes usually have simple square planar to tetragonally distorted octahedral stereochemistry. However, irrespective of the stereochemistry involved the magnetic moment has been found to be (with spin-orbit coupling constant of 850cm^{-1}) about 1.90 BM. Generally octahedral coordinated Cu(II) complexes have magnetic moment in the range 1.90-2.20 BM and the value are independent of temperature. Figgis predicted a magnetic moment > 1.90 BM for tetrahedral and < 1.90 BM for square planar and octahedral Cu(II) complexes. The square planar complexes of Cu(II) ion may slightly be called as extreme cases of tetragonally distorted octahedral geometry around the central metal ion and in such environment the separation between the ground level $^2B_{1g}$ and the components of $^2T_{2g}$ term of the Cu(II) ion is layer than in octahedral complexes which possibly seems to be responsible for the lower magnetic moment value of square planar complexes. However no significant conclusion concerning the stereochemistry of Cu(II) compounds can be drawn nearly on the basis of magnetic data.

The electronic spectra of Cu(II) complex show only one broad absorption band at 16000 cm^{-1} which may be assigned to the transition ^3E_g

$^2T_{2g}$ characteristic of distorted Cu(II) complex. The magnetic moment value of Cu(II) complex is 1.86 B.M. suggesting distorted octahedral stereochemistry.

Fungicidal Testing of mixed ligand complexes : The idea that fungi toxicants reacts mainly with ligands on conidial surfaces and are primarily accumulated on the surfaces does not have valid experimental support. However the migration of fungicides to the sites of action consists a complicated series of reactions that involves both electronic and hydrophobic nature of the toxicants. Since the life processes of organism are controlled and directed by a complex and inter related series of enzyme systems it is however between that the metal complexes may penetrate the wall on lipoid membrane in the form of simple chelate inhibiting specific

enzymes, causing toxic reactions among cellular constituents and ultimately causing death of the organism.

The bound metal mostly attacks the functional groups contained in the living tissues. The functional groups most frequently attached on the thiol and the amino groups. Several amino groups from the amino acids comprise amino pool in the cellular fluids which are particularly the targets of pesticides. Cu(II) known to exert a striking influence in the sporulation of fungi. However, different fungi seem to differ in their quantities may be cited its fungicidal effect on majority of the fungi as various Cu-fungicides at higher concentrations.

It has been shown that chemical control of plant disease have dependent much on heavy metals for its success and in many cases the activity increases after complex formation with an organic radicals. The data in colony growth responses of Drechlera tetramera, Alterntria alternate and Fusarium oxysporum at different concentration 500, 200 and 100 ppm using three replications in each cases are recorded. The analysis of fungicidal result showed a definite pattern existing between fungi toxicity and chemical structure. The result indicate that in untreated control the test fungi grew, on the other hand the growth of fungi inhibited well by all the complexes. It may be concluded that the primary ligand possess good fungicidal activity against all the three fungi.

The antifungal activity Cu(II) complex is most active fungicide. The fungicidal action of Cu(II) complex may be explained due to inactivation of enzymes.

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