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Farheen Jahan
 Research Scholar, Department
 of Chemistry, L.N.M.U.,
 Darbhanga, Bihar, India

Structural and physiological studies on transition metal complexes of some substituted thiozoline

Farheen Jahan

Abstract

Metal complexes of the type ML_2X_2 , $M'L_3X$ [$M = Cu(II), Co(II), Ni(II)$ and $Fe(II)$, and $M' = Fe(III)$, $L = 2$ -aminophenyl-3-phenyl-4-(*p*-m3thoxyphenyl- Δ^4 -thiazoline and $X = Cl^-, NO_3^-$)] were prepared and characterized with the help of their elemental analysis, spectral and magnetic susceptibility studies. IR studies show that sulphur of thiazole ring took part in coordination. These complexes were also screened for their antifungal activity against *Phoma-exigua*, *Macrophomina-phaseoli* and *Colletotrichum capsici* at 100, 50 and 20 ppm. The activity decreases with decrease of concentration

Keywords: Thiazole, co-ordination, *Phoma-exigua*, *macrophomina-phaseoli*, *Colletotrichum capsici*, antifungal activity

Introduction

Thiazolines and their derivatives have recently attracted the attention of many Scholars, because of the wide range of activity^[1-8]. Survey of literature revealed that no work has been done on transition metal complex of 2-aminophenyl-3-phenyl-4-(*p*-m3thoxyphenyl- Δ^4 -thiazoline. So, it is worthwhile to prepare transition metal complex with this ligand.

The present paper deals with the preparation and characterization of complexes of first series of transition metal especially $Cu(II)$, $Co(II)$, $Ni(II)$, $Fe(II)$ and $Fe(III)$ complexes with 2-aminophenyl-3-phenyl-4-(*p*-m3thoxyphenyl- Δ^4 -thiazoline. The newly synthesized complexes were also screened against different fungi at different concentrations.

Experimental

Materials and Methods

All chemicals used were of B.D.H. AR grad otherwise used after purification. The methoxy acetophenone was obtained by market. The ligand was prepared by using standard method. The C, H and N were estimated from C.D.R.I., Lucknow and B.H.U. the IR and far IR were recorded or nujol-mull from G.N.B. Amritsar. The magnetic moment was obtained at room temperature using mercury tetrathiocyanato cobaltate as calibrant. The fungicidal activity were determined by using Gouy's method at different concentration against *Phoma-exigua*, *macrophomina-phaseoli* and *Colletotrichum capsici*. The ligand was prepared from *p*-methoxy acetophenone using standard method reported in literature^[10].

In general these complexes were prepared by refluxing the respective metal salts with ligand 2-aminophenyl-3-phenyl-4-(*p*-m3thoxyphenyl- Δ^4 -thiazoline in 1:2 molar in case of trivalent metal salt in ethanolic medium on water bath. The product was then filtered, washed with alcohol and dried in vacuum.

Result and Discussion

In all the cases stoichiometric ratio was found to be 1:2 except in $Fe(III)$ where it is 1:3. In IR spectra the ligand has absorption bands in the region 1530-1595, 1495 and 1405 cm^{-1} characteristic of five membered thiazole ring. The main absorption bands in the ligand lie in region 1630, 3095, and 1695-1470 cm^{-1} assignable to $\nu_{C=O}$, ν_{C-H} , and the conjugated cyclic system $-C=C-N-C$ respectively. The ν_{CN} of thiazole ring, which are similar to those of Schiff bases and oximes where it occurs in the range 1475-1680 cm^{-1} . On comparing the spectra of metal complexes those of ligands it has been observed that frequency associated

Correspondence

Farheen Jahan
 Research Scholar, Department
 of Chemistry, L.N.M.U.,
 Darbhanga, Bihar, India

with ν_{C-S} stretching mode shifts to lower range by 1025 cm^{-1} giving an indication of the coordination of ring sulphur atom with the metal ion.

The magnetic moment of Fe (II) complex observed at room temperature lie in the range 5.62-5.65 B.M. The value is suggestive of high spin nature of Fe (II) complexes^[12, 13]. The octahedral Fe (II) complexes exhibit broad band assigned to ${}^5T_{2g} \rightarrow {}^5E_g$ transition. Here two bands are observed near 8650 and 1055, which are split component of one band assigned to ${}^5T_{2g} \rightarrow {}^5E_g$.

The spectra of present Co (II) complexes were very similar and there spin allowed transition ${}^4A_2 \rightarrow {}^4T_2(\nu_1)$, ${}^4A_2 \rightarrow {}^4T_1(F)(\nu_2)$ and ${}^4A_2 \rightarrow {}^4T_1(P)(\nu_2)$ expected to occur in tetrahedral field. The reflectance spectra exhibit bands a 1900-10250, 16050, 8700-8850 and 7050 cm^{-1} in conformity with the spectra of other tetrahedral Co (II) complexes. The observed value of magnetic moment 4.97 B.M. at room temperature lies well within the range expected for diamagnetic of coordination geometry around the metal ion.

The present six coordinated Ni (II) complexes exhibit a magnetic moment 2.80-3.90 B.M. expected for two unpaired electrons in an octahedral geometry. The electronic spectra indicates^[15] that an octahedral or tetrahedral arrangements of the ligand. Although the complexes formally have D_{4h} symmetry, the electronic spectra in the range $8000\text{--}8350\text{ cm}^{-1}$ and magnetic moment values are typical of octahedral coordinated Ni (II) complexes. The observed energies of the three spins allowed transition ${}^3A_{2g} \rightarrow {}^3T_{2g}$ at $8400\text{--}8750\text{ cm}^{-1}$, ${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$ at 14000 cm^{-1} and ${}^3A_{2g} \rightarrow {}^4T_{1g}(P)$ at $24000\text{--}24150\text{ cm}^{-1}$ agree well with those predicted from Liehe and Ballhausen¹⁶ energy level diagram for Ni (II) in a ligand field of octahedral symmetry.

In electronic spectra of Cu (II) complexes two bands were observed in the region $15300\text{--}15600$ and $19200\text{--}19300\text{ cm}^{-1}$ which may be attributed to d-d transition ${}^2B_{1g} \rightarrow {}^2A_{1g}$ and ${}^2B_{1g} \rightarrow {}^2E_g$ respectively in a planar field distorted of the planar complexes towards a tetrahedral configuration lower the band frequency and relatively low intensities to crystal field transition of Cu (II) on a pseudotetrahedral environment. Hence the absence of a band 10050 cm^{-1} in these complexes eliminates the possibility of tetrahedral structure. However a distorted effectively planar structure is likely as ${}^3B_{1g} \rightarrow {}^3E_g$ transition is likely to be more intense.

Antifungal activity

The fungicidal activity of the ligand as well as metal complexes were screened against *Phoma-exigua*, *macrophomina-phaseoli* and *Colletotrichum capsici* at 100, 50 and 20 ppm in czapek's dox agar medium. It has been concluded that the fungi toxicity of the ligand decreases on complex formation and complex are less toxic than ligand. Both ligand and metal complexes are more toxic at higher concentration i.e. the fungicidal activity decreases with the decrease of concentration.

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