SYNTHESIS AND FUNGICIDAL ACTIVITIES OF TRANSITION METAL COMPLEXES OF THE LIGAND 2- AMINO -4- (P- HYDROXY PHENYL) OXAZOLE

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ABSTRACT

The ligand 2-amino-4-(p-hydroxy phenyl) oxazole ($C_9H_8N_2O_2$) and its metal complexes were synthesized and the structures were characterized with the help of their elemental analysis, IR, electronic and magnetic susceptibility studies. The magnetic and electronic spectral studies indicate an octahedral geometry for the complexes with the ($M_2L_2X_2$) formula. These newly synthesized complexes were also screened for their antifungal activity against different fungi at different concentrations. The activity decreases with decrease of concentration and the metal complexes are less toxic than the parent ligand.

Key Words: *Fungicidal activity, Oxazole Complexes, Toxicity.*

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INTRODUCTION

Recently the chemistry of transition metal complexes of biologically active ligands has created an interest. Several heterocyclic compounds are known which form complexes with various transition metal ions. Heterocyclic compounds are cyclic compound containing a hetero atom in the ring. The common hetero atoms are nitrogen and oxygen. Oxazole derivatives have attracted the interest because in addition to nitrogen atom, it has also oxygen atom which acts as donor site. Such study has been motivated not only by a desire to understand the interaction between the donor site and metal atoms but also by the development of metal complexes into antifungal, antiviral and antibacterial agent. These metal complexes have shown importance in the field of medicine and analytical chemistry. A critical review of literature revealed that no systematic work on transition metal complexes of 2- amino-4-(p-hydroxy phenyl) oxazole has been carried out. Khamamkar et. al. 2012 studied the synthesis, spectral characterization and biological activity of Schiff's base derived metal complexes. Schiff's base derived complexes of derivatives of DHA were also studied by Mane et.al.2001. Malik et. al. 2013 studied the structural and biological aspects of transition metal complexes of the ligand 2-amino-4-(p-hydroxy phenyl) thiazole. The present paper deals with the preparation and characterization of Cu(II),Co(II) and Ni(II) complexes with 2-amino-4-(p-hydroxy phenyl) oxazole. Metal complexes play an important role in biological activity. In many cases metal complexes are more potent than free ligands. The newly prepared complexes were also screened for their antifungal activity against different fungi at different concentrations (Bharti et al. 2010). Singh et. al. 1988 synthesised some new schiff bases containing thiazole and oxazole nuclei and studied their fungicidal activity. Reddy et. al. 2008 studied the synthesis, characterization and antimicrobial Activity of Cu(II), Co(II) and Ni(II) Complexes with O, N, and S Donor Ligands Similar experiments on fungicidal and antimicrobial activity of Cu(II), Co(II) and Ni(II) Complexes with O, N, and S Donor were also conducted by Pandeya et. al. 2000, Shriodkar et. al. 2001, Ravanasiddappa et. al. 2008, Belaid et. al.2008 and Mapari et. al. 2011. EPR and electronic spectral studies on copper (II) complexes of some N-O donor ligands were studied by Chandra et. al. 2004**.**

EXPERIMENTAL

Materials and methods:

All the chemicals and reagents used were of anlytical grade; otherwise they were purified before use. Organic solvent used was absolute alcohol. IR spectra of the ligand and complexes are recorded in nujolmull. The fungicidal activity of ligands as well as complexes was determined by using the Growth method. The electronic spectra were recorded in MgO at room temperature on VSU-22 spectrophotometer. The measurements were carried out Guru Nanak Dev University, Amristar. Metal and oxygen contents of these complexes were estimated using the standard procedures reported in literature (Vogal 1961 and Vogal 1958). The estimation of carbon, hydrogen and nitrogen were carried out at BHU, Varanasi and CDRI, Lucknow and results are given in Table 1. Magnetic measurements were carried out at IIT Roorkee at room temperature using Co [Hg $(CNS)_4$] as a calibrant.

Table 1

Elemental Analysis Data

Complexes	**%Calc./ Obs.**				
	C	H	N	O	M
$C_9H_8N_2O_2$	61.36 61.30	4.54 4.52	15.90 15.88	18.18 18.14	-----
$[Cu(C_9H_8N_2O_2)_2Cl_2]$	44.39 44.30	3.28 3.21	11.51 11.46	13.15 13.10	13.85 13.79
$[Ni(C_9H_8N_2O_2)_2Cl_2]$	44.81 44.79	3.31 3.28	11.61 11.55	13.27 13.23	12.24 12.19
$[Co(C_9H_8N_2O_2)_2Cl_2]$	44.84 44.77	3.33 3.30	11.60 11.58	13.28 13.24	12.23 12.17
$[Cu(C_9H_8N_2O_2)_2(CH_3COO^-$	49.48		10.49	23.99	11.90

$)_2]$	49.41	4.12 4.09	10.42	23.95	11.87
$[Ni(C_9H_8N_2O_2)_2(CH_3COO^-)_2]$	49.91 49.88	4.14 4.11	10.57 10.53	24.18 24.14	11.16 11.12
$[Co(C_9H_8N_2O_2)_2(CH_3COO^-)_2]$	49.90 49.86	4.15 4.11	10.58 10.55	24.19 24.13	11.15 11.12

The ligand 2-amino-4-(p-hydroxy phenyl) oxazole was prepared using the procedure reported in the literature (Dodson et al. 1945).

Preparation of metal complexes

[2-amino-4-(p-hydroxy phenyl) oxazole] Dichloride/Diacetate ligands and M(II) salts where M= Ni(II), Cu(II) and Co(II) are taken to synthesize the complex. Alcoholic solution of metal salts (0.01 M) and ligand (0.02 M) were mixed and few drops of ammonia solution were added to raise the pH of the solution. The reaction mixture was then refluxed on water bath for an hour. The precipitate separates out which was filtered and washed with alcohol and dried in vaccum.

RESULTS AND DISCUSSION

In general the absorption frequencies of ligand get affected after complex formation. Here also absorption band due to amino and ν (C-O) are affected most. The main absorption bands of the ligand are obtained in the region 3450-3400, 3335-3300 and 1565-1558 cm^{-1}. These are due to anti-symmetric and symmetric ν (N-H) and – N = C-O ring stretching frequencies. The characteristic band of oxazole system appeared at 1640-1615, 1600-1590 and 1545-1530 cm^{-1}. The absorption band due to ν C-H, ν C=O, -C-O-C and ν C-Cl were observed in the region 3065-3005, 1620-1595, 1155-1103 and 800-605 cm^{-1}. The presence of these bands supports the aromatic character of the ligand. On comparison of the spectra of the metal complexes with those of the ligand it is observed that on complexation the ν(C=N) stretching frequencies observed at 1475-1455 cm^{-1} in the free ligand remain practically unchanged after complex formation. This shows that the ring nitrogen does not take part in co-ordination. The anti-symmetric and symmetric ν (N-H) stretching frequencies in the free ligand get shifted to the lower frequencies after complex formation. This shows that the lone pair of electron available on nitrogen atom of amino group is taking part in complex formation. Considerable lowering in these frequencies along with the change in deformation wagging and rocking amino vibrations suggests that metal are co-ordinated through nitrogen of the amino group because the lone pair of electrons on the nitrogen of the amino group is more basic than those on nitrogen in the ring-system and is used to explain both the reasons of high electron density and formation of co-ordinate linkage. In the present complexes bands are observed in the region 375-275 cm^{-1} which was assigned to M-O band. This shows that the oxygen of oxazole ring is taking part in the co-ordination. From the above observations it is clear that nitrogen of amino group and oxygen of the oxazole ring are taking part in complex formation.

The different types of cobalt complexes show different magnetic moment. In case of square planar complexes the value lie between 2.1-2.9 B.M. while in case of high spin five co-ordinate complexes it lie in the region 4.2-4.8 B.M. The electronic spectra of acetate complexes shows band around 8500, 17000 and 20500 cm^{-1} which may be assigned to $^4T_{1g}$ (F) → $^4T_{2g}$(F) (ν_1), $^4T_{1g}$ (F) → $^4A_{2g}$ (F) (ν_2) and $^4T_{1g}$ (F) → $^4T_{1g}$ (P) (ν_3) respectively for octahedral complexes. The magnetic moment value 4.52 B. M. also support the octahedral geometry. In case of chloro complexes the bands are obtained in the region 15000-18000 cm^{-1} which may be assigned to $^4A_2$ (F) → $^4T_1$(F) (ν_3). The magnetic moment value of these complexes is found in the region 4.2-4.5 B.M. The magnetic and electronic data suggest tetrahedral structure of the complexes similar results were also obtained by other workers.

For Ni (II) ion having d^8 electronic configuration in an octahedral ligand field. Three spin allowed transitions are expected to occur from $^3A_{2g}$ (F) ground state. The electronic spectra of Ni (II) complexes shows bands in the region 8300-9000, 14000-15750 and 24055-24200 cm^{-1}, these may be assigned to $^3A_{2g} \rightarrow {}^3T_{2g}$, $^3A_{2g} \rightarrow {}^3T_{1g}$ (F) and $^3A_{2g} \rightarrow {}^3T_{1g}$ (P) transitions. The magnetic moment value lies in the range 2.90-3.22 B.M. suggests octahedral geometry of the metal complexes. The magnetic moment value lie in the range 2.80-3.48 B.M. showing the presence of three unpaired electrons and support the distorted octahedral geometry **(Earnshaw 1968)**

The cupric ion has $3d^9$ configuration having one unpaired electron. In the present study the magnetic moment value are found in the range of 1.80-2.13 B.M. The magnetic moment value of octahedral complexes lie in the range 1.91-2.22 B.M. According to Figgis the magnetic moment value 1.89 B.M. is for tetrahedral and 1.91 B.M. is for square planar and octahedral complexes.

The present Cu (II) complexes are paramagnetic in moment value 1.81-1.87 B.M. The electronic spectra of Cu (II) complexes shows absorption bands in the region 15000-15600 and 18000-19000 cm^{-1} assignable to $^2B_{1g} \rightarrow {}^2A_{1g}$ and $^2B_{1g} \rightarrow {}^2E_g$ transitions, respectively. These are in quite agreement to the square planar configuration. In the electronic spectra of the complex a unique strong band is obtained around 13000 cm^{-1} which is characteristic of planar geometry.

The fungicidal activity of ligand and metal complexes was determined using growth method and from the data it is clear that ligand is more toxic than metal complexes. The activity also decreases with decrease of concentration. The reason for less reactivity of metal complexes is might be one reason that in the free ligand the functional group and the atom are free which are responsible for the reactivity but in complexes they are co-ordinated to metal so they are not free. This is the reason that metal complexes are less toxic than ligand.

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