
BIOLOGICAL STUDIES ON TRANSITION METAL COMPLEXES OF SUBSTITUTED OXAZOLE

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ABSTRACT:

The chemistry of transition metal complexes of biologically active ligands has attracted attention of several workers for the last few years. There are various heterocyclic compounds known which form complexes with various metal ions. These metal complexes are of great importance in the field of medicines and analytical chemistry. Various complexes of platinum and palladium with sulphur and nitrogen donor ligands are used in cancer chemotherapy¹, metal complex of amino acids have been found to possess antitumour activity.

INTRODUCTION:

The chemistry and wide range of application of oxazole compounds have been reported in literature. These compounds have shown wide range of applications, they can be used as hypertensive, analgesic, anti-inflammatory, antibacterial, antiviral, anti-tubercular, anticonvulsant urinary tract infection sedative, cardiac stimulant, antihistaminic muscle relaxant and hypotensive.

Recently Pattanayak has reported, that addition of chlorine increases the fungicidal activity, he also reported that with increase of chlorine atom in the molecule the activity increases regularly. Survey of the literature shows that few references are available but no systematic study has been done so far so is worthwhile to study the preparation and characterization of substituted oxazole. The present paper with the preparation of 2-Amino-4-(p-hydroxy phenyl)-5-chloro oxazole and its metal complexes. The stoichiometries of the newly synthesized complexes were established by their elemental analysis. They U.V., I.R., far I.R., magnetic measurements were carried out to establish their structure. The ligands as well as the metal complexes were screened for their fungicidal activity against various fungi at different concentration.

EXPERIMENTAL:**(a) SYNTHESIS OF THE LIGAND:**

The ligand 2-Amino-4-(p-hydroxy phenyl)-5-chloro oxazole was prepared by the method reported in literature.

(b) PREPARATION AND ISOLATION OF METAL COMPLEXES:

All the complexes were prepared by mixing ethanolic solution of ligand with appropriate metal salts in the same solvent and in proper ratio. The mixed solutions were refluxed on water bath. The contents were concentrated and cooled, crystals were separated out. These crystals were filtered washed thoroughly with ethanol and dried.

I.R. SPECTRAL STUDIES:

On comparison of the spectra of ligand with that of metal complexes it is observed that the ν (C–N) stretching frequency observed at 3450 cm^{-1} in the free ligand remains practically unchanged after complexation, they show that ring nitrogen is not taking part in complexation. The antisymmetric and symmetric ν (NH) stretching frequencies appeared in the region $3440\text{--}3400$, $3340\text{--}3300\text{ cm}^{-1}$ in the free ligand get shifted to lower frequency after complexation. This shows that nitrogen of the amino group is

taking part in complex formation. In all the complexes a band appeared in the region $375\text{-}280\text{ cm}^{-1}$ assigned to ν (M– O) bond. This shows that the oxygen of the oxazole ring is taking part in coordination. The characteristic band of oxazole system were observed in the region $1640\text{-}1600$, $1595\text{-}1580$ and $1560\text{-}1530\text{ cm}^{-1}$. In the ligand as well as in all the complexes a band appeared in the region $600\text{-}500\text{ cm}^{-1}$. This is due to ν (C– Cl) band.

MAGNETIC AND ELECTRONIC SPECTRAL STUDIES:

Fe (III) COMPLEXES:

The magnetic moment value of Fe (III) complexes were found in the region 4.9-5.3 B.M. The electronic spectra shows bands in the region $14000\text{-}15000$, $16000\text{-}17000$, $24500\text{-}25500\text{ cm}^{-1}$ assigned to ${}^6A_{1g} \rightarrow {}^4T_1$ (4D) (ν_1) ${}^6A_{1g} \rightarrow {}^4T_{1g}$ (ν_2) and ${}^6A_{1g} \rightarrow {}^4A_{2g}$ (ν_3) transitions respectively the spectral and magnetic suggest octahedral structure of Fe (III) complexes.

Co (II) COMPLEXES:

In the case of Co(II) nitrate, chloro and sulphato complexes bands are observed in the range $8000\text{-}8500$, $15000\text{-}18000$, $20000\text{-}23000\text{ cm}^{-1}$. These bands are assigned to 4A_2 (F) $\rightarrow {}^4T_2$, (ν_1), 4A_2 (F) $\rightarrow {}^4T_1$ (ν_2) and 4A_2 (F) $\rightarrow {}^4T_1$ (P) (ν_3) respectively¹⁶. The magnetic moment value 4.0-4.42 B.M. and spectral data suggest tetrahedral structure¹⁷. In the acetato complexes bands are observed at 8600 , 17000 , 21000 cm^{-1} assigned to ${}^4T_{1g}$ (F) $\rightarrow {}^4T_{2g}$ (F) (ν_1), ${}^4A_{2g}$ (F) (ν_2) and ${}^4T_{1g}$ (P) (ν_3) respectively. The magnetic moment value observed 5.0 B.M. This and the spectral studies shows into octahedral geometry.

Ni (II) COMPLEXES:

The electronic spectra of Ni(II) complexes show bands in the region $8500\text{-}9000\text{ cm}^{-1}$, $14000\text{-}15750\text{ cm}^{-1}$ and $24050\text{-}24200\text{ cm}^{-1}$ characteristic of octahedral Ni(II) ion. These observed energies of three spin allowed transitions ${}^3A_{2g} \rightarrow {}^3T_{2g}$, ${}^3A_{2g} \rightarrow {}^3T_{1g}$ (F) and ${}^3A_{2g} \rightarrow {}^3T_{1g}$ (P) agree well with those predicted from Liehr and Ballhausen¹⁸ energy level diagram for Ni(II) in a ligand field of octahedral symmetry. The magnetic moment value are in between 2.90-3.20 B.M. which is in support of high spin octahedral structure.

Cu(II) Complexes :

The electronic spectra of Cu(II) complexes show absorption bands in the region $15500\text{-}16000$, $18500\text{-}20000\text{ cm}^{-1}$ assignable to ${}^2B_{1g} \rightarrow {}^2A_{1g}$ and ${}^2B_{1g} \rightarrow {}^2E_g$ transitions respectively. A unique peaks also obtained in all the cases around 14000 cm^{-1} this is characteristic of planar geometry. The Cu(II) complexes are paramagnetic in nature and are having magnetic moment value suggest square planar configuration of Cu(II) complexes.

FUNGICIDAL ACTIVITY:

The fungicidal activity of ligand and metal complexes were determined using growth method. The fungitoxicity data (table-I) revealed that the ligand is more toxic than its metal complexes. The Fungitoxicity also varies from fungus to fungus as well as on the change of concentration. At higher concentration the ligands as well as the metal complexes are more toxic. The toxicity decreases with decrease of concentration.

Table -1

Growth responses of Phoma-exigua, Macrophomina- phaseoli and Collectotrichum-capsici at three concentrations in relation to the ligand and its metal complexes

Test Samples	AVERAGE PERCENTAGE INHIBITION AFTER 168 HOURS								
	Phoma-exigua			Macrophomina- phaseoli			Colletotrichum- capsici		
	Concentetrations used in ppm.								
	100	50	20	100	50	20	100	20	50
ABPO	74.4	56.4	40.8	65.7	50.8	43.6	75.6	44.3	54.0
[Mn (L) ₂ Cl ₂]	52.3	36.6	208	45.7	30.6	23.4	55.4	24.2	24.4
[Mn (L) ₂ (NO ₃) ₂]	52.2	36.4	20.7	45.5	30.4	22.9	54.8	23.9	24.2
[Mn (L) ₂ (CH ₃ COO) ₂]	52.0	36.3	20.6	45.0	30.3	22.8	54.7	23.8	24.2
[Mn (L) ₂ SO ₄)]	52.0	36.2	20.6	45.0	30.2	22.8	54.6	23.7	24.2
[Fe (L) ₃] Cl ₃	32.2	16.0	1.0	25.1	10.8	2.2	34.7	4.1	4.2
[Fe (L) ₃] (NO ₃) ₃	32.8	16.6	1.2	25.7	11.0	2.7	35.3	4.7	4.8
[Fe (L) ₃] (CH ₃ COO) ₃	33.0	17.2	1.4	26.7	11.2	3.0	35.5	4.9	5.0
[Fe ₂ (L) ₆] (SO ₄) ₃	32.6	16.0	1.0	25.7	10.8	2.5	35.1	4.4	5.5
[Co (L) ₂] Cl ₂ .2H ₂ O	47.8	31.2	15.8	40.7	25.0	17.6	50.6	19.8	19.7
[Co (L) ₂] (NO ₃) ₂ .2H ₂ O	47.0	30.7	15.2	40.4	25.2	17.8	50.0	19.2	19.1
									2
[Co (L) ₂ (CH ₃ COO) ₂]. 2H ₂ O	47.2	29.6	15.0	40.1	25.0	17.9	49.8	19.0	19.1
[Co (L) ₂] (CH ₃ CO ₄) . 2H ₂ O	47.3	30.5	15.4	40.4	25.4	18.3	50.0	19.3	19.4
[Ni (L) ₂ Cl ₂] .H ₂ O	46.6	31.2	14.7	39.8	24.5	17.6	49.2	19.6	19.5
[Ni (L) ₂ (NO ₃) ₂].H ₂ O	46.2	30.6	14.2	39.6	24.3	17.2	49.2	19.4	19.2
[Ni (L) ₂ (CH ₃ COO) ₂]. H ₂ O	46.8	31.5	14.8	39.9	24.7	17.8	49.6	19.8	19.7
[Ni (L) ₂ (SO ₄)]. H ₂ O	46.4	31.1	14.5	39.4	24.4	17.3	49.4	19.4	19.3
[Cu (L) ₂] CL ₂	42.2	26.5	13.2	35.1	20.4	13.2	45.3	14.2	15.2
[Cu (L) ₂] (NO ₃) ₂	42.3	26.4	13.4	35.0	20.6	13.3	45.5	14.3	15.4

[Cu (L) ₂] (CL ₃ COO) ₂	42.4	26.4	13.2	35.1	20.8	13.4	45.8	14.6	15.5
[Cu (L) ₂] ((SO ₄)	42.2	26.6	13.0	34.9	20.6	13.2	45.6	14.4	15.3

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