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ANALYSIS OF OXAZOLE COMPEXES OF BI AND TRI VALENT METAL IONS

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ABSTRACT:

2-Amino-4-(p-chloro phenyl)-5-chloro oxazole complexes Cu(II), Co (II), Ni(II), Zn (II), Mn (II), Fe (III) were prepared and characterized by their elemental analysis. The structure of these complexes were established by their spectral and magnetic studies in the case of bivalent 1 : 2 and in the case of trivalent 1 : 3 complexes were obtained. These complexes were screened for their antifungal activity against different fungi at different concentrations.

Key words: magnetic studies, antifungal activity

INTRODUCTION:

The chemistry and wide range of pharmaceutical applications of oxazole derivatives like hypertensive[1], analgesic anti-inflammatory[2, 3], antibacterial, antiviral[4], antitubercular[5], anti-convulsant[6], urinary tract infection sedative[7] and similar such diseases have been reported in literature. Recently Pattnayak[8] prepared a large number of 2-Amino-4-substituted oxazole and chlorinated these oxazole. He points out that the presence of chlorine increases fungicidal activity and this increase with increase in the number of chlorine atom in the molecule. The survey of literature revealed that only few scattered references[9-16] are available but no systematic work has been done on 2-Amino-4-(p-chloro phenyl)-5-chloro oxazole complexes.

The present paper deals wit the preparation of 2-Amino-4-(p-chloro-phenyl)-5-chloro oxazole and its complexes with various metal ions. The stoichiometry of metal complexes has been established by their elemental analysis. The structures of the complexes have been confirmed by I.R., U.V. and magnetic studies. The ligand and their metal complexes are also screened for their antifungal activity against various fungi viz. Phomaexigna, Colletotrichum-capsici and Macrophomina-Phaseoli at different concentrations viz. 100 ppm. 50 ppm and 20 ppm.

EXPERIMENTAL:

All the reagents used were of AR grade.

Preparation of ligand:

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

Preparation of metal-complexes:

All the metal complexes were prepared by mixing metal and ligand in proper molar ratio in an appropriate solvent. The reaction mixture were refluxed on water bath and then concentrated and kept overnight. Crystals of complexes are separated, filtered, washed with alcohol and dried in vaccuo.

RESULT AND DISCUSSION:

From the elemental analysis table-1 the stoichiometery of the metal complexes were found to be 1: 2 except in the Fe (III) complexes where it is 1: 3.

I.R. SPECTRAL STUDIES:

The I.R. spectra of the ligand and the metal complexes were done to know the place of coordination. On comparison of the spectra of metal complexes with that of the ligand, it is observed that on complexation the υ(C=N) stretching frequencies observed at 1470 cm^{-1}, in the free ligand remain practically unchanged supporting that the ring nitrogen does not take any part in complex formation or co-ordination. The antisymmetric and symmetric υ(NH) stretching frequencies appear in the region 3450-3400 and 3335-3300 cm^{-1} in the free ligand get shifted to the lower frequencies after complex formation. This shows that the nitrogen of the amino group is taking part in coordination. Considerable lowering in these frequencies along with the changes in the deformation, wagging and rocking amino vibrations suggest that metal are coordinated through nitrogen of the amino group. The anti-symmetric and symmetric υ(NH) and – N= C– O ring stretching frequencies were observed in the region 3460-3400, 3350-3300, 1560-1550 cm^{-1}, respectively. The characteristic bands of oxazole system were also observed at 1640-1610, 1600-1585 and 1560-1530 cm^{-1}. The absorption bands due to υ (CH), υ(C=O), –C–O–C and υ(C–Cl) were observed in the region 3060-3000, 1620-1590, 1150-1100, 800-600 cm^{-1}. The presence of these bands supports the aromatic character. In all the metal complexes and the ligand the band observed in the region 1450-1100 this is due to υ(C–Cl) frequency. In the present complexes the band observed in the region 370-260 cm^{-1} assigned to (M–O) band[15-20], this shows that the oxygen of the oxazole ring is taking part in the coordination.

WATER OF CRYSTALLIZATION:

In the case of Co (II) and Ni (II) complexes a medium strong absorption band in the region 3450-3250 is observed, which is due to antisymmetric and symmetric υOH and υ(HOH) band is observed in the region 1650-1610 cm^{-1}. These observation shows that Co (II) and Ni (II) complexes are containing water molecule in their lattice structure.

INFRA RED SPECTRA OF CHLORO COMPLEXES:

In the metal chloro complexes the band observed in the region 275-250 cm^{-1} assigned to υ(M–Cl) band which are in agreement with the reported data[21]. In the case of Cu (II) complexes is observed at 250 cm^{-1} assigned to υ(Cu–Cl) this is in support of square planar nature of the complexes[22].

INFRA RED SPECTRA OF NITRATO COMPLEXES:

In the nitrato complexes, bands are observed in the region 1400-1370, 1300-1270, 1000-900, 820-790 cm^{-1} these bands are due to asymmetric NO_2, symmetric NO_2, stretching NO and out of plane rocking vibration respectively.

INFRA RED SPECTRA OF ACETATO COMPLEXES:

The asymmetric and symmetric C=O stretching frequencies of free acetate ion reported at 1578 cm^{-1} and 1425 cm^{-1} respectively in acetato complexes. The separation of 122-110 cm^{-1} in these modes on complexation suggests that the acetato group is behaving as unidentate ligand in these complexes[23].

INFRA RED SPECTRA OF SULPHATO COMPLEXES:

The free sulphate ion belongs to the high symmetry point group Td. of the four fundamentals only υ_3 and υ_4 are infrared active. If the ion is coordinated to a metal, the symmetry is lowered and splitting of the degenerate modes occurs together with the appearance of new bands in infra red spectrum corresponding to Raman active bands in the free ion. The lowering of symmetry caused by coordination is different for the uni dentate and bidentate complexes. In the case of sulphato complexes bands are obtained in the region 1110 and 620 cm^{-1}, which may be assigned to υ(S-O) stretching frequency.

MAGNETIC AND ELECTRONIC SPECTRAL STUDIES:

In the present study attempts were made to correlate spectral and magnetic property.

Mn (II) COMPLEXES :

At room temperature magnetic susceptibility measurement of Mn (II) complexes suggest that Mn (II) complexes are high spin and show magnetic moment value in the range 5.8 -6.0 B.M. expected for five unpaired electron in a weak octahedral field. In the electronic spectra four bands are obtained in the region 18500-19500, 22000-23000, 27200-28000, 31000-31600 cm^{-1} assigned to $^6A_{1g} \rightarrow {}^4T_{1g}(G)$, $^6A_{1g} \rightarrow {}^4T_{2g}(D)$, $^6A_{1g} \rightarrow {}^4A_{2g}(D)$, $^6A_{1g} \rightarrow {}^4T_{1g}(P)$ respectively. The magnetic and electronic spectra support the octahedral configuration.

Fe (III) COMPLEXES:

In the Fe(III) complexes bands are obtained in the region 14000-15000, 16000-16500, 24000-25500 cm^{-1} these band may be assigned to $^6A_{1g} \rightarrow {}^4T_{1g}({}^4D)$ (υ_1), $^6A_{1g} \rightarrow {}^4T_{1g}(\upsilon_2)$ and $^6A_{1g} \rightarrow {}^4A_{2g}(\upsilon_3)$ transitions respectively. The magnetic susceptibility of Fe(III) complexes in the present study were lie in the range. 4.8-5.2 B.M. The magnetic moment value and the electronic studies suggest the octahedral stereochemistry of the Fe (III) complexes.

Fe (II) COMPLEXES:

In the spectra of Fe (II) complexes only one weak band is observed around 1000 nm this is due to Five $^5T_{2g} \rightarrow {}^5E_g$ transition and this is characteristic of high spin octahedral Fe (II) complexes. The magnetic moment value 5.6-6.62 B.M. also support octahedral stereochemistry.

Co (II) COMPLEXES:

In the case of nitrato, chloro and sulphato complexes three bands are obtained in the range 7800-8100, 15000-18000, 20000-22000 assignable to $^4A_2(F) \rightarrow {}^4T_2$ (υ_1) , $^4A_2(F) \rightarrow {}^4T_1$ (F) (υ_2) , and $^4A_2(F) \rightarrow {}^4T_1$ (P) (υ_3) , respectively[24]. The magnetic moment values of these complexes were obtained in the region 4.1-4.4 B.M. The magnetic moment value and electronic spectra suggest the tetrahedral structure of the complexes, this is in quite agreement with the reported values.[25] Acetato complexes shows bands around 8500, 17000, 20500 cm^{-1}, which may be assigned to $^4T_{1g}(F) \rightarrow {}^4T_{2g}$ (F) (υ_1) $\rightarrow {}^4A_{2g}$ (F) (υ_2) and $^4T_{1g}$ (P) (υ_3) respectively for octahedral complexes. The magnetic moment value 4.51 B.M. also support the octahedrald geometry.

Ni (II) COMPLEXES:

Ni ion is having d^8 electronic configuration in the ground state. The electronic spectra of Ni (II) complexes show bands in the region 8500-9000, 14000-15750 and 24050-24200 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 Balhausen[26] energy level diagram for Ni(II) in a ligand field of octahedral symmetry. The magnetic moment values 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 band in the region 15000-15500, 18000-19500 cm^{-1} assignable to $^2B_{1g} \rightarrow {}^2A_{1g}$ and $^2B_{1g} \rightarrow {}^2E_g$ transitions, respectively. A unique peak is also obtained in all the cases around 13500 cm^{-1} this is characteristic of planar geometry. The Cu (II) complexes are paramagnetic in nature and are having magnetic moment value 1.8-1.85 B.M. The electronic spectra and magnetic moment value suggest square-planar configuration of Cu (II) complexes.

Zn (II) COMPLEXES:

Zn (II) having the configuration $3d^{10}$ is expected to form diamagnetic complex and on the basis of elemental analysis and I.R. spectra of the complex, an octahedral structure for the complex may be proposed.

CONDUCTANCE MEASUREMENTS OF METAL COMPLEXES:

The conductance measurements of metal complexes were measured at room temperature in nitro-methane. The molar conductance in all the Mn (II) and Ni (II) complexes were found in the range ~ 18 ohm^{-1} cm^2 $mole^{-1.}$ These value shows non-electrolytic nature, while in the case of Fe(III), Cu(II), chloro and nitrato complexes of Co(II) the value lie in the range 72-80 ohm^{-1} cm^2 $mole^{-1}$ showing the electrolytic nature.

FUNGICIDAL ACTIVITY:

From the fungicidal activity, it is clear that the ligand is more toxic than its metal complexes. In the case of ligand the amino group which is free, plays a significant role in toxicity but in the complexes the NH_2 group is not free due to coordination with the metal ion that might be the cause by which the metal complexes is less toxic than the free ligand. The fungicidal activity varies with the variation of concentration. In general the fungicidal activity increases with increase of concentration. However, a Co-relation between toxicity of metal and their ability to form stable metal chelates revealed the following order: Cu (II) > Ni (II) = Co (II) > MN (II) > Fe (III). It is evident that 1: 2 (M: L) complexes are more active than 1: 3 complexes. Toxicity of Ni (II) and Co (II) is almost equal. Fe (III) complexes have been found to be least toxic while Cu (II) complexes possess maximum fungitoxicity.

Table –1

Growth responses of Phoma-exigua, Macrophomina- phaseoli and Collectotrichun-capsici (After 168 hours at 25 ± 1° on Czepeck's Dox Agar Medium) at three concentrations (in ppm.) 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	74.2	56.4	40.8	65.7	50.8	43.6	75.6	44.3	54.0
[Mn $(L)_2$ Cl_2]	52.1	36.6	208	45.7	30.6	23.4	55.4	24.3	24.4

$[Mn\ (L)_2\ (NO_3)_2]$	52.3	36.4	20.7	45.5	30.4	22.9	54.8	23.1	24.2
$[Mn\ (L)_2\ (CH_3\ COO)_2]$	52.4	36.3	20.6	45.0	30.3	22.8	54.7	23.2	24.2
$[Mn\ (L)_2\ SO_4)]$	52.5	36.2	20.6	45.0	30.2	22.8	54.6	23.3	24.2
$[Fe\ (L)_3]\ Cl_3$	32.3	16.0	1.0	25.1	10.8	2.2	34.7	4.2	4.2
$[Fe\ (L)_3]\ (NO_3)_3$	32.8	16.6	1.2	25.7	11.0	2.7	35.3	4.3	4.8
$[Fe\ (L)_3]\ (CH_3\ COO)_3$	33.3	17.2	1.4	26.7	11.2	3.0	35.5	4.5	5.0
$[Fe_2\ (L)_6]\ (SO_4)_3$	32.5	16.0	1.0	25.7	10.8	2.5	35.1	4.3	5.5
$[Co\ (L)_2]\ Cl_2\ .2H_2O$	47.6	31.2	15.8	40.7	25.0	17.6	50.6	19.2	19.7
$[Co\ (L)_2]\ (NO_3)_2\ .2H_2O$	47.1	30.7	15.2	40.4	25.2	17.8	50.0	19.2	19.12
$[Co\ (L)_2\ (CH_3\ COO)_2]$. $2H_2O$	47.3	29.6	15.0	40.1	25.0	17.9	49.8	19.1	19.1
$[Co\ (L)_2\ ]\ (CH_3\ CO_4)$. $2H_2O$	47.3	30.5	15.4	40.4	25.4	18.3	50.0	19.1	19.4
$[Ni\ (L)_2\ Cl_2]\ .H_2O$	46.6	31.2	14.7	39.8	24.5	17.6	49.2	19.1	19.5
$[Ni\ (L)_2\ (NO_3)_2].H_2O$	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_2O	46.8	31.5	14.8	39.9	24.7	17.8	49.6	19.8	19.7
$[Ni\ (L)_2\ (SO_4)]$. H_2O	46.4	31.1	14.5	39.4	24.4	17.3	49.4	19.3	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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