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Research Article

SYNTHESIS, ELEMENTAL ANALYSIS, IR AND ELECTRONIC STUDIES OF THE LIGAND 2- AMINO -4- (P- METHOXY PHENYL) OXAZOLE COMPLEXES OF TRANSITION METAL (II) IONS

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ABSTRACT
2-amino-4-(p-methoxy phenyl) oxazole ($C_{10}H_{10}N_2O_2$) has been prepared from the condensation of p-methoxy acetophenone, urea and iodine and finally crystallized from alcohol. The ligand is then converted into respective transition metal (II) complexes of the type ($M_2L_2X_2$) where M= Cu, Co and Ni. These newly synthesized complexes were also screened for their antifungal activity against Drechslera-tetramera and Fusarium-oxysporum at different concentrations. The activity decreases with decrease of concentration and the metal complexes are less toxic than the parent ligand. The structure of complexes was 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.

Keywords: *Oxygen Donor Atom, Oxazole, Bidentate Ligand, IR Studies Toxicity*

INTRODUCTION
Many biologically important 2-amino-4-(p-methoxy phenyl) oxazole complexes have been reported in the literature possessing, antimicrobial, antibacterial, antifungal, anti-inflammatory, anticonvulsant and antitumor activities. . Oxazole derivatives have been of great interest because of their plant growing regulating activity as well as anti-fungal activity. The present work deals with the preparation and characterization of Cu(II),Co(II) and Ni(II) complexes with the ligand 2-amino-4-(p-methoxy phenyl) oxazole. Oxazole derivatives have attracted the interest because in addition to nitrogen atom, it has also oxygen atom which acts as donor site. A critical review of literature revealed that no systematic work on transition metal complexes of 2- amino-4-(p-methoxy phenyl) oxazole has been carried out. Malik *et al.*, (2013, 2014, 2015) studied the structural and biological aspects of transition metal complexes of the ligands oxazole and thiazole. 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). Schiff's base derived complexes of derivatives of DHA were also studied by Mane *et al.*, (2001). Khamamkar *et al.*, (2012) studied the synthesis, spectral characterization and biological activity of Schiff's base derived metal complexes. Synthesis, spectral characterization and biological activity of Schiff's base derived metal complexes of Cu(II), CO(II) and Ni(II) were studied by Reddy *et al.*, (2008). Similar experiments on fungicidal and antimicrobial activites of Cu (II), Co (II) and Ni (II) Complexes with O, N, and S donor, their EPR and electronic spectral studies were also conducted by many workers (Pandeya *et al.*, 2000; Shriodkar *et al.*, 2001; Chandra *et al.*, 2004; Ravanasiddappa *et al.*, 2008; Belaid *et al.*, 2008; Mapari *et al.*, 2011).

MATERIALS AND METHODS
All the chemicals and reagents used were of analytical 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 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; 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**
$C_{10}H_{10}N_2O_2$	63.15	11.11	14.71	16.84	-----
	63.11	11.08	14.61	16.19	
$[Cu(C_{10}H_{10}N_2O_2)_2Cl_2]$	46.64	3.88	10.88	12.43	12.34
	46.56	3.80	10.78	12.40	12.31
$[Ni(C_{10}H_{10}N_2O_2)_2Cl_2]$	47.05	3.92	10.98	12.54	11.56
	47.00	3.87	10.97	12.52	11.49
$[Co(C_{10}H_{10}N_2O_2)_2Cl_2]$	47.11	3.91	10.93	12.57	11.54
	47.08	3.89	10.90	12.53	11.50
$[Cu(C_{10}H_{10}N_2O_2)_2(CH_3\ COO)_2]$	51.29	4.63	9.97	22.79	11.31
	51.22	4.58	9.96	22.74	11.28
$[Ni(C_{10}H_{10}N_2O_2)_2(CH_3\ COO)_2]$	51.70	4.66	10.05	22.98	10.59
	51.68	4.61	10.03	22.91	10.54
$[Co(C_{10}H_{10}N_2O_2)_2(CH_3\ COO)_2]$	51.73	4.63	10.08	22.92	10.57
	51.69	4.58	10.00	22.89	10.55

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

Table 2: Characteristic IR bands of ligands and complexes

Complexes	IR Bands (cm^{-1})					
	νN-H	**νN=C-O**	**νC-H**	**νC=O**	**νC=N**	**νM-O**
$C_{10}H_{10}N_2O_2$	3320-3150	1570-1560	3065-3005	1620-1595	1471-1459	--
$[Cu(C_{10}H_{10}N_2O_2)_2Cl_2]$	3270-3131	1565-1557	3061-3001	1241-1189	1470-1454	370-271
$[Ni(C_{10}H_{10}N_2O_2)_2Cl_2]$	3275-3125	1561-1559	3063-3000	1297-1187	1468-1450	369-282
$[Co(C_{10}H_{10}N_2O_2)_2Cl_2]$	3268-3120	1567-1558	3063-3002	1248-1186	1472-1449	373-275
$[Cu(C_{10}H_{10}N_2O_2)_2(CH_3COO)_2]$	3262-3112	1567-1556	3064-2999	1239-1196	1470-1447	375-280
$[Ni(C_{10}H_{10}N_2O_2)_2(CH_3COO)_2]$	3261-3114	1569-1557	3061-3002	1243-1196	1473-1451	373-277
$[Co(C_{10}H_{10}N_2O_2)_2(CH_3COO)_2]$	3168-3118	1566-1556	3063-2997	1240-1190	1476-1454	371-274

A shift in the νC=O and νN-H band frequencies is observed in all the complexes. This shows that the lone pair of electron presents on the oxygen atom of oxazole ring and nitrogen atom of free amino group is taking part in co-ordination (Table 2).

Table 3: Electronic spectral bands and their assignments

Complexes	Bands (cm^{-1})	Assignment
$[Cu(C_{10}H_{10}N_2O_2)_2(CH_3COO)_2]$	15240-15660	$^2B_{1g} \rightarrow {}^2A_{1g}$
	18070-19120	$^2B_{1g} \rightarrow {}^2E_g$
$[Ni(C_{10}H_{10}N_2O_2)_2(CH_3COO)_2]$	8290-9150	$^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ (ν_1)
	14065-15785	$^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ (ν_2)
	24098-26188	$^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ (ν_3)
$[Co(C_{10}H_{10}N_2O_2)_2(CH_3COO)_2]$	8487-8764	$^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ (ν_1)
	17235-17515	$^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ (ν_2)
	20568-21078	$^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ (ν_3)

CZ-record UV-Viz. spectrometer provided with an automatic recorder was used to record the electronic spectra of the complexes in ethanol at room temperature (Table 3).

Preparation of Metal Complexes

Metal salts and ligand [2-amino-4-(p-methoxy phenyl) oxazole] Dichloride/Diacetate were dissolved in ethanol. Few drops of ammonia solution were added to raise the pH of the solution. The mixed solutions were refluxed on water bath for an hour. The precipitate obtained were filtered after cooling, washed with ethanol and finally with ether. Now these were dried in vacuum.

RESULTS AND DISCUSSION

The elemental analysis shown in the Table 1 indicates that, all the metal complexes have 1:2 stoichiometry with respect to metal and ligand {where M = Co(II) , Ni(II) and Cu(II)} and are dark colored amorphous substances.

The important infrared frequencies exhibited by the ligands and their complexes are given in the Table 2. The ligand shows an absorption band is in the region 1570-1560 cm^{-1} which is characteristics of five member oxazole ring. The absorption band due to ν C-H, ν C=O, -C-O-C and ν C-Cl were observed in the region 3065-3050, 1620-1595, 1155-1103 and 800-605 cm^{-1}. The presence of these bands supports the aromatic character of the ligand. The ν (N-H) stretching frequencies in the free ligand are lowered by 45-50 cm^{-1} after complex formation.

This shows that the lone pair of electron available on nitrogen atom of amino group is taking part in complex formation. 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 370-271 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 electronic spectral studies of the Complexes of Co(II) , Ni(II) and Cu(II) with 2-amino-4-(p-methoxy phenyl) oxazole were carried out in MgO at room temperature on VSU-22 spectrophotometer. Cu (II) complexes observed bands in the region 15240-15660 and 18070-19120 cm^{-1} which may be assigned to $^2B_{1g} \rightarrow {}^2A_{1g}$ and $^2B_{1g} \rightarrow {}^2E_{1g}$ transitions respectively. In the electronic spectra of Ni (II) complexes, bands were observed in the region 14065-15785 cm^{-1} which can be assigned to $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ (ν_2), the highest energy transition ν_3 obtained in the region 24098-26188 cm^{-1} may probably be due to $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ while the spin allowed transition 8290- 9150 cm^{-1} of the lowest energy ν_1 may be assigned to $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$. In Co (II) complexes, three bands at 8487-8764, 17235-17515 and 20568-21078 cm^{-1} were observed which may be assigned for $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ (ν_1), $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$(ν_2) and $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ (ν_3) respectively.

Synthesized ligand metal complexes were screened against Drechlera-tetramera, Fusarium-oxysporum and Macroohomia-phaseoli at different concentrations in Czapek's Dox Agar medium to assess their potential as fungicidal activity by Growth measurements. The metal complexes are less toxic than the free ligand. This might be due to the fact that free oxygen is present in the ligand, responsible for toxicity is

coordinated to metal in the complex. It is also observed that the ligand as well as their metal complexes is more toxic at higher concentration and the activity decreases with decrease in concentration.

Conclusion

The elemental analysis, magnetic susceptibility and electronic spectral observations suggest the octahedral geometry for the Co(II), Ni(II) and Cu(II) complexes and exhibit coordination number six (Earnshaw, 1968). The ligand and the complexes were screened for their antifungal activity by using growth method and it is found that the complexes are less toxic than the free ligand. Further the toxicity decreases with decrease in concentration.

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