



Synthesis Characterization and Fungicidal activity of 2- Amino -4- (P-Ethoxy Phenyl) Oxazole Complexes of Transition Metal (II) ions

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Abstract

Transition metal (II) complexes of the ligand 2-amino-4-(p-ethoxy phenyl) oxazole ($C_{11}H_{12}N_2O_2$) have been prepared. The complex is of the type ($M_2L_2X_2$) where $M = Cu, Co$ and Ni . The infrared studies suggest that 2-amino-4-(p-ethoxy phenyl) oxazole behaves as a bidentate ligand with nitrogen of amino group and oxygen of oxazole ring as two co-ordination sites. 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. 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.

Keywords: Oxazole, fungicidal activity, bidentate ligand, complexes, toxicity.

Introduction

Complexes of oxazole with paramagnetic transition metal ions have attracted close attention. A number of oxazole transition metal complexes have gained wide interest, because they show a broad spectrum of biological and pharmaceutical activities such as anti-bacterial, anti-viral, anti-tubercular and hypertensive action. Oxazole derivatives have been of great interest because of their plant growing regulating activity as well as anti-fungal activity. 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. 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-ethoxy phenyl) oxazole has been carried out. The present paper deals with the preparation and characterization of Cu(II), Co(II) and Ni(II) complexes with the ligand 2-amino-4-(p-ethoxy 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 concentrations¹ Some new schiff bases containing thiazole and oxazole nuclei were synthesized and their fungicidal activity

were also studied². Synthesis, spectral characterization and biological activity of Schiff's base derived metal complexes and complexes of Cu(II), Co(II) and Ni(II) were studied by many workers³⁻⁴. Similar experiments on fungicidal and antimicrobial activities 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 workers⁵⁻¹⁰. Schiff's base derived complexes of derivatives of DHA, their spectra and synthesis under microwave irradiation were also studied by many workers¹¹⁻¹³. Thermal study of the metal complexes Cr and Mo with some nitrogen-oxygen donors ligands were studied by many workers¹⁴.

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 nujol mull. 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 at Guru Nanak Dev University, Amritsar. Metal and oxygen contents of these complexes were estimated using the standard procedures reported in literature¹⁵⁻¹⁶.

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.

The ligand 2-amino-4-(p-ethoxy phenyl) oxazole was prepared using the procedure reported in the literature¹⁷.

A shift in the ν_{C-O-C} and ν_{N-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). 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).

Table 1
Elemental Analysis Data

Complexes	%Calc./ Obs.				
	C	H	N	O	M
C ₁₁ H ₁₂ N ₂ O ₂	64.70	5.88	13.72	15.68	-----
	64.64	5.82	13.66	15.61	
[Cu(C ₁₁ H ₁₂ N ₂ O ₂) ₂ Cl ₂]	48.66	4.42	10.32	11.79	11.70
	48.57	4.38	10.27	11.70	11.66
[Ni(C ₁₁ H ₁₂ N ₂ O ₂) ₂ Cl ₂]	49.11	4.45	10.41	11.90	10.97
	49.09	4.41	10.35	11.83	10.88
[Co(C ₁₁ H ₁₂ N ₂ O ₂) ₂ Cl ₂]	49.10	4.46	10.40	11.91	10.98
	49.04	4.40	10.37	11.85	10.87
[Cu(C ₁₁ H ₁₂ N ₂ O ₂) ₂ (CH ₃ COO ⁻) ₂]	52.92	5.08	9.49	21.71	10.77
	52.87	5.01	9.38	21.66	10.70
[Ni(C ₁₁ H ₁₂ N ₂ O ₂) ₂ (CH ₃ COO ⁻) ₂]	53.36	5.13	9.58	21.89	10.07
	53.28	5.05	9.50	21.78	10.01
[Co(C ₁₁ H ₁₂ N ₂ O ₂) ₂ (CH ₃ COO ⁻) ₂]	53.35	5.14	9.57	21.88	10.08
	53.27	5.07	9.49	21.79	10.04

Table 2
Characteristic IR bands of ligands and complexes

Complexes	IR Bands (cm ⁻¹)					
	ν_{N-H}	$\nu_{N=C-O}$	ν_{C-H}	ν_{C-O-C}	$\nu_{C=N}$	ν_{M-O}
C ₁₁ H ₁₂ N ₂ O ₂	3300-3135	1565-1558	3065-3005	1155-1103	1475-1453	--
[Cu(C ₁₁ H ₁₂ N ₂ O ₂) ₂ Cl ₂]	3280-3130	1564-1557	3064-3000	1131-1088	1474-1452	375-275
[Ni(C ₁₁ H ₁₂ N ₂ O ₂) ₂ Cl ₂]	3285-3128	1563-1557	3062-2999	1139-1081	1473-1453	374-272
[Co(C ₁₁ H ₁₂ N ₂ O ₂) ₂ Cl ₂]	3288-3129	1565-1554	3064-3001	1138-1080	1473-1452	370-271
[Cu(C ₁₁ H ₁₂ N ₂ O ₂) ₂ (CH ₃ COO ⁻) ₂]	3282-3122	1562-1556	3062-2998	1135-1093	1474-1450	374-270
[Ni(C ₁₁ H ₁₂ N ₂ O ₂) ₂ (CH ₃ COO ⁻) ₂]	3281-3124	1561-1557	3062-3001	1138-1089	1472-1452	372-269
[Co(C ₁₁ H ₁₂ N ₂ O ₂) ₂ (CH ₃ COO ⁻) ₂]	3288-3128	1563-1555	3061-2998	1140-1090	1473-1453	374-272

Table 3
Electronic spectral bands and their assignments

Complexes	Bands (cm ⁻¹)	Assignment
[Cu(C ₁₁ H ₁₂ N ₂ O ₂) ₂ Cl ₂ /(CH ₃ COO ⁻) ₂]	15000-15600	² B _{1g} → ² A _{1g}
	18000-19000	² B _{1g} → ² E _g
[Ni(C ₁₁ H ₁₂ N ₂ O ₂) ₂ Cl ₂ /(CH ₃ COO ⁻) ₂]	8300-9000	³ A _{2g} → ³ T _{2g}
	14000-15750	³ A _{2g} → ³ T _{1g} (F)
	24055-24200	³ A _{2g} → ³ T _{1g} (P)
[Co(C ₁₁ H ₁₂ N ₂ O ₂) ₂ Cl ₂ /(CH ₃ COO ⁻) ₂]	8500-8750	⁴ T _{1g} (F) → ⁴ T _{2g} (F)
	17000-17500	⁴ T _{1g} (F) → ⁴ A _{2g} (F) (v ₂)
	20500-21000	⁴ T _{1g} (F) → ⁴ T _{1g} (P) (v ₃)

Preparation of metal complexes: Metal salts and ligand [2-amino-4-(p-ethoxy 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 I.R. spectra of the ligand and metal complexes were recorded in order to know co-ordination behavior of the ligand with metal¹⁸⁻²⁰. The absorption frequencies of ligand get affected after complex formation. The ligand shows an absorption band in the region 1640-1615, 1600-1590 and 1545-1530 cm⁻¹ which are 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 3065-3005, 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 ν (N-H) stretching frequencies in the free ligand are lowered by 15-20 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. Considerable lowering in these frequencies along with the change in deformation wagging and rocking amino vibrations suggests that metal are co-ordinate 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.

In the electronic spectra of Co(II) complexes bands are obtained in the regions around 8500-8750, 17000-17500 and 20500-21000 cm⁻¹ which may be assigned to $^4T_{1g}(F) \rightarrow ^4T_{2g}(F)$ (ν_1), $^4T_{1g}(F) \rightarrow ^4A_{2g}(F)$ (ν_2) and $^4T_{1g}(F) \rightarrow ^4T_{1g}(P)$ (ν_3) respectively. In case of square planar complexes the magnetic moment 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 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.

The magnetic moment values of Cu (II) complexes are in the range of 1.79-2.11 B.M. The magnetic moment value 1.90 B.M.

is for tetrahedral and 1.93 B.M. is for square planar and octahedral complexes²¹. The present Cu (II) complexes are paramagnetic in moment value 1.84-1.90 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.

In case of Ni (II) complexes, having d⁸ electronic configuration three transitions are expected $^3A_{2g} \rightarrow ^3T_{2g}$, $^3A_{2g} \rightarrow ^3T_{1g}(F)$ and $^3A_{2g} \rightarrow ^3T_{1g}(P)$. These transitions show bands in the region 8300-9000, 14000-15750 and 24055-24200 cm⁻¹. The magnetic moment value lies in the range 2.88-3.19 B.M. suggests octahedral geometry of the metal complexes. The magnetic moment value lie in the range 2.78-3.50 B.M. showing the presence of three unpaired electrons and support the distorted octahedral geometry²².

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-ordinate to metal so they are not free. This is the reason that metal complexes are less toxic than ligand.

Conclusion

Six transition metal complexes of the ligand 2-amino-4-(p-ethoxy phenyl) oxazole of general formula (ML₂X₂) were synthesized. 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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