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Research Article

SYNTHESIS AND ANTIFUNGAL ACTIVITY OF COMPLEXES OF 2-AMINO-4-PHENYL-5-CHLORO OXAZOLE & PYRIDINE WITH FEW TRANSITION METAL IONS AND ITS Cu (II), Zn (II), Ni (II), Co (II) COMPLEXES

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ABSTRACT

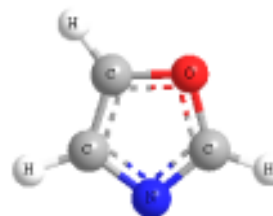
The present work deals in the preparation and characterization of mixed ligand complexes of transition metal co-ordination Metal complexes of the type $[ML_2Py_2] x$, Where $M=Cu(II)$, $Ni(II)$ and $Mn(II)$ $L=2$ -Amino-4-phenyl-5-chloro oxazole $Py=$ Pyridine and $[X=Cl^-, CH_3COO^-$ or $NO_3^-]$ were prepared and characterized by their elemental analysis, IR, electronic and magnetic studies. These studies confirms the co-ordination of amino, nitrogen and ring oxygen magnetic and electronic spectral study shows that all the complexes are octahedral except chloro and nitrate complexes of CO (II) which are tetrahedral however Cu (II) complexes are square planar. The fungicidal activity shows that legends are more toxic than complexes. However the activity decreases with decrease of concentration.

Keywords: Oxazole, Antifungal activity, IR, Pyridine, Metal complexes

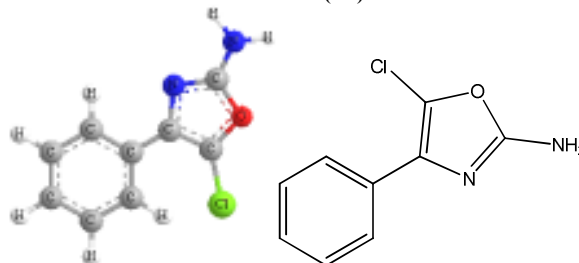
INTRODUCTION

Several H.C. are known which form complexes with various transition metal ions. These metal complexes have shown importance in the field of medicine and analytical chemistry metal ions play an important role in the biological system. antitumor activity of complexes of amino acids⁵ and complexes of platinum and palladium with sulphur and nitrogen donor ligands has been reported⁶ Recently a large number of pharmaceutical applications of heterocyclic compounds like hypertensive¹⁵, antiviral¹⁸, antitubercular¹⁹, anticonvulsant²⁰, urinary tract infection, sedative²¹, cardiac stimulant²², antihistaminic muscle relaxant²³ and hypotensive²⁴ have been reported. Oxazoline derivatives have been of great interest because of their plant growth regulating activity²⁵ as well as their antibacterial²⁶ and antifungal²⁷ character. However survey of the literature revealed that no systematic work has been done so far on the mixed ligand complexes with chloro oxazole as primary ligands and pyridine and its derivatives as co-ligands. The present study is an attempt in the direction to establish a relationship between spectral and magnetic properties in an environment of ligand of unequal

size and strength. Attempts have also been made to study whether fungicidal activities of these organic ligands are increased, decreased or remain unaffected after complex formation.



Oxazole (3D)



2-AMINO-4-PHENYL-5-CHLORO OXAZOLE

EXPERIMENTAL

Synthesis of the primary ligand-

The ligand 2-amino-4-phenyl-5-chloro-oxazole was prepared by acetophenone using the procedure reported in literature.

PREPARATION & ISOLATION OF MIXED LIGAND COMPLEXES

The ethanolic solution of appropriate metal salts such as chloride, nitrate and acetates of Cu(II), Ni(II), Co(II), Mn(II),

and Zn(II), were taken in a flask and primary ligand oxazole is added then ethanolic solution of pyridine (the secondary ligand) is added the whole mass is refluxed for few hours on water bath. On concentration mixed ligand complexes separate out which were filtered, washed & dried.

Table 1: Percentage calculation in compound

Compound	(% observed/calculated)			
	C	H	N	Cl
C ₉ H ₇ N ₂ OCl	55.52	3.60	14.39	18.25
	55.54	3.58	14.36	18.30

Table 2: Analytical Data of Dichloro/dinitrato and diacetato bis (2-Amino-4- phenyl-5-chloro-oxazole pyridine With Mn (II) complexes

Complexes	Elemental analysis (%) Observed/calculated				
	C	H	N	Cl	Mn
[Mn L2Py2]Cl2	49.96	3.56	12.46	21.12	8.14
	49.73	3.56	12.48	21.10	8.16
[Mn L2Py2](NO3)2	46.30	3.32	15.44	9.77	7.54
	46.28	3.30	15.42	9.78	7.56

L=C₉H₇N₂OCl, Py=C₅H₅N

Table 3: Analytical Data of Dichloro/dinitrato and diacetato bis (2-Amino-4- phenyl-5-chloro-oxazole pyridine With Cu (II) complexes

Complexes	Elemental analysis (%) Observed/calculated				
	C	H	N	Cl	Cu
[Cu L Py2]Cl2	46.84	3.50	11.51	21.88	13.02
	46.81	3.49	11.49	21.86	13.04
[Cu L Py2](NO3)2	42.24	3.18	15.58	6.60	11.75
	42.21	3.14	15.55	6.57	11.76
[Cu L Py2]CH3COO)2	51.70	4.32	10.52	6.62	11.90
	51.68	4.30	10.48	6.64	11.89

L=C₉H₇N₂OCl, Py=C₅H₅N

Table 4: Analytical Data of Dichloro/dinitrato and diacetato bis 2-Amino-4- phenyl-5-chloro-oxazole pyridine With Zn (II) complexes

Complexes	Elemental analysis (%)			Observed/calculated	
	C	H	N	Cl	Ni
[Zn L2Py2]Cl2	49.18	3.52	12.30	20.78	9.58
	49.16	3.51	12.29	20.77	9.56
[Zn L2Py2](NO3)2	45.64	3.26	15.20	9.68	8.88
	45.62	3.25	15.20	9.64	8.87

L=C₉H₇N₂OCl, Py=C₅H₅N

Table-5: Analytical Data of Dichloro/dinitrato and diacetato bis 2-Amino-4- phenyl-5-chloro-oxazole pyridine Ni (II) complexes

Complexes	Elemental analysis (%) Observed/calculated				
	C	H	N	Cl	Ni
[Ni L2Py2]Cl2	49.68	3.54	12.42	20.99	8.68
	49.65	3.54	12.41	20.98	8.67
[Ni L2Py2](NO3)2	46.03	3.30	15.36	9.76	8.02
	46.04	3.28	15.34	9.72	8.04
[Ni L2Py2]CH3COO)2	53.06	4.16	11.62	9.86	8.12
	53.05	4.14	11.60	9.81	8.11

L=C₉H₇N₂OCl, Py=C₅H₅N

Table 6: Analytical Data of Dichloro/dinitrato and diacetato bis 2-Amino-4- phenyl-5-chloro-oxazole pyridine With Co (II) complexes

Complexes	Elemental analysis (%) Observed/calculated				
	C	H	N	Cl	Co
[Co L2Py2]Cl2	49.64	3.52	12.42	20.98	8.72
	49.63	3.54	12.40	20.97	8.70
[Co L2Py2](NO3)2	46.02	3.26	15.36	9.74	8.06
	46.03	3.28	15.34	9.72	8.07
[Co L2Py2]CH3COO)2	53.03	4.20	11.62	9.82	8.16
	53.04	4.14	10.60	9.80	8.14

L=C₉H₇N₂OCl, Py=C₅H₅N**IR spectral studies-**

In the present complexes bands are observed in the region 375-275 cm⁻¹ which was assigned to M-O band²⁷⁻³². This shows that the oxygen of the 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 only taking part in complex formation. In all the complexes a new band appeared in the region 230-240 cm⁻¹ assigned to M-N band. This shows that nitrogen of pyridine ring is taking part in co-ordination.

Table 7: INFRA-RED SPECTRAL DATA IN Cm⁻¹ OF (2-Amino-4-phenyl)-5-chloro-oxazole pyridine

LIGAND	COMPLEXES					Tentative Assignment	Zn	Complexes
	Mn(II)	Cu(II)	Co(II)	Ni(II)	Zn(II)			
3450	3400	3450	3440	3450	3440	Asymm. NH ₂	8.65 8.68	[Co L2Py2]Cl2
3335	3330	3325	3300	3315	3320	Symm. NH ₂	8.10 8.05	
1560	1560	1560	1555	1555	1550	ν (N=C-O)Ring Stretching		[Co L2Py2](NO3)2
1470	1470	1470	1470	1470	1470	ν (C=N)		[Co 2Py2]CH3COO)2
800	790	785	800	790	780	ν (C-Cl)		[Co 2Py2]CH3COO)2
	350	270	315	300	365	ν (M-O)		
	300	235	238	240	240	ν (M-N)		

Magnetic Moment and Electronic Spectral Studies

In the present investigation attempts were made to correlate spectral and magnetic properties of metal complexes.

Co(II) Complexes

The electronic spectra of acetato complexes shows band around 8500, 17000, 20500 cm⁻¹ which may be assigned to 4T_{1g}(F)4 → T_{2g}(F)(v₁), 4T_{1g}(F) → 4A_{2g}(F)(v₂) and 4T_{1g}(F) → 4T_{1g}(P)(v₃) 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 which may be assigned to 4A_{2g}(F) → 4T_{1g}(F)(v₃)³⁵. 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

Ni(II) Complexes

The electronic spectra of Ni (II) complex shows bands in the region 8300-9000, 14000-15750 and 24055-2420 cm⁻¹ these may be assigned to 3A_{2g} → 3T_{2g}, 3A_{2g} → 3T_{1g}(F) and 3A_{2g} → 3T_{1g}(P) transitions the magnetic moment value lie in the range 2.90-3.22 suggests three unpaired electron spectral data, suggesting octahedral geometry of the metal complexes.

Cu(II) complexes

The present Cu (II) complexes are paramagnetic in moment value 1.81-1.87 B.M. The electronic spectra Cu(II) complexes

shows absorption bands in the region 15000-15600, 18000-19000 cm⁻¹ assignable to 2B_{1g} → 2A_{1g} and 2B_{1g} → 2E_g transition, respectively. These are in quite agreement to the square planer configuration. In the electronic spectra of the complexes a unique strong band is obtained around 13000 cm⁻¹, which is characteristic of planer geometry.

Mn(II) complexes- In the present study these complexes show magnetic moment show in the range 5.85-5.95 B.M. suggesting there by that these are spin free octahedral complexes having five unpaired electron. The absorption bands in the spectra correspond to the spin forbidden transition from ground state (6A₁) to the levels arising from 4G, 4P, 4D excited states of the free ion. Further these absorb. The complexes display three absorption bands in the region 18500-18680 cm⁻¹, 22000-22485 cm⁻¹ and 28065-28300 cm⁻¹ assigned to sextet, quartet, transitions.

6A_{1g} → 4T_{1g} (4E)(v₁), 6A_{1g} → 4E_g (4D) (v₂) and 6A_{1g} → 4T_{1g} (4P) (v₃) respectively using the figgis equation.

FUNGICIDAL ACTIVITY

The fungicidal activity of ligand as well as their complexes was determined using the Growth method. The fungicidal activity of ligand as well as their complexes was determined using the Growth method. The activity was determined against various fungi i.e. *Drechslera*, *tetramera*, *Fusarium-oxysporum*, *Macrophomera-phaseoli*, at different

temperature. The data were statistically analyzed according to the following formula:

$$\% \text{ inhibition} = [(C-T) \times 100]/C$$

Where,

C=diameter of fungus colony in control plates after 96 hours.

T=Diameter of fungus colony in treated plates after 96 hours.

RESULTS AND DISCUSSION

From the elemental analysis it is clear that stoichiometric composition in all the complexes were found to be 1:2:2(metal :primary ligand: secondary ligand) except in the case of Cu(II) where it was found to be 1:1:2(metal :primary ligand: secondary ligand).

CONCLUSION

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 atoms 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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