Research Article

Synthesis and Structural Studies of Cu(II), Co(II) and Mn(II) Ions Complexes of 2-(8-Quinolinol-5-yl) - Amino Methyl-3(4-methoxy phenyl)-5-(Phenyl)-Pyrazoline

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ABSTRACT

Complexes of 2-(8-Quinolinol-5-yl) - amino methyl-3(4-methoxy phenyl)-5-(Phenyl)-Pyrazoline with Cu(II), Co(II) and Mn(II) have been synthesized and characterized using elemental analysis, IR spectra, PMR spectra, Reflectance spectra, Conductivity measurements and antimicrobial activity. These studies revealed that they are having octahedral geometry of the type $[ML_2 (H_2O)_2]$.The compounds show net enhancement in activity on coordination of metals with ligand but moderate activity as compared to standard drugs.

Key Words : pyrazoline, hexahydrate, chalcones , chelates.

INTRODUCTION

During the last few decades, a considerable attention has bean devoted to synthesis of heterocyclic Compounds and their derivatives possessing such comprehensive bioactivities as antimicrobial[1-3],anti inflammatory[4] ,anlagesic[5], antitumorial[6], antihypertensives[7], anti convalsant[8] and antiviral[9] activities.

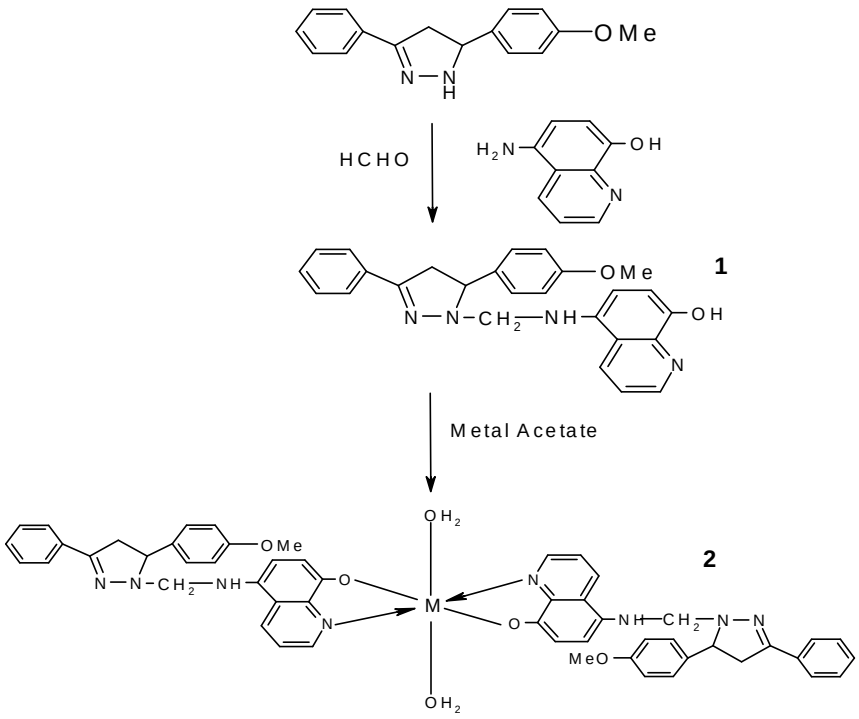
From the literature, we found that several Metal Chelates of Pyrazolines are known to display antimicrobial and therapeutic activies. Literature survey reveals scant mention of the above compounds with antimicrobial properties and hence more and more derivatives are worth tested for the possible medicinal applications. So we have decieded to synthesis Metal Chelates of 2-(8-Quinolinol-5-yl) - amino methyl-3(4-methoxy phenyl)-5-(Phenyl)-Pyrazoline

EXPERIMENTAL

Melting points were taken in open capillary tube and were uncorrected. IR spectra (KBr) were recorded on Nicollet FTIR 760 and PMR spectra were recorded on Bruker NMR spectro-photometer. PMR chemical shifts are recorded in ðvalue using TMS as an internal standard in $CDCl_3/D_6$-DMSO. Purity of the compounds were checked by tlc on silica- G plates. The fungicidal activity of all the compounds was studied at 1000 ppm concentration in vitro. Plant pathogenic organisms used were Penicillium expansum, Botrydepladia thiobromine, Nigrospora Sp., Trichothesium Sp., and Rhizopus nigricum. Anti bacterial activities were tested by Agar Cup method.

Preparation of 2-(8-Quinolinol-5-yl) - amino methyl-3(4-methoxy phenyl)-5-(Phenyl)-Pyrazoline. [HL] (1).

A mixture of 3-(4-methoxy phenyl)-5-(phenyl) -2H- Pyrazoline (0.01 mole) and formaldehyde (40%, 1.5 ml) in ethanol (20 ml) was stirred at room temp. With a solution of 5-Amino-8-Quinolinol (0.01 mole) in ethanol (10 ml) for 30 min. The solid product that separated out on standing for a 1 hrs was collected by filtration, washed with ethanol & dried. It was recrystallized from ethanol to yield the ligand compounds having m.p- 236°C. (Uncorrected). The yield of the product was 83 % .Found: C(73.4%) H(5.6%) N(13.1%), Calcd. for $C_{26}H_{24}N_4O_2$: C(73.6%) H(5.7%) N(13.2%)



Metal Complex

Where, M = Cu^{+2}, Co^{+2}, Mn^{+2}

IR (KBr); [HL]: (cm^{-1})**:** 3800-2960 (-OH), 1599,1507,3028 (Aromatic), 1638, 1575,1698, 1470 (8-HQ Moiety), 1275-1298 (C-N), 2850,2920,1450 (>CH_2)

PMR ; [HL]: δppm 7.13 to 7.54 Multiplet, quinoline, δppm 8.5 to 9.2 Singlet of phenolic- OH, δppm 4.75 - CH_2-, δppm 3.45 - CH_2-, δppm 0.95 – OCH_3

Preparation of Metal Chelates of 2-(8-Quinolinol-5-yl) - amino methyl-3(4-methoxy phenyl)-5-(Phenyl)-Pyrazoline. (2)

Formation of Cu^{2+} Chelates

The reagent solution of ligand (0.01 mole) was added drop wise to a solution of cupric nitrate hexahydrate (0.005 mole) in 100 ml. of water with rapid stirring. The pH of the resultant solution was maintained at 4.5 by NH_3. A greenish blue solid precipitated out. It was allowed to settle. Then it was digested on water bath at 70^0C for about 2 hours. The solid mass was filtered, washed with 1:1 mixture of water - ethanol and finally with acetone, and the yield of complex 78 %. The resulting complex was powdered well and further dried at 70^0C over a period of 24 hrs.

Formation of Co^{2+} Chelates

It was obtained as mist colored precipitate by mixing a reagent solution of ligand (0.01 mole) with that of cobalt nitrate hexahydrate (0.005 mole) in 100 ml. of water. The final pH was adjusted 6.0. A brown complex was purified in the same manner described earlier. The yield of a purified complex was 86%.

Formation of Mn^{2+} Chelates

The reagent solution of ligand (0.005 mole) was stirred in a solution of manganese chloride hexahydrate (0.005 mole) in 100 ml. of water. The final pH adjusted was 5.6. The yield of complex was 80%.

Characterization of Metal Chelates of Ligand

Metal Complexes	Molecular formula	M.W	Yield %	% Metal analysis		Elemental analysis					
						%C		%H		%N	
				Cald.	Found	Cald	Found	Cald.	Found	Cald.	Found
$(HL)_2$ Cu^{+2}	$C_{52}H_{46}N_8O_4$ $Cu^{+2}2H_2O$	945.5	78	6.7	6.6	65.9	65.8	5.2	5.2	11.8	11.8
$(HL)_2$ Co^{+2}	$C_{52}H_{46}N_8O_4$ $Co^{+2}2H_2O$	941	86	6.2	6.1	66.3	66.2	5.3	5.2	11.9	11.8
$(HL)_2$ Mn^{+2}	$C_{52}H_{46}N_8O_4$ $Mn^{+2}2H_2O$	937	80	5.8	5.8	66.6	66.5	5.3	5.3	11.9	11.9

IR (KBr); $(HL)_2$-Co^{+2} : (cm^{-1})**:** 3500-2600 broad (-OH), 1609,1459,2989 (Aromatic), 1609,1577, 1509, 1459 (8-HQ Moiety), 1269 (C-N), 2839,2901,1459 (>CH_2).

Experimental data of magnetic moment and conductivity of metal chelate of Ligand

Metal complexes	$\chi_\gamma \times 01^{6-}$ (cgs)	$\chi_\mu \times 01^{6-}$ (cgs)	Magnetic moment μeff (BM)	μeff = $\sqrt{n(n+2)}$ BM	μeff (BM) Expected	$\wedge_M^a$
$(HL)_2$ Cu+2	1.59	1504	1.91	1.73	1.7-2.2	7.98
$(HL)_2$ Co^{+2}	11.75	11057	5.18	3.87	4.4-5.2	29.10
$(HL)_2$ Mn^{+2}	15.57	14589	5.95	5.91	5.2-6.0	9.10

Reflectance spectral data of metal complexes of ligand

Metal complex	Absorption, cm^{-1}	Transional
$(HL)_2$ Cu^{+2}	24387 15620	CT $^2B_{1g} \rightarrow {}^2A_{1g}$
$(HL)_2$ Co^{+2}	24125 19715 8665	$^4T_{1g}(F) \rightarrow {}^4T_{2g}(P)$ $^4T_{1g}(F) \rightarrow {}^4A_{2g}$ $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$
$(HL)_2$ Mn^{+2}	23985 17641 15467	$^6A_{1g} \rightarrow {}^4A_{1g}$ ($4E_g$) $^6A_{1g} \rightarrow {}^4T_{2g}$ (4G) $^6A_{1g} \rightarrow {}^4T_{1g}$ (4G)

Antifungal activity of ligand HL and their metal Chelate

Sample	Zone of inhibition at 1000 ppm (%)				
	Penicillium Expansum	C.Albicans	Nigras Pora Sp.	Trichothesium Sp.	A. Niger
HL	66	60	56	54	64
$(HL)_2Cu^{+2}$	78	75	84	88	84
$(HL)_2$ Co^{+2}	68	69	78	74	80
(HL)2 Mn+2	54	54	68	66	55

Antibacterial activity of ligands HL and their metal Chelate

Sample	Zone of inhibition (in mm)			
	Gram + Ve		*Gram -Ve*	
	B.Cereus	Micrococcus	P. Aeruginosa	E-Coli
HL	13	15	18	20
$(HL)_2 Cu^{+2}$	14	19	21	22
$(HL)_2 Co^{+2}$	14	19	19	19
$(HL)_2 Mn^{+2}$	09	14	11	15

RESULT AND DISCUSSION

All the complexes are toxic more or less to fungi. The substitution of phenyl rings does not have more effect on the fungicidal activity of complexes. Out of all metal complexes, Cu^{+2} metal complexes are more toxic than others and the order for is $Cu^{+2} > Co^{+2} > Mn^{+2}$.

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