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Synthesis and antimicrobial activity of some Pyrazoline derivatives and their metal complexes

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ABSTRACT

Complexes of 2-(8-Quinolinol-5-yl) - amino methyl-3(4- nitro phenyl)-5-(Phenyl)-Pyrazoline with Cu(II), Mn(II) and Zn(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.

Keywords : pyrazoline, quinoline, chalcones , chelates.

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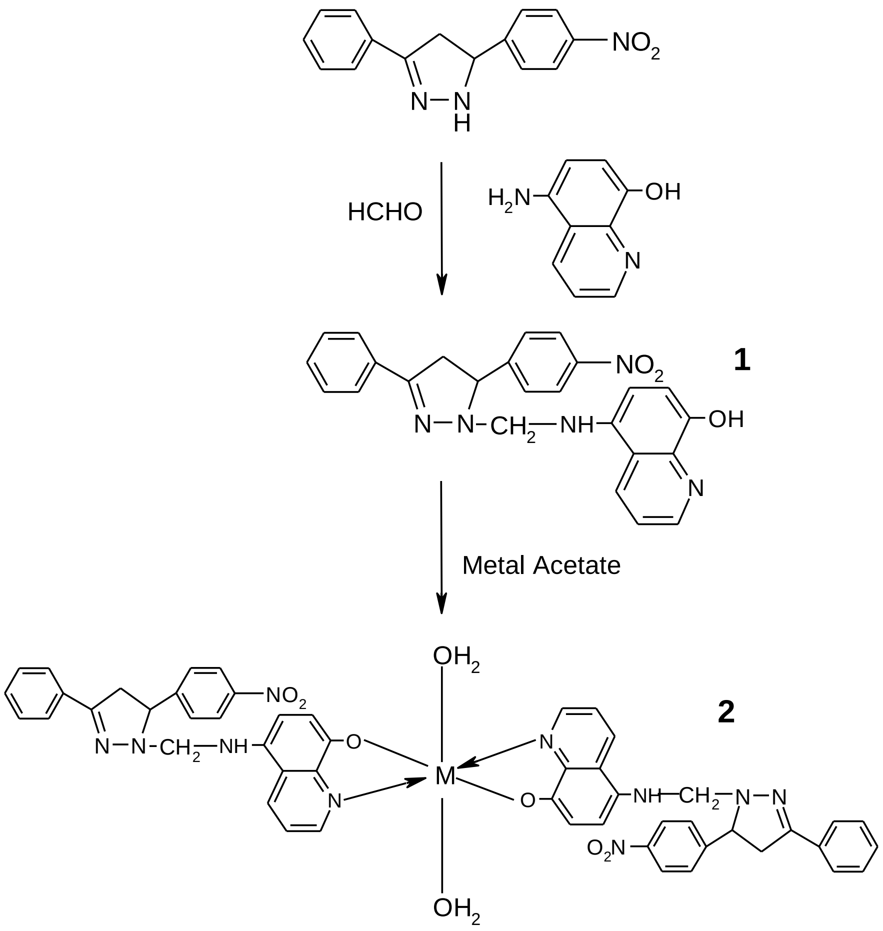
INTRODUCTION

Pyrazoslines are reported as antibacterial, antifungal, antimicrobial, antiviral, anti-arthritis and anti-inflammatory agents [1-9]. Encouraged by these facts, we selected to work on some Pyrazoline derivatives and their metal complexes.

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 δvalue 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.



Metal Complex

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

Preparation of 2-(8-Quinolinol-5-yl) - amino methyl-3(4- nitro phenyl)-5-(Phenyl)-Pyrazoline. (1).

A mixture of 3-(4-nitro 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- 256°C. (Uncorrected). The yield of the product was 64 % .Found: C(68.2%) H(4.7%) N(15.8%) Calcd. for $C_{25}H_{22}N_5O_3$: C(68.3%) H(4.8%) N(15.9%)

IR (KBr); [HL]: (cm^{-1})**:** 3800-2700 (-OH), 1599,1507,3028 (Aromatic), 1638, 1575,1698, (8-HQ Moiety), 1275-1298 (C-N), 2850,2910,1450 (>CH_2)

NMR ; [HL]: δ ppm 7.1 to 7.64 Multiplet, quinoline, δ ppm 8.5 to 9.2 Singlet of phenolic- OH, δ ppm 4.75 - CH_2-, δ ppm 4.05 - CH_2-

Preparation of Metal Chelates of 2-(8-Quinolinol-5-yl) - amino methyl-3(4- nitro 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 65%. The resulting complex was powdered well and further dried at 70^0C over a period of 24 hrs.

Formation of Mn^{2+} Chelates

The reagent solution of each 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 70%.

Formation of Zn^{2+} Chelates

The reagent solution of ligand (0.01 mole) was added to that of zinc nitrate hexahydrate (0.005 mole) in 100 ml of water. The resultant pH was 5.6. The product was purified in the same manner described earlier. The dried complex was in pale yellow powder. The yield was 73%.

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Characterization of Metal Chelates of Ligand HL -1.

Metal Complexes	Molecular formula	M.Wt Gm/mole	Yield %	% Metal analysis		Elemental analysis					
						%C		%H		%N	
				Cald.	Found	Cald.	Found	Cald.	Found	Cald.	Found
$(HL)_2\ Cu^{+2}$	$C_{50}H_{42}N_{10}O_6\ Cu^{+2}.2H_2O$	975.5	65	6.5	6.4	61.5	61.5	4.5	4.4	14.3	14.3
$(HL)_2\ Mn^{+2}$	$C_{50}H_{42}N_{10}O_6\ Mn^{+2}.2H_2O$	967	70	5.6	5.6	62.0	62.0	4.5	4.4	14.4	14.3
$(HL)_2\ Zn^{+2}$	$C_{50}H_{42}N_{10}O_6\ Zn^{+2}.2H_2O$	977	73	6.6	6.5	61.4	61.4	4.5	4.4	14.3	14.3

IR (KBr); $(HL)_2$-Zn^{+2} : (cm^{-1}): 3500-2600 broad (-OH), 1577,1457,2989 (Aromatic), 1667,1577,1508,1390 (8-HQ Moiety), 1269 (C-N), 2989,1457 (>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	1551	1.94	1.73	1.7-2.2	4.12
$(HL)_2\ Mn^{+2}$	14.93	14442	5.92	5.91	5.2-6.0	6.72
$(HL)_2\ Zn^{+2}$	-	-	-	-	D(*)	9.12

Reflectance spectral data of metal complexes of ligand.

Metal complex	Absorption, cm^{-1}	Transional
$(HL)_2\ Cu^{+2}$	24613	CT
14970	$^2B_{1g} \rightarrow {}^2A_{1g}$	
$(HL)_2\ Mn^{+2}$	23786	$^6A_{1g} \rightarrow {}^4A_{1g}$ (4Eg)
18410	$^6A_{1g} \rightarrow {}^4T_{2g}$ (4G)	
16722	$^6A_{1g} \rightarrow {}^4T_{1g}$ (4G)	

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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	67	63	72	60	62
$(HL)_2\ Cu^{+2}$	88	86	82	92	88
$(HL)_2\ Mn^{+2}$	66	56	58	58	61
$(HL)_2\ Zn^{+2}$	84	84	79	89	82

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	20	18	20	13
$(HL)_2\ Cu^{+2}$	22	22	22	22
$(HL)_2\ Mn^{+2}$	11	12	13	16
$(HL)_2\ Zn^{+2}$	18	22	18	18

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. In each series the Cu-complexes have much toxicity. This is expected because the copper salts are mostly used as fungicides. Most of the complexes inhibit the growth of the above organisms which cause decease in many plants. Out of all metal complexes, Cu^{+2} metal complexes are more toxic than others and the order for is $Cu^{+2} > Zn^{+2} > Mn^{+2}$.

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