

Synthesis, characterization and chelating properties of novel ligands containing Pyrazoline ring

B. N. Patel¹, P.S. Patel^{2*} and V. G.Patel¹

¹Department of Chemistry, Municipal Arts and Urban Bank Science College, Mehsana, India.

²Department of Chemistry, Sheth L.H. Science College, Mansa.-382845, India.

*Corres.author: pspatel_mansa@yahoo.co.in

Abstract: Complexes of 2-(8-Quinololinol-5-yl) - amino methyl-3- (4- Methoxy Phenyl)-5-(4-chloro Phenyl)-Pyrazoline with Cu(II), Mn(II) and Co(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, antidiabetic, anaesthetic, chalcones , chelates.

Introduction

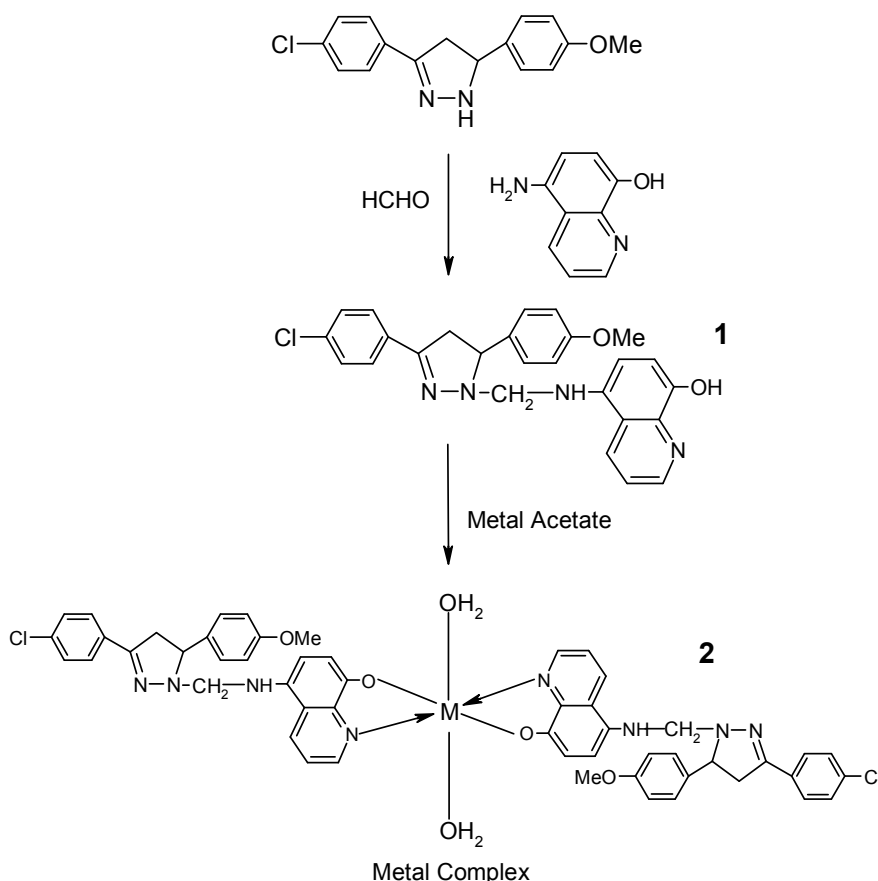
Heterocyclic compounds have so far been synthesized mainly due to the wide range of biological activities. Much attention has paid to the synthesis of heterocyclic compounds bearing nitrogen and oxygen containing ring system, like pyrazoline mainly due to their higher pharmacological activity.

Pyrazoline are prominent nitrogen containing heterocyclic compounds play important role in medicinal chemistry. Considerable attention has been focused on pyrazoline derivatives due to their interesting biological activities. They have found to possess antifungal¹, antibacterial², antidepressant³, anticonvulsant^{4,5}, anti-inflammatory⁶, anti-tumor⁷, antidiabetic, anaesthetic and analgesic⁸⁻¹⁰ properties. Owing to the mentioned biological activities of

pyrazoline prompted us to synthesize various substituted pyrazoline derivatives.

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 δ value 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 thibromine*, *Nigrospora Sp.*, *Trichothesium Sp.*, and *Rhizopus nigricum*. Anti bacterial activities were tested by Agar Cup method.



Where, M = Ni²⁺, Mn²⁺, Co²⁺

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

A mixture of 3-(4-methoxy phenyl)-5-(4-chloro 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- 228°C. (Uncorrected). The yield of the product was 62 % .Found: C(67.9%) H(4.9%) N(12.1%) Cl(7.6%) Calcd. for C₂₆H₂₃N₄O₂Cl: C(68.1%) H(5.0%) N(12.2%) Cl(7.7%)

IR (KBr); [HL]: (cm⁻¹): 3650-2700 (-OH), 1598,1507,3028 (Aromatic), 1638, 1575,1698, (8-HQ Moiety), 1275-1298 (C-N), 2850,2920,1450 (>CH₂)

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 to 4.95 - CH₂-, δ ppm 3.45 - CH₂-, δ ppm 0.92 - OCH₃

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

Formation of Ni²⁺ Chelates :

A reagent solution of ligand (0.01 mole) mixed with a solution of nickel nitrate hexahydrate (0.005 mole) in 100 ml. of water. A dull greenish precipitate was formed at pH 6.0. The product was purified in the manner described above. The yield was 86 %.

Formation of Mn²⁺ 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 77%.

Formation of Co²⁺ 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 78%.

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 Ni ⁺²	C ₅₂ H ₄₄ N ₈ O ₄ Cl ₂ Ni ⁺² ·2H ₂ O	1010	86	5.8	5.7	61.7	61.7	4.7	4.6	11.0	11.0	
(HL) ₂ Mn ⁺²	C ₅₂ H ₄₄ N ₈ O ₄ Cl ₂ Mn ⁺² ·2H ₂ O	1006	77	5.4	5.4	62.0	61.9	4.7	4.6	11.1	11.0	
(HL) ₂ Co ⁺²	C ₅₂ H ₄₄ N ₈ O ₄ Cl ₂ Co ⁺² ·2H ₂ O	1010	78	5.8	5.8	61.7	61.6	4.7	4.7	11.0	11.0	

IR (KBr); (HL)₂-Co⁺² : (cm⁻¹): 3500-2600 broad (-OH), 1649,1459,2931 (Aromatic), 1649,1510,1459 (8-HQ Moiety), 1279 (C-N), 2838, 2838, 1459 (>CH₂).

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

Metal complexes]	$\chi_v \times 10^{16}$ (cgs)	$\chi_\mu \times 10^{16}$ (cgs)	Magnetic moment μ_{eff} (BM)	$\mu_{eff} = \sqrt{n(n+2)}$ BM	μ_{eff} (BM) Expected	\wedge_M^a
(HL) ₂ Ni ⁺²	4.69	4736	3.39	2.82	2.9-3.4	7.92
(HL) ₂ Mn ⁺²	14.50	14589	5.95	5.91	5.2-6.0	6.10
(HL) ₂ Co ⁺²	10.91	11015	5.17	3.87	4.4-5.2	20.04

Reflectance spectral data of metal complexes of ligand.

Metal complex	Absorption, cm ⁻¹	Transional
(HL) ₂ Ni ⁺²	22465	³ A _{2g} → ³ T _{1g} (P)
	14973	³ A _{2g} → ³ T _{1g} (F)
(HL) ₂ Mn ⁺²	23817	⁶ A _{1g} → ⁴ A _{1g} (4Eg)
	17795	⁶ A _{1g} → ⁴ T _{2g} (4G)
	15893	⁶ A _{1g} → ⁴ T _{1g} (4G)
(HL) ₂ Co ⁺²	22985	⁴ T _{1g} (F) → ⁴ T _{2g} (P)
	17195	⁴ T _{1g} (F) → ⁴ A _{2g}
	8875	⁴ T _{1g} (F) → ⁴ T _{2g} (F)

Antifungal activity of ligand HL and their metal Chelate.

Sample	Zone of inhibition at 1000 ppm (%)				
	Penicillium Expansum	C.Albicans	Nigras Pora Sp.	Trichothesi um Sp.	A. Niger
HL	75	77	83	81	82
(HL) ₂ Ni ⁺²	75	65	67	71	69
(HL) ₂ Mn ⁺²	65	60	58	64	60
(HL) ₂ Co ⁺²	80	73	70	80	70

GFBGAntibacterial 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	21	20	18	21
(HL) ₂ Ni ⁺²	14	11	15	15
(HL) ₂ Mn ⁺²	11	08	12	12
(HL) ₂ Co ⁺²	15	12	16	16

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 Co-complexes have much toxicity. This is expected because the cobalt salts are mostly used as fungicides. Most of the complexes inhibit the growth of the above organisms which cause disease in many plants. Out of all metal complexes, Co⁺² metal

complexes are more toxic than others and the order for is Co⁺² > Ni⁺² > Mn⁺².

Acknowledgements

The authors are thankful to Dr. D.R. Patel, principal, Municipal Arts and Urban Bank Science College, Mehsana for providing me with all possible research facilities. One of the author of this paper Pankaj S. Patel is thankful to UGC. Ganeshkhind, pune. for Teacher Research Fellowship.

References.

1. Kargaokar S S, Patil P H, Shah M T and Parekh H H, *Indian J Pharm Sci.*,1996 ,58, 222.
2. Palaskar E, Aytemir M, Uzbay I T and Erol D, *Eur J Med Chem.*, 2001, 36, 539-543.
3. Bilgin A A, Palaskar E and Sunal R, *Aezneim Forsch Drug Res.*, 1993, 43, 1041.
4. Ozdemir Z, Kandilici H B, Gumusel B, Calis U and Bilgin A A, *Eur J Med Chem.*, 2007, 42, 373-379.
5. Ruhoglus O, Ozdemir Z, Calis U, Gumusel B and Bilgin A A, *Aezneim Forsch Drug Res.*, 2005, 55, 431-436.
6. Udipi R H, Kushnoor A R and Bhat A R, *Indian J Hetrocyclic Chem.*, 1998, 8, 63.
7. Taylor E C and Patel H H, *Tetrahedron*, 1992, 48, 8089-8100.
8. Regaila H A, El-Bayanki A K and Hammad M, *Egypt J Chem.*, 1979, 20, 197.
9. Krishna R B, Panade R, Bhaithwal S P and Parmar S S, *Eur Med J Chem.*, 1980, 15567.
10. Husain M J and Shukla S, *Indian J Chem.*, 1986, 25B, 983.
