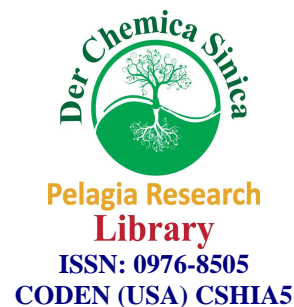




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Novel of Cu(II), Mn(II) and Co(II) metal complexes with Pyrazoline ligands: Synthesis and spectral characterization

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ABSTRACT

Complexes of 2-(8-Quinololinol-5-yl) - amino methyl-3-(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, hexahydrate, chalcones , chelates.

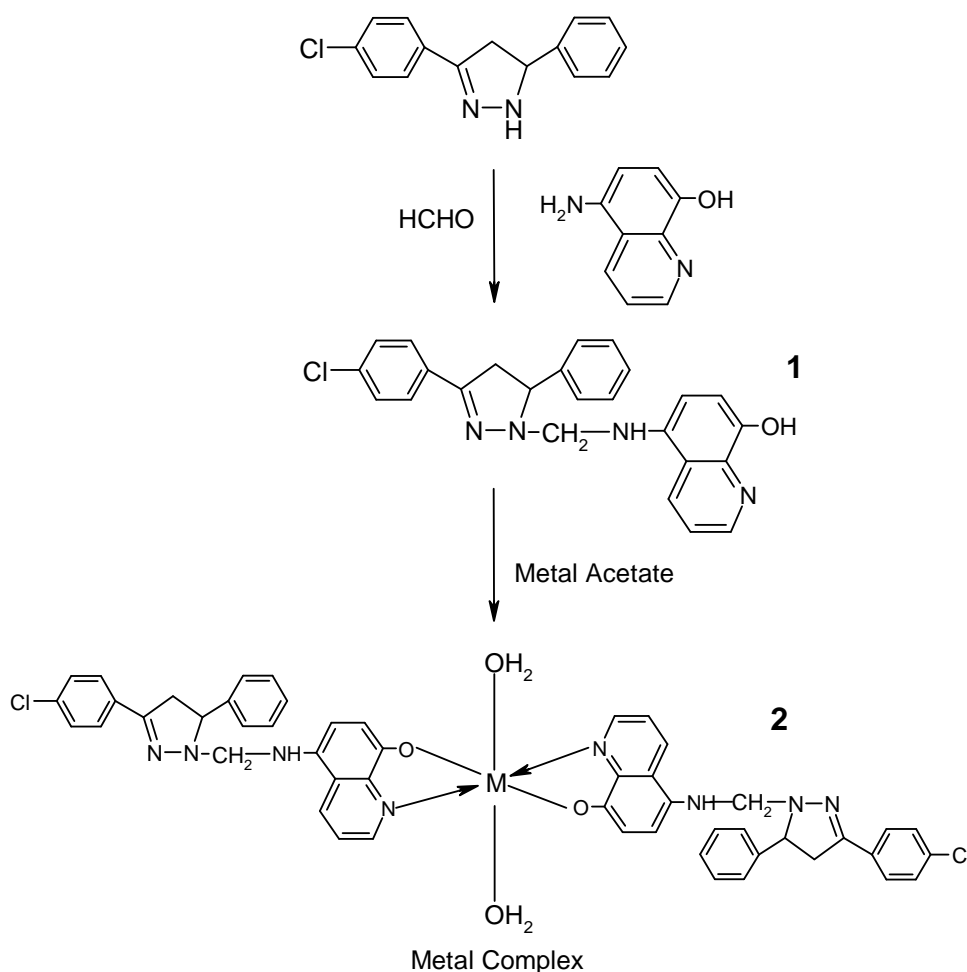
INTRODUCTION

Pyrazoline derivatives are found to be bactericidal [1], fungicidal [2] and biodegradable agrochemical [3] also, used as intermediate in the dye industry [4]. The substituted pyrazolines effectively utilized as antitumor [5], antidiabetic [6], anaesthetic [7] and analgesic [8]. While the pyrazoline structure has shown a special ability to interact with UV and VIS radiation in linear and nonlinear optical sense; some of them used as drugs for prevention and diagnosis of many diseases [9]. Also, pyrazoline derivatives with different substitution show the electroluminescence and photoluminescence in OLED [10-11].

MATERIALS AND METHODS

Melting points were taken in open capillary tube and were uncorrected. IR spectra (KBr) were recorded on Nicolet FTIR 760 and PMR spectra were recorded on Bruker NMR spectrophotometer. 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 thiobromine*, *Nigrospora* Sp., *Trichothesium* Sp., and *Rhizopus nigricum*. Anti bacterial activities were tested by Agar Cup method.



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

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

A mixture of 3-(phenyl)-5-(4-chlorophenyl)-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- 245°C. (Uncorrected). The yield of the product was 74 % .Found: C(69.8%) H(4.8%) N(13.0%) Cl(8.2%) Calcd. for $C_{25}H_{21}N_4OCl$: C(70.0%) H(4.9%) N(13.1%) Cl(8.3%)

IR (KBr); [HL]: (cm^{-1}): 3800-2600 (-OH), 1599,1507,3028 (Aromatic), 1638, 1575,1698, (8-HQ Moiety), 1275-1298 (C-N), 2850,2920,1450 ($>CH_2$) **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 3.55 - CH_2 -

Preparation of Metal Chelates of 2-(8-Quinolinol-5-yl) - amino methyl-3-(Phenyl)-5-(4-chloro 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°C 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°C over a period of 24 hrs.

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 68%.

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 64%.

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 |
| $(\text{HL})_2 \text{Cu}^{+2}$ | $\text{C}_{50}\text{H}_{42}\text{N}_8\text{O}_2\text{Cl}_2 \text{Cu}^{+2} 2\text{H}_2\text{O}$ | 954.5 | 65 | 6.6 | 6.6 | 62.8 | 62.8 | 4.6 | 4.5 | 11.7 | 11.6 |
| $(\text{HL})_2 \text{Mn}^{+2}$ | $\text{C}_{50}\text{H}_{42}\text{N}_8\text{O}_2\text{Cl}_2 \text{Mn}^{+2} 2\text{H}_2\text{O}$ | 946 | 68 | 5.8 | 5.7 | 63.4 | 63.3 | 4.6 | 4.5 | 11.8 | 11.7 |
| $(\text{HL})_2 \text{Co}^{+2}$ | $\text{C}_{50}\text{H}_{42}\text{N}_8\text{O}_2\text{Cl}_2 \text{Co}^{+2} 2\text{H}_2\text{O}$ | 950 | 64 | 6.2 | 6.1 | 63.1 | 63.1 | 4.6 | 4.5 | 11.7 | 11.7 |

IR (KBr); $(\text{HL})_2\text{-Cu}^{+2}$: (cm^{-1}): 3500-2600 broad (-OH), 1577,1467,3028 (Aromatic), 1669,1577,1509,1466 (8-HQ Moiety), 1289 (C-N), 2850, 3174, 1466 ($>\text{CH}_2$).

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

| Metal complexes | $\chi_r \times 10^6$ (cgs) | $\chi_m \times 10^6$ (cgs) | Magnetic moment μ_{eff} (BM) | $\mu_{\text{eff}} = \sqrt{n(n+2)}$ BM | μ_{eff} (BM) Expected | Δ_M^a |
|--------------------------------|----------------------------|----------------------------|---|---------------------------------------|----------------------------------|--------------|
| $(\text{HL})_2 \text{Cu}^{+2}$ | 1.57 | 1503 | 1.91 | 1.73 | 1.7-2.2 | 7.10 |
| $(\text{HL})_2 \text{Mn}^{+2}$ | 15.53 | 14687 | 5.97 | 5.91 | 5.2-6.0 | 7.92 |
| $(\text{HL})_2 \text{Co}^{+2}$ | 11.46 | 10887 | 5.14 | 3.87 | 4.4-5.2 | 27.20 |

Reflectance spectral data of metal complexes of ligand.

| Metal complex | Absorption, cm^{-1} | Transitional |
|--------------------------------|------------------------------|---|
| $(\text{HL})_2 \text{Cu}^{+2}$ | 23885 | CT |
| | 15653 | ${}^2\text{B}_{1g} \rightarrow {}^2\text{A}_{1g}$ |
| $(\text{HL})_2 \text{Mn}^{+2}$ | 22124 | ${}^6\text{A}_{1g} \rightarrow {}^4\text{A}_{1g}$ (4Eg) |
| | 18538 | ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{2g}$ (4G) |
| | 16105 | ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{1g}$ (4G) |
| $(\text{HL})_2 \text{Co}^{+2}$ | 24125 | ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{2g}(\text{P})$ |
| | 19888 | ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{A}_{2g}$ |
| | 9824 | ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{2g}(\text{F})$ |

Antifungal activity of ligand HL and their metal Chelate

| Sample | Zone of inhibition at 1000 ppm (%) | | | | |
|--------------------------------|------------------------------------|-------------------|----------------------------|--------------------------------|-----------------|
| | <i>Penicillium Expansum</i> | <i>C.Albicans</i> | <i>Nigras Pora Sp.</i> | <i>Trichothesium m Sp.</i> | <i>A. Niger</i> |
| HL | 75 | 72 | 67 | 69 | 67 |
| $(\text{HL})_2 \text{Cu}^{+2}$ | 85 | 84 | 83 | 77 | 85 |
| $(\text{HL})_2 \text{Mn}^{+2}$ | 59 | 57 | 55 | 55 | 55 |
| $(\text{HL})_2 \text{Co}^{+2}$ | 65 | 78 | 64 | 64 | 75 |

Antibacterial activity of ligands HL and their metal Chelate.

| Sample | Zone of inhibition (in mm) | | | |
|--------------------------------|----------------------------|--------------------|----------------------|---------------|
| | Gram + Ve | | Gram -Ve | |
| | <i>B.Cereus</i> | <i>Micrococcus</i> | <i>P. Aeruginosa</i> | <i>E-Coli</i> |
| HL | 21 | 20 | 18 | 21 |
| $(\text{HL})_2 \text{Cu}^{+2}$ | 22 | 21 | 21 | 20 |
| $(\text{HL})_2 \text{Mn}^{+2}$ | 11 | 08 | 12 | 12 |
| $(\text{HL})_2 \text{Co}^{+2}$ | 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 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 disease in many plants. Out of all metal complexes, Cu^{+2} metal complexes are more toxic than others and the order for is $\text{Cu}^{+2} > \text{Co}^{+2} > \text{Mn}^{+2}$.

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REFERENCES

- [1] Das, N.B. and Mittra A.S., *Ind. J. Chem.*, 16B: 638(1978)
- [2] Roelofvan, S.G., Arnold C., and Wellmgak, *J.Agric. Food Chem.*, 27: 406(1979)
- [3] Cremtyu, R., *Pesticides preparation and mode of action*, Wiley and sons New York(1978)

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- [4] Lubs, H.A., *The Chemistry of synthetic dyes and pigments*, Am. Chem. Soc. (1970)
- [5] Chen, K., Kuo S., Hsieh M. and Authoner, *J. Med. Chem.*, 40: 3049(1997)
- [6] Regila, H.A., El-Boyounk A.K. and Hammad M., *Egypt J. Chem.*, 20: 197(1979)
- [7] Krishna R., Pande B.R., Bharghawal S., Parmar S., *Eur. J. Med. Chem.*, 15: 567 (1980)
- [8] Kumar A., Sharma S., Bajaj K., Bansal D., Sharma, Sexena A.K., Lata S., Gupta B. and Srivastava, (2003). *Ind. J. Chem.*, 42B(1979)
- [9] Joaquin, B., Koen C., Raquel G., Stephen H., Persoons A., Luis J. and Sexena, (1998). *J. Med. Chem.*, 8(8), (1725)
- [10] Zhang, X.H., Lai W.Y., Wong T.C., Gao Z.Q., Jing Y.C., Wu S.K., Kwong H.L., Lee C. S., Lee S.T., *Synthetic Metal*. 114,115(2000)
- [11] Zhang, X.H., Lai W.Y., Gao Z.Q., Wong T.C., Lee C.S., Kwong H.L., Lee S.T. and Wu S.K., *Chemical Physics Lett.*, 320,7(2000)