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**SYNTHESIS, CHARACTERISATION AND ANTIMICROBIAL  
 ACTIVITY OF Mn (II), Co (II), Ni (II) AND Cu (II) COMPLEXES OF 4-  
 CARBOXALDEHYDE DINITRO PHENYLHYDRAZONE-1-PHENYL-  
 3-METHYL-2-PYRAZOLINE-5-ONE**

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**ABSTRACT**

4-Carboxaldehyde-1-phenyl-3-methyl-2-pyrazoline-5-one condensed with Dinitro Phenyl hydrazine to form ligand (HL). These metal complexes are of type  $[ML_2(H_2O)_2]$  [M= Mn(II), Co(II), Ni(II) and Cu(II)]. Elemental analysis, magnetic susceptibility, electrical conductance, electronic and infrared data suggest octahedral structure for the metal complexes. All the compounds were tested for their antimicrobial activity. The result indicates that the growth of the tested organisms was inhibited by most of the compounds.

**Keywords:** Dinitrophenylhydrazine, Antimicrobial activity, Complexes.

**INTRODUCTION**

$\beta$ -Diketone hydrazone derivatives are known to act as good chelating agents[1-4]. The interest in studying these compounds and their metal complexes arises from their behavior as efficient antituberculous agents[5]. Furthermore, some hydrazones are used as quantitative analytical reagents, especially in colorimetric and fluorimetric determinations of metal ions[6,7]. In continuation of our earlier work [8,9], we report here some new transition metal complexes of ligand (HL) derived from 4-Carboxaldehyde-1-phenyl-3-methyl-2-pyrazolin-5-one with phenyl hydrazine[10].

**MATERIALS AND METHODS**

All the chemicals used in the preparation of ligand and their metal complexes were of reagent grade. The ligand was prepared by condensation of equimolar amount of 4-Carboxaldehyde-1-phenyl-3-methyl-2-pyrazolin-5-one with dinitrophenyl hydrazine in ethanol on water bath for 2-3 hours. The crude product was collected by filtration, then washed several times with water. The phenyl hydrazone CDPHPz were than purified

by recrystallization in ethanol. The following general procedure was used in the syntheses of the entire metal complex. Metal salts were dissolved in a minimum quantity of hot double distilled water. The warm ethanolic solution of the ligand and metal salts solution were mix in the stoichiometric proportions 1:2, metal: ligand ratio for all divalent metal ions. To the resulting mixture 2g of sodium acetate was added and then refluxed for 2 hours on water bath. The product obtained on cooling was filtered and washed several times with hot water, followed by ethanol and finally dried in the air. The ligand and their metal complexes were tested for antibacterial activity against *Escherichia coli*, *Bacillus subtilis*, *Aspergillus niger* and *Saccharomyces cerevisiae*. Elemental analysis of all the compound carried out on a "Perkin Elmer seriesII, 2400". The FT-IR spectra of the compounds studied in the present work were recorded on a Fourier Transmission in KBr pellets in the range of 4000 - 400  $cm^{-1}$ . The electronic spectra of the solid compounds were recorded in DMF (spectral grade) on Perkin-Elmer Lambda-19 UV-Visible spectrophotometer. The conductivities of the metal chelates in DMF were

measured using “Equiptronics EQ-660 digital conductivity meter” and a calibrated conductivity cell at room temperature. The magnetic susceptibilities at room temperature were measured by Gouy method [11-13]. Dimagnetic correction were made using Pascal constants [14,15]. Molecular weight were determined by Rast Camphor method. Metal were estimated gravimetrically [16,17] and volumetrically [18].

## RESULT AND DISCUSSION

All the complexes are coloured solids, insoluble in common organic solvents but sparingly soluble in dioxane and DMF. The analytical data (table-1.0) suggest molecular formula  $[ML_2(H_2O)_2]$  for all the metal complexes. All complexes are found to be non-electrolyte in nature. Their probable structures have been derived on the basis of their elemental analyses, magnetic, electronic and infrared spectral measurements. Ligand show bidentate behavior. Electronic spectral data and magnetic moment values suggest octahedral geometry of these complexes. Elemental analysis, magnetic moment and conductance data are given in the table -1

The electronic spectra of the Mn(II) complexes show three weak bands in the region  $18,610 - 15,130\text{cm}^{-1}$  and  $25,600 - 18,000\text{cm}^{-1}$ . Considering an octahedral structure for these complexes, these bands may be assigned to the  ${}^6A_{1g} \longrightarrow {}^4T_{1g}$  (G), and  ${}^6A_{1g} \longrightarrow {}^4E_g$ ,  ${}^4A_{1g}$  (G) transitions respectively [19,20].

Electronic spectra of Co(II) complexes show three bands in the regions,  $9,330-8,390$ ,  $19,800-18,500$  and  $29,000-25,000\text{cm}^{-1}$  [20,21]. The first two bands may correspond to

${}^4T_{1g}(F) \longrightarrow {}^4T_{2g}(F)$  ( $\nu_1$ ) and  ${}^4T_{1g}(F) \longrightarrow {}^4T_{1g}$  (p) ( $\nu_3$ ) transitions respectively. The latter highest energy band may be due to tetragonal distortion along the Z - axis.

The transition energy ratio  $\nu_2^{\text{calcd.}}/\nu_1$  is very close to the reported values required for an octahedral structure for all the complexes [22,23].

The electronic spectra of all the Ni(II) complexes studied in the present work have the general appearance of typical octahedral Ni(II) spectra consisting of three bands as under [24].

$\text{cm}^{-1}$	$\nu_1$	:	${}^3A_{2g} \longrightarrow {}^3T_{2g}$	$11,000 - 8,000$
$\text{cm}^{-1}$	$\nu_2$	:	${}^3A_{2g} \longrightarrow {}^3T_{1g}$	$21,000 - 16,000$
$\text{cm}^{-1}$	$\nu_3$	:	${}^3A_{2g} \longrightarrow {}^3T_{1g}$ (p)	$27,000 - 24,000$

The  $\nu_2/\nu_1$  ratio is greater than the range required for an octahedral structure [24].

The electronic spectrum of all Cu(II) complexes studied in the present work show only one absorption band in the region  $20,250-12,850\text{cm}^{-1}$ . This band is resolved into two or three components, which presumably contain d

- d transition [25]. The much more intense band in all the complexes in the region  $28,880-26,100\text{cm}^{-1}$ , might be due to charge transfer in origin [26]. Absence of any band below  $10,000\text{cm}^{-1}$ , excludes the possibility of tetrahedral structure for the complexes [27]. The infrared spectra of all the ligand new  $\nu_{O-H}$  band appears at the region  $3550 - 2900\text{cm}^{-1}$  indicate the involvement of a 5-OH group in the intramolecular or intermolecular hydrogen bonding with the  $\pi$ -electrons of the azomethine group and may be also correlated with the lone pair of nitrogen [4,21]. The ligands show a strong band due to  $\delta_{O-H}$  in the region  $1274\text{cm}^{-1}$ . This band disappear in the infrared spectra of all the metal complexes. This may be due to deprotonation of the 5-OH group of the ligand and participation of oxygen atom in the co-ordination [11,27]. The infrared spectra of all the ligand show strong band due to  $\nu_{C-O}$  in the region  $1345 - 1315\text{cm}^{-1}$  suggesting structure-II for the ligands [28]. On the co-ordination, this band is shifted toward higher frequency by  $2-30\text{cm}^{-1}$  indicating that the 4-methylene proton is transferred to 5-oxygen making the 5-OH group of the ligand to participate in the co-ordination [28].

The infrared spectra of all the ligand show a strong absorption band in the region  $1620$  and  $1005\text{cm}^{-1}$ , which may be due to  $\nu_{C=N}$  of the azomethine group [27] and  $\nu_{N-N}$  mode [29] respectively. In the spectra of all the metal complexes  $\nu_{C=N}$  (azomethine) shifts to lower frequency by  $15-51\text{cm}^{-1}$  and  $\nu_{N-N}$  to higher frequency by  $\sim 10\text{cm}^{-1}$  suggesting involvement of azomethine nitrogen in co-ordination. The increase in double bond character offsetting the loss of electron density via donation to metal, suggesting the participation of azomethine nitrogen atom in the coordination [30]. The infrared spectra of all the ligand studied in the present work show strong band in the region  $1615-1595\text{cm}^{-1}$ , which may be assigned to  $\nu_{C=N}$  (pyrazolin ring). This band remains at the same position in the spectra of all the metal complexes indicating that non-participation of this group on coordination [31].

The coordination through azomethine nitrogen atom and oxygen atom of 5 -OH group pyrazolin ring of all the ligands is further strengthened by the appearance of the new non - ligand bands in the infrared spectra of all metal complexes in the region  $540 - 500\text{cm}^{-1}$  and  $470 - 420\text{cm}^{-1}$ , which may be assigned to  $\nu_{M-O}$  and  $\nu_{M-N}$  modes respectively [32] In the light of the above discussion, octahedral structures for Ni(II), Co(II), Mn(II) and distorted octahedral structure for Cu(II) complexes are proposed.

## ANTIBACTERIAL ACTIVITY

The compound tested in vitro for the the antibacterial activity against *Escherichia coli*, *Bacillus subtilis*, *Aspergillus niger* and *Saccharomyces cerevisiae* using agar cup assay method. The degree of effectiveness was measured by determining the diameter of the zone of inhibition caused by the compound. Effectivity was

classified into three zones on the basis of the diameter of zone of inhibition:

++ : Most effective  
 ++ : Moderate effective

+ : Slightly effective

- : Non effective

Most of the compound were active against bacteria and yeast. The result are as under :

**Table 1. Physical and analytical data of metal complex**

Complexes	Colour	Empirical formula	Found (Calculated) %				$\lambda_m$ ohm <sup>-1</sup> cm <sup>2</sup> mole <sup>-1</sup> in DMF	$\mu_{\text{eff.}}$ in B. M.
			Metal	Carbon	Hydrogen	Nitrogen		
[Mn(CDHPZ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]	Golden-Brown	MnC <sub>34</sub> H <sub>30</sub> N <sub>12</sub> O <sub>12</sub>	6.44 (6.43)	47.76 (47.84)	3.53 (3.54)	19.68 (19.69)	2.8	5.83
[Co(CDHPZ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]	Black	CoC <sub>34</sub> H <sub>30</sub> N <sub>12</sub> O <sub>12</sub>	6.89 (6.87)	47.53 (47.62)	3.52 (3.52)	19.59 (19.60)	1.93	4.77
[Ni(CDHPZ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]	Orange	NiC <sub>34</sub> H <sub>30</sub> N <sub>12</sub> O <sub>12</sub>	6.86 (6.84)	47.55 (47.63)	3.53 (3.52)	19.60 (19.60)	1.5	3.02
[Cu(CDHPZ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]	Brown Ash	CuC <sub>34</sub> H <sub>30</sub> N <sub>12</sub> O <sub>12</sub>	7.38 (7.37)	47.29 (47.36)	3.52 (3.50)	19.50 (19.49)	1.99	1.78

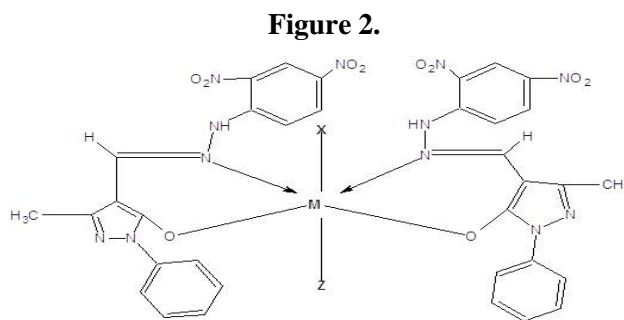
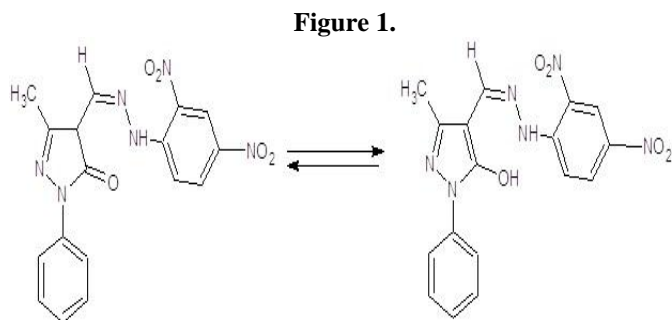
Where CDHPZ = 4-Carboxaldehyde-dinitrophenylhydrazone-1-phenyl-3-methyl-2-pyrazolin-5-one

**Table 2. Infrared Spectral DATA (cm<sup>-1</sup>) OF CDHPZ<sub>Z</sub> and its Metal Complexes**

[Mn(CDHPZ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]	[Co(CDHPZ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]	[Ni(CDHPZ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]	[Cu(CDHPZ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]	Assignment
-	-	-	-	$\nu_{\text{O-H}}$ (enolic)
3309 (s.vb)	3350 (w.br)	3300 (w.br)	3346 (w.br)	$\nu_{\text{O-H}}$ (Coordinated water)
3100 (m.br)	3100 (m.br)	3140 (m.br)	3100 (m.br)	Aryl $\nu_{\text{(C-H)}}$
2905 (w.br)	2905 (w.br)	2904 (w.br)	2910 (w.br)	Saturated $\nu_{\text{(C-H)}}$
1613 (s.s)	1615 (s.s)	1620 (s.s)	1625 (s.s)	$\nu_{\text{(C=N)}}$ (azomethine)
1584 (s.br)	1595 (s.br)	1584(s.br)	1595 (s.br)	$\nu_{\text{(C=N)}}$ (Pyrazolin)
1490 (s.s.)	1490 (s.s.)	1491 (s.s.)	1490 (s.s.)	Pyrazolin ring stretch
1451 (s.s)	1457 (s.s)	1457 (s.s)	1457 (s.s)	Phenyl ring $\nu_{\text{(C=C)}}$
1320 (s.s)	1327 (w.sh)	1304(w.sh)	1335(w.sh)	$\nu_{\text{NO}_2}$ (2,4-dinitrophenyl ring)
1310 (s.s)	1349 (s.s)	1321 (s.s)	1346 (s.s)	$\nu_{\text{(C-O)}}$ (enol)
-	-	-	-	$\delta_{\text{O-H}}$ (enol)
1063(w.sh)	1061 (w.sh)	1061(w.sh)	1076(w.sh)	Pyrazolin ring breathing
1007 (w.sh)	1007 (w.sh)	1005 (w.sh)	1005 (w.sh)	CH <sub>3</sub> rocking
984 (m.s)	960 (m.s)	986 (m.s)	980 (m.s)	C-C <sub>6</sub> H <sub>5</sub> stretch
913 (m.s)	904 (m.s)	916 (m.s)	905 (m.s)	C-CH <sub>3</sub> stretch
820 (m.s)	812(m.br)	814 (m.br)	810 (m.br)	$\nu_{\text{(O-H)}}$ (wagging mode of coordinated water)
508(m.vb)	510 (m.vb)	508 (m.vb)	511 (m.vb)	$\nu_{\text{(M-O)}}$
437 (m.br)	420 (m.br)	419 (m.br)	447 (m.br)	$\nu_{\text{(M-N)}}$

**Table 3. Antibacterial activity of the CDPHP<sub>Z</sub> (control – DMF)**

Compounds	<i>E-Coli</i>	<i>B-Subtilis</i>	<i>Saccharonyces Cerevisiae</i>	<i>Aspegillus niger</i>
[Mn(CDPHP <sub>Z</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]	+	++	-	++
[Co(CDPHP <sub>Z</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]	+	+	-	-
[Ni(CDPHP <sub>Z</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]	-	++	++	+++
[Cu(CDPHP <sub>Z</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]	++	+++	+	+++



Where Z=X= H<sub>2</sub>O M= Mn (II), Co (II), Ni (II) and Cu (II)

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