Synthesis, Characterization and Antibacterial Activity of Mn(II), Co(II), Ni(II) and Cu(II) Complexes of 4-Carboxaldehyde Phenylhydrazine-1-phenyl-3-methyl-2-pyrazolin-5-one


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Abstract: 4-Carboxaldehyde-1-phenyl-3-methyl-2-pyrazolin-5-one condensed with phenylhydrazine to form ligand (HL). These metal complexes are of type [ML₂(H₂O)₂] (M = Mn, Co, Ni and Cu). Elemental analysis, magnetic susceptibility, electrical conductance, electronic and infrared data suggest octahedral structure for the metal complexes. All the compounds were tested for their antibacterial activity. The result indicates that the growth of the tested organisms was inhibited by most of the compounds.

Keywords: Phenylhydrazone, Antibacterial activity, Synthesis, Complexes.

Introduction
In continuation of our earlier work¹, we report here some new transition metal complexes of ligand (HL) derived from 4-carboxaldehyde-1-phenyl-3-methyl-2-pyrazolin-5-one with phenylhydrazine².

Experimental
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 phenyl hydrazine in ethanol on water bath for 2-3 hours. The crude product was collected by filtration, and then washed several times with water. The phenylhydrazone CPHPz were then purified by recrystallization in ethanol. The following general procedure was used in the syntheses of all the 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 2 g of sodium acetate was added and than refluxed for 2 h 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 againsts Escherichia coli, Bacillus subtilis, Aspergillus niger and Saccharomyces cerevisiae, Elemental analysis of all the compound carried out on a “Perkin Elmer series II, 2400”. The FT-IR spectra of the compounds studied in the present work were recorded on a Fouier Transmition 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 conductance cell at room temperature. The magnetic susceptibilities at room temperature were measured by Gouy method\(^{3,4}\). Dimagnetic correction were made using Pascal constants\(^{5,6}\). Molecular weights were determined by Rast Camphor method. Metal were estimated gravimetrically\(^{7}\) and volumetrically\(^{8}\).

![Chemical structures](image)

**Figure 1.** 4-Carboxaldehyde-1-phenyl-3-methyl-2-pyrazolin-5-one with phenylhydrazine

**Results 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) suggest molecular formula [ML\(_2\) (H\(_2\)O)\(_2\)] 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 cm\(^{-1}\) and 25,600-18,000 cm\(^{-1}\). Considering an octahedral structure for these complexes, these bands may be assigned to the \(^6A_{lg} \rightarrow {^4}T_{lg} (G)\) and \(^6A_{lg} \rightarrow {^4}E_g, ^4A_{lg} (G)\) transitions respectively\(^{9,10}\).

Electronic spectra of Co(II) complexes show\(^{11}\) three bands in the regions, 9,330-8,390, 19,800-18, 500 and 29,000-25,000 cm\(^{-1}\). The first two bands may correspond to \(^4T_{lg} (F) \rightarrow {^4}T_{2g} (F) (\nu_1)\) and \(^4T_{lg}(F) \rightarrow {^4}T_{lg} (p) (\nu_3)\) transitions respectively. The latter highest energy band may be due to tetragonal distortion along the Z – axis.
<table>
<thead>
<tr>
<th>Complexes</th>
<th>Colour</th>
<th>Empirical formula</th>
<th>Found (Calculated) %</th>
<th>$\lambda_{\text{em}}$ in DMF</th>
<th>$\mu_{\text{eff}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Mn(CPHP$_2$)$_2$ (H$_2$O)$_2$] Brown</td>
<td>MnC$_{34}$</td>
<td>H$<em>{34}$N$</em>{8}$O$_{4}$</td>
<td>7.99 (8.15) 60.83 (60.62) 4.79 (5.08) 16.71 (16.63)</td>
<td>1.25</td>
<td>5.68</td>
</tr>
<tr>
<td>Co(CPHP$_2$)$_2$ (H$_2$O)$_2$ Orange</td>
<td>CoC$_{34}$</td>
<td>H$<em>{34}$N$</em>{8}$O$_{4}$</td>
<td>8.68 (8.69) 60.48 (60.26) 4.77 (5.05) 16.63 (16.53)</td>
<td>1.19</td>
<td>4.78</td>
</tr>
<tr>
<td>[Ni(CPHP$_2$)$_2$ (H$_2$O)$_2$] Brown</td>
<td>NiC$_{34}$</td>
<td>H$<em>{34}$N$</em>{8}$O$_{4}$</td>
<td>8.70 (8.66) 60.51 (60.28) 4.78 (5.05) 16.63 (16.54)</td>
<td>1.63</td>
<td>2.97</td>
</tr>
<tr>
<td>[Cu(CPHP$_2$)$_2$ (H$_2$O)$_2$] Ash</td>
<td>CuC$_{34}$</td>
<td>H$<em>{34}$N$</em>{8}$O$_{4}$</td>
<td>9.6 (9.31) 59.51 (59.85) 4.76 (5.02) 16.55 (16.42)</td>
<td>2.7</td>
<td>1.81</td>
</tr>
</tbody>
</table>

Where CPHP$_2$ = 4-Carboxaldehyde phenylhydrazone-1-phenyl-3-methyl-2-pyrazolin-5-one

The transition energy ratio $\nu_2/\nu_1$ is very close to the reported values required for an octahedral structure for all the complexes.$^{12,13}$ 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$^{14}$.

\[
\begin{align*}
\nu_1 & : {^3}A_{2g} \rightarrow {^3}T_{2g} & \text{11,000 – 8,000 cm}^{-1} \\
\nu_2 & : {^3}A_{2g} \rightarrow {^3}T_{1g} & \text{21,000 – 16,000 cm}^{-1} \\
\nu_3 & : {^3}A_{2g} \rightarrow {^3}T_{1g} \text{(p)} & \text{27,000 – 24,000 cm}^{-1}
\end{align*}
\]

The $\nu_2/\nu_1$ ratio is greater than the range required for an octahedral structure$^{14}$. 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 cm$^{-1}$. This band is resolved into two or three components, which presumably contain d - d transition$^{15}$. The much more intense band in all the complexes in the region 28,880-26,100 cm$^{-1}$, might be due to charge transfer$^{16}$. Absence of any band below 10,000 cm$^{-1}$, excludes the possibility of tetrahedral structure for the complexes$^{17}$.

The infrared spectra of all the ligand new $\nu_{\text{O-H}}$ band appears at the region 3550 - 2900 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. The ligands show a strong band due to $\delta_{\text{O-H}}$ in the region 1274 cm$^{-1}$. This band disappears 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 coordination$^{17}$.

The infrared spectra of all the ligand show strong absorption band in the region 1345-1315 cm$^{-1}$ suggesting structure-II for the ligands. On the coordination, this band is shifted toward higher frequency by 2-30 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 coordination$^{4}$.

The infrared spectra of all the ligand show a strong absorption band in the region 1620 and 1005 cm$^{-1}$, which may be due to $\nu_{\text{C=N}}$ of the azomethine group$^{17}$ and $\nu_{\text{N=N}}$ mode respectively. In the spectra of all the metal complexes $\nu_{\text{C=N}}$ (azomethine) shifts to lower frequency by 15-51 cm$^{-1}$ and $\nu_{\text{N=N}}$ to higher frequency by $\sim$10 cm$^{-1}$ suggesting involvement of azomethine nitrogen in coordination. 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.
The infrared spectra of all the ligand studied in the present work show strong band in the region 1615-1595 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\(^\text{18}\).

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 a complexes in the region 540 - 500 cm\(^{-1}\) and 470-420 cm\(^{-1}\), which may be assigned to \(\nu_{M-O}\) and \(\nu_{M-N}\) modes respectively\(^\text{19}\). 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 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 was active against bacteria and yeast. The result is shown in Table 2.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>E. coli</th>
<th>B. Subtilis</th>
<th>Saccharomyces Cerevisiae</th>
<th>Aspegillus niger</th>
</tr>
</thead>
<tbody>
<tr>
<td>CPHP(_Z)</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>[Mn(CPHP(_Z))(_2)(H(_2)O)(_2)]</td>
<td>-</td>
<td>++</td>
<td>+</td>
<td>++</td>
</tr>
<tr>
<td>[Co(CPHP(_Z))(_2)(H(_2)O)(_2)]</td>
<td>-</td>
<td>++</td>
<td>+</td>
<td>++</td>
</tr>
<tr>
<td>[Ni(CPHP(_Z))(_2)(H(_2)O)(_2)]</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>[Cu(CPHP(_Z))(_2)(H(_2)O)(_2)]</td>
<td>++</td>
<td>+</td>
<td>+</td>
<td>++</td>
</tr>
</tbody>
</table>

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