ELECTRONIC, IR AND THERMAL STUDIES ON BIOLOGICALLY ACTIVE COMPLEX OF Ni (II) WITH BENZIMIDAZOLE OXIMES

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ABSTRACT: The Electronic, IR and Thermal studies on biologically active complexes of Ni (II)-has been reported. The bands observed and discussed assuming the molecule under C\textsubscript{3} point group symmetry. The IR spectral studies of this compound have been discussed. The thermal study of complex compound has been calculated. The electronic study in nujol phase has been calculated.

Keywords: Electonic Spectra, IR, Thermal studies,EPR and Benzimidazole oxime.

INTRODUCTION:
Extensive studies of various carbonic anhydrases (1) and alkaline phosphatases (2) indicate the presence of a catalytic Zn\textsuperscript{2+} bound to three imidazole residues of enzyme histidines. In the carboxy peptidases (3) and in thermolysin (4), the critical Zn\textsuperscript{2+} is bound to two imidazoles and a carboxylate group of the enzyme. Inspite of the obvious interest such systems would have few chelating ligands using imidazole rings have been made so far, and none which combine three simple imidazole rings as models for the metal binding sites of carbonic anhydrase.

Holmes et.al (5) have investigated metal binding by 2, 2−bis (imidazole) (1) while Gruenwedel (6) has studied Zn\textsuperscript{2+} and Co\textsuperscript{2+} binding by the tetradentate ligands(2). An important study by Fruton (7) led to the synthesis and metal binding constants for bis \{4(5) −imidazolyl\} methane (3). Fruton’s synthesis from histidine is not adaptable for the preparation of related tris (imidazoles). Thompson et.al (8) has described some metal binding properties of a tris (benzimidazole) ligand system (4). Finally the tris (pyrazolyl) borohydride ligand (5) first reported by Trofimenko (9) but studied by Marks and Ibers (10). The X−ray studies (11) on carbonic anhydrase show that the three imidazole ligands have distorted tetrahedral coordination to the Zn\textsuperscript{2+}. Molecular models suggested that a similar geometry could be attained with a tris (imidazolyl) methane derivative.
Benzimidazole complexes of transition metals exhibit interesting spectral and magnetic properties. Oxime function located adjacent to another donor atom in an organic molecule, can act as a versatile chelating group and may make the molecule useful in the separation and estimation of metal ions. These considerations prompted us to synthesise new polydentate ligands containing both oxime and imidazole functions together. Here we discuss the synthesis and characteriz.
<table>
<thead>
<tr>
<th>No.</th>
<th>Formula</th>
<th>Color</th>
<th>% C</th>
<th>% H</th>
<th>% N</th>
<th>% O</th>
<th>% Cl</th>
<th>Molar Conductivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.</td>
<td>[Ni(C_{10}H_{10}N_{2}O)]Cl.3H_{2}O</td>
<td>Green</td>
<td>50.82(50.98)</td>
<td>4.90(5.09)</td>
<td>17.70(17.84)</td>
<td>12.30(12.47)</td>
<td>–</td>
<td>2.94</td>
</tr>
<tr>
<td>3.</td>
<td>[Ni(C_{15}H_{12}N_{3}O)]Cl.3H_{2}O</td>
<td>Greening yellow</td>
<td>45.03(45.20)</td>
<td>4.40(4.52)</td>
<td>10.40(10.54)</td>
<td>14.60(14.74)</td>
<td>8.72(8.91)</td>
<td>2.96</td>
</tr>
<tr>
<td>4.</td>
<td>[Ni(C_{15}H_{11}N_{3}O)].3H_{2}O</td>
<td>Yellowish green</td>
<td>49.60(49.76)</td>
<td>4.52(4.69)</td>
<td>11.50(11.61)</td>
<td>16.10(16.23)</td>
<td>–</td>
<td>3.10</td>
</tr>
</tbody>
</table>

**Electronic Spectra:**

The electronic spectra of Ni(II) complexes [Ni (C_{10}H_{10}N_{2}O)]Cl.2H_{2}O; [Ni(C_{15}H_{10}N_{2})].2H_{2}O; [Ni(C_{15}H_{12}N_{3}O)]Cl.3H_{2}O; [Ni(C_{15}H_{11}N_{3}O)].3H_{2}O showed three bands in the regions 25920−24692, 17391−16130 and 10638−10205 cm⁻¹. these are assigned to ν[^3]T₁g(P) ←[^3]A₂g; ν[^3]T₁g(F) ←[^3]A₂g] and ν[^3]T₂g ←[^3]A₂g] transitions respectively, expected for nickel(II) octahedral complexes. One of these the low energy band (ν₁) has been equated to 10Dq. The various spectral parameters have been calculated table-2. The ratio ν₂/ν₁ is close to that required for octahedral geometry[^24].

**Infrared Spectra:** A comparison of the infrared spectra of the ligands and their complexes indicated that the benzimidazole oximes were coordinated to the metal in the present complexes in five different ways (a − d)
In type (a) [Ni(C5H2N4O)2]Cl2.2H2O and [Ni(C5H2N4O)(NO3)2]2H2O; [Ni(C5H2N4O)2]SO4.2H2O complexes, ligand functions as a neutral bidentate ligand coordinating through the nitrogen of oxime function and the tertiary nitrogen of benzimidazole moiety. Here ν(C=N) (oxime group) is lowered by about 20 cm⁻¹ on coordination ν(C=N) (benzimidazole ring) is lowered from its position at 1570–1580 cm⁻¹ in ligands and is probably merged with ν(C=C) band at ~ 1540 cm⁻¹. A band at 3300–3460 cm⁻¹ is assigned to ν(OH) of coordinated water. A medium intensity band in the region 3250–3280 cm⁻¹ in the ligand is assigned to intramolecularly hydrogen bonded (OH) structure (I, II) of the following type.

\[
\begin{align*}
&\text{In type (a) [Ni(C5H2N4O)2]Cl2.2H2O and [Ni(C5H2N4O)(NO3)2]2H2O; [Ni(C5H2N4O)2]SO4.2H2O complexes, ligand functions as a neutral bidentate ligand coordinating through the nitrogen of oxime function and the tertiary nitrogen of benzimidazole moiety. Here } \nu(C=N) \text{ (oxime group) is lowered by about 20 cm}^{-1} \text{ on coordination } \nu(C=N) \text{ (benzimidazole ring) is lowered from its position at 1570–1580 cm}^{-1} \text{ in ligands and is probably merged with } \nu(C=C) \text{ band at ~ 1540 cm}^{-1}. \text{ A band at 3300–3460 cm}^{-1} \text{ is assigned to } \nu(OH) \text{ of coordinated water. A medium intensity band in the region 3250–3280 cm}^{-1} \text{ in the ligand is assigned to intramolecularly hydrogen bonded (OH) structure (I, II) of the following type.}
\end{align*}
\]

Similar type of hydrogen bonding is reported to be present in pyridine−2− Aldoxime\(^{26}\). The band due to \nu(OH) is expected in these complexes as no deprotonation occurs. In [Ni(C5H2N4O)Cl2.2H2O this band is observed at 3240 cm⁻¹ respectively. The shift of \nu(OH) to higher frequency might be consequence of breaking of the intramolecular hydrogen bonding with the chloride. The band due to pyrrolic NH appears at 3100–3120 cm⁻¹ in these complexes (table-3).

\[
\begin{align*}
&\text{In type [Ni(C5H2N4O)2]2H2O and [Ni(C5H2N4O)Cl3H2O the ligands function in a monobasic bidentate manner, } \nu(OH) \text{ of oxime function is observed at 3240 cm}^{-1} \text{ due to hydrogen bonding with chloride/tertiary nitrogen of benzimidazole moiety. } N(NH) \text{ disappears confirming deprotonation and coordination through the pyrrolic nitrogen } \nu(C=N) \text{ (imidazole) appears at the same frequency as in ligands.}
\end{align*}
\]

\[
\begin{align*}
&\text{In type [Ni(C5H2N4O)3]3H2O; complexes the ligands function as dibasic tridentate bridging ligands. Bands assignable to } \nu \text{ (OH) and } \nu \text{ (NH) disappear indicating deprotonation at these sites and replacement of protons by metal. The ligands coordinate to the metal through pyrrolic nitrogen and oxide nitrogen. Tertiary nitrogen of imidazole is free as suggested by the presence of a band at 1580 cm}^{-1}. \text{ EPR Spectra: EPR−spectra of the [Ni(C5H2N4O)3]Cl3H2O and [Ni(C5H2N4O)3]2H2O were recorded in polycrystalline samples and in DMF solution, both at room temperature (RT) and liquid nitrogen temperature (LNT). The EPR−parameters computed from spectra are indicative of octahedral or square planar geometry for the complexes.}
\end{align*}
\]

\[
\begin{align*}
&\text{Thermal Studies: [Ni(C5H2N4O)2]2H2O; and [Ni(C5H2N4O)Cl3H2O were examined complexes at high temperature underwent endothermic mass loss in the temperature ranges, 120–170; 160–180 and 150–170°C respectively. The mass losses (8.5%), 10.0% and 8.0% respectively) agree well with the loss of coordinated water (table-4).}
\end{align*}
\]
### Table-2: Electronic Spectral data and ligand field parameters of the complexes

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Complex</th>
<th>$\lambda_{\text{max}}$ (cm$^{-1}$)</th>
<th>Dq (cm$^{-1}$)</th>
<th>B (cm$^{-1}$)</th>
<th>$\beta$</th>
<th>$\nu_2/\nu_1$</th>
<th>LFSE (Kcal mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>[Ni(C$<em>{10}$H$</em>{11}$N$_3$O)Cl$_2$]2H$_2$O</td>
<td>10604</td>
<td>16130</td>
<td>24936</td>
<td>1060.4</td>
<td>663.7</td>
<td>0.637</td>
</tr>
<tr>
<td>2</td>
<td>[Ni(C$<em>{10}$H$</em>{10}$N$_3$O)$_2$]Cl.3H$_2$O</td>
<td>10416</td>
<td>17361</td>
<td>25000</td>
<td>1041.6</td>
<td>740.8</td>
<td>0.712</td>
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<tr>
<td>3</td>
<td>[Ni(C$<em>{15}$H$</em>{12}$N$_3$O)]Cl.3H$_2$O</td>
<td>10363</td>
<td>17391</td>
<td>24690</td>
<td>1036.7</td>
<td>732</td>
<td>0.702</td>
</tr>
<tr>
<td>4</td>
<td>[Ni(C$<em>{15}$H$</em>{11}$N$_3$O)].3H$_2$O</td>
<td>10204</td>
<td>1600</td>
<td>25316</td>
<td>1020.4</td>
<td>713.6</td>
<td>0.685</td>
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</tbody>
</table>

* Values in nujol phase are given in parentheses calculated value

### Table -3: Infrared Spectral Data (cm$^{-1}$) of complexes

<table>
<thead>
<tr>
<th>Compounds</th>
<th>ν(OH) water</th>
<th>ν(OH) oxime</th>
<th>ν(NH)</th>
<th>ν(C=N) oxime</th>
<th>ν(C=N imidazole)</th>
<th>ν(C=O)</th>
<th>ν(N−O)</th>
<th>ν(M−N)</th>
<th>ν(M−O)</th>
<th>ν(M−Cl)</th>
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<tr>
<td>Ligands</td>
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<tr>
<td>4−methyl−2−Acetylbenzimidazoleoxime (MACBZOXH$_2$)</td>
<td></td>
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<tr>
<td>4−methyl−2−benzoylbenzimidazoleoxime (MBZBZOXH$_2$)</td>
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<tr>
<td>Complexes</td>
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<tr>
<td>[Ni(C$<em>{10}$H$</em>{11}$N$_3$O)]Cl$_2$2H$_2$O</td>
<td>3460</td>
<td>3240</td>
<td>3190</td>
<td>1610</td>
<td>1550</td>
<td>1025</td>
<td>480</td>
<td>410</td>
<td>280</td>
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<tr>
<td>[Ni(C$<em>{10}$H$</em>{10}$N$_3$O)$_2$.2H$_2$O]</td>
<td>3360</td>
<td>3270</td>
<td></td>
<td>1600</td>
<td>1575</td>
<td>1535</td>
<td>975</td>
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<tr>
<td>[Ni(C$<em>{15}$H$</em>{12}$N$_3$O)]Cl.3H$_2$O</td>
<td>3400</td>
<td>3250</td>
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<td>1605</td>
<td>1580</td>
<td>1560</td>
<td>1020</td>
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<tr>
<td>[Ni(C$<em>{15}$H$</em>{11}$N$_3$O)].3H$_2$O</td>
<td>3450</td>
<td></td>
<td></td>
<td>1610</td>
<td>1580</td>
<td>1540</td>
<td>1000</td>
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</table>

### Table -4: Thermal analysis data on Ni (II) complex

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Complexes</th>
<th>Decomposition Temperature °C</th>
<th>Decomposition Product</th>
<th>Weight Loss (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Initial</td>
<td>Final</td>
<td>Found</td>
</tr>
<tr>
<td>1</td>
<td>[Ni(C$<em>{10}$H$</em>{10}$N$_3$O)$_2$.2H$_2$O]</td>
<td>320</td>
<td>300</td>
<td>[Ni(C$<em>{10}$H$</em>{10}$N$_3$O)$_2$]</td>
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<tr>
<td></td>
<td></td>
<td>310</td>
<td>440</td>
<td>[NiO]</td>
</tr>
</tbody>
</table>
Fig. 1: IR SPECTRA OF ORGANIC COMPOUNDS
(i) C$_{10}$H$_{13}$N$_{3}$O (ii) C$_{15}$H$_{13}$N$_{3}$O

Fig. 2: IR SPECTRA OF COMPLEXES
(i) [Ni (C$_{10}$H$_{13}$N$_{3}$O)]Cl.2H$_{2}$O (ii) [Ni (C$_{10}$H$_{13}$N$_{3}$O)$_{2}$]. 2H$_{2}$O (iii) [Ni (C$_{15}$H$_{13}$N$_{3}$O) Cl.3H$_{2}$O]
REFERENCES

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