NUCLEAR MAGNETIC RESONANCE (¹HNMR) STUDY OF CHROMIUM (III) SALICYLATE AND BENZOATE COMPLEXES

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ABSTRACT
Chromium (III) salicylate and Chromium (III) benzoate complexes were prepared using Chromium trioxide and different molar concentrations of salicylic and benzoic acid. Tertiary amyl alcohol and ethanol are used as a solvent. ¹HNMR spectra of solid samples were recorded. ¹HNMR spectra of metal complexes suggest that deprotonation of –COOH group took place, and the complex formed was not through the –OH of the acid. It confirms the coordination of the ligand to the metal ion through the carboxylic oxygen atom.

Keywords: Chromium Metal Complexes, Salicylic Acid, Benzoic Acid, ¹HNMR

INTRODUCTION
Nuclear Magnetic resonance is a powerful spectroscopic technique for investigating molecular structure and dynamics. It involves the reorientation of nuclear spins concerning an applied static magnetic field. NMR also provides crucial insight into the nature of the coordination sphere of the metal, stereochemistry and metal-ligand bonding. ¹ This spectroscopy applies to organometallic clusters, in studying the movement of hydrides and carbonyls around the metal core and transition metal complexes with organic ligands. It is also well reported that Hexavalent chromium is a powerful oxidant and finds a number of applications in organic synthesis. ²–⁶ Thus it was thought to prepare Chromium (III) salicylate and Chromium (III) benzoate complexes using chromium (VI) oxide and tertiary amyl alcohol as a solvent. ¹HNMR spectra have been studied and the results are discussed in this research paper.

EXPERIMENTAL
Preparation of Complexes
Chromium trioxide solution was prepared by dissolving in tertiary amyl alcohol. This solution was mixed with ethanolic solution of salicylic and benzoic acid in different molar ratios. The resulting solution was left standing in a closed flask at room temperature. After 24 hrs, precipitation began to separate from the solution. The process continued for 5 days, after which time no further precipitation was observed. The stable suspension was filtered, and the solid was washed with ethanol and TAA and dried in air.

Characterization of Samples by ¹HNMR Spectrometry
The ¹HNMR spectra of complexes were recorded on Bruker DRX-300 instruments in DMSO using Tetramethylsilane as an internal standard at Sophisticated Analytical Instrument Facility, Central Drug Research Institute, Lucknow, India.

Table-1: Details of Samples and their Identification

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>CrO₃ : Organic acid(Salicylic/Benzoic acid) : Solvent (Molar Ratio)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr/H₃sal/1</td>
<td>CrO₃ : Salicylic acid : Tertiary amyl alcohol (1:1)</td>
</tr>
<tr>
<td>Cr/H₃sal/2</td>
<td>CrO₃ : Salicylic acid : Tertiary amyl alcohol (1:2)</td>
</tr>
<tr>
<td>Cr/Hben/1</td>
<td>CrO₃ : Benzoic acid : Tertiary amyl alcohol (1:1)</td>
</tr>
<tr>
<td>Cr/Hben/2</td>
<td>CrO₃ : Benzoic acid : Tertiary amyl alcohol (1:2)</td>
</tr>
</tbody>
</table>
RESULTS AND DISCUSSION

The NMR resonance and their assignments are given in Table-2. Proton resonance spectral data of complexes are shown in Fig.-1 to Fig.-4.

<table>
<thead>
<tr>
<th>Complexes</th>
<th>Chemical Shift</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr/Hsal/1</td>
<td>7.76, 7.40, 6.84, 3.97, 3.40, 2.50, 1.36, 1.05, 0.82</td>
<td>7.76-6.84 ((4H,ArH), 3.97 (-OH,Ar) 3.40 (-OH, ethanol), 2.56-2.50 (Protio-solvent component), 1.36 (2H, -CH₃), 1.05 (-OH of complex) 0.82 (3H,-CH₃)</td>
</tr>
<tr>
<td>Cr/Hsal/2</td>
<td>4.00, 3.37, 3.31, 3.24, 2.56, 2.50, 1.36, 1.34, 1.23, 1.11, 1.04, 0.84, 0.82, 0.79</td>
<td>4.00 (-OH, Ar), 3.37-3.24 (-OH, ethanol), 2.56-2.50 (Protio-solvent component), 1.39-1.31 (2H, -CH₃), 1.23 (-OH of complex), 0.84-0.79 (3H, -CH₃)</td>
</tr>
<tr>
<td>Cr/Hben/1</td>
<td>7.94,6.86,4.00,3.31,3.25,3.18,3.16,2.50,2.27,1.39,1.34,1.31,1.23,1.10,0.94,0.84,0.82,0.79</td>
<td>6.86-7.94 (ArH), 3.16-3.31 (-OH of ethanol), 2.27-2.50 (Protio-solvent component), 1.31-1.39 (2H,-CH₃) 1.23 (-OH of complex), 0.79-0.84 (3H, -CH₃)</td>
</tr>
<tr>
<td>Cr/Hben/2</td>
<td>7.94, 7.60, 7.49, 4.00, 3.33, 2.49, 1.34, 1.23, 1.04, 0.82</td>
<td>7.49-7.94 (4H,ArH), 3.33 (-OH of ethanol), 2.49 (Protio-solvent component), 1.34 (-OH, ethanol), 1.04-1.23 (2H,-CH₃), 0.82 (3H, -CH₃)</td>
</tr>
</tbody>
</table>
Results show that the peaks of protons belonging to different groups were very broad and could not be distinguished. The $^1$HNMR spectra of Chromium (III) salicylate and Chromium (III) benzoate complexes slightly changed compared to those of the corresponding ligand. The aromatic ring protons of complex Cr/H$_2$sal/1 show a peak at 6.8-7.7 ppm while the aromatic ring protons of complexes Cr/Hben/1 and Cr/Hben/2 show a peak at 6.86-8.02 ppm. Comparison of these spectrums with the spectrum of the free ligand confirmed a downfield shift due to coordination.

The $^1$H NMR spectrum of the complex Cr/H$_2$sal/1 showed resonances at 0.82, 1.36 and 3.40 ppm, which may be for the presence of methyl, methylene and -OH protons of ethanol molecule, respectively. Similarly, the $^1$H NMR spectrum of the complex Cr/H$_2$sal/2 showed resonances at 0.84-0.79, 1.39-1.31 and 3.37-3.24 ppm, which may be for the presence of methyl, methylene and -OH protons of ethanol.
molecule, respectively. The complex also showed resonances at 1.04 and 1.11 ppm, which may be due to the protons of the tertiary amyl group. The $^1$H NMR spectrum of the complex Cr/Hben/1 showed resonances at 0.79-0.84, 1.31-1.39 and 3.16-3.31 ppm, which may be for the presence of methyl, methylene and -OH protons, respectively. The peaks at 0.99-1.10 ppm may represent the methyl and methylene protons of amyl group. Similarly, the $^1$H NMR spectrum of the complex Cr/Hben/2 showed resonance at 3.332 and 0.821-1.347 ppm, which may be for the presence of methyl and methylene protons, respectively. All the complexes show resonances at 2.27-2.72 ppm, which may be for the presence of protio-solvent component. The $^1$H NMR spectrum of the complexes absence of signals due to –OH proton of Carboxylic group suggests the deprotonation of the carboxylic group of the ligand during complex formation. It may be due to the coordination of the ligand to the metal ion through carboxylic oxygen atom.

CONCLUSION

It may be concluded that: - $^1$HNMR spectrum of Chromium (III) salicylate and Chromium (III) benzoate complexes showed that deprotonation of –COOH group took place, and the complex formed was not through the –OH of the acid. It confirms the coordination of the ligand to the metal ion through the carboxylic oxygen atom.

REFERENCES