Mixed Ligand Complexes of Alkali Metal Salts of Some Organic Acids with O-Hydroxyacetophenone Phenylhydrazone –2, 4 – Dinitrophenyl Hydrazone

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Abstract: In continuation to our project for exploring the mechanism of selective absorption of alkali metals by plants as well as the possible role of alkali metals cations in plant metabolism Chemistry of alkali metals would facilitate fuller understanding of the mechanism. The study of the Coordinator Chemistry of these metals has been undertaken.Our aim has been to synthesize new alkali metals complexes and to identify the various structural features in the ligands, which enhance their selectivity for complex formation with alkali metals icons.

Keywords: O-hydroxyacetophenone phenylhydrazone, -hydroxyacetophenone – 2 , 4 – dinitrophenyl hydrazine salicylaldehyde, anthranilic acid, Picolinic acid and Quinaldinic acid

1. Introduction

In previous chapters, we have described the preparation of a large number of mixed ligand alkali complexes involving potential chelating ligand, having oxygen and nitrogen as the donor atoms.

In both O-hydroxyacetophenone hydrazone (OHAHz) and O-hydroxyacetophenone phenylhydrazone (OHAPHz), the donors are the nitrogen atoms of the hydrazone moiety and the oxygen atom of – OH moiety. Both the types of hydrazones formed mixed ligand complexes of the typeML.HL’, where M = Li, Na or K; L = deprotonated organic acid and HL’= O-hydroxyacetophenone hydrazine or O-hydroxyacetophenone phenylhydrazone.

It has been observed that the chelating ability of O-hydroxyacetophenone hydrazine is greater than that of O-hydroxyacetophenone phenylhydrazone, suggesting thereby that substituted hydrazones become more selective in their behaviour towards alkali metal cations. We now extend our investigation to study the possible complex formation by alkali metals with the ligand O-hydroxyacetophenone –2, 4 - dinitrophenyl hydrazine, hereafter abbreviated as OHA –2, 4 – DNPz.

Our usual method of preparing these complexes was to take equimolar proportion of the alkali metal salt (ML) and the title ligand O-hydroxyacetophenone – 2, 4 - dinitrophenyl hydrazine (HL’) in absolute ethanol in a conical flask and to reflux the contents for four to six hours with continuous stirring. A clear solution was obtained. It was concentrated and cooled, when adduct came apart. It was filtered, washed with absolute ethanol and then dried in an electric oven at 80°c. Adducts did not separated in case of potassium oxinate and potassium 1 – nitroso –2 – naptholate.

Table 6.1 lists the mixed ligand complexes of O-hydroxyacetophenone – 2, 4 - dinitrophenyl hydrazine which we have obtained.

Table 6.1: Mixed Ligand Complexes of O-Hydroxyacetophenone –2, 4 - dinitrophenylhydrazine

2. Physical Properties

All the complexes of O-hydroxyacetophenone – 2, 4 - dinitrophenyl hydrazine with alkali metal salts are characteristically coloured. They are stable in air under dry conditions for reasonable long periods of time. They are stored in corked sample tubes over anhydrous calcium
chloride in a desiccator. They are hygroscopic in nature. They are soluble in most polar solvents, but are insoluble in non-polar solvents. The additional ligand molecule is not removed by benzene or ether. However, studies in solution and measurements of the common solvents in which they dissolve. Also the solvents used, e.g. ethanol, acetone and N – methyl – 2 – pyrrolidine can not be regarded as inert, since they may coordinate to the metal or interact with the ligand by hydrogen bonding.

The complexes are unstable in moist air, in the presence of which they appear to decompose giving brown solids of indeterminate composition. The order of stability is Li>Na>K.

From the table – 6.2, it is apparent that these complexes undergo transformation at a temperature higher than the melting point of the ligand, indicating thereby their greater thermal stability.

<table>
<thead>
<tr>
<th>Table 6.2: Some physical properties of OHADNPz and its complexes</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Compound</strong></td>
</tr>
<tr>
<td>OHADNPz</td>
</tr>
<tr>
<td>Liacac. OHADNPz</td>
</tr>
<tr>
<td>Naacac. OHADNPz</td>
</tr>
<tr>
<td>Kacac. OHADNPz</td>
</tr>
<tr>
<td>LiSalH. OHADNPz</td>
</tr>
<tr>
<td>NaSalH. OHADNPz</td>
</tr>
<tr>
<td>KSalH. OHADNPz</td>
</tr>
<tr>
<td>LiAnc. OHADNPz</td>
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<td>KAnc. OHADNPz</td>
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<td>LiPicA. OHADNPz</td>
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<td>NaPicA. OHADNPz</td>
</tr>
<tr>
<td>KPicA. OHADNPz</td>
</tr>
<tr>
<td>LiQinA. OHADNPz</td>
</tr>
<tr>
<td>NaQinA. OHADNPz</td>
</tr>
<tr>
<td>KQinA. OHADNPz</td>
</tr>
</tbody>
</table>
* Molar Conductivity (ohm -1 cm2 mol-1) of 10-3 M solution in DMF.

3. Infrared Spectra

Infrared measurements for the ligands, their alkali metal salts and the complexes were made between 4000-650 cm-1 in Nujol mulls. Pertinent IR data for these compounds are shown in Table – 6.3.

The absorption bands of our principal interest in the IR spectra of Q-hydroxyacetophenone – 2, 4 - dinitrophenylhydrazone are 3360,3255,1605,1255 and 905 cm-1. The moderately strong bands at 3255 cm-1 in the spectra of the ligands may be attributed to stretching antisymmetric and symmetric – NH vibrations respectively. In the IR spectra of the complexes , these band exhibit a considerable downward . While the ~ 3360 cm-1 band is observed at about 3200 cm-1, the v symmetric NH band is observed at 3160 cm-1.

The 905 cm-1 band, most probably due to νN-H vibrations, is observed in the complexes as split bands at 945,940 and 870 cm-2 as in complexes of alkali metal salts of organic acids with Q-Hydroxyacetophenone - hydrazone and Q- Hydroxyacetophenone phenylhydrazone . The 605 cm-1 bands, most probably owing to νC=N vibrations in the molecules of the ligand, has undergone a downward shift to an extent of 10 – 15 cm-1. These observations suggest that the coordination of ligands with alkali metals has taken place through the nitrogen atom of the hydrazone moiety.

The absorption band of 1255 cm-1 has been ascribed to the stretching CO (Phenolic) vibration in the ligand molecules. In the complexes, this band has undergone an upward shift to an extent of 1520 cm-1, indicating strong chelation owing to the intrinsicality of oxygen atom of the – OH group of the ligand.

In addition to these bands, a new broad band of weak to medium intensity in the region 2300 – 1950 cm-1 is observed in all the complexes. No such bands are observed in the spectra of either the alkali metal salts of the ligand or in the molecules of the ligand OHADNPz. This band could be assigned to O – H ...... O/N ...... H – O absorption. This may be one of the dominant factors stabilising these complexes.

4. Conductivities

Molar conductivities were measured in DMF at 250°C at a concentration of 10-3 M. A value of ~ 35 – 40 ohm-1 cm2 mole-1 appears characteristic of a 1:1 electrolyte16, whereas ideally moral conductivity of a neutral complex should be zero. From the result (Table 6.2), it is observed that molar conductivities of none of the complexes approach either ideal or 1:1 electrolyte. However, significantly low values of their molar conductivities suggest them to be non – electrolytes.

5. Probable Structure

On the basis of element analyses, the general molecular formula of these complexes comes out to be MLHL’ where M=Li, Na or K; L=deprotonated O – nitrophenol,1 – nitroso – 2 – naphthol, 8 – Hydroxyquinoline, 2 – hydroxyl – 3 – naphthoic acid and Salicylic Acid; HL’= Q- hydroxyacetophenone -2, 4 – dinitrophenyl hydrazone. The Infrared spectra of these complexes suggest the coordination of alkali metals with Q-hydroxyacetophenone -2, 4 – dinitrophenylhydrazone through oxygen atom of the hydroxyl group as well as the nitrogen atom of the hydrazone moiety. The infrared spectra of these complexes indicate the presence of hydrazone bonding in them. Keeping in view the fact that the six member chelate rings are most stable and that the ligand Q-hydroxyacetophenone - 2, 4 – dinitrophenylhydrazone behaves as a bidentate ligands.
The following structure may be suggested for these complexes.

**Figure 6.2**

### Table 6.3: I.R. Spectral data for the ligand OHADNPz and its alkali metal complexes

<table>
<thead>
<tr>
<th>Compound</th>
<th>Vibrant IR bands (cm⁻¹)</th>
<th>ν(ester)</th>
<th>ν(amide)</th>
<th>ν(carboxyl)</th>
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<tr>
<td>OHADNPz</td>
<td>3300 3190 1670 1555 985</td>
<td>1770</td>
<td>3250</td>
<td>1660</td>
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<tr>
<td>Liacac.OHADNPz</td>
<td>3300 3190 1670 1555 985</td>
<td>1770</td>
<td>3250</td>
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</tr>
<tr>
<td>Naacac.OHADNPz</td>
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<td>1770</td>
<td>3250</td>
<td>1660</td>
</tr>
<tr>
<td>Kacac.OHADNPz</td>
<td>3300 3190 1670 1555 985</td>
<td>1770</td>
<td>3250</td>
<td>1660</td>
</tr>
<tr>
<td>LiSal.OHADNPz</td>
<td>3205 3134 1670 1555 985</td>
<td>1770</td>
<td>3250</td>
<td>1660</td>
</tr>
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<td>3250</td>
<td>1660</td>
</tr>
</tbody>
</table>

### 6. Experimental

**Preparation of the Ligand O-Hydroxyacetophenone 2,4 – dintrophenylhydrazone**

The title ligand O-Hydroxyacetophenone 2,4 – dintrophenylhydrazone, was prepared as described by Vishnoi.

In a 250ml conical flask, 4gm. of 2,4 dintrophenylhydrazone was taken. 10ml absolute ethanol was added to it, following by 1ml conc. H₂SO₄. The contents were shaken and then heated to dissolve any solid. To, the warm solution, 10ml O-Hydroxyacetophenone was added. The contents were reshenaken and cooled, when red crystalline solid O-Hydroxyacetophenone 2,4 – dintrophenylhydrazone appeared as crystals. The crystals were filtered, washed with cold water, recrystallized from alcohol and then dried in an electric oven at 80°C.

Its authenticity was established by elemental analyses and IR spectra. Red crystallized sample, obtained by us, has the melting point 250°C.

Results of its elemental analyses are as follows:

- Found: C, 53.25; H, 3.80; N, 17.58%
- C₁₂H₁₂N₂O₄ requires: C, 53.16; H, 3.79; N, 17.72%

**Adducts of O-Hydroxyacetophenone 2,4 – dintrophenylhydrazone**

1) **Adducts with alkali metal salts of acetylacetone with O-Hydroxyacetophenone 2,4 – dintrophenylhydrazone**

Alkali metal salt of acetylacetone with O-Hydroxyacetophenone - 2,4 – dintrophenylhydrazone were taken in a 30ml conical flask. About 30ml of absolute ethanol was added to it. The contents were refluxed on an electrically maintained hot plate, while constantly stirring the solution with the help of a magnetic stirrer. It was refluxed for about 6 hours. A clear solution was obtained. On cooling, coloured crystals came apart. It was filtered, washed with the solvent and then dried in an electric oven at 120°C.

- (a) Liacac.OHADNPz
  - Found: C, 53.84; H, 4.54; N, 13.27%
  - C₂₁H₂₁N₂O₄Li requires: C, 54.03; H, 4.50; N, 13.27%
- (b) Naacac.OHADNPz
  - Found: C, 52.24; H, 4.30; Na, 12.70; Na, 5.25%
  - C₂₁H₂₁N₂O₄Na requires: C, 52.05; H, 4.34; N, 12.78; Na, 5.25%
- (c) Kacac.OHADNPz
  - Found: C, 50.37; H, 4.12; Na, 12.25; K, 8.50%
  - C₂₁H₂₁N₂O₄K requires: C, 50.22; H, 4.18; Na, 12.33; K, 8.59%

2) **Adducts with alkali metal salts of salicylaldehyde with O-Hydroxyacetophenone 2,4 – dintrophenylhydrazone**

Alkali metal salt of salicylaldehyde and O-Hydroxyacetophenone - 2,4 – dintrophenylhydrazone were taken in a conical flask. About 30ml of absolute ethanol was added to it. The contents were refluxed on an electrically maintained hot plate, while constantly stirring the solution with the help of a magnetic stirrer. It was refluxed for about 6 hours. A clear solution was obtained. On cooling, coloured crystals came apart. It was filtered, washed with the solvent and then dried in an electric oven at 120°C.

- (a) LiSal.OHADNPz
  - Found: C, 56.95; H, 3.72; Na, 12.24%
  - C₂₁H₂₁N₂O₄Li requires: C, 56.76; H, 3.83; N, 12.61%
- (b) NaSal.OHADNPz
  - Found: C, 54.84; H, 3.54; Na, 12.00; Na, 5.0%
  - C₂₁H₂₁N₂O₄Na requires: C, 54.78; H, 3.69; N, 12.17; Na, 5.0%
- (c) KSal.OHADNPz
  - Found: C, 52.08; H, 3.45; K, 11.65; K, 8.00%
  - C₂₁H₂₁N₂O₄K requires: C, 52.94; H, 3.57; N, 11.76; K, 8.19%

3) **Adducts with alkali metal salts of anthranilic acid with O-Hydroxyacetophenone 2,4 – dintrophenylhydrazone**

Equimolar proportions of alkali metal anthranilate and O-Hydroxyacetophenone - 2,4 – dintrophenylhydrazone were taken in a 150ml conical flask. About 30ml of absolute ethanol was added to it. The contents were refluxed on an electrically maintained hot plate, while constantly stirring the solution with the help of a magnetic stirrer. It was refluxed for about 6 hours. A clear solution was obtained. On cooling, coloured crystals came apart. It was filtered,
washed with the solvent and then dried in an electric oven at 120°C.

(a) LiAnc.OHADNPz
Found: C, 53.98; H, 3.65; N, 15.78%
C_{25}H_{16}N_{2}O_{2}Li requires: C, 53.98; H, 3.59; N, 15.73%

(b) NaAnc.OHADNPz
Found: C, 53.11; H, 3.52; N, 15.23; Na, 5.00%
C_{25}H_{16}N_{2}O_{2}Na requires: C, 52.06; H, 3.47; N, 15.18; Na, 4.99%

(c) KAnc.OHADNPz
Found: C, 50.36; H, 3.40; N, 14.70; K, 8.25%
C_{25}H_{16}N_{2}O_{2}K requires: C, 50.31; H, 3.35; N, 14.67; K, 8.18%

5) Adducts with alkali metal salts of quinaldinic acid with O-hydroxyacetophenone - 2,4 – dintrophenylhydrazone
Equimolar proportions of alkali metal salt of quinaldinic acid and O-Hydroxyacetophenone - 2,4 – dintrophenylhydrazone were taken in a conical flask. About 30ml of absolute ethanol was added to it. The contents were refluxed. A clear solution was obtained. It was refluxed for about 6 hours. A clear solution was obtained. It was concentrated and dried in an electric oven at 120°C.

(a) LiQuinA.OHADNPz
Found: C, 58.23; H, 3.69; N, 14.09%
C_{24}H_{16}N_{2}O_{2}Li requires: C, 58.18; H, 3.64; N, 14.14%

(b) NaQuinA.OHADNPz
Found: C, 56.40; H, 3.57; N, 13.62; Na, 4.45%
C_{24}H_{16}N_{2}O_{2}Na requires: C, 56.36; H, 3.52; N, 13.69; Na, 4.50%

(c) KQuinA.OHADNPz
Found: C, 54.70; H, 3.45; N, 13.23; K, 7.35%

References

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