

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.

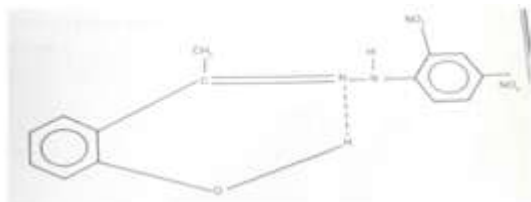
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1. Introduction

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 (OHAPHz) 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 type ML.HL', where M = Li, Na or K ; L = deprotonated organic acid and HL' = O-hydroxyacetophenone hydrazone or O-hydroxyacetophenone phenylhydrazone.

It has been observed that the chelating ability of O-hydroxyacetophenone hydrazone 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 hydrazone, 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 hydrazone (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^oc. Adducts did not separated in case of potassium oxinate and potassium 1 – nitroso – 2 – naphtholate.

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

Mixed Ligand Complexes of O-Hydroxyacetophenone – 2, 4 - dinitrophenylhydrazone

The three corners of the triangle shown in the above table represent the alkali metals Li, Na and K. Where the symbol appears, the complex ML.HL'. Could be obtained. Crosses indicate that the corresponding complexes could not be obtained.

2. Physical Properties

All the complexes of O-hydroxyacetophenone – 2, 4 - dinitrophenyl hydrazone 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 – pyrrolidone 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 6.2: Some physical properties of OHADNPz and its complexes

Compound	Colour	Melting Point / decomposition (°c)	Conductivity*
OHADNPz	Red	250m	-
Liaca. OHADNPz	Cream colour	280d	1.5
Naaca. OHADNPz	Cream colour	275d	2.0
Kaca. OHADNPz	Cream colour	265d	2.0
LiSalH. OHADNPz	Grey colour	268d	1.5
NaSalH. OHADNPz	Grey colour	265d	2.5
KsalH. OHADNPz	Grey colour	260d	6.0
LiAnc. OHADNPz	Brown colour	274d	2.5
NaAnc. OHADNPz	Brown colour	272d	2.8
KAnc. OHADNPz	Brown colour	269d	4.5
LiPicA. OHADNPz	Cream colour	276d	2.0
NaPicA. OHADNPz	Cream colour	270d	2.5
KPicA. OHADNPz	Cream colour	268d	5.5
LiQinA. OHADNPz	Cream colour	>300	1.5
NaQinA. OHADNPz	Cream colour	>300	2.5
KQinA. OHADNPz	Cream colour	>300	5.0

* Molar Conductivity ($\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$) of 10^{-3} M solution in DMF.

Infrared Spectra

Infrared measurements for the ligands, their alkali metal salts and the complexes were made between $4000\text{-}650 \text{ cm}^{-1}$ 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 O-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 $\sim 3360 \text{ cm}^{-1}$ band is observed at about 3200 cm^{-1} , the vsymmetric NH band is observed at 3160 cm^{-1} .

The 905 cm^{-1} band, most probably due to $\nu\text{N-H}$ vibrations, is observed in the complexes as aplit bands at $945, 940$ and 870 cm^{-1} as in complexes of alkali metal salts of organic acids with O-Hydroxyacetophenone hydrazone and O-Hydroxyacetophenone phenylhydrazone . The 605 cm^{-1} bands, most probably owing to $\nu\text{C=N}$ vibrations in the molecules of the ligand, has undergone a downward shift to an extent of $10 - 15 \text{ cm}^{-1}$. 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 $2300 - 1950 \text{ cm}^{-1}$ 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.

Conductivities:

Molar conductivities were measured in DMF at 25°c at a concentration of 10^{-3} M. A value of $\sim 35 - 40 \text{ ohm}^{-1} \text{Cm}^2 \text{mole}^{-1}$ 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.

Probable Structure:

On the basis of element analyses, the general molecular formula of these complexes comes out to be $\text{ML.HL}'$ where $\text{M}=\text{Li, Na or K}$; $\text{L}=\text{deprotonated O - nitrophenol, 1 - nitroso - 2 - naphthol, 8 - Hydroxyquinoline, 2 - hydroxyl - 3 - naphthoic acid and Salicylic Acid}$; $\text{HL}'=\text{O - hydroxyacetophenone -2, 4 - dinitrophenyl hydrazone}$. The Infrared spectra of these complexes suggest the coordination of alkali metals with O-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 O-hydroxyacetophenone -2, 4 - dinitrophenylhydrazone behaves as a bidentate ligands.

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

Compound	Pertinent IR bands (in cm ⁻¹)				
	Vasy NH	Vsym NH	VC=N	VCO (Phenolic)	VN=N
OHADNPz	3360	3255	1605	1255	905
LiAcac. OHADNPz	3200	3160	1595	1270	940, 935, 875
Naacac. OHADNPz	3200	3160	1595	1270	945, 940, 870
Kacac. OHADNPz	3200	3160	1590	1270	945, 940, 870
LiSalH. OHADNPz	3205	3164	1595	1265	942, 937, 865
NaSalH. OHADNPz	3205	3163	1590	1270	945, 940, 870
KsalH. OHADNPz	3205	3162	1590	1270	945, 940, 870
LiAsc. OHADNPz	3200	3160	1590	1270	945, 940, 870
NaAsc. OHADNPz	3200	3164	1590	1270	945, 940, 870
Kasc. OHADNPz	3200	3164	1590	1270	945, 940, 870
LiPicA. OHADNPz	3200	3167	1595	1265	945, 940, 870
NaPicA. OHADNPz	3205	3165	1593	1270	945, 940, 870
KpicA. OHADNPz	3205	3160	1592	1270	945, 940, 870
LiQinA. OHADNPz	3205	3160	1590	1265	945, 940, 870
NaQinA. OHADNPz	3210	3168	1590	1265	942, 937, 865
KqinA. OHADNPz	3210	3167	1590	1265	942, 937, 865

The following structure may be suggested for these complexes.

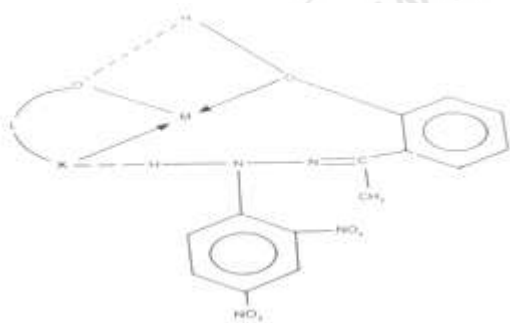


Figure 6.2

3. Experimental

Preparation of the Ligand O-Hydroxyacetophenone 2,4-dinitrophenylhydrazone

The title ligand O-Hydroxyacetophenone 2,4-dinitrophenylhydrazone, was prepared as described by vishnoi.¹¹⁷

In a 250ml conical flask, 4gm. of 2,4-dinitrophenylhydrazone 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 reshaken and cooled, when red crystalline solid O-Hydroxyacetophenone 2,4-dinitrophenylhydrazone appeared as crystals. The crystals were filtered, washed with cold water, recrystallized from alcohol and then dried in an electric oven at 80^oc. Its authenticity was established by elemental analyses and IR spectra. Red crystallized sample, obtained by us, has the melting point 250^oc.

Results of its elemental analyses are as follows:
 Found: C, 53.25 ; H, 3.80 ; N, 17.58%
 C₁₄H₁₂N₄O₅ requires : C, 53.16 ; H, 3.79 ; N, 17.72%

Adducts of O-Hydroxyacetophenone - 2,4-dinitrophenylhydrazone

1. Adducts with alkali metal salts of acetylacetone with O-Hydroxyacetophenone - 2,4-dinitrophenylhydrazone

Alkali metal salt of acetylacetone with O-Hydroxyacetophenone - 2,4-dinitrophenylhydrazone 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^oc.

(a) LiAcac.OHADNPz

Found : C, 53.84 ; H, 4.54; N, 13.27%
 C₁₉H₁₉N₄O₇Li requires
 : C, 54.03 ; H, 4.50 ; N, 13.27%

(b) Naacac. OHADNPz

Found : C, 52.24 ; H, 4.30; N, 12.70 ; Na, 5.25%
 C₁₉H₁₉N₄O₇Na requires
 : C, 52.05 ; H, 4.34; N, 12.78 ; Na, 5.25%

(c) Kacac. OHADNPz

Found : C, 50.37 ; H, 4.12; N, 12.25 ; K, 8.50%
 C₁₉H₁₉N₄O₇K requires
 : C, 50.22 ; H, 4.18; N, 12.33 ; K, 8.59%

2. Adducts with alkali metal salts of salicylaldehyde with O-Hydroxyacetophenone - 2,4-dinitrophenylhydrazone

Alkali metal salt of salicylaldehyde and O-Hydroxyacetophenone - 2,4-dinitrophenylhydrazone 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^oc.

(a) LiSalH.OHADNPz

Found : C, 56.95 ; H, 3.72; N, 12.24%
 C₂₁H₁₇N₄O₇Li requires
 : C, 56.76 ; H, 3.83; N, 12.61%

(b) NaSalH. OHADNPz

Found : C, 54.84 ; H, 3.54; N, 12.00 ; Na, 5.0%
 C₂₁H₁₇N₄O₇Na requires
 : C, 54.78 ; H, 3.69; N, 12.17 ; Na, 5.0%

(c) KSalH. OHADNPz

Found : C, 52.08 ; H, 3.45; N, 11.65; K, 8.00%
 C₂₁H₁₇N₄O₇K 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-dinitrophenylhydrazone

Equimolar proportions of alkali metal anthranilate and O-Hydroxyacetophenone - 2,4-dinitrophenylhydrazone 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^oc.

- (a) LiAnc.OHADNPz
Found : C, 54.95 ; H, 3.85; N, 15.20%
C₂₁H₁₈N₅O₇Li requires
: C, 54.90 ; H, 3.92 ; N, 15.25%
- (b) NaAnc. OHADNPz
Found : C, 53.15 ; H, 3.82; N, 14.80 ; Na, 4.50%
C₂₁H₁₈N₅O₇Na requires
: C, 53.05 ; H, 3.79; N, 14.74 ; Na, 4.84%
- (c) KAnc. OHADNPz
Found : C, 51.37 ; H, 3.72; N, 14.30; K, 7.85%
C₂₁H₁₈N₅O₇K requires
: C, 51.32 ; H, 3.66; N, 14.26; K,7.94%

4. Adducts of alkali metal salts of picolinic acid with O-Hydroxyacetophenone - 2,4 – dintrophenylhydrazone

Alkali metal salt of picolinic acid and the ligand 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. It was concentrated and cooled, when coloured crystals came apart. It was filtered, washed with the solvent and then dried in an electric oven at 120^oc.

- (a) LiPicA.OHADNPz
Found : C, 53.98 ; H, 3.65; N, 15.78%
C₂₀H₁₆N₅O₇Li requires
: C, 53.98 ; H, 3.59 ; N, 15.73%
- (b) NaPicA. OHADNPz
Found : C, 52.11 ; H, 3.52; N, 15.23 ; Na, 5.00%
C₂₀H₁₆N₅O₇Na requires
:C, 52.06 ; H, 3.47; N, 15.18 ; Na, 4.99%
- (c) KPicA. OHADNPz
Found : C, 50.36 ; H, 3.40; N, 14.70; K, 8.25%
C₂₀H₁₆N₅O₇K requires
: C, 50.31 ; H, 3.35; N, 14.67; K,8.18%

5. Adducts with alkali metal salts of Quinaldonic acid with O-Hydroxyacetophenone - 2,4 – dintrophenylhydrazone

Equimolar proportions of alkali metal salt of quinaldonic acid 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. It was concentrated and then cooled, when the adduct came apart. It was filtered, washed with the solvent and then dried in an electric oven at 120^oc.

- (a) LiQuinA.OHADNPz
Found : C, 58.23 ; H, 3.69; N, 14.09%
C₂₄H₁₈N₅O₇Li 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%
C₂₄H₁₈N₅O₇Na 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%
C₂₄H₁₈N₅O₇K requires
: C, 54.65 ; H, 3.41; N, 13.28; K,7.40%

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