

Mixed Ligand Complexes of Alkali Metal Salts of Some Organic Acids with O-Hydroxyacetophenone Phenylhydrazone

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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, salicylaldehyde, anthranilic acid, Picolinic acid and Quinaldinic acid

1. Introduction

In this chapter, we extend our investigation study the possible complex formation by alkali metals with ligand O-hydroxyacetophenone phenylhydrazone (Fig. 5.1), hereafter abbreviated as OHAPz

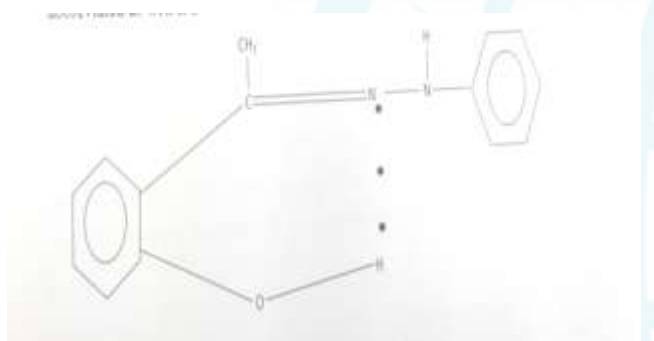


Figure 5.1

In the previous chapter, we observed that O-hydroxyacetophenone was hydrazone forms stable complexes with alkali metal salts of acetyl acetone, salicylaldehyde, anthranilic acid, Picolinic acid and Quinaldinic acid.

Ease of complexation was found to increase with the atomic number of the central metal ion.

Literature survey reveals that no complex formation by alkali metals with this ligand has yet been reported. Accordingly, it was decided to examine this ligand for possible complex formation with this ligand.

We have been able to isolate a number of coordination compounds of alkali metal salts of some organic acids with the title ligand. They have the general formula $ML.HL'$, where $M=Li, Na$ or K ; L =deprotonated acetylacetone (acac), salicylaldehyde (SalH), anthranilic acid (AnC), picolinic acid (PicA) Quinaldinic acid (QuinA) and HL' =O-hydroxyacetophenone phenylhydrazone. Analytical data confirm the stoichiometry. Thermal,

Infrared and solution studies reveal that there adducts are genuine complexes.

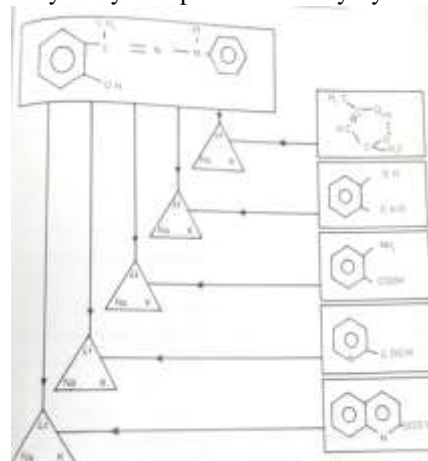
Our usual method of preparing these complexes was to take equimolar proportion of the alkali metal salt (ML) and the title ligand O-hydroxyacetophenone hydrazone (HL') in absolute ethanol in a conical flask and to reflux the contents for four to six hours with continuous stirring. A clear solution was obtained. It was filtered, washed with absolute ethanol and then dried in an electric oven at $80^{\circ}C$.

Table 5.1 lists the complexes of alkali metal salts of some organic acid with O-hydroxyacetophenone phenylhydrazone.

Physical Properties

O-hydroxyacetophenone phenylhydrazone is light yellow in colour. Its complexes with alkali metal salts are characteristically coloured, the colour depending upon the acid from which alkali metal salt has been derived. They are stable in air under dry conditions for reasonable long periods of time. They were stored in corked sample tubes over anhydrous calcium chloride in desiccator. They are hygroscopic in nature.

Table 5.1: Mixed Ligand Complexes of O – Hydroxyacetophenone Phenylhydrazone



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

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 colligative properties are hampered by the dissociation of the adducts in the common solvents in which they dissolve. Also the solvent 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.

Table 5.2 lists some physical properties of the ligand O-hydroxyacetophenone phenylhydrazone and its complexes with alkali metal salts of some organic acids.

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

Table 5.2: Some physical properties of OHAPz and its complexes

TABLE – 5.2
Some physical properties of OHAPz and its complexes

Compound	Colour	Melting Point / decomposition (°C)	Conductivity*
OHAPz	Light Yellow	114m	-
LiAc.OHAPz	Cream colour	165d	2.0
NaAc.OHAPz	Cream colour	163d	2.0
KAc.OHAPz	Cream colour	166d	3.0
LiSalH.OHAPz	Grey colour	160d	1.5
NaSalH.OHAPz	Grey colour	158d	1.5
KsalH.OHAPz	Grey colour	155d	2.8
LiAnc.OHAPz	Brown colour	150d	2.0
NaAnc.OHAPz	Brown colour	155d	2.0
Kanc.OHAPz	Brown colour	158d	2.0
LiPicA.OHAPz	Cream colour	160d	2.5
NaPicA.OHAPz	Cream colour	165d	3.0
KpicA.OHAPz	Cream colour	145d	4.5
LiQinA.OHAPz	Cream colour	170d	2.8
NaQinA.OHAPz	Cream colour	165d	3.5
KqinA.OHAPz	Cream colour	162d	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 4000-650 cm^{-1} in Nujol mulls. Pertinent IR data for these compounds are shown in Table – 5.3.

The absorption bands of our principal interest in the IR spectra of OHAPz are 3380, 3275, 1615, 1270 and 920 cm^{-1} . The moderately strong bands at 3380 cm^{-1} and 3275 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 shift (Table – 5.3), while the $\sim 3380 \text{ cm}^{-1}$ vband is observed at 3210 cm^{-1} , the Sym. N-H band is observed at 3180 cm^{-1} .

The 920 cm^{-1} band, attributed to $\nu\text{N-N}$ vibrations, is observed in the complexes as split band at 960, 950 and 890 cm^{-1} . The 1615 cm^{-1} band, most probably owing to $\nu\text{C}=\text{N}$ vibrations in the molecules of the ligand, has undergone a downward shift to an extent of 10 – 15 cm^{-1} . These observations suggest that coordination of the ligand with alkali metals has taken place through the nitrogen atom of the hydrazone moiety.

Table 5.3: I.R. Spectral data for the ligand OHAPz and its alkali metal complexes

Compound	$\nu_{\text{asy NH}}$	$\nu_{\text{sym NH}}$	$\nu\text{C}=\text{N}$	$\nu\text{C}=\text{O}$ (Phenolic)	$\nu\text{N-N}$
OHAPz	3380	3275	1615	1270	920
LiAc.OHAPz	3210	3180	1605	1290	960, 950, 890
NaAc.OHAPz	3205	3170	1605	1285	960, 950, 890
KAc.OHAPz	3205	3180	1600	1290	960, 950, 890
LiSalH.OHAPz	3210	3170	1600	1285	960, 945, 890
NaSalH.OHAPz	3210	3170	1602	1285	958, 945, 895
KsalH.OHAPz	3210	3170	1604	1285	958, 955, 898
LiAnc.OHAPz	3200	3165	1600	1288	960, 950, 890
NaAnc.OHAPz	3200	3165	1600	1288	960, 950, 890
Kanc.OHAPz	3200	3165	1600	1290	960, 950, 890
LiPicA.OHAPz	3205	3170	1605	1287	960, 955, 895
NaPicA.OHAPz	3205	3170	1605	1287	960, 955, 895
KpicA.OHAPz	3208	3170	1605	1285	960, 955, 895
LiQinA.OHAPz	3210	3170	1600	1290	960, 950, 890
NaQinA.OHAPz	3205	3170	1600	1290	960, 950, 890
KqinA.OHAPz	3210	3165	1600	1290	960, 950, 890

The absorption band at 1270 cm^{-1} has been ascribed to the stretching $\nu\text{C}=\text{O}$ (phenolic) vibrations in the ligand molecule. In the 15-20 cm^{-1} , indicating strong chelation^{115,119,120}. Owing to the intrinsicity 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 ligands or the ligands or the molecules of the ligands OHAPz. This band could be assigned to O.H. O/N H.O. absorption. This may be one the dominant factors stabilizing the complexes.

Conductivities

Molar conductivities were measured in DMF (N,N – dimethylformamide) at 25^oc at a concentration of 10^{-3} M. Using a Systronic Direct Reading Conductivity Meter Bridge Model No. 303 using conventional dip type bright platinum electrodes.

A value of $\sim 34 - 40 \text{ ohm}^{-1} \text{ Cm}^2 \text{ mol}^{-1}$ appears characteristic of a 1:1 electrolyte¹⁶, whereas ideally molar conductivity of a neutral complex should be zero.

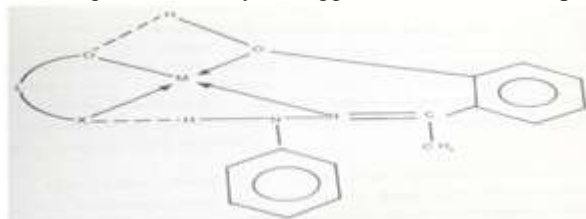
From the result (Table 5.2), it is observed that molar conductivities of none of the complexes approach either ideal or 1:1 electrolyte. However, significantly low values of their molar conductivities suggest them to be non – electrolytes.

2. Probable Structure

On the basis of element analyses, the general molecular formula of these complexes comes out to be $ML.HL'$ where $M=Li, Na$ or K , $L=$ deprotonated acetylacetone (acac), salicylaldehyde (SalH), anthranilic acid (Anc.), Picolinic acid (Pic.A) or quinaldine acid (Quin.A) and $HL'=O$ -hydroxyacetophenone phenylhydrazone.

The Infrared spectra of these complexes suggest the coordination of alkali metals with O -hydroxyacetophenone phenylhydrazone through oxygen atoms of hydrazone moiety. The infrared spectra of these complexes indicate the presence of hydrazone bonding in them.

Keeping in view the fact that the six membered chelate rings are most stable and that the ligand O -hydroxyacetophenone phenylhydrazone behaves as a bidentate ligand, the following structure may be suggested for these complexes :



($M=Li, Na$ or K and $X = O$ or N)
(Fig. 5.2)

3. Experimental

Perparation of the ligand O -hydroxyacetophenone Phenylhydrazone

The title ligand O -hydroxyacetophenone phenylhydrazone, was prepared as described in literature.¹¹⁷

40ml 50% acetic acid solution was taken in a R.B. flask. 5ml phenylhydrazine was added, followed by 5ml O -hydroxyacetophenone. Contents were shaken well. 100ml water was added to it. The contents were reshaken and cooled, when O -hydroxyacetophenone phenylhydrazone separated as light yellow crystals. The crystals were filtered, washed with cooled water, recrystallized from alcohol and then dried in an electric oven at 180^oc.

Its authenticity was established by elemental analyses, melting point determination and IR spectra. Fine light yellow crystals of O -hydroxyacetophenone phenylhydrazone, that we obtained has the melting point 114^oc which is identical with reported value.¹¹⁸

Results of its elemental analyses are as follows :

Found : C, 74.58 ; H, 6.28 ; N, 12.20%
 $C_{14}H_{14}N_2O$ requires : C, 74.34 ; H, 6.19 ; N, 12.39%

4. Preparation of Alkali Metal Complexes of O -Hydroxyacetophenone Phenylhydrazone

1. Adducts with alkali metal salts of acetylacetone with O -hydroxyacetophenone phenylhydrazone

Alkali metal salt of acetylacetone with O -hydroxyacetophenone phenylhydrazone 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) LiAcac.OHAPz

Found : C, 68.95 ; H, 6.54; N, 8.40%

$C_{19}H_{21}N_2O_3Li$ requires: C, 68.67 ; H, 6.32 ; N, 8.43%

(b) Naacac.OHAPz

Found : C, 65.80 ; H, 6.42; N, 8.00 ; Na, 6.50%

$C_{19}H_{21}N_2O_3Na$ requires : C, 65.52 ; H, 6.03; N, 8.04 ; Na, 6.61%

(c) Kacac.OHAPz

Found : C, 63.64 ; H, 5.99; N, 7.70 ; K, 10.80%

$C_{19}H_{21}N_2O_3K$ requires: C, 63.33 ; H, 5.83; N, 7.78 ; K, 10.83%

2. Adducts with alkali metal salts of salicylaldehyde with O -hydroxyacetophenone phenylhydrazone

Alkali metal salt of salicylaldehyde and O -hydroxyacetophenone phenylhydrazone 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) LiSalH.OHAPz

Found : C, 71.38 ; H, 5.79; N, 8.02%

$C_{21}H_{19}N_2O_3Li$ requires: C, 71.19 ; H, 5.37 ; N, 7.91%

(b) NaSalH.OHAPz

Found : C, 67.98 ; H, 5.45; N, 7.50 ; Na, 6.00%

$C_{21}H_{19}N_2O_3Na$ requires: C, 68.11 ; H, 5.13; N, 7.57 ; Na, 6.22%

(c) KSalH.OHAPz

Found : C, 65.24 ; H, 5.00; N, 7.13; K, 10.00%

$C_{21}H_{19}N_2O_3K$ requires : C, 65.28 ; H, 4.92; N, 7.25 ; K, 10.10%

3. Adducts with alkali metal salts of anthranilic acid with O -hydroxyacetophenone phenylhydrazone

Equimolar proportions of alkali metal anthranilate and O -hydroxyacetophenone phenylhydrazone 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. In half an hour, a clear solution was obtained. It was concentrated and then cooled, when yellow colour precipitate of the adduct separated. It was filtered, washed with the solvent and then dried in an electric oven at 120^oc.

(a) LiAnc.OHAPz

Found : C, 68.58 ; H, 5.67; N, 11.25%

$C_{21}H_{20}N_3O_3Li$ requires : C, 68.29 ; H, 5.42 ; N, 11.38%

(b) NaAnc.OHAPz

Found : C, 65.81 ; H, 5.20; N, 11.00 ; Na, 6.00%
 $C_{21}H_{20}N_3O_3Na$ requires: C, 65.45 ; H, 5.19; N, 10.91 ;
 Na, 5.97%

(c) KAnc.OHAPz

Found : C, 63.18 ; H, 5.24; N, 10.52; K, 9.50%
 $C_{21}H_{20}N_3O_3K$ requires : C, 62.84 ; H, 4.99; N, 10.47;
 K, 9.72%

4. Adducts of alkali metal salts of picolinic acid with O-hydroxyacetophenone phenylhydrazine

Alkali metal salt of picolinic acid and the ligand O-hydroxyacetophenone phenylhydrazine were taken in a molar proportions (1:1) in a conical flask. About 30c.c. 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.OHAPz

Found : C, 67.59 ; H, 5.44; N, 11.70%
 $C_{20}H_{18}N_3O_3Li$ requires: C, 67.60 ; H, 5.07 ; N, 11.83%

(b) NaPicA.OHAPz

Found : C, 64.14 ; H, 5.19; N, 11.12 ; Na, 6.00%
 $C_{20}H_{18}N_3O_3Na$ requires: C, 64.69 ; H, 4.85; N, 11.32 ; Na,
 6.19%

(c) KPicA.OHAPz

Found : C, 62.24 ; H, 4.94; N, 10.78; K, 10.00%
 $C_{20}H_{18}N_3O_3K$ requires: C, 62.01 ; H, 4.65; N, 10.85;
 K, 10.08%

5. Adducts with alkali metal salts of Quinaldinic acid with O-hydroxyacetophenone phenylhydrazine

Equimolar proportions of alkali metal salt of quinaldinic acid and O-hydroxyacetophenone phenylhydrazine 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. In half an hour, a clear solution was obtained. It was filtered, washed with the solvent and then dried in an electric oven at 120^oc.

(a) LiQuinA.OHAPz

Found: C, 71.48 ; H, 5.32; N, 10.25%
 $C_{24}H_{20}N_3O_3Li$ requires: C, 71.11 ; H, 4.94 ; N, 10.37%

(b) NaQuinA.OHAPz

Found : C, 68.54 ; H, 4.84; N, 9.78 ; Na, 5.25%
 $C_{24}H_{20}N_3O_3Na$ requires : C, 68.41 ; H, 4.75; N, 9.98 ; Na,
 5.46%

(c) KQuinA.OHAPz

Found: C, 66.39 ; H, 4.81; N, 9.50; K, 8.80%
 $C_{24}H_{20}N_3O_3K$ requires: C, 65.90 ; H, 4.58; N, 9.61;
 K, 8.92%

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