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Alkali Metal Salts of Some Organic Acids with Q-Hydroxy

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Abstract: *The study of the coordination chemistry of alkali metals^{1,2} would be interesting and useful as the subject remained neglected and receive very little attention until recently. In recent years, the synthesis of complexes containing two or more different ligands has been of special interest to coordination chemists. Mixed complexes in which the metal ion is simultaneously bonded to two or more different types complexing species, are probably formed in most solution which contain ion of a particular metal as well as more than one kind of ligands..*

Keywords: Q-hydroxycetophenone hydrazone, bidentate ligand, n-hexene and benzene

I. INTRODUCTION

When two or more different types of ion are simultaneously present in the solution, these may exist polynuclear complex. Such complexes are likely to be important as model for metalloenzyme-substrate complexes and also component of the multi metal multi ligand system in biological fluids. In this communication we have taken the ligand Q-hydroxycetophenone hydrazone as this ligand behaves as the bidentate ligand and has been shown to form stable³ complexes with a number of transition metals.

II. EXPERIMENTAL

Preparation of Ligand : The Q-hydroxycetophenone hydrazone abbreviated as OHAHz was prepared as described by Vishnoi⁴, while the other chemical used in this study were AnalaR. Grade. In order to prepare the ML.HL type mixed ligand complexes, the complexes of alkali metal salts (ML) with the title ligand (HL') was refluxed at 120⁰C in their molar proportions (ML;HL'=1:1) in absolute ethanol for four to six hours, with constantly stirring the solutions with the help of a magnetic stirrer. Clear solution was obtained which on cooling gave the characteristically coloured adducts. They were filtered, washed with absolute ethanol and dried in an electric oven at 80⁰C.

III. RESULTS AND DISCUSSION

Some physical properties of the ligand and newly formed mixed legand complexes are listed in table – I. All the complexes are coloured and stable under dry condition for reasonably long period of time but decompose rapidly on exposure to moist air. Their decomposition temperatures are higher than the melting point of the ligand Q-hydroxycetophenone hydrazones, showing their greater thermal stability and strong bonding between ML and HL'. They are in soluble in non-polar solvents namely chloroform, diethyl ether, n-hexene and benzene, but are soluble in polar solvents such as methanol and ethanol. The molar conductivities of all the complexes are measured in DMF and 25⁰C at a concentration of 10⁻³ M. The lower values 35-40 ohm⁻¹ cm² mol⁻¹ of molar conductivities of the complexes suggest the non electrolytic nature of the complexes.

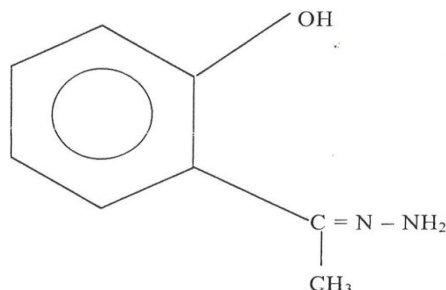
Infra red spectra of the ligand and the complexes were recorded in the region 4000-650 cm⁻¹ in NUJOL Mulls. Pertinent I.R. data are listed in table – 2.

The moderately strong bonds at 3390 cm⁻¹ and 3295 cm⁻¹ in the I.R. spectrum of the title ligand Q-hydroxy acetophenone are attributed³ to stretching ant symmetric and symmetric NH vibration respectively. In the spectra of the complexes these band exhibit a considerable downward shift while the 3390 cm⁻¹band was observed at V 3220 cm⁻¹, the V sym NH-band was observed at 3190 cm⁻¹.

The 930 cm⁻¹ band, due to V N – N vibrations^{3,5} is observed in the complexes at ~970 cm⁻¹. The 1625 cm⁻¹ band, attributed to V C = N vibrations in the ligand molecule has undergone a downward shift by about 10-15 cm⁻¹. These spectral observations suggest that the coordination of the ligand with the alkali metal has taken place through the nitrogen atom of the hydrazone moiety.

The absorption band of 1825 cm⁻¹ has been ascribed to the stretching CO (phenolic) vibrations in the ligand molecule. In the complexes, this band has undergone an upward shift to 15-20 cm⁻¹ suggesting strong chelation³ owing to the intrinsically of the oxygen atom of the OH-group of the ligand.

In addition to the above bands, a new broad band of weak to medium intensity in the region $2300-1950\text{ cm}^{-1}$ is observed in all the complexes. This band is absent in the spectra of either the alkali metal salt of the ligand or in the ligand O-hydroxycetophenone hydrazone. This could be assigned to $\text{O} \cdots \text{H} \cdots \text{O} / \text{N} \cdots \text{H} - \text{O}$ absorption. This band may be one of the important forces that bind the alkali metal salt with the ligand. I.R. spectra of the title ligand O-hydroxycetophenone hydrazone and a representative alkali metal complex of this ligand are shown in Fig. 1

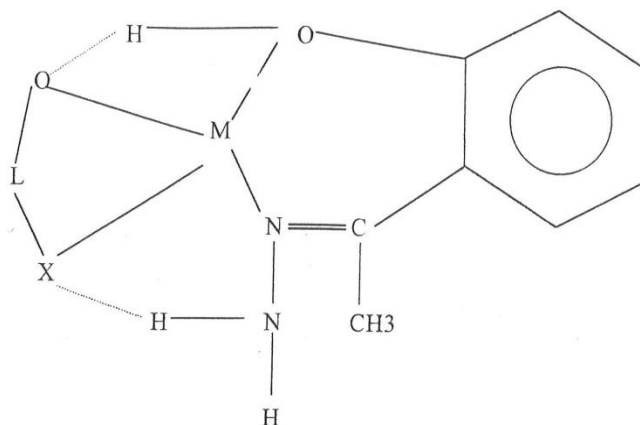


O - hydroxycetophenone Hydrazone (OHAHz)

Fig.1

IV. PROBABLE STRUCTURE

On the basis of element analysis, the general molecular formula of these complexes comes out to be $\text{ML} \cdot \text{HL}'$ where $\text{M} = \text{Li}, \text{Na}$ or K ; $\text{L} =$ acetylacetone, O-Salicylaldehyde, Anathranilic acid, Picolinic acid, Quinaldinic acid etc and $\text{HL}' =$ O-hydroxycetophenone hydrazone. The infra-red spectra of these complexes also indicate the presence of hydrogen bonding in them. Keeping in view the fact that six member chelate rings are most stable and that the ligand O-hydroxycetophenone hydrazone behaves as a bidentate ligand, the following structure may be suggested for these complexes.



(X = O or N, M=Li, Na, K)

Fig.2

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