

Alkali Metal Complexes: Mixed Ligand Complexes of Alkali Metal Salts of Some Organic Acids with *o*-Hydroxy Acetophenone Hydrazone

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Mixed ligand complexes of alkali metal salts of organic acids, viz., acetylacetone, salicylaldehyde, anthranilic acid, picolinic acid and quinaldinic acid with *o*-hydroxy acetophenone hydrazone have been synthesized and characterised on the basis of elemental analyses, conductivity measurement and infra-red spectral data. The probable structure has also been assigned. Low values of molecular conductivity suggest the covalent nature of bond in these complexes.

INTRODUCTION

The study of the coordination chemistry of alkali metals¹ would be interesting and useful as the subject remained neglected and received 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 of complexing species, are probably formed in most solutions which contain ion of a particular metal as well as more than one kind of ligands. When two or more different types of ions are simultaneously present in the solution, these may exist as polynuclear complexes. Such complexes are likely to be important as models for metalloenzyme-substrate complexes and also components of the multi-metal multi-ligand system in biological fluids. In this communication we have taken the ligand *o*-hydroxyacetophenone hydrazone (Fig. 1) which behaves as a bidentate ligand and has been shown to form stable² complexes with a number of transition metals.

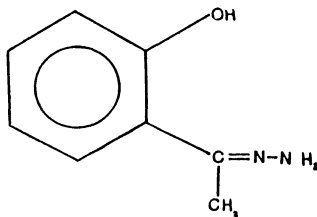


Fig. 1

EXPERIMENTAL

Preparation of Ligand: The ligand *o*-hydroxyacetophenone hydrazone abbreviated as OHAHZ was prepared as described by Vishnoi³, while the other chemicals 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) (as prepared

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by reported method¹) with the title ligand (HL') were refluxed at 120°C in their molar proportions (ML : HL' = 1 : 1) in absolute ethanol for 4–6 h, with constantly stirring the solutions with the help of a magnetic stirrer. Clear solutions were obtained which on cooling gave the coloured adducts. They were filtered, washed with absolute ethanol and dried in an electric oven at 80°C.

RESULTS AND DISCUSSION

Some physical properties of the ligand and newly formed mixed ligand complexes are listed in Table-1. All the complexes are coloured and stable under dry

TABLE-1

Compound (colour)	m.p./dec.p. (°C)	Conducti- vity	% Found (calcd.)			
			C	H	N	M
OHAHz (Light yellow)	84m	—	64.38 (64.00)	6.60 (6.67)	19.18 (18.67)	—
Li Acac. OHAHz (Cream)	145d	1.0	61.25 (60.94)	6.81 (6.64)	10.85 (10.94)	—
Na Acac. OHAHz (Cream)	142d	1.8	57.12 (57.35)	6.40 (6.25)	10.25 (10.29)	8.40 (8.45)
K Acac OHAHz (Cream)	140d	3.0	54.00 (54.17)	6.24 (5.90)	9.52 (9.27)	13.50 (13.54)
Li Sal. H. OHAHz (Grey)	155d	1.8	64.34 (64.75)	5.79 (5.39)	10.25 (10.07)	—
Na Sal. H.OHAHz (Grey)	150d	2.0	60.64 (61.22)	5.58 (5.10)	9.35 (9.52)	7.50 (7.82)
K Sal. H. OHAHz (Grey)	148d	3.5	57.98 (58.06)	5.08 (4.89)	8.89 (9.03)	12.50 (12.58)
Li Anc. OHAHz (Brown)	160d	2.5	61.50 (61.43)	5.68 (5.46)	14.15 (14.33)	—
Na Anc. OHAHz (Brown)	155d	2.5	58.00 (58.25)	5.39 (5.18)	13.28 (13.59)	7.24 (7.44)
K Anc. OHAHz (Brown)	152d	3.8	55.48 (55.38)	5.20 (4.92)	12.85 (12.92)	12.00 (12.00)
Li Pic. A. OHAHz (Cream)	150d	1.8	59.75 (60.21)	5.45 (5.01)	14.78 (15.05)	—
Na Pic. A. OHAHz (Cream)	155d	2.0	56.54 (56.95)	4.98 (4.74)	14.00 (14.24)	7.67 (7.79)
K Pic. A. OHAHz (Cream)	160d	2.4	53.90 (54.02)	4.80 (4.50)	13.26 (13.50)	12.21 (12.54)
Li Quin. A. OHAHz (Cream)	165d	2.0	65.51 (65.65)	4.90 (4.86)	12.75 (12.76)	—
Na Quin. A. OHAHz (Cream)	160d	3.0	62.50 (62.61)	4.75 (4.64)	12.00 (12.17)	6.60 (6.67)
K Quin. A. OHAHz (Cream)	150d	4.8	59.70 (59.83)	4.59 (4.43)	11.50 (11.63)	10.78 (10.80)

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

Acace (acetylacetone), Sal. H. (salicylaldehyde), Anc. (anthranilic acid), Pic. A (Picolinic acid), Quin. A. (quinaldinic acid)

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 *o*-hydroxy acetophenone hydrazone, showing their greater thermal stability and strong bonding between ML and HL'. They are insoluble 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 were measured in DMF at 25°C 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 IR data are listed in Table-2.

TABLE-2
PERTINENT IR BANDS (cm⁻¹) IN THE LIGAND OHAHz AND ITS ALKALI METAL COMPLEXES

Compounds	$\nu_{\text{asym}}(\text{NH})$	$\nu_{\text{sym}}(\text{NH})$	$\nu(\text{C}=\text{N})$	$\nu(\text{CO})$ (Phenolic)	$\nu(\text{N}-\text{N})$
OHAHz	3390	3295	1625	1285	930
Li Acac. OHAHz	3220	3180	1610	1295	970, 965, 895
Na Acac. OHAHz	3220	3180	1610	1300	970, 965, 895
K Acac. OHAHz	3220	3185	1610	1305	970, 965, 895
Li Sal. H. OHAHz	3210	3180	1615	1295	970, 965, 898
Na Sal. H. OHAHz	3210	3180	1618	1300	970, 965, 898
K Sal. H. OHAHz	3210	3180	1615	1300	970, 965, 898
Li Anc. OHAHz	3215	3185	1610	1305	970, 960, 890
Na Anc. OHAHz	3210	3185	1610	1305	970, 960, 890
K Anc. OHAHz	3220	3185	1610	1305	970, 960, 890
Li Pic. OHAHz	3220	3190	1615	1300	970, 960, 895
Na Pic. OHAHz	3220	3190	1615	1300	970, 960, 895
K Pic. OHAHz	3220	3190	1615	1300	970, 960, 895
Li Quin. A. OHAHz	3215	3185	1615	1305	970, 965, 890
Na Quin. A. OHAHz	3215	3185	1615	1295	970, 967, 890
K Quin. A. OHAHz	3215	3185	1615	1295	970, 965, 890

The moderately strong bands at 3990 and 3295 cm⁻¹ in the IR spectrum of the free ligand *o*-hydroxy acetophenone are attributed² to stretching antisymmetric and symmetric NH vibrations respectively. In the spectra of the complexes these bands exhibit a considerable downward shift at 3220 and 3190 cm⁻¹.

The 930 cm⁻¹ band, due to $\nu(\text{N}-\text{N})$ vibrations^{2, 4} is observed in the complexes at *ca.* 970 cm⁻¹. The 1625 cm⁻¹ band, attributed to $\nu(\text{C}=\text{N})$ 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 at 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 chelation² owing to 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 cm^{-1} is observed in all the complexes. This band is absent in the spectra of either the alkali metal complexes or in the free ligand *o*-hydroxy acetophenone hydrazone. This could be assigned to $\text{O}^{\cdot\cdot}\text{H} \cdots \text{O}/\text{N} \cdots \text{H}-\text{O}$ absorption. This band may be one of the important forces that bind the alkali metal salt with the ligand.

Probable Structure: On the basis of elemental 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 ; $\text{L} =$ acetylacetonone, *o*-salicylaldehyde, anthranilic acid, picolinic acid, quinaldinic acid etc. and $\text{HL}' =$ *o*-hydroxyacetophenone 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*-hydroxyacetophenone hydrazone behaves as a bidentate ligand, the following structure may be suggested for these complexes. (Fig. 2)

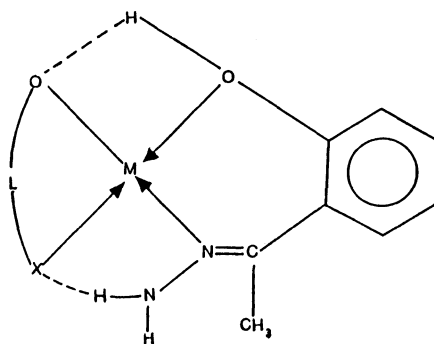


Fig. 2.

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