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Physical Properties of Mixed Ligand Complexes of Alkali Metal Salts

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Abstract: 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,

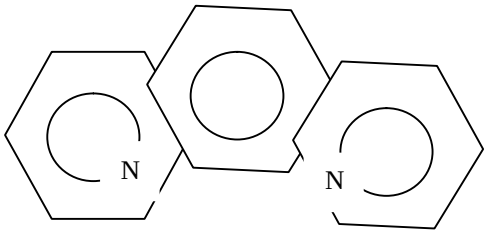
I. INTRODUCTION

All the ligands, namely O-hydroxyacetophenone hydrazone, O-hydroxyacetophenone phenylhydrazone and Ohydroxyacetophenone – 2, 4 – dinitrophenylhydrazone formed mixed ligand complexes of the type ML.HL', where M=Li, Na or K, L=deprotonated organic acid and HL'= any of the above named ligand.

possibly of class a character of the cation. We also found that the hydrogen bonding is an important feature of these solid adducts and this may be one of the factors stabilizing them. Another feature of these adducts is that the ligand must be capable of chelation to form 5 – or 6 – membered ring. Thus, m – nitrophenol and n – nitrophenol , which are expected to form 7 – membered and 8-membered rings respectively, do not form adducts with alkali metal salts. Further, no adduct was formed by reaction between acetic acid (HL) and its alkali metal salt (ML), or by reaction between an alkali metal salt of acetic acid (ML) and organic acids (ML') which are potential ligands having the

It has been observed that the chelating ability of hydrazone decreases in the order : O-hydroxyacetophenone hydrazone > O-hydroxyacetophenone phenylhydrazone > O-hydroxyacetophenone – 2, 4 – dinitrophenylhydrazone. Thus subsitituted hydrazones become more selective in their behavior towards alkali metal cation.

We now extend our investigation to study the possible complex formation by alkali metal salts with the ligand 1, 10 – phenanthroline (Fig. 7.1) because it is devoid of acidic hydrogen atoms, consequently rulling our any possibility of hydrogen bonding complexes.



Complexes of transition metal [121,122] with 1,10 – phenanthorline, which is a well known hetrocyclic base and behaves as a bidentate ligand, are well established. The metal chelates of 1,10 – phenanthorline and the related ligands have been revived by Brandt et.al.[123].

Recently Banerjee et.al. [31] reported obtaining a number of stable complexes of alkali metal salts of 8-hydroxyquinoline and O – nitrobenzoic acid with 1,10 – phenanthorline in organic solvents. Very recently, Singh and Prakash 48 have synthesized and characterized some mixed ligand complexes of alkali metal salts of some organic acids, namely acetyl acetone, salicylaldehyde and O-Hydroxyacetophenone with 1, 10 – phenanthroline.

We have synthesized and characterized a number of mixed ligand complexes of alkali metal salts of O-Hydroxyacetophenone hydrazone (OHAHz) and O-Hydroxyacetophenone phenylhydrazone (OHAPHz) and O-hydroxyacetophenone – 2, 4 - dinitrophenyl hydrazone (OHADNPz) with 1,10 – phenanthorline. They have the general formula ML.nL'where M = Li, Na or K; L=deprotonated O-Hydroxyacetophenone hydrazone, O-Hydroxyacetophenone phenylhydrazone or O-hydroxyacetophenone – 2, 4 - dinitrophenyl hydrazone, n= 1 and L = 1,10 – phenanthorline. These

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are thermally very stable. Thermal, IR spectra and the solution studies of these solid adducts reveal that these are genuine complexes.

Our usual method of synthesizing these adducts was to take a suspension of the alkali metal salt in benzene in a test tube and then to add 1,10 – phenanthorline to it in the mole ratio 1:4. Greater excess of the second ligand was avoided to prevent Crystallization of the base in preference to the adduct. On stirring the mixture slowly, all the solids went into solution. Frequently some crystals were deposited after a new minures, but they redissolved on heating the contents were warmed for 5 minutes on a steam bath and cooled, when the crystals of the adduct came apart. These were filtered, washed with cold benzene and dried in an electric oven at 80^0c.

The existence of an interaction was demonstrated by the solubilisation of the suspended alkali metal salt on addition of 1,10 – phenanthorline during the preparation of the adduct.

II. PHYSICAL PROPERTIES

All the complexes are characteristically coloured. They are stable when stored under dry conditions, e.g. in a desicator over anhydrous CaCl2. They showd no change in stoichiometry or in their physical properties even after one year. On exposure to moisture, the hydrolysis of the complexes to give the three ligand and metal salt appears to take place. The transition / decomposition temperatures of all these complexes are much higher than the melting point of the ligand. This would seem to indicate that 1,10 – phenanthorline present in the complexes is certainly not present as free base or even as its hydrate, which melt at 117^0c and 93 – 94^0c respectively. This would also seem to indicate that the compounds are held together by forces stronger than the Vander Waal's forces.

This apparent stability of alkali metal complexes of 1,10 – phenanthorline has been previously observed for Class A complexes by other workers also. Hart et.al.[124] noted that the decomposition points for tris – (1,10 – phenanthorline) lanthanide isocyanides were often in excess of 250^0c.

Table – 7.1 lists the complexes of alkali metal salts with 1,10 – phenanthorline, which was have obtained.

Complexes of Alkali Metal Salts Or some organic acids with 1,10 – phenanthorline

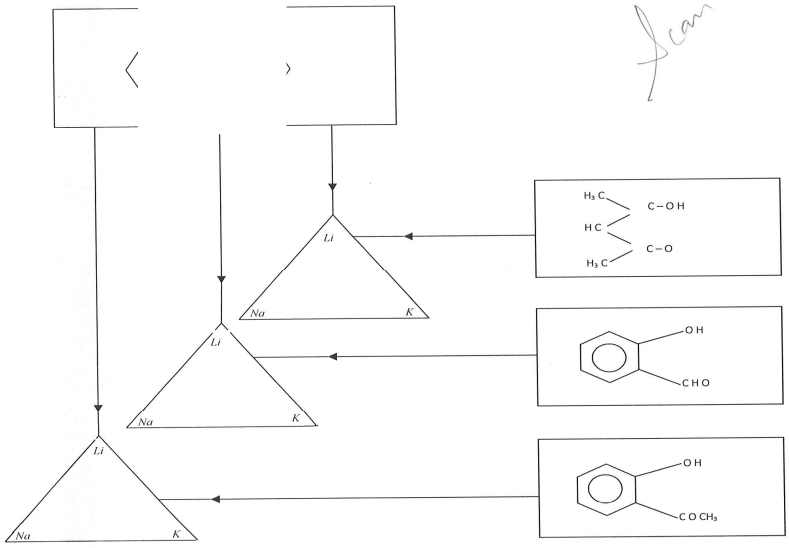


TABLE – 7.1

Three corners of the triangles shown in the above table represent the alkali metals Li, Na and K. Symbols indicate that the corresponding complexes were obtained.

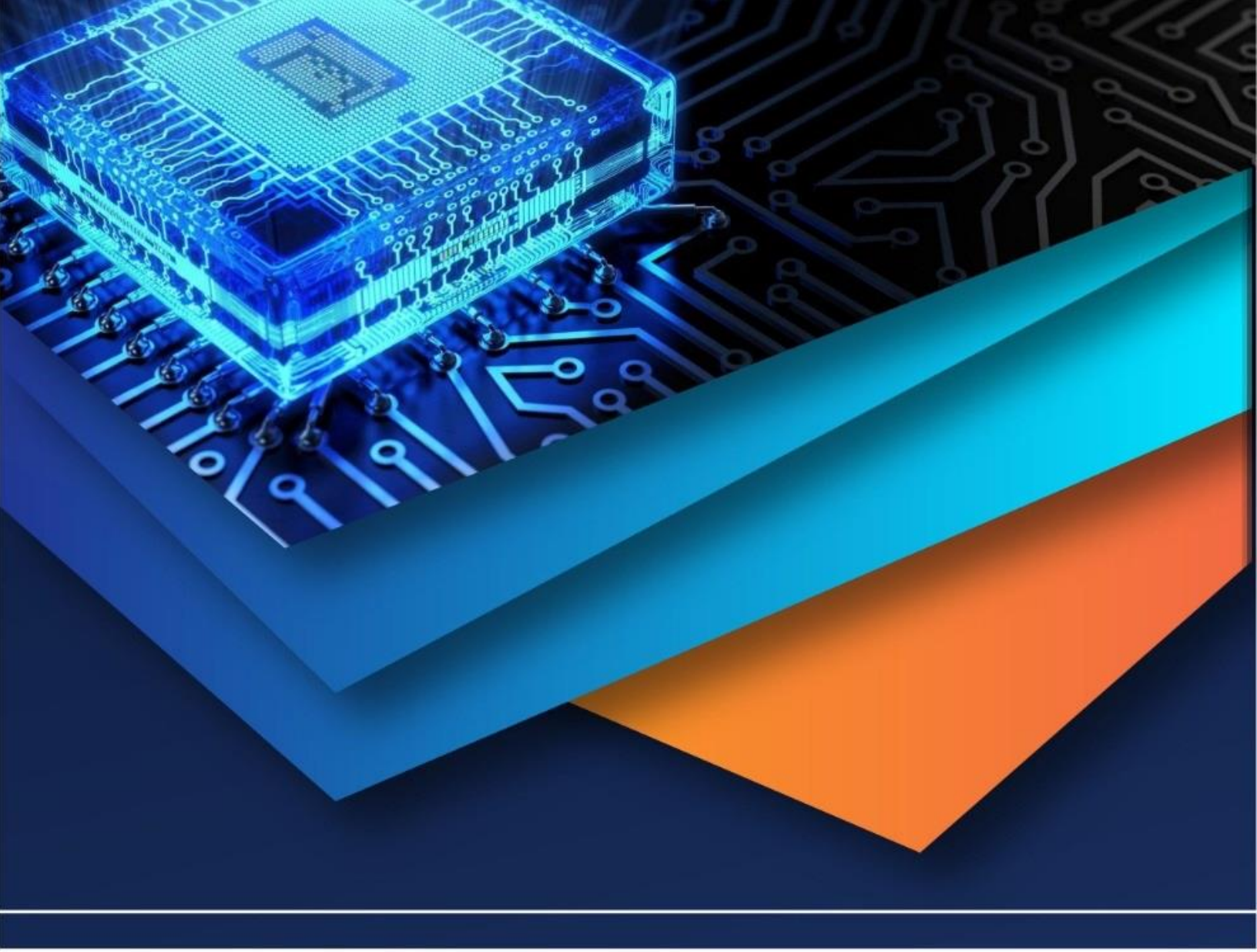
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