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Conductivity of Mixed Ligand Complexes of Alkali Metal Salts

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Abstract: Our present work shows that hydrogen bonding is not necessary for formation of adducts between a chelating legend and the alkali metal salt of a chelate ion.
Keywords: hydroxyacetophenone phenylhydrazone,

I. INTRODUCTION

Only two bands are observed : one at 738 cm^{-1} (assigned to out – of – plane motion of the H – atoms on the heterocyclic rings) and the other at 854 cm^{-1} (assigned to out of plane motion of hydrogen atoms on the central ring). On complication, the multiple splitting of these two bands arise from out – of – plane motions other than those in phase and also probably from overtones of low lying fundamentals in resonance. The splitting of these two bands appears to be metal sensitive.

These facts suggest the coordination of the alkali metals with 1,10 – phenanthorline through the nitrogen atoms of its pyridine fragments 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. Only two bands are observed : one at 738 cm^{-1} (assigned to out – of – plane motion of the H – atoms on the heterocyclic rings) and the other at 854 cm^{-1} (assigned to out of plane motion of hydrogen atoms on the central ring). On complication, the multiple splitting of these two bands arise from out – of – plane motions other than those in phase and also probably from overtones of low lying fundamentals in resonance. The splitting of these two bands appears to be metal sensitive. These facts suggest the coordination of the alkali metals with 1,10 – phenanthorline through the nitrogen atoms of its pyridine fragments. Our present work shows that hydrogen bonding is not necessary for formation of adducts between a chelating ligand and the alkali metal salt of a chelate ion.

II. CONDUCTIVIES

Molar conductivities of all the complexes were measured in N – methyl – 2 – pyrrolidone at 250^0c at a concentration of 10^{-3} M.

The solvent has been calibrated by Banerjee et.al[16] and they have observed that the values of molar conductivities in the range 35 – 40 cm^{-1} correspond to 1:1 electrolyte. Detail studies [125,126] of this solvent have shown that significantly different values as obtained with different anions, even for tetra – alkylammonium cations, and that 1:1 electrolytes may give values as low as 25 ohm^{-1} cm^{-1} $mole^{-1}$. From the results (Table – 7.2), it is observed that none of the values approach either ideal or 1:1 electrolyte. Low values of molar conductivities of these complexes would seem to indicate neutral complexes. However, low values are also obtained for the simple salts, which may be due to ion-pair formation and the consequent preliminary chelation. The trend Li > Na > K would seem to indicate that the lithium complexes is the strongest in solution. Significantly high values of molar conductivities of these complexes in N – methyl – 2 – pyrrolidone suggest that they have undergone dissociation

III. STRUCTURE AND BONDING

Analytical data lead to the general molecular formula M1.L' for these complexes, where M = alkali metal salt of the O-Hydroxyacetophenone hydrazone, O-Hydroxyacetophenone phenyl hydrazone or O-Hydroxyacetophenone – 2, 4 - dinitrophenyl hydrazone and L'= 1,10 – phenanthorline. Their IR spectra suggest the coordination of the ligand L'with alkali metals through nitrogen atom of the pyridine fragments. Accordingly, these complexes should have the following structure :

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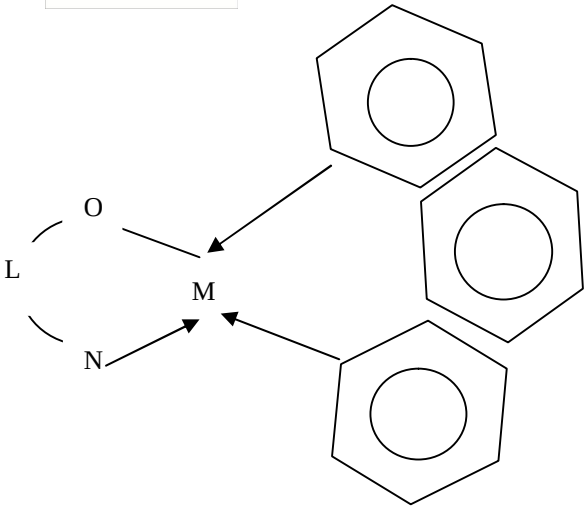


Fig 7.5

IV. EXPERIMENTAL

Ligand 1,10 - phenanthroline
The ligand 1,10 – phenanthroline of E. Merck quality was used as such.

A. Adducts of 1,10 – phenanthroline

1) Adducts with alkali metal salts of O-Hydroxyacetophenone hydrazine: To the hot suspension of an alkali metal salt of O-Hydroxyacetophenone hydrazone (OHAHz) in acetone, excess of solid 1,10 – phenanthorline was added. On stirring, the contents went into solution and almost instantaneously, pale yellow coloured adduct came apart. It was redis solved by warming the contents on a steam bath for 5 minutes. On cooling, the pale yellow adduct reappeared. It was filtered, washed with cold benzene dried in a desicator over anhydrous $CaCl_2$.

a) Li OHAHz.phen

Found : C, 71.38 ; H, 5.00; N, 16.62%
$C_{20}H_{17}N_4OLi$ requires
: C, 71.42 ; H, 5.06 ; N, 16.67%

b) NaOHAHz.phen

Found : C, 68.13 ; H, 4.87; N, 15.85 ; Na, 6.50%
$C_{20}H_{17}N_4ONa$ requires
: C, 68.18 ; H, 4.83; N, 15.91 ; Na, 6.53%

c) KOHAHz.phen

Found : C, 65.17 ; H, 4.58; N, 15.20 ; K, 10.52%
$C_{20}H_{17}N_4OK$ requires
: C, 65.22 ; H, 4.62; N, 15.22 ; K, 10.59%

2) Adducts with alkali metal salts of O-Hydroxyacetophenone phenylhydrazone : These adducts were obtained by the method strictly analogous to that described for the preparation of adducts of 1,10 – phenanthroline with alkali metal salts of O-Hydroxyacetophenone phenylhydrazone **.** Ease of formation of the adducts was found to be greater in comparison to the formation of the adducts in case of OHAHz.

a) Li OHAPz. phen

Found : C, 75.69 ; H, 5.01; N, 13.51%
$C_{26}H_{21}N_4OLi$ requires
: C, 75.73 ; H, 5.09; N, 13.59%

b) Na OHAPz.phen

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Found : C, 72.82 ; H, 4.89; N, 13.02 ; Na, 5.32%
$C_{26}H_{21}N_4O$ Na requires
:C, 72.89 ; H, 4.91; N, 13.08 ; Na, 5.37%

c) KOHAPz.phen

Found : C, 70.22 ; H, 4.69; N, 12.66; K, 8.74%
$C_{26}H_{21}N_4O$ K requires
: C, 70.27 ; H, 4.73; N, 12.61; K,8.78%

3) Adducts with alkali metal salts of O-Hydroxyacetophenone - 2,4 – dintrophenylhydrazone

These adducts too could be obtained by the procedure as described above for the preparation of adducts of OHAPz.

a) LiOHADNPz.phen

Found : C, 62.23 ; H, 3.62; N, 16.72%
$C_{20}H_{18}N_6O_5Li$ requires
: C, 62.28 ; H, 3.59 ; N, 16.77%

b) NaOHADNPz.phen

Found : C, 60.30 ; H, 3.52; N, 16.20 ; Na, 4.50%
$C_{20}H_{18}N_6O_5Na$ requires
: C, 60.35 ; H, 3.48; N, 16.25 ; Na, 4.45%

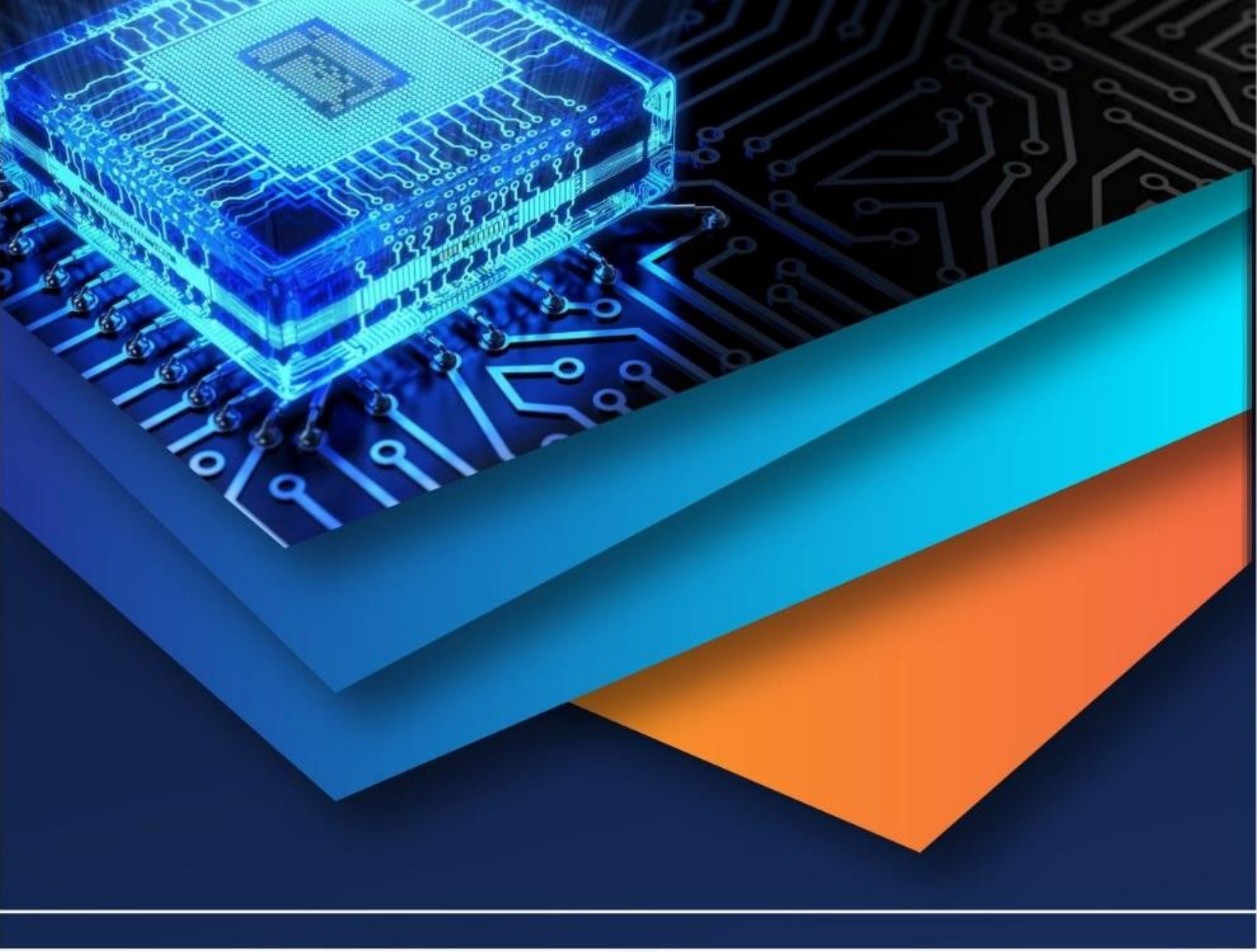
c) KOHADNPz.phen

Found : C, 58.50 ; H, 3.42; N, 15.72; K, 7.36%
$C_{20}H_{18}N_6O_5K$ requires
: C, 58.54 ; H, 3.48; N, 15.76; K,7.32%

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