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Mixed Ligand Complexes of Alkali Metal Salts of Some Organic Acids with Isonitroso Ethylacetoacetate

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Some mixed ligand complexes of alkali metal salts of 1-nitroso-2-naphthol. 8-hydroxy quinoline, *o*-amino phenol, *o*-amino benzoic acid, *o*-nitro benzoic acid with isonitroso ethylacetoacetate have been synthesised and characterised on the basis of elemental analysis, conductivity measurement and IR spectral data.

INTRODUCTION

Complexing ability of isonitroso compounds has been well documented with transition metals[1–4] as well as with alkali metals[5–8]. We have extended the investigation to synthesise the mixed ligand complexes of alkali metals having the general formula ML·HL′, where M = Li, Na or K, L = deprotonated 1-nitroso-2-naphthol (1N2N), 8-hydroxy quinoline (8HQ), *o*-amino phenol (OAP), *o*-amino benzoic acid (OABA), *o*-nitro benzoic acid (ONBA), HL′ = isonitroso ethylacetoacetate (INEAA).

EXPERIMENTAL

1-Nitroso-2-naphthol, 8-hydroxy quinoline, *o*-amino benzoic acid, *o*-amino phenol, *o*-nitro benzoic acid of AnalaR grade was taken and made to react with alkali metal hydroxides in an ethanolic medium to produce their respective salts. Reagents used for the preparation of ligand (INEAA) too were of AnalaR grade. Isonitroso ethylacetoacetate (INEAA) was prepared by the method of Liebig[9].

1 : 1 Stoichiometric amounts of alkali metal salts of 1N2N, OAP, 8HQ, OABA, ONBA and INEAA were used in absolute ethanolic medium with constant stirring and heating, which on concentration and cooling of the solution led to the separation of coloured adducts of respective complexes. The precipitates were filtered, washed with absolute ethanol and dried in an electric oven at 80°C.

RESULTS AND DISCUSSIONN

Some physical properties of ligand (INEAA) and its mixed ligand complexes are listed in Table-1. From the result, it is evident that almost all the complexes of INEAA have been found to be coloured and stable under dry conditions. They undergo transformation at temperatures which are considerably higher than the melting point of the ligand (INEAA), indicating their greater thermal stability. Most of the complexes are soluble in polar solvents, *e.g.*, methanol, ethanol, DMF,

However, a few complexes have also been found to be sparingly soluble in non-polar solvents, *e.g.*, chloroform. Ease of complexation and the quantum of yield was found to increase with increase in radius of alkali metal ions (*i.e.*, $Li^+ < Na^+ < K^+$).

TABLE-1
PHYSICAL PROPERTIES AND ANALYTICAL DATA OF METAL COMPLEXES

Compound	Colour	M.P./decomp./ trans. temp. (°C)	Conduc-tivity*	Analysis % (Found/Calcd.)			
				C	H	N	M
H·INEAA	Colourless	57m	–	47.23 (45.28)	5.60 (5.66)	8.70 (8.80)	–
Li1N2N·INEAA	Yellow	245d	5.7	56.7 (56.8)	4.2 (4.4)	8.0 (8.3)	2.0 (2.1)
Na1N2N·INEAA	Pale green	250d	7.0	54.0 (54.2)	4.1 (4.2)	7.6 (7.9)	6.3 (6.5)
K1N2N·.NEAA	Brownish green	260d	8.3	51.5 (51.9)	3.9 (4.1)	7.3 (7.6)	10.6 (10.5)
Li8HQ·INEAA	White	245d	3.0	57.8 (58.0)	4.6 (4.8)	8.0 (8.1)	2.0 (2.3)
Na8HQ·INEAA	Blackish white	230d	6.0	55.0 (55.2)	4.5 (4.6)	8.5 (8.6)	7.0 (7.1)
K8HQ·INEAA	White	270d	3.2	52.5 (52.6)	4.5 (4.4)	8.1 (8.2)	11.3 (11.4)
LiOAP·INEAA	Light orange	270d	5.0	52.48 (51.65)	5.41 (5.47)	10.16 (10.22)	2.50 (2.55)
NaOAP·INEAA	Blackish white	225d	7.0	49.59 (49.65)	5.11 (5.17)	9.60 (9.65)	7.90 (7.93)
KOAP·INEAA	Pinkish white	270d	3.3	47.0 (47.06)	4.85 (4.90)	9.12 (9.15)	12.69 (12.74)
LiOABA·INEAA	Blackish white	250d	2.9	51.60 (51.65)	4.91 (4.97)	9.23 (9.27)	2.26 (2.32)
NaOABA·INEAA	Blackish white	220d	5.5	48.97 (49.05)	4.66 (4.72)	8.75 (8.80)	7.20 (7.25)
KOABA·INEAA	White	270d	4.9	46.67 (46.71)	4.43 (4.49)	8.34 (8.38)	11.60 (11.67)
LiONBA·INEAA	White	245d	5.0	46.91 (46.99)	3.85 (3.91)	8.99 (8.43)	2.05 (2.11)

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

Molar conductivities of all complexes were measured in DMF at 23°C at a concentration of 10^{-3} M. A value of *ca.* 35–40 ohm^{-1} cm^2 mol^{-1} corresponds to 1 : 1 electrolyte[10]. From the result, it is evident that the molar conductivities of none of the complexes approach either ideal or 1 : 1 electrolyte. However, the significantly low values of molar conductivities of these complexes suggest them to be covalent compounds.

Infrared spectra of the ligand (HL′) and its mixed ligand alkali metal complexes (ML·HL′) have been recorded in the region 4000–650 cm^{-1} in KBr phase with the help of a Perkin Elmer spectrometer, model 257. The selected absorption bands of the ligand as well as of the complexes are given in Table-2.

TABLE-2

Compound	ν(O—H/O—H . . O)	ν(C=O)	ν(C=N)	ν(N—O) or ν(N=O)
H·INEAA	3300–3200br, 2850br	1720m, 1660m	1590w	990s
Li1N2N·INEAA	2900–2800br 2200br	1710m, 1640w	1570m	960w
Na1N2N·INEAA	3050br, 2350br	1710m, 1630m	1575m	970m
K1N2N·INEAA	3100br, 2500br	1720sh, 1625m, 1605w	1575m	980m
Li8HQ·INEAA	3150br	1720m, 1640m, 1605m	1580s	960m
Na8HQ·INEAA	3340br, 2350br	1720w, 1610m	1575m	980m
K8HQ·INEAA	3200br	1710w, 1650m, 1600m	1570m	970m
LiOAP·INEAA	3050br, 2500br	1720m, 1630m, 1620m	1575m	970m
NaOAP·INEAA	3150br, 2850br	1630m, 1610s	1570m	980m
KOAP·INEAA	3100br, 2320br	1720w, 1640sh 1600s	1560m	980w
LiOABA·INEAA	3370s, 3350m, 3050br	1615s	1575m	980m
NaOABA·INEAA	3480m, 3340s, 3050br, 2350br	1700s, 1610s	1570m	960m
KOABA·INEAA	3450m, 3350m, 3100br	1710m, 1630m, 1600m	1575m	970m
LiONBA·INEAA	3100br, 2800br	1620m	1575m	970m

Spectra of mixed ligand complexes of alkali metal salts of some organic acids with isonitroso ethylacetoacetate: The broad absorption bands in the region 3200–2800 cm^{-1} in the spectrum of the ligand point out to the presence of strong intramolecular hydrogen bonding involving the isonitroso hydrogen atom and the carbonyl oxygen atom.

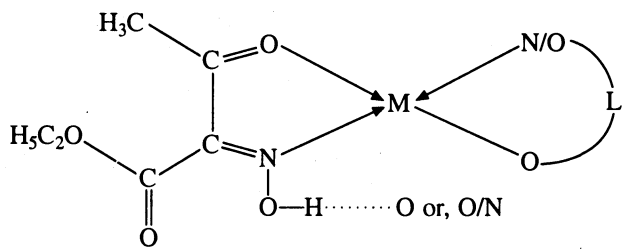
In general, the IR spectra of mixed ligand complexes are very complicated, hence difficult in interpretation precisely because of both the ligand having different or somewhat similar functional group which rise to absorption bands in the similar region, *i.e.*, 1700–950 cm^{-1}. New broad absorption bands of medium to strong intensity in the region 3100–2200 cm^{-1} (shifted from 3200–2800 cm^{-1}) in its mixed ligand complexes except Na8HQ·INEAA and K8HQ·INEAA suggest that there is strong hydrogen bonding. Only MOABA·INEAA, where M = Li, Na or K, shows medium absorption bands in the region 3500–3300 cm^{-1} also which appear most probably due to presence of $—NH_2$ group in the first ligand *o*-amino benzoic acid (used as anion of alkali metal salts).

None of these mixed ligand complexes showed anomalous broad absorption

bands between 1100–700 cm^{-1} characteristic of acid salt structure with very short O . . H—O (about 2.7 Å). The two peaks at 1720 cm^{-1} and 1660 cm^{-1} are assigned to free and bonded carbonyl groups in the ligand. The 1720 cm^{-1} absorption bands of the ligand remain unaffected, due to presence of free >C=O group in them also. On the other hand the 1660 cm^{-1} absorption band of the ligand shifts towards lower frequency by 10–50 cm^{-1} in the case of its mixed ligand alkali metal complexes. This indicates the participation of second >C=O group of the ligand in coordination. In some cases absorption band at 1660 cm^{-1} splits into two peaks of lower frequencies. This is due to presence of various functional groups like —NH_2, —NO_2, —COOH bending etc. in the various alkali metal anions of organic acids (first ligand). The 1590 cm^{-1} absorption band of the ligand assigned to the stretching ν(C=N) absorption, shifted towards lower frequency by 10–30 cm^{-1}. These features suggest the coordination of the ligand with alkali metals through nitrogen atom. The 990 cm^{-1} absorption band of the ligand assigned to the N—O absorption was generally found to be shifted towards lower frequency. The lower shifting by 10–30 cm^{-1} implies the coordination through nitrogen atom of —NO group in the complexes.

Structure and Bonding

The probable structure on the basis of above studies can be produced schematically as given below:



where M = Li, Na, or K: L = 1N2N, OAP, ONBA, OABA, 8HQ

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