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Alkali Metal Complexes: Mixed Ligand Complexes of Alkali Metal Salts of Some Organic Acids with Isonitrosoethylmethylketone

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A number of mixed ligand complexes of alkali metal salts of *o*-nitrophenol, 2,4-dinitrophenol, 2,4,6-trinitrophenol, 1-nitroso-2-naphthol, salicylic acid, 8-hydroxyquinoline and *o*-aminobenzoic acid with isonitrosoethylmethylketone have been synthesised in absolute ethanol and characterised by elemental analysis, conductivity measurement and IR spectral data. Their IR spectral data indicate the presence of hydrogen bonding in them, which may be one of the dominant factors for their stability.

INTRODUCTION

Coordinating ability of alkali metal salts with isonitrosoacetophenone,[1-3] isonitrosopropiophenone and isonitrosobenzoylacetone[4] have been reported earlier. However, a survey of the literature revealed that no mixed ligand complexes of alkali metal salts of organic acids with isonitrosoethylmethylketone (INEMK) have previously been reported. In the present communication, we report the synthesis and characterisation of a number of mixed ligand complexes of alkali metal salts of some organic acids with isonitrosoethylmethylketone.

EXPERIMENTAL

The ligand, isonitrosoethylmethylketone (INEMK) was prepared by the method described by Semon and Domerill.[5] 1-Nitroso-2-naphthol (1N2N), *o*-nitrophenol (ONP), 2,4-dinitrophenol (DNP), 2,4,6-trinitrophenol (TNP), salicyalic acid (SalA), 8-hydroxyquinoline (8HQ) and *o*-aminobenzoic acid (OABA) of AnalaR grade were used as such.

Preparation of Alkali Metal Salts of Various Organic Acids

Equimolar proportions of alkali metal hydroxide and the organic acids (ONP, DNP, TNP, 1N2N, 8HQ, SalA and OABA) were refluxed in 95% ethanol for *ca.* 1/2 h. The solution was concentrated and then cooled, when the alkali metal salt precipitated out. It was filtered, washed with solvent and then dried in an electric oven at 80°C.

Preparation of the Complexes

The complexes were prepared by taking equimolar proportions of the alkali metal salt and the ligand (INEMK) in absolute ethanol. On refluxing with

continuous stirring for 1–2 h, a clear solution was obtained. On concentration and cooling, the adduct got separated which was filtered, washed with absolute ethanol and dried in an electric oven at 80°C.

RESULTS AND DISCUSSION

The physical properties and analytical data of the ligand isonitrosoethylmethylketone (HL′) and its mixed ligand complexes (ML·HL) with various other organic acids (HL) are listed in Table 1.

TABLE 1
ANALYTICAL DATA OF ALKALI METAL COMPLEXES

Compound/ Colour	m.p./decom./ trans. temp. (°C)	Analysis % (Found/calculated)			
		C	H	N	M
INEMK (White)	75 m	47.8 (47.5)	6.8 (6.9)	13.6 (13.8)	—
Li(IN2N)INEMK (Dark brown)	200 t	58.65 (60.00)	4.68 (4.64)	9.85 (10.00)	2.3 (2.5)
Na(IN2N)INEMK (Dark brown)	80 t	55.25 (56.75)	4.41 (4.39)	9.45 (9.46)	7.70 (7.76)
K(IN2N)INEMK (Brown)	85 t	52.90 (53.84)	4.20 (4.17)	8.78 (8.98)	12.00 (12.50)
K(ONP)INEMK (Orange yellow)	130 t, 180 d	45.91 (45.16)	4.05 (3.96)	9.85 (10.07)	13.80 (14.03)
Na(DNP)INEMK (Deep yellow)	270 d	40.25 (39.09)	3.30 (3.26)	13.20 (13.68)	7.25 (7.49)
K(DNP)INEMK (Deep yellow)	280 d	36.50 (37.15)	3.25 (3.09)	12.63 (13.00)	11.81 (12.07)
Na(TNP)INEMK (Deep yellow)	258 d	35.25 (34.09)	2.41 (2.55)	15.45 (15.91)	6.25 (6.53)
K(TNP)INEMK (Bright yellow)	270 d	33.80 (32.61)	2.50 (2.44)	15.80 (15.22)	9.85 (10.59)
Li(SalA)INEMK (Cream)	280 d	53.55 (53.87)	4.71 (4.89)	5.04 (5.17)	2.98 (2.85)
Na(SalA)INEMK (Dirty white)	260 d	50.13 (50.57)	5.02 (4.59)	5.22 (5.36)	8.96 (8.81)
K(SalA)INEMK (Dirty white)	250 d	48.50 (47.65)	4.38 (4.33)	4.95 (5.05)	13.68 (14.08)
Li(8HQ)INEMK (Dirty white)	300 d	60.98 (61.90)	5.20 (5.16)	10.95 (11.11)	2.75 (2.77)
K(8HQ)INEMK (Yellow)	232 d	53.75 (54.93)	4.60 (4.57)	9.78 (9.86)	13.62 (13.73)
Li(OABA)INEMK (Dirty white)	300 d	55.20 (54.09)	5.38 (5.33)	10.45 (11.47)	2.70 (2.87)
K(OABA)INEMK (Dirty white)	265 d	47.75 (47.83)	4.65 (4.71)	10.24 (10.15)	14.26 (14.13)

From the results it is evident that almost all the complexes undergo transformation at temperatures which are considerably higher than the melting points of the ligand used, indicating their greater thermal stability. Ease of complexation and yield was found to increase with increase in radius of the alkali metal ions. Most of these complexes are found to be sparingly soluble in most polar solvents such as methanol, ethanol, DMF, etc. but they are insoluble in non-polar solvents such as benzene, chloroform, diethyl ether etc.

Molar conductivities were measured in MeOH at 23°C at concentration of 10^{-3} M. The significantly low values of molar conductivity (1.5–8.0 ohm^{-1} cm^2 $mole^{-1}$) from the mixed ligand complexes of Li and Na with INEMK would seem to suggest that they are non-electrolytes.[6] The slightly higher values for the K-complexes of INEMK imply that they have undergone partial dissociation in the solvent (MeOH) used.

Infrared spectra for the ligand and its mixed ligand alkali metal complexes have been recorded in the region 4000–650 cm^{-1} in KBr disc.

The spectrum of isonitrosoethylmethylketone shows multiple medium broad absorption bands over a wide range (3300–3200 cm^{-1}). The presence of absorption features in this region points out to the presence of intramolecular hydrogen bonding involving isonitroso hydrogen atom and the carbonyl oxygen atom of the ligand.

The spectra of all the mixed ligand alkali metal complexes (ML·HL′) differ from that of ligand (HL′) by the absence of a medium broad hydrogen bonded O—H stretching absorption bands in the region 3300–3200 cm^{-1} except complexes with Li-OABA and K-OABA. However shifting of broad adsorption bands in the region 3300–3200 cm^{-1} of the ligand (INEMK) to 3100–1800 cm^{-1} in its mixed ligand complexes suggest that there is a strong hydrogen bonding. In case of Li-OABA and K-OABA two strong and medium absorption bands between 3400–3200 cm^{-1} can also be seen, which appear only due to the presence of NH_2 group in the first ligand (L^-). None of these mixed ligand complexes showed anomalous broad absorption band between region 1100–700 cm^{-1} characteristic of acid salt structure with very short O - - - H—O (about 2.7 Å).

The IR spectrum of the ligand shows characteristic absorption at 1670 cm^{-1}, 1680 cm^{-1} and 1010 cm^{-1} which may be assigned to ν(C=O), ν(C=N) and ν(N—O) modes respectively. In all the mixed ligand alkali metal complexes shifting by 30–70 cm^{-1} in the region 1670 cm^{-1} has been found. In some of the mixed ligand complexes another band appears in this region which may be attributed to the presence of groups like —COOH, ν(C=O), ν(–NO_2), —NH_2 bending etc. in the various alkali metal anions of organic acid (first ligands).

The 1580 cm^{-1} absorption band of the ligand has been assigned to the stretching ν(C=N) absorption has shifted towards lower frequency[7,8] by 10–20 cm^{-1}. These features suggest the coordination of the ligand with alkali metals through nitrogen atoms.

The 1010 cm^{-1} strong absorption band of the ligand which has been assigned to the stretching ν(N—O) absorption has shifted towards lower frequency by 20–50 cm^{-1}. The higher shifting implies that the double bond character of the

(NO) linkage increases on complexation and suggests the coordination through nitrogen atom of the NO group in the complexes.

TABLE 2
PERTINENT IR DATA (cm^{-1}) FOR LIGAND (INENK) AND ITS MIXED LIGAND ALKALI METAL COMPLEXES

Compound	ν(O—H/O—H - - - O)	ν(C=O)	ν(C=N)	ν(N—O)
INEMK	3300–3200 br	1670 s	1580 w	1010 s
Li(1N2N)INEMK	2900–2800 br, 2200 br	1640 w	1570 m	970 m
Na(1N2N)INEMK	2500–2400 br	1640 s	1565 m	980 m
K(ONP)INEMK	3100 br	1630 s	1560 s	980 m
Li(8HQ)INEMK	3050 br	1610 m	1580 s	960 m
K(8HQ)INEMK	3060 br	1620 m	1575 s	960 m
Na(Sal A)INEMK	3050 br, 2650–2550 br	1635 m	1580 s	995 m
K(Sal A)INEMK	3550 br, 2600–2500 br	1630 m	1570 s	990 m
Na(DNP)INEMK	3100 br, 2500–2400 br 2000–1900 br	1640 sh, 1600 s	1570 m	980 w
K(DNP)INEMK	3100 br, 2320 br	1600 s, 1640 sh	1560 m	980 w
Na(TNP)INEMK	3100 s, 1870 br	1635 s, 1615 sh	1570 s	990 w
K(TNP)INEMK	3100 br, 2850 br	1635 s, 2625 sh	1560 s	960 m
Li(OABA)INEMK	3380 s, 3270 s, 3050 br	1615 s	1580 s	980 m
K(OABA)INEMK	3380m, 3320 m, 3100–2800 br	1630 m, 1610 m, 1590 m	1560 s	990 m

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