Alkali Metal Complexes: Mixed Ligand Complexes of Some Alkali Metal Salts of Some Organic Acids with Isonitroso-P-Methyl Ace to phenone

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Abstract
A number of mixed ligand complexes of alkali metal salts of o-nitrophenol,2,4-dinitrophenol, 2,4,6,-trinitrophenol, 1-nitroso-2- naphthol and 8- hydroxyquinoline with Insoniroso–p methylacetopheone have been synthesized in absolute ethanol & characterized by elemental analysis and I .B. spectral data. Their I.R spectral data indicate the presence of hydrogen bonding in them, which many be one of the dominant factors of their stability. Further appreciable shift in 1650 cm^{-1} band (possibly vC=O) and 1600 cm^{-1}band (possibly vC=N)Suggests their coordination behavior in these mixed ligand complexes
The reactions that take place in natural systems are highly specific and selective. Alkali metal ions actively participate in most of the reaction occurring in the biological systems, which are dominated by mixed ligand complexes. Studies of such mixed ligand complexes of alkali metals can threw light in understanding the role and mechanism of selective absorption of alkali metals ions by plants
Coordinating ability of alkali metal with isonitrosoacetophenone[1-2] and transition metals with isonitrosoacetophenone[3] and isonitroso-p-methylacetophenone[4] have been reported earlier. In the present paper we report the mixed ligand complexes of alkali metal salts having the general formula ML.HL, ' where M=Li, Na & K and L=deprotonated o- nitrophenol, 2,4 dinitrophenol, 2, 4, 6- trinitrophenol, 1-nitroso-2-naphthol or 8-hydroxquinoline; HL'= p-MeHINAP (isonitroso-p-methylacetophenone).

I. EXPERIMENT AL

Preparation of p-Me HINAP

The ligand ML' was prepared by the method V.Pechmann and Muller[5].

Preparation of the complexes

To a suspension of alkali metal salts(ML)in absolute ethanol, the ligand(HL')was added (1:1 mole ratio) and the reaction mixture was heated under reflux with stirring for half an hour when a uniform solution was obtained. The contents were slightly concentrated and cooled when the colored adducts got separated. The separated adduct was filtered, washed ethanol and dried at 80^0 C in an electric oven.

II. RESULTS AND DISCUTION

The complexes of these ligands with alkali metal salts are characteristically colored.The
Colors, the decomposition/transition temperatures as well as analytical data of these
Complexes are listed in table 1.

Table-1

Compound	Colour	M.p./ Decom/trans temp (c)	%Found				(%)calculated			
			C	H	N	M	C	H	N	M
P-MeHINAP	Light cream	98-99 M	66.28	5.55	8.58		66.26	5.52	8.58	
Li(ONP)p-MeHINAP	Pale yellow	220 d	57.88	4.20	8.98	2.33	58.44	4.22	9.09	2.77
Na(ONP)p-MeHINAP	Yellowish green	284 d	56.80	4,20	8.78	7.06	55.56	4.04	8.64	7.09
K(ONP)p-MeHINAP	Pale pinkish yellow	300 d	53.25	3.85	8.28	11.44	52.94	3.82	8.24	11.47
Li(DNP)p-MeHINAP	Light yellow	132.d	51.06	3.42	11.95	1.63	50.99	3.39	11.89	1.98
Na(DNP)P-MeHINAP	Bright yellow	150.d	48.60	3.27	11.35	6.26	48.78	3.25	1138	6.23
K(TNP)p-MeHINAP	Deep yellow	230.m	44.98	3.15	10.88	10.21	47.75	3.12	10 91	10.13
Li(TNP)p-MeHINAP	Yellow	223.d	46.00	2,82	14.14	1.71	45.23	2.76	14.07	1.76
Na(TNP)P-MeHINAP	Deep yellow	248 d	42.50	2,68	13.45	5.60	43.48	2.66	13.53	5.58
K(TNP)p-MeHINAP	Deep yellow	260 d	40.28	2.54	12,15	9.09	41.46	2.59	12.00	9.01
Li(IN2N)p-MeHINAP	Yellowish green	225.d	66.41	4.33	812	2.10	66.76	4.39	8.19	2.05
Na(IN2N)p-MeHINAP	Dark brown	180.d	63.60	418	7.78	6.48	63.69	4.19	7.82	6.42
K(IN2N)p-MeHINAP	Brownish green	210.d	58.70	420	7.05	10.45	60.96	4.21	7.49	10.43

Li(8HQ)p-MeHINAP	Cream	220 m	67.68	5.00	8.80	2.31	68.79	4.78	8.92	2.23
Na(8HQ)p-MeHINAP	Brownish yellow	135 d	65.28	4.58	8.52	6.91	65.46	4.55	8.49	6.97
K(8HQ)p-MeHINAP	Yellow	112 d	61.20	4.38	7.75	11.35	62.43	4.34	8.09	11.27

Ease of complexation and yield was found to increases 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 etc. but are insoluble in non-polar solvents such as benzene diethyletheretc.

They are stable in dry air but stability decreased on exposure to moisture leading ultimately to decomposition hence all the complex were kept in desiccator over solid anhydrous calcium chloride.

They either decompose or undergo a transformation at temperatures, which are considerably higher than the melting point of the corresponding ligand, indicating their greater thermal stability.

III. INFRARED SPECTRA:

Infrared measurements for the title ligand and its hitherto unknown mixed ligand alkali metal complexes of the type (ML.HL') were recorded in the region between 4000 to 650 cm^{-1} in Nujol mulls. Pertinent IR data for these compounds are recorded in Table 2.

Table 2.
Pertinent IR data (cm^{-1}) for ligand (p-MeHINAP) and its mixed ligand complexes.

Compound	*v*OH	*v*C=0	*v*C=N	*v*N-O
p- MEHINAP	3300-3200 br	1650 s	1600s	980s
Li(ONP)p-MeHINAP	2800-2600br	1640sh,1620sh	1590s	1000m
Na(ONP)p-MeHINAP	2300br	16070s,1620sh	1580m	1000sh
K(ONP)P-MeHINAP	1900-1800br	1630 sh	1590s	980s
	2320 br			1010w
	2000-1900 br			
	2320 br			
Na (DNP)p-MeHINAP	2320br,1950br	1670 s, 1640w	1590s	1020m
K(DNP)p-MeHINAP	2340 br	1640m,1630m	1590m	1000m
Li(TNP)p-MeHINAP	2340 br,1830 br	1640sh, 1600s	1575 m	1010 m
Na(TNP)p-MeHINAP	2320br,1870 br	1630,1610sh	1560 s	1005 s
K(TNP)p-MeHINAP	2350 br	1630 m,1610 w	1560 m	1000 w
Li(IN2N)p-MeHINAP	2350 br	1630 m,1610 m	1555 s	1020 m
Na(IN2N)p-MeHINAP	2340 br,1950 br	1640 s,1600 m	1570 s	1025 m
K(IN2N)p-MeHINAP	2320 br	1640 sh,1625 m	1590 m	1000 m
Li(8HQ)p-MeHINAP	2340 br	1615 m,1600 s	1580 m	1010 s
Na(8HQ)p-MeHINAP	2340 br, 1950 br	1620 m,1610 m	1590 m	1015 sh
K(8HQ)p-MeHINAP	2340 br	1630 m, 1605 m	1590 m	1000 m

m=medium, s=strong, br=broad, sh=shoulder, w=weak.

The spectra of p-MeHINAP shows multiple medium broad absorption bands over a wide range (3330-3200 cm-1 & 2800-2600 cm-1. The presence of absorption features in this region points out to the presence of strong intramolecular hydrogen bonding involving oximino hydrogen atom and the carbonyl oxygen atom of the ligand.

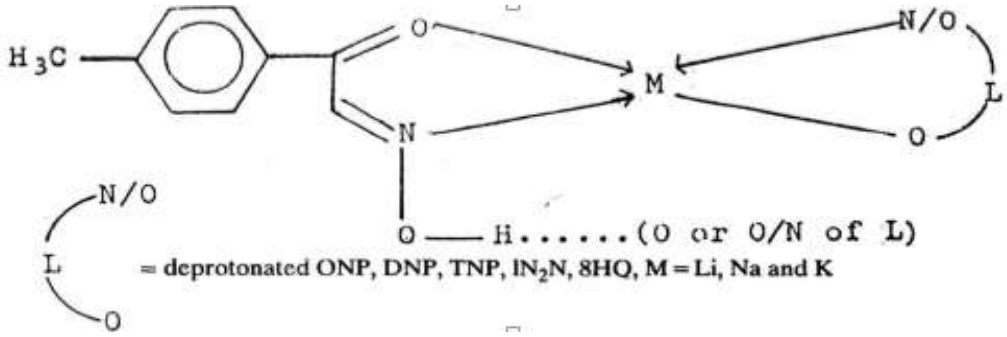
Shifting of board absorption bands in the region 3300-1800 cm^{-1} of the ligand (HL') to 2490-1800 cm^{-1} in its mixed ligand complexes suggest that there is strong hydrogen bonding[6-8]. None of these mixed ligand complexes showed anomalous broad absorption band between 1100-700 cm^{-1} characteristic of acid salt structure with very short O…H – O (Ca, 2.7 AE).

The IR spectrum of the ligand shows characteristic absorption at 1650 cm^{-1}, 1600 cm^{-1} and 980. Cm^{-1} which may be assigned to *v*C=O, vC=N and N-O modes respectively. In all the mixed ligand complexes shifting by 10-50 cm^{-1} in the region 1650 cm^{-1} was found. Some of the mixed ligand complexes also showed another band in this region which may be attributed to the presence of groups like C=O, NO_2etc. in the various alkali metal anions of organic acids (first ligands). Shifting to lower frequency by 10-40 cm^{-1} in the region 1600cm^{-1} (for *v*C=N stretching) suggest of the coordination of the legand (HL) with alkali metal through nitrogen atom.

Shifting of the absorption band in the region 980 $^{cm-1}$ to higher frequency suggest the coordination through nitrogen atom of N-O group in the complexes and higher shifting also implies the double bond character of the N-O group linkage.

IV. PROBABLE STRUCTURE

The probable structures on the basis of above factual information can be produced schematically as such.



= deprotonated ONP, DNP, TNP, IN_2N, 8HQ, M = Li, Na and K

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