

Mixed Ligand Complexes of Alkali Metal Salts of Some Organic Acids with Picolinic Acid

D. PRAKASH,* K.B. SINHA, B. KUMAR and ANJU K. GUPTA
Department of Chemistry, Patna University, Patna-800 005, India

The mixed ligand complexes of the general formula $ML \cdot HL'$ where $M = Li, Na$ or K , $L =$ deprotonated 2,4-dinitrophenol, 2,4,6-trinitrophenol, *o*-nitronaphthol, 2,4-dinitronaphthol and $HL' =$ picolinic acid, have been synthesised and characterised by physical methods. IR spectral data show that hydrogen bonding in these complexes are dominant factors for their stability.

INTRODUCTION

The study of mixed ligand complexes has evinced considerable interest among coordination chemists due to the biological importance in the living system^{1,2}. Transition metals, rare earth metals as well as alkaline earth metals complexes with picolinic acid have been well investigated earlier³⁻⁵. In this communication we have taken picolinic acid to investigate the coordination behaviour towards various alkali metal salts of some organic acids such as 2,4-dinitrophenol (DNP), 2,4,6-trinitrophenol (TNP), *o*-nitronaphthol (ONN) and 2,4-dinitronaphthol (DNN).

EXPERIMENTAL

2,4-Dinitrophenol, 2,4,6-trinitrophenol, *o*-nitronaphthol, 2,4-dinitronaphthol and picolinic acid or AnalaR grade were used as such.

Preparation of alkali metal salts of various organic acids: Equimolar proportions of metal hydroxide and organic acid were refluxed in an ethanolic medium for about 30 min. The clear solution was then cooled when the coloured alkali metal salts precipitated out. It was filtered, washed with absolute alcohol and dried in an electric oven at 80°C.

Preparation of the Complexes: 1 : 1 stoichiometric amount of alkali metal salts of DNP, TNP, ONN, OND and DNN and picolinic acid 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 DISCUSSION

The colours, melting/transition temperatures and analytical data of the ligand (picolinic acid) and its mixed ligand alkali metal complexes are listed in Table-1.

All the complexes are light coloured (yellow or brownish yellow) and are stable under dry condition. Most of the complexes are soluble in polar solvents, *e.g.*, methanol, ethanol, but a few of them are sparingly soluble in non-polar solvents. They undergo a transformation at temperatures which are considerably higher than the melting point of the corresponding ligand, indicating thereby their greater thermal stability.

TABLE-1

Compound	Colour	m.p./decomp./ trans. temp. (°C)	Analysis % (found/calcd.)			
			C	H	N	M
Picolinic acid (HPicA)	White	135m	58.48 (58.54)	4.01 (4.06)	11.21 (11.38)	– –
Li(DNP)·HPicA	Yellow	220t	45.78 (46.15)	2.50 (2.56)	13.00 (13.48)	2.20 (1.92)
Na(DNP)·HPicA	Yellow	240t	42.92 (43.76)	2.45 (2.43)	12.58 (12.76)	6.70 (6.99)
K(DNP)·HPicA	Yellow	260t	41.66 (41.70)	2.30 (2.31)	12.15 (12.17)	11.00 (11.30)
Li(TNP)·HPicA	Yellow	265t	40.00 (40.33)	1.97 (1.96)	15.25 (15.68)	1.80 (1.68)
Na(TNP)·HPicA	Yellow	260t	38.00 (38.42)	1.85 (1.87)	14.50 (14.97)	6.00 (6.14)
K(TNP)·HPicA	Yellow	268t	36.25 (36.92)	1.72 (1.79)	14.20 (14.35)	9.90 (10.00)
Li(ONN)·HPicA	Yellow	240t	59.85 (60.50)	3.50 (3.47)	8.80 (8.83)	1.85 (1.89)
Na(ONN)·HPicA	Yellow	218t	57.20 (57.48)	3.30 (3.29)	8.35 (8.38)	6.80 (6.88)
K(ONN)·HPicA	Yellow	200t	54.95 (54.80)	3.12 (3.14)	8.05 (8.00)	10.95 (11.10)
Li(DNN)·HPicA	Brownish yellow	235t	53.75 (53.03)	2.80 (2.76)	11.50 (11.60)	1.70 (1.65)
Na(DNN)·HPicA	Brownish yellow	262t	52.20 (50.60)	2.70 (2.63)	10.75 (11.08)	5.50 (6.06)
K(DNN)·HPicA	Brownish yellow	272t	49.05 (48.60)	2.68 (2.53)	10.28 (10.06)	9.60 (9.87)

Pertinent IR data for these compounds are recorded in Table-2. The broad band at 3400 cm^{-1} in the spectrum of the ligand points to strong intermolecular hydrogen bonding in it. The spectra of all the complexes differ from the ligand molecule by the absence of this weak broad band. However, the spectra of Li(ONN)·HPicA, Na(ONN)·HPicA and K(ONN)·HPicA show a broad band of medium intensity between $2400\text{--}2300\text{ cm}^{-1}$. All other complexes show absorptions between $3140\text{--}3050\text{ cm}^{-1}$. Na(DNP) showed additional band between $2500\text{--}2300\text{ cm}^{-1}$ and Li(TNP)·HPicA showed broad band at 2500 cm^{-1} and

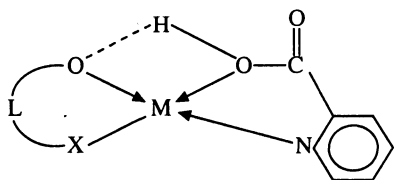
2250 cm^{-1} . $\text{Na}(\text{ONN})\cdot\text{HPicA}$ also showed an additional broad band at 2200 cm^{-1} . These may be assigned to $\text{O}-\text{H} \cdots \text{O}/\text{N} \cdots \text{H}-\text{O}$ absorption and this suggests hydrogen bonding to be a dominant factor in stabilising these complexes. The shifting of 1650 cm^{-1} band to lower frequencies by 10–30 cm^{-1} and negative shifting of 1520 cm^{-1} band by 10–40 cm^{-1} in almost all the complexes as well as shifting of the 1600 cm^{-1} band to lower frequencies by 5–10 cm^{-1} . But in a few cases [$\text{K}(\text{DNP})\cdot\text{HPicA}$, $\text{K}(\text{TNP})\cdot\text{HPicA}$, $\text{Na}(\text{ONN})\cdot\text{HPicA}$, $\text{K}(\text{ONN})\cdot\text{HPicA}$], the absorption band shifted to higher frequencies this is probably due to the increase in double bond character. The 1580 cm^{-1} band of the ligand has shifted to lower frequencies by 10–20 cm^{-1} . These features of the aforesaid vibrational modes demonstrate that coordination of the ligand with alkali metals has taken place through the carboxylic acid moiety and its ring N-atom in all the complexes examined. Coordination through the nitrogen atom of the pyridine fragments of the ligand is suggested by frequency shifts of bands in the region 1650–1500 cm^{-1} associated with the vibrational modes of aromatic amine ring¹⁰⁻¹³.

TABLE-2

Compound	O—H	O—H...O/N...H—O	$\nu(\text{COOH})$		$\nu(\text{C}=\text{N})$	
HpicA	3400br	—	1650s	1600s	1580s	1520s
$\text{Na}(\text{DNP})\cdot\text{HPicA}$	—	3400–3100br, 2500–2300br	1640m	1590m	1570m	1500m
$\text{K}(\text{DNP})\cdot\text{HPicA}$	—	3100br	1690m	1610sh	1590m	1500m
$\text{Li}(\text{DNP})\cdot\text{HPicA}$	—	3080br, 2500br, 2250 br	1630m	1600w	1570m	1480w
$\text{K}(\text{TNP})\cdot\text{HPicA}$	—	3050br	1620s	1590m	1560m	—
$\text{Li}(\text{ONN})\cdot\text{HPicA}$	—	2400–2300br	1640m	1610m	1590m	1505s
$\text{Na}(\text{ONN})\cdot\text{HPicA}$	—	2400–2300br, 2200br	1640s	1610m	1570m	1510s
$\text{K}(\text{ONN})\cdot\text{HPicA}$	—	2400–2300br	1635w	1605w	1590s	1510s
$\text{Li}(\text{DNN})\cdot\text{HPicA}$	—	3100br	1660sh	1590m	1570m	1480m
$\text{Na}(\text{DNN})\cdot\text{HPicA}$	—	3050br	1630m	1590m	1570m	1500w

In conclusion, the probable coordination number of central metal is found to be four.

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



(M=Li, Na or K and X=O or N)

Fig. I

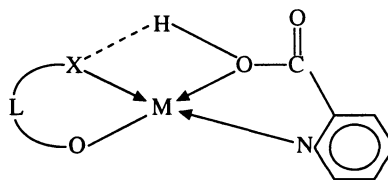


Fig. II

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