Asian Journal of Chemistry Vol. 5. No. 4 (1993), 916–919

Alkali Metal Complexes: Mixed Ligand Complexes of Alkali Metal Salts of Picolinic acid, Quinaldinic acid and their N-Oxides with 1, 10-Phenanthroline Mono-N-Oxide

D. PRAKASH*, S.S. PRASAD, R. CHANDRA and O.P. GUPTA
Chemistry Department, Patna University
Patna-800 005, India

Complexes having the general formula ML. L' where M = Li, Na and K, HL = picolinic acid, quinaldinic acid and their N–oxides and L' = 1,10– phenanthroline mono-N-oxide have been synthesized. Complexes have been characterised on the basis of elemental analysis, IR spectral studies and conductivity measurements.

INTRODUCTION

Transition metal complexes of 1,10–phenanthroline mono-oxide have been widely investigated[1–3]. However, the mixed ligand complexes of alkali metal salts of picolinic acid, quinaldinic acid and their N–oxides with 1, 10–phenanthroline mono–N-oxide have not been investigated. The present study involves the synthesis and characterisation of mixed ligand complexes of alkali metals with above mentioned ligands.

EXPERIMENTAL

Picolinic acid and quinaldinic acid used were of AnalaR grade and the ligand picolinic acid N–oxide[4] and quinaldinic acid N–oxide[5] were prepared by the method as described in the literature. 1, 10–Phenanthroline mono-N–oxide was prepared by a slight modification of the method of Corey *et al*[6].

Preparation of the complexes

Alkali metal salts of picolinic acid, quinaldinic acid and their N–oxide were prepared by the reported methods[7,8]

To a suspension of alkali metal salt of picolinic acid in absolute alcohol, 1, 10–phenanthroline mono N–oxide was added in mole ratio 1 : 1. On refluxing about 2 hrs., with constant stirring on a hot plate a clear solution was obtained. The solution was concentrated and cooled. Adducts separated was filtered, washed with the solvent and dried in an electric oven below 100°C.

The adducts with sodium salt of picolinic acid could not be separated.

RESULTS AND DISCUSSION

The colours, the decomposition/transition temperature and analytical data of these complexes are listed in Table 1. All the complexes are generally of cream colour with exceptions in few cases. They are partialy soluble in polar solvents. The complexes are stable under dry conditions *e.g.* over anhydrous calcium chloride in a desiccator. They show no change in stoichiometry or in physical properties even after a long time. But the complexes are unstable in moist air; in presence of which they appear to decompose into solid of indeterminate composition. From Table 1, it is evident that all these complexes are fairly stable at higher temperatures above the melting or boiling point of the ligand, indicating thereby their greater thermal stability. The conductance values (3.5–7.2 $ohm^{-1}cm^2mole^{-1}$) in methanol at 25°C reveal the non-electrolytic nature of these complexes.

TABLE 1

Compounds	M. Pt./Decom./ Trans Temp. (°C)	Analysis % Found/(Calculated)			
		C	H	N	M
PhenO (Pale yellow)	180	73.48 (73.47)	4.12 (4.08)	14.28 (14.28)	—
LiPicA. PhenO (Cream)	290 d	65.80 (66.46)	3.75 (3.69)	12.85 (12.92)	2.10 (2.15)
KPicA. PhenO (Cream)	250 d	58.90 (60.50)	3.48 (3.36)	11.20 (11.76)	10.25 (10.92)
LiPicO. PhenO (Cream)	275 t	63.25 (63.34)	3.55 (3.51)	12.35 (12.31)	1.90 (2.05)
NaPicO. PhenO (Cream)	260 t	58.90 (60.50)	3.00 (3.36)	11.15 (11.76)	6.17 (6.44)
KPicO. PhenO (Pale yellow)	225 d	58.20 (57.90)	3.20 (3.20)	11.00 (11.26)	9.90 (10.45)
LiQuinA. PhenO (Light yellow)	300	70.25 (70.40)	3.75 (3.73)	11.25 (11.20)	1.80 (1.86)
NaQuinA. PhenO (Cream)	280 d	65.95 (67.51)	3.65 (3.58)	10.60 (10.74)	5.90 (5.81)
KQuinA. PhenO (Cream)	275 t	62.90 (64.86)	3.50 (3.43)	9.98 (10.31)	9.20 (9.58)
LiQuinO. PhenO (Brown)	300	66.80 (67.51)	3.60 (3.50)	10.70 (10.74)	1.70 (1.79)

Infrared spectra

The infrared measurements of all the compounds have been carried out in the region 4000–650 cm^{-1} in KBr phase. Pertinet IR data are given in Table 2.

TABLE 2

Compounds	Key IR absorption bands (cm^{-1})		
	1650–1540 region	νNO	δNO
PhenO	1612 w 1590 m 1558 sh 1550 m 1546 sh	1269 s 1246 s	811 sh 808 s
LiPicA. PhenO	1600 s 1580 m 1550 m	1285 m 1220 w	830 s 800 w
KPicA. PhenO	1600 s 1580 m 1550 m	1280 m 1240 w	830 s
LiQuinA. PhenO	1600 sh 1540 sh 1500 br	1280 w 1220 w	850 s 800 m
NaQuinA. PhenO	1600 s 1550 m 1500 m	1290 m 1210 m	840 m 800 s
KQuinA. PhenO	1600 s 1550 m 1500 m	1290 m 1200 w	835 m 790 s
LiPicO. PhenO	1600 sh 1540 w 1520 sh	1285 w 1235 w	850 s 795 w
NaPicO. PhenO	1630 m 1600 m 1500 w	1280 m 1240 s	830 m 790 m
LiQuinO. PhenO	1600 br 1580 m 1555 m	1280 m 1230 m	840 m 800 m

Free 1, 10–phenanthroline mono N–oxide (Pheno) shows a rich IR spectrum in the 1650–650 cm^{-1} region[9]. The ν (N–O) vibration occurs as doublet in the free ligand[10]. The doublet occurs at 1269 and 1249 cm^{-1}. Both these bands exhibit positive or negative frequency shifts upon metal complex formation. While 1269 cm^{-1} band shift to higher frequency by 10–20 cm^{-1}, the 1249 cm^{-1} band shift to lower frequency by 9–49 cm^{-1} in the spectra of the complexes. The 811 and 808 cm^{-1} bands of the ligand assigned to the bending N–O vibrations[11–15], too shift towards higher and lower frequencies respectively on complex formation. However, in the spectra of all the complexes of alkali metal salts of picolinic acid, quinaldinic acid and their N–oxides; the two bands at 1269 and 811 cm^{-1} corresponing N–O stretching as well as N–O bending vibrations have shifted to

higher frequencies. These features of the aforesaid vibrational modes demonstrate that coordination of the ligand with alkali metals has taken place through the oxygen atom N–O moiety[11-15], in all the complexes examined.

Coordination through the nitrogen atom of the pyridine fragments of the ligand is suggested by frequency shifts of several bands in the region 1650–1500 cm^{-1} associated with the vibrational modes of aromatic amine ring.[9,16-18] In conclusion, the probable coordination number of central metal in found to be four.

ACKNOWLEDGEMENT

One of the authors (O.P.G.) expresses his thanks to U.G. C., New-Delhi for the award of Teacher-fellowship.

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(*Received*: 13 April 1992; *Accepted*: 12 February 1993) AJC-550