Asian Journal of Chemistry Vol. 7, No. 1 (1995), 85–88

Neutral Complexes of Alkali Metals with Picolinic Acid N-Oxide and Quinaldinic Acid N-Oxide

D. PRAKASH*, K.B. SINHA, O.P. GUPTA and R.N. SHUKLA
Department of Chemistry
Patna University, Patna-806 005, India

Neutral complexes of alkali metals, belonging to ML · HL type, where M = K, Rb or Cs and HL = picolinic acid N-oxide and quinaldinic acid N-oxide have been synthesised and characterised by elemental analysis, conductance and infrared spectral studies.

INTRODUCTION

Significant studies on coordination behaviour of alkali metals with picolinic acid, quinaldinic acid[1] and 8-hydroxyquinoline-N-oxide[2] have been extensively studied. In the present communication we report the complexing behaviour of picolinic acid N-oxide (HPicO) and quinaldinic acid N-oxide (HQuinO) towards alkali metal ions.

EXPERIMENTAL

Picolinic acid N-oxide and quinaldinic acid N-oxide were prepared by the method as described in the literature[3].

Preparation of the complexes

Metal hydroxide was added to a solution of picolinic acid N-oxide or quinaldinic acid N-oxide in absolute alcohol in 1:2 mole ratio. The solution was refluxed on a water bath for 1–3 h under a constant stream of nitrogen and then left to stand at 0°C for 24 h. Cream-coloured crystals were filtered off, washed with a small volume of ethanol and dried at 80°C in an electric oven. Li and Na complexes could not be separated but K, Rb, Cs complexes could very well be isolated.

RESULTS AND DISCUSSION

Some physical properties of the ligand and the new neutral complexes obtained are listed in Table 1. All the complexes are cream coloured and are stable in dry air but decompose rapidly on exposure to moisture. These compounds were kept in a desiccator over solid anhydrous $CaCl_2$. All these complexes undergo a transformation at temperatures which are considerably higher than the melting point of the ligands, indicating their greater thermal stability. Most of the complexes are soluble in most polar solvents such as methanol but are insoluble in non-polar solvents such as benzene, toluene and diethyl ether. Ease of complexation and the quantum of yield was found to increase with increase in radius of the alkali metal ion. Low values of molar conductance (8.8–10.9 ohm^{-1} cm^{2} mol^{-1}) in methanol suggest the non-electrolytics nature of the complexes.

The multiple bands that occur in the spectrum of the ligands HpicO and HQuinO indicate that in the solid state, they contain strong H-bonds, possibly of the symmetrical type resulting in the dimer[4] shown in Fig. 1 and Fig. 2. In the spectra of the complexes these multiple bands have disappeared.

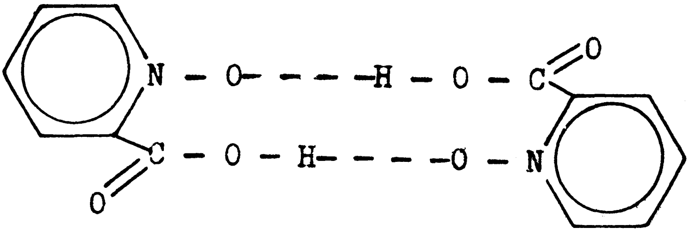


Fig. 1

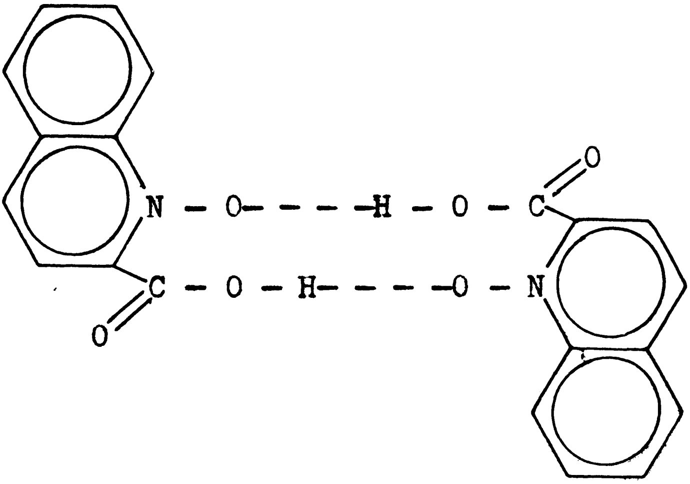


Fig. 2

However the spectra of all the complexes contain a broad band in the region 2300–2400 cm^{-1}. Presence of these bands in the spectra of the complexes suggests hydrogen bonding as a dominant factor in stabilizing them.

The bands at 1720 cm^{-1} and 1680 cm^{-1} in HPicO and the band at 1680 cm^{-1} in HQuinO have been assigned to asymmetric —COOH absorption[5], while the bands at 1295 cm^{-1} (HPicO) and 1280 cm^{-1} (HQuinO) are in all probability due to symmetric stretching —COOH vibrations. The shifting of all these bands to lower frequency regions in almost all the complexes is indicative of the coordination through the oxygen atom of the —COOH group of the ligand.

TABLE-1
ANALYTICAL DATA OF ALKALI METAL COMPLEXES

Compound (Colour)	M.P./decomp./ transition temp. (°C)	% Found (Calculated)			
		C	H	N	M
HPicO (Pale yellow)	161 m	57.74 (51.80)	3.68 (3.60)	10.45 (10.70)	—
KPicO·HPicO (Cream)	220 t	45.00 (45.56)	2.82 (2.84)	8.56 (8.86)	12.00 (12.34)
RbPicO·HPicO (Cream)	195 t	38.95 (39.72)	2.82 (2.48)	7.56 (7.72)	23.20 (23.58)
CsPicO·HPicO (Cream)	180 t	35.00 (35.13)	2.20 (2.19)	6.65 (6.83)	32.00 (32.42)
HQuinO·HQuinO (Light yellow)	168–170 d	51.70 (51.80)	3.70 (3.60)	10.50 (10.10)	—
KQuinO·HQuinO (Cream)	205 d	56.25 (57.69)	3.15 (3.12)	6.77 (6.73)	9.30 (9.37)
RbQuinO·HQuinO (Cream)	185 d	52.00 (51.89)	2.84 (2.81)	5.95 (6.05)	18.00 (18.48)
CsQuino·HQuinO (Cream)	180 d	46.50 (47.06)	2.55 (2.54)	5.40 (5.49)	25.90 (26.06)

In the spectra of the complexes, the 1620 cm^{-1} band (HPicO) and 1610 cm^{-1} band of medium intensity (HQuinO) have been assigned to $\nu(C-C) + \nu(C-N)$ absorption, which have shifted to lower frequencies by 10–20 cm^{-1}. Similarly the band at 1267 cm^{-1} (HPicO) and the band at 1300 cm^{-1} of medium intensity (HQuinO), which are attributed to stretching N-oxide vibrations, have shifted to lower frequencies in the complexes by 5–17 cm^{-1}. These features suggest that the coordination of the ligand with the alkali metals has taken place through the oxygen atom of the N—O group. Similar shifts have also been observed in case of complexes of the ligand picolinic acid N-oxide with transition metals[6, 7].

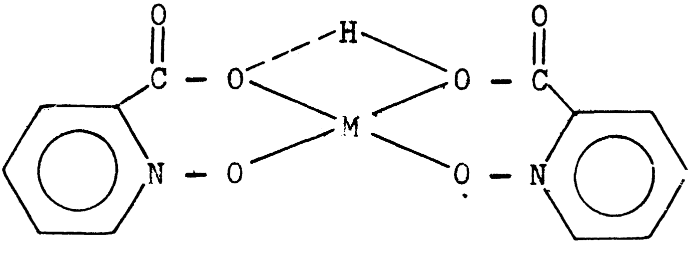
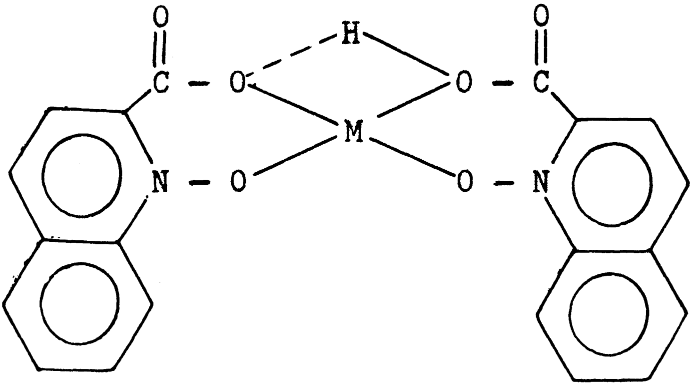


Fig. 3

On the basis of elemental analysis, conductivity measurement and IR spectral data studies, the following probable structure of the neutral complexes of alkali metals can be proposed as such.



Where M = K, Rb or Cs.

Fig. 4

ACKNOWLEDGEMENT

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

REFERENCES

1. Dharm Prakash and S.P. Singh, *Polyhedron*, **3**, 243 (1984).
2. ________ , *J. Indian Chem. Soc.*, **62**, 424 (1985).
3. Otto Diels, Kurt Adler, W. Friedrichen, Petersen, Brodersen and Kech, *Ann.*, **510**, 87 (1934).
4. M. Zafran, *Bull. Acad. Polon. Sci. Ser. Sci. Chim.*, **13**, 245 (1965).
5. T.J. Delia, M.A. Little and D.X. West., *J. Inorg. Nucl. Chem.*, **35**, 1400 (1973).
6. A.B.P. Lever, J. Lewis and R.S. Nyholm, *Proc. 7 ICCC, Stockholm and Uppsala, Sweden*, **49** (1962).
7. ________ , *J. Chem. Soc.*, 526 (1962).
8. A.K. Banerjee, A.J. Layton, R.S. Nyholm and M.R. Truter, *J. Chem. Soc. (A)*, 2536 (1969).

(*Received*: 12 November 1993; *Accepted*: 14 May 1994) AJC-817