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Netural Complexes of Alkaline Earth Metals with Picolinic Acid-N-Oxide and Quinaldinic Acid-N-Oxide

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Complexes of alkaline earth metals belonging to $ML_2 \cdot nH_2O$ type, where M = Mg, Ca, Sr and Ba, HL = picolinic acid-N-oxide and quinaldinic acid-N-oxide and n = 0 or 2 have been synthesised and characterised on the basis of elemental analysis, conductivity measurements and IR spectral studies.

The coordination behaviour of picolinic acid-N-oxide (HPicO) towards transition and alkaline earth metals such as calcium and magnesium ions were studied earlier[1–5]. The literature survey also reveals that the ligand quinaldinic acid-N-oxide (HQuinO), has two possible coordination sites remained neglected and no attempt has yet been made to examine its chelating ability towards the alkaline earth metals. In the present work, we have synthesised a number of chelate neutral complexes with these ligands having the general formula $ML_2 \cdot nH_2O$ where M = Mg, Ca, Sr or Ba; HL = HPicO or HQuinO and n = 0 or 2.

The ligand picolinic acid-N-oxide[6] and quinaldinic acid-N-oxide[7] were prepared by the method as described in the literature. The complexes were synthesized by the following general method. To the suspension of alkaline earth metal acetate in 95% ethanol the ligand (HPicO or HQuinO) was added in 1 : 2 molar ratio. A clear solution was obtained. The solution was refluxed for about 1–2 h on a hot plate with continuous stirring. On cooling the solution adduct got seperated. In some cases the adduct got seperated in hot condition also. Adduct so obtained was filtered, washed with ethanol and then dried in an electric oven at 100°C.

The colours, the decomposition, transition temperatures, molar conductance values and analytical data of these complexes are listed in Table 1. These complexes are soluble in most polar solvents such as methanol, but are insoluble in non-polar solvents such as benzene, toluene and diethyl ether. The lower values of molar conductivities (4.0–7.3 ohm^{-1} mole^{-1}) of the complexes in methanol (25°C) indicate their non-electrolytic nature. All these complexes are stable under dry conditions, *e.g.*, over anhydrous $CaCl_2$ in a desiccator. They showed no change in stoichiometry or in physical properties even after one year. They undergo a transformation at temperatures which are considerably higher than the melting point of the corresponding ligand, indicating thereby their greater thermal stability. Only magnesium complexes lose water moleculs at *ca.* 130–150°C showing these water moleculs are coordinated.

TABLE 1

Compound/ Colour	M.P./decomp./ transition temp. (°C)	Conductivity ($Ohm^{-1} cm^2 mol^{-1}$)	(%) Found (Cald.) C	H	N	M
HPicO (Pale Yellow)	161 m	—	51.70 (51.80)	3.70 (3.60)	10.50 (10.10)	—
$Mg(PicO)_2 \cdot 2H_2O$ (White)	270 t	4.0	45.50 (46.66)	3.12 (3.35)	7.74 (7.77)	6.60 (6.66)
$Ca(PicO)_2$ (White)	290 d	5.4	48.62 (49.41)	2.30 (2.35)	8.10 (8.23)	11.43 (11.67)
$Sr(PicO)_2$ (White)	265 t	6.3	42.68 (43.29)	2.00 (2.06)	7.01 (7.21)	22.50 (22.68)
$Ba(PicO)_2$ (White)	250 d	7.3	37.82 (38.44)	1.80 (1.83)	6.25 (6.40)	30.80 (31.35)
HQuinO (Lighe Yellow)	168–170 d	—	63.70 (63.50)	3.80 (3.70)	7.40 (7.60)	—
$Mg(QuinO)_2 \cdot 2H_2O$ (White)	295 t	4.3	54.60 (55.04)	3.45 (3.67)	6.31 (6.42)	5.37 (5.50)
$Ca(QuinO)_2$ (Cream)	255 d	5.1	56.63 (57.69)	2.75 (2.88)	6.64 (6.73)	9.40 (9.61)
$Sr(QuinO)_2$ (White)	300 d	5.8	50.62 (51.72)	2.34 (2.58)	5.65 (6.03)	18.24 (18.96)
$Ba(QuinO)_2$ (White)	245 d	6.2	45.60 (46.78)	2.26 (2.33)	5.36 (5.45)	25.80 (26.70)

Pertinent IR data for these compounds are recorded in Table 2. The multiple band that occur in the spectra of the ligands HPicO & HQuinO indicate that in the solid state, they contain strong hydrogen bonds, possibly of the symmetrical type resulting in the dimer[8]. In the spectra of the complexes, these multiple bands have disappeared (except in the case of magnesium complex). In the magnesium complexes the two water molecule are coordinated and lose at a temperature *ca.* 150°C, showing greater association. Broad –OH peak has been observed at 3200 cm^{-1}. The rocking δH_2O has also been identified at 860 and 855 cm^{-1}.

The lower shifting of the band at 1720 cm^{-1}, 1680 cm^{-1} (HPicO) and 1680 cm^{-1} (HQuinO) (Assigned to asymmetric –COOH absorption) while the band 1295 cm^{-1} in HPicO and 1280 cm^{-1} in HQuinO (symmetric streching –COOH vibration) and the band at 1620 cm^{-1} (HPicO) and 1610 cm^{-1} (HQuinO) (assigned to $\nu C = C + \nu C = N$ absorption), indicate the bonding with alkaline earth metal through oxygen atom of the carboxyl moiety.

The band at 1267 cm^{-1} (HPicO) and 1300 cm^{-1} (HQuinO) which is attributed to stretching N-oxide vibration, have shifted to lower frequency. The lower shift of the band at 847 cm^{-1} and 845 cm^{-1} of HPicO and HQuinO respectively, which have been assigned to bending N–O vibration have also been observed in the complexes. These features suggest that the coordination of the ligand with alkaline earth metals have been taken through the oxygen atom of the N–O group.

TABLE 2
KEY IR BANDS (cm^{-1}) OF THE COMPOUNDS

HPicO	2800–1850 w	1720 s	1680 s	1620 s	1295 s	1267 s	—	847 s
$Mg(PicO)_2 \cdot 2H_2O$	3200 br	1695 m	1660 sh	1615 s	1290 s	1260 m	860 s	835 sh
$Ca(PicO)_2$	—	1660 m	1660 m	1610 m	1290 s	1255 m	—	840 sh
$Sr(PicO)_2$	—	1690 m	1658 sh	1610 m	1290 m	1255 m	—	840 s
$Ba(PicO)_2$	—	1700 m	1670 m	1610 s	1290 m	1255 m	—	840 s
HQuinO	2800–1800 br		1680 br	1610 m	1300 m	1280 m	—	845 s
$Mg(QuinO)_2 \cdot 2H_2O$	3200 br		1640 s	1600 m	1290 w	1268 m	855 s	835 s
$Ca(QuinO)_2$	—		1640 m	1600 m	1295 w	1265 m	—	830 m
$Sr(QuinO)_2$	—		1670 s	1610 s	1295 m	1270 m	—	825 s
$Ba(QuinO)_2$	—		1640 m	1600 m	1290 w	1265 m	—	840 s

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