Oriental Journal of Chemistry Vol. **25**(1), 241-244 (2009)

Mixed ligand complexes of alkali metal salts of salicylic acid, acetyl salicylic acid and 2-hydroxy-3-naphthoic acid with 2,5 dihydroxybenzoquinone

PRAMOD KUMAR[1], ASHOK KUMAR GUPTA[2], V.K. TIWARY[1], VIJAY KUMAR[2], SANTOSH KUMAR[3], SUBHASH PRASAD[4] and AJAY KUMAR[5]

[1]Research Scholar, Department of Chemistry, M.U. Bodh Gaya (India).
[2]Department of Chemistry, R.K.D. College (M.U.) Patna-20 (India).
[1]Department of Chemistry, S.G.G.S. College, Patna City, M.U. Bodh Gaya (India).
[2]H.O.D. Chemistry, R.R.P. College, Bhergawan, Masaurhi, Patna (India).
[3]Department of Chemistry, P.U. Patna (India).
[4]Department of Chemistry, R.K. D. College, Patna M.U. Bodh Gaya, Bihar (India).
[5]Department of Chemistry, G.D.M. College, Patna (India).

(Received: September 28, 2008; Accepted: November 03, 2008)

ABSTRACT

Mixed ligand complexes of general formula $(ML)_2$. H_2BQ, where M = Li, Na or K, L = deprotonated salicylic acid, acetylsalicyilc acid or 2-hydroxy-3-napthoic acid; H_2BQ = 2, 5-idhydroxybenzoquinone have been synthesized and characteriszed. The infrared studies indicate the presence of intramolecular hydrogen bonding in the complexes, whcih may be one of the factors for stabilizing them.

Key words: Mixed ligand complexes, IR studies.

INTRODUCTION

Most of the hydroxquinones are present in plant system and have important analytical applicaitons[1]. Coplexing behaviour or 2,5-dihydroxybenzquinone have been well documented with transition metals and non-transition metals2[-5]. We have extended the investigation to synthesis and characterise some new mixed ligand complexes of alkali metal salts of salicylic acid, acetylsalicylic acid and 2-hydroxy-3-naphthoic acid with 2,5-dihydroxybenzoquinone.

EXPERIMENTAL

Preparation of ligand

2,5 -dihydroxybenzoquinone have been prepared from hydroquinone by the method of jones and shonle[6].

Preparation of alkali metal salts of organic acids

0.01 Mole of alkali metal hydroxide (MOH) and 0.01 mole of organic acid (HL) were refluxed in 95% ethanol on a hot plat of magnetic stirrer at 60°C with constant stirring for half an hour. The clear solution was decanted, concentrated and cooled when colourless or white crystals of alkali metal salts (ML) precipitated out. The Precipitate was filtered, washed with 95% ethanol and dried in electric oven at 80°C.

Preparation of complexes

0.001 Mole of alkali metal salt (ML) of organic acid and 0.001 mole of 2,5 dihydroxybenzoquione were taken in 25ml absolute alcohol. The suspension of refluxed at 60-70^{0}C for 2-3 hours on a hot plate of magnetic stirrer with constant stirring, when whole mass went into solution. A Solution was concentrated and cooled to give Characteristic colour solid. It was filtered washed with absolute alcohol and dried in an electric oven at 80°C.

RESULTS AND DISCUSSION

Some Physical properties of the ligand and mixed ligand alkali metal complexes are listed in Table 1. From the results, it is evident that the colour of complexes are different from the ligand or alkali metal salts. The complexes are generally soluble in methanol, ethanol, DMF etc. but insoluble in non-poplar solvents namely chloroform, n-hexane, benzene etc. All complexe undergo decomposition/ transition at temperature higher than the melting point of the ligand, indicating thereby greater thermal stability. They are stable under dry condition e.g. over anhydrous $CaCl_2$ in a desiccator.

Table 1:

Compound	Colour	M.P./Decomp/ Trans. Temp (°C)	Conductivity (ohm-1 cm² mol^{-1})	% Analysis found / (Calc.) C	H	M
2, 5-Dihydroxy-benzoquinone (H_2BQ)	Orange yellow	198m	-	51.40	2.83	-
				(51.43)	(2.86)	
$(LiSalA)_2H_2BQ$	Deep Brown	255t	5.5	55.96	3.20	3.19
				(56.07)	(3.27)	(3.27)
$(NaSalA)_2H_2BQ$	Light red	270d	4.9	52.02	2.95	9.86
				(52.17)	(3.04)	(10.00)
$(KSalA)_2H_2BQ$	Brick red	258d	7.8	49.69	2.75	15.71
				(48.78)	(2.84)	(15.85)
$(LiSalA)_2H_2BQ$	Reddish brown	245t	3.8	56.14	3.47	2.68
				(56.25)	(3.51)	(2.73)
$(NaAcSalA)_2H_2BQ$	Orange brown	280d	3.8	52.85	3.26	8.37
				(52.94)	(3.31)	(8.45)
$(KAcSalA)_2H_2BQ$	Brick red	253d	3.8	49.75	3.04	13.40
				(49.82)	(3.11)	(13.49)
$(Li_2H_3NA)_2H_2BQ$	Dark brown	265d	3.8	63.51	3.35	2.51
				(63.63)	(3.41)	(2.65)
$(Na_2H_3NA)_2H_2BQ$	Dark brown	255t	10.1	59.85	3.08	8.05
				(60.00)	(3.21)	(8.21)
$(K_2H_3NA)_2H_2BQ$	Dark brown	268d	8.6	56.68	2.96	13.02
				(56.75)	(3.04)	(13.17)

Table 2: Pertinent IR data for ligand (2,5 Dihydroxybenzoquinone) & its mixed ligand alkali metal complexes

Compound	υ0-H	υc=0	υc-0	υm=0
2, 5-Dihydroxy- benzoquinone (H_2BQ)	3264	1618	1308	—-
$(LiSalA)_2H_2BQ$	3370	1570,1530	1267	540, 424
$(NaAcSalA)_2H_2BQ$	3397	15971560	1267	525, 463, 415
$(Na_2H_3NA)_2H_2BQ$	3405	1551	1256	540, 463
$(Li_2H_3NA)_2H_2BQ$	3432	1535	1254	521, 461

Table 3: Carbonyl frequency (in cm^{-1}) of metal chelates

Metal	Frequency	Metal	Frequency
Cobalt	1529	Lithium	1550
Nickel	1507	Sodium	1555
Copper	1472	Potassium	1560
Zinc	1527	-	-

Molar conductivities

Molar conductivities (in ohm^{-1}cm^{2} mol^{-1}) of compounds were measured in method at 30^{0}C at a concentration of 10^{-3}M (Table-1). The Compounds show low values (3.8-10.1ohm^{-1}Cm^{2} mol^{-1}) of model conductivity inchacting that they are non-electrolyte. A value of ca. 35-40 ohm^{-1} cm^{2} mol-1 appears characteristic of 1:1 electrolyte, whereas ideally molar condctivity of a neutral complex should be zero[7].

Infrared spectra

IR spectra of ligand and alkali metal complexes were recorded in KBr phase between 4000-400cm-1. with the help of JASCO-FT/IR spectrophotometer model-5300. Selected absorption bands are shown in Table 2.

The absorption bands of our interests in the infrared spectrum of 2,5 dihydroxy benzoquinone (H_2BQ) are 3263cm^{-1} & 1618cm^{-1}.

The dihydroxy benzoquinone molecule has a sharp absorption peak in the 3263Cm-1 region due to the -OH stretching vibration. The hydrogen bonded carbonyl is assigned to 1618cm^{-1}.

The infrared spectra H2BQ and its divalent transition metals chelates have been reported by Bottei and Fangman[8]. They observed that the C=O peak of 2,5-dihydroxy benzoquinone at 1618 cm^{-1} shifted down in the region 1527-1472 cm^{-1} due to chelation

In the spectra of dialkali metal salt, the O-H absorption bands is missing both of the hydrogenatom of phenolic group in dihydroxybenzoquinone are replaced by two alkali metals. For all the alkali metals salts, the sgrongest absorption near 1618 cm^{-1} is shifted below 1600 cm^{1-}, assuming that the absorption in the region 1600-1500cm^{-1} is due to the chelated carbonyl, these assignments for the alkali metal salts are given in the Table 3.

The amount of shifting of the carbonyl absorption mode of the alkali metal salts of dihydroxbenzoquinone can be compared to the carbonyl peak shifts in the chelate of transition metals (Table 3)

We are discussing the infrared spectra of mixed ligand complexes of alkali metal salts of some orgranic acids, viz, salicylic acid, acetylsalicylic acid and 2-hydroxy-3-naphthoic acid with 2,5 dihydorxybenzoquinone. In general, it is very difficult

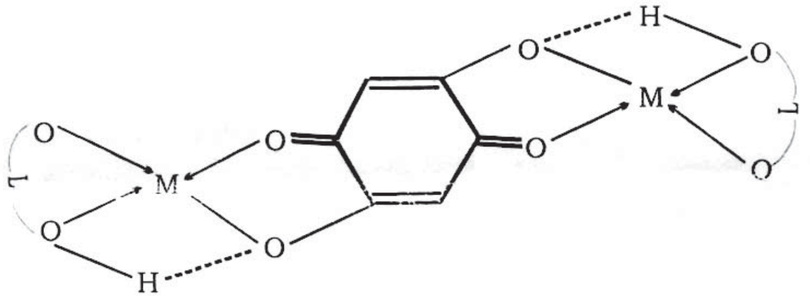

Fig. 1: (where M = Li, Na or K, L = deprotonated SalA, AcSalA or 2H3NA)

to interpret the infrared spectra of mixed ligand complexes because both ligands (First and Second) of different functional groups occur at the same region.

The moderately strong broad at 3264 cm^{-1} in the spectrum of ligand (H^2BQ) is attributed to the stretching O-H vibration frequency. The complexes also exhibit a broad band in the region 3370-3442 cm-1 suggest that there is intramolecular hydrogen bonding in these complexes.

The ν_{C-O} stretch is observed in the free ligand in the region at 1308cm-1, on complexation, this band shift to lower frequency region 1267-1254 cm^{-1}, indicating coordination through oxygen atom of the phenolic group and the shifting of the strongest absorption band of carbonyl (C=O) group at 1618 cm^{-1} to lower frequency region 1597-1530 cm^{-1} also suggest chelation through carbonyl oxygen atom.

In the mixed ligand alkali metal complexes, the lower shift of Uc-$_0$ stretching frequency shows the increased bond order between the C & D atoms as a result of coordination of oxygen atom to the alkali metals. Slight shift in UC-0 stretching frequencies are also found in all complexes probably due to change in stereochemistry of the complex.

Further, in low frequency region 540-415cm^{-1}, the bands observed in the complexes are assigned to ^{u}m-0.

Structure and bonding

On the basis of elemental analysis, the general formula of the mixed ligand complexes of 2,5 dihydroxybenzo-quinone (H_2BQ) comes out to be $(ML)_2$. H_2BQ. The infrared spectra of these complexes suggest the coordination of alkali metal with H_2BQ through oxygen atoms of 0-H (Phenolic) and C=0 (Quinine) groups. These facts suggest the following structure for these complexes (Fig.1).

REFERENCES

1. Shields T.C., *Chem. Commun,* 832 (1968)
2. Prakash, D. and Singh S.P*., Ind. Chem. Soc*, **58**: 1143 (1981)
3. Banerjee, A.K. Mahapatra B., Prakash D. and Roy S.K. Ibid., **62**: 552 (1985).
4. Banerjee, A.K. Prakash D. and Roy S.K. *Ibid,* **59**: 1303 (1982).
5. Banerjee. A.K. Ghosh M.K. Sinha S.K. and Roy S.K. *Ibid.* **62**: 272 (1985).
6. Jones R.G. and Shonle H.A.. *J. Amer Chem. Soc*. **67**: 1034 (1945).
7. Banerjee, A.K. Layton A.J. Nyholm R.S. and Truter M.R*. Nature*, **5134**: 1147 (1968)
8. Bottei R.S. and Fangman. J.T. *J. Inorg. Nucl. Chem*. **26**: 1259 (1966).