Asian Journal of Chemistry Vol. 13, No. 3 (2001), 854–858

Alkali Metal Complexes: Mixed Ligand Complexes of Alkali Metal Salts of 1-Hydroxy Anthraquinone with Oxygen Donor Ligands

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

Complexes of alkali metals belonging to ML·nHL′ type, where M = Li, Na or K, L = 1-hydroxy anthraquinone, n = 1 or 2 and HL′ = acetyl acetone, benzoyl acetone, ethylacetoacetate, ethyl malonate, salicylaldehyde, *o*-hydroxy acetophenone and 2-hydroxy-1-naphthaldehyde have been synthesised and characterised on the basis of elemental analysis, conductivity measurements and IR spectral studies.

INTRODUCTION

The hydroxy anthraquinones are of practical interest and importance on account of their occurrence in nature, their extensive use in technology as mordant dyes and dye intermediates. The coordination behaviour of 1-hydroxy anthraquinone towards alkaline earth metals such as magnesium and calcium ions were studied earlier[1, 2]. In this communication, we have taken the above mentioned ligand to investigate the coordination behaviour towards alkali metals.

EXPERIMENTAL

Acetyl acetone (AcAc), benzoyl acetone (BzAc), ethylacetoacetate (EAA), ethyl malonate (EM), salicylaldehyde (SalH), and *o*-hydroxy acetophenone (OHA) of AnalaR grade were used as such. 2-Hydroxy-1-naphthaldehyde (HNaph) was prepared as described in literature[3]. Ligand, 1-hydroxy anthraquinone (HAQ) was prepared by the method of Breadford *et al.*[3]

Preparation of alkali metal salts of 1-hydroxy anthraquinone

Equimolar proportions of metal hydroxide and the 1-hydroxy anthraquinone were refluxed in 95% ethanol for about 30 min. The solution was filtered and concentrated when alkali metal salt separated out. It was filtered, washed with the solvent and dried in an electric oven at 80°C.

Preparation of the Complexes: Alkali metal salt of 1-hydroxy anthraquinone and organic acid were taken in absolute ethanol in 1 : 2 molar ratio. The contents were refluxed for about 2–3 h with constant stirring, when a clear solution was obtained. It was concentrated and cooled, when coloured adduct separated out. It was filtered, washed with absolute ethanol and dried in an electric oven at 80°C.

RESULTS AND DISCUSSION

Some physical properties of the first ligand (HL), its alkali metal salts (ML), second ligand (HL′) and the new mixed ligand complexes are listed in Table-1. All the complexes are generally brown in colour except in few cases and stable under dry conditions. They show no change in stoichiometry or in physical properties even after a long period. In general, the complexes are appreciably soluble in polar solvents like methanol but sparingly soluble in non-polar solvents namely, carbon tetrachloride, benzene and toluene etc.

TABLE-1
PHYSICAL PROPERTIES AND ANALYTICAL DATA OF METAL COMPLEXES

Compound	Colour	m.p./b.p./ decomp./trans. temp. (°C)	Conductivity*	Analysis % (Found/Calcd.)		
				C	H	M
HAQ	Yellow	193 m	–	74.80 (75.00)	3.56 (3.57)	–
LiHAQ	Purple	300 d	5.5	72.80 (73.04)	3.20 (3.04)	–
NaHAQ	Purple	300 d	7.0	68.20 (68.29)	2.85 (2.84)	9.30 (9.34)
KHAQ	Deep violet	300 d	8.5	63.85 (64.12)	2.70 (2.67)	14.50 (14.88)
AcAc	Colourless	133 bp	–	–	–	–
LiHAQ·(AcAc)	Orange yellow	190 md	2.8	67.85 (69.09)	4.60 (4.54)	–
NaHAQ·(AcAc)$_2$	Brown	170 md	3.0	62.95 (64.57)	5.25 (5.15)	5.00 (5.15)
Bzac	White	61 mp	–	–	–	–
LiHAQ·(BzAc)	Yellowish brown	185 md	1.0	72.50 (73.46)	4.35 (4.33)	–
NaHAQ·(BzAc)$_2$	Brown	170 md	2.3	70.75 (71.57)	4.95 (4.73)	3.90 (4.03)
KHAQ·(BzAc)$_2$	Brown	163 d	2.8	67.88 (69.62)	5.02 (4.60)	6.50 (6.65)
EAA	Colourless	181 bp	–	–	–	–
LiHAQ·(EAA)	Brown	195 md	3.2	64.70 (66.66)	5.02 (94.72)	–
NaHAQ·(EAA)$_2$	Brown	180 d	3.6	60.86 (61.66)	5.50 (5.33)	4.50 (4.54)
EM	Colourless	197 bp	–	–	–	–
LiHAQ·(EM)	Yellowish brown	175 md	2.7	62.33 (64.61)	4.97 (4.87)	–
NaHAQ·(EM)$_2$	Deep brown	223 d	3.5	60.50 (62.06)	4.98 (4.67)	5.60 (5.66)

Compound	Colour	m.p./b.p./ decomp./trans. temp. (°C)	Conductivity*	Analysis % (Found/Calcd.)		
				C	H	M
SalH	Colourless	192 bp	–	–	–	–
LiHAQ·(SalH)	Salmon pink	120 md	3.3	71.50 (71.59)	3.70 (3.69)	–
$NaHAQ\cdot(SalH)_2$	Salmon pink	280 t	3.8	68.48 (68.57)	3.90 (3.87)	4.70 (4.69)
OHA	Colourless	106 m	–	–	–	–
LiHAQ·(OHA)	Dark brown	280 d	4.0	70.85 (72.13)	4.25 (4.09)	–
$NaHAQ\cdot(OHA)_2$	Reddish brown	220 d	4.8	68.25 (69.49)	4.60 (4.44)	4.40 (4.44)
HNaph	Cream	80 mp	–	–	–	–
LiHAQ·(HNaph)	Brown	180 md	3.6	72.90 (74.62)	4.40 (3.73)	–
$NaHAQ\cdot(HNaph)_2$	Deep brown	195 t	4.8	72.35 (72.36)	5.20 (5.02)	3.90 (3.85)
$KHAQ\cdot(HNaph)_2$	Deep brown	190 t	10.2	67.95 (70.47)	5.60 (4.89)	7.00 (6.36)

*molar conductivity in ohm^{-1} cm^2 $mole^{-1}$ in DMP at 23°C

All the complexes undergo a transformation at temperatures which are considerably higher than the melting or boiling point of the ligand except LiHAQ·SalH, indicating thereby their greater thermal stability. The molar conductivities of all these complexes were measured in DMF at 23°C. The lower values (1.0–10.2 ohm^{-1} cm^2 $mole^{-1}$) of molar conductivities of the complexes suggest the covalent nature of the complexes.

Infrared Spectra

The pertinent IR data for these compounds are shown in Table-2. The absence of —OH absorption band in the region 3500–1800 cm^{-1} suggests that there is strong hydrogen bonding[5]. The absence of hydroxyl band and shifting to 1635 cm^{-1} of C=O indicates marked weakening of the —OH and C=O band frequencies. The band is attributed to the chelated hydroxyl group of the quinone (C=O . . H . . O) and indicates the presence of intramolecular hydrogen bonding in the anthrquinone.

The ν(OH) is also missing in alkali metal salts and complexes of 1-hydroxy anthraquinone. But in some cases a new broad band of weak to medium intensity in the region 2700–1800 cm^{-1} is observed. The absence of —OH band and new broad band in the region 2700–1800 cm^{-1} suggests that there is strong hydrogen bonding in these complexes[6–7]. None of these mixed ligand complexes show anomalous broad absorption band between 1100–700 cm^{-1} and as such the acid-salt structure with very short O—H . . O (*ca.* 2.7 Å) is most improbable.

The free C=O and hydrogen bonded carbonyl are assigned to 1675 cm^{-1} and 1635 cm^{-1} respectively. In the spectra of mixed ligand complexes of alkali metals, TABLE-2

Compound	ν(O—H . . O)	ν(free C=O)	ν(C=O/C=C)	ν(C—O)
HAQ		1675 m	1635 s	1300 s
LiHAQ		1672 m	1625 s	1305 s
NaHAQ		1675 w	1625 s	1305 s
KHAQ		1672 m	1620 s	1305 s
AcAc	3000–2700 br	1725 sh	1705 m 1625 s	–
LiHAQ·AcAc	2700–2500 br	1670 m	1625 s 1585 m 1560 sh 1290 s	–
NaHaQ(AcAc)$_2$	2700–2500 br, 1850 br	1680 sh	1650 m 1618 s 1600 sh 1570 m	1280 m
EAA	3000–2800 br	1720 br	1650 sh	–
LiHAQ·EAA		1715 m	1675 m 1650 w 1620 s 1570 w	1280 m
NaHAQ·(EAA)$_2$		1690 w	1670 m 1625 s	1290 s
EM		1720 s		–
LiHAQ·EM		1710 w	1675 m 1640 s 1625 w 1580 m	1310 w
NaHAQ(EM)$_2$		1700 w	1670 m 1638 s 1580 m 1570 w	1310 w
SalH	3100–2900 br	1660 br		1282 m
LiHAQ·SalH	2750–1900 br	1675 s	1638 s 1605 m 1575 w 1560 w	1315 w
NaHAQ·(SalH)$_2$	2720 br–1900 br	1670 s	1640 w 1630 w 1620 sh 1585 m	1300 m
OHA	3100–3000 br		1640 s	1300 s
LiHAQ·OHA	1900 br	1675 m	1648 s 1638 w 1610 s 1575 w	1300 sh
NaHAQ·(OHA)$_2$	1900 br	1678 m	1640 sh 1615 s 1575 w 1562 w	1280 s
Bzac			1603 s 1580–1540 hr	–
LiHAQ·BzAc	2700 br–2500 br	1675 s	1638 w 1620 sh 1590 m 1580 w	1310 w
KHAQ·(BzAc)$_2$	2700 br–1900 br	1680 m	1650 w 1620 s 1575 m 1560 w	1305 sh
HNaph	3000–2800 br		1650 s	1310 s
LiHAQ·HNaph	2700–2500 br 2000–1800 br	1680 m	1650 m 1620 m 1600 sh 1572 w	1300 sh
KHAQ·(HNaph)$_2$	2700–2600 br 2000–1800 br	1670 w	1640 w 1620 w 1610 w 1580 w	1300 w

br = broad, m = medium, w = weak, sh = shoulder, s = strong

the free C=O band at 1675 cm^{-1} remains unaffected but hydrogen bonded at 1635 cm^{-1} band splits into two; one of the split bands is due to the presence of free C=O group in alkali metal salts of 1-hydroxy anthraquinone and other bands appear due to chelated enolic form of C=O and C=C stretching bands. This splitting and shifting in C=O group suggests that the coordination has taken place through oxygen of the carbonyl group. The strong band at 1300 cm^{-1} in the spectrum of 1-hydroxy anthraquinone is in all probability due to the C—O (phenolic) stretching vibration. On complexation, there is slight appreciable change in C—O band.

Structure and Bonding

On the basis of elemental analysis and IR spectral data the following probable structures have been assigned to the mixed ligand complexes:

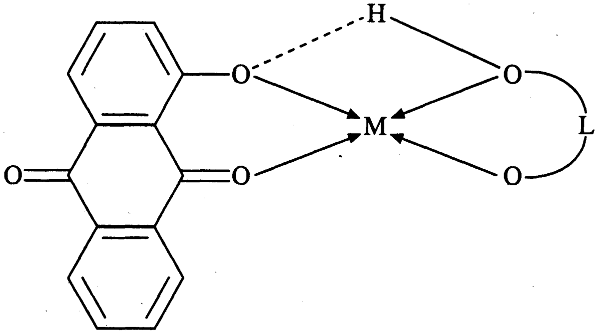

Fig. 1

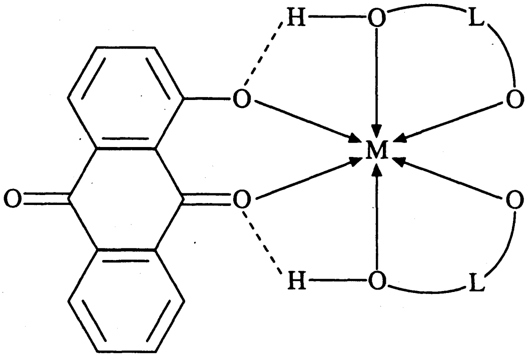

Fig. 2

(where M = Li, Na or K)

REFERENCES

1. B.P. Geyer and George Mcp Smith, *J. Am. Chem. Soc.*, **64**, 1649 (1942).
2. V.M. Dziomko, *Zhur. Vsesoyuz. Khim. Obschestva in D.I. Mendeleeva*, **6**, 108 (1961).
3. Horning, Organic Synthesis, Collective Vol-III, p. 463 (1955).
4. M. Stc. Flett., *J. Chem. Soc.*, 1441 (1948).
5. R.C. Lord and R.E. Merryfield, *J. Chem. Phys.*, **21**, 166 (1953).
6. A. Corsini and J. Abraham, *Chem. Comm.*, 856 (1968).
7. A. Corsini, J. Abraham and M. Thompson, *Chem. Comm.*, 1101 (1967).

(*Received:* 24 November 2000; *Accepted:* 9 March 2001) AJC-2280