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Neutral Complexes of Alkali Metals with 5,7-Substituted Oximes

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Complexes of alkali metals with 5,7-dinitro-oxine, 5,7-dichloro-oxine and 5,7-dibromo-oxine have been synthesised and characterised on the basis of physico-chemical data. The IR spectral data indicate that the ligands are coordinated to the metal atom via hydroxyl oxygen and 'N' atom of the quinoline ring. It also indicates the presence of hydrogen bonding in them, which may be one of the dominant factors for the stability of these complexes.

INTRODUCTION

Coordinating ability of alkali metals with 8-hydroxyquinoline[1–3] and 8-hydroxyquinoline-N-oxide[4] have been extensively studied. In the present paper investigation has been undertaken to examine the complexing ability of the derivatives of 8-hydroxyquinoline *e.g.* 5,7-dinitro-oxine, 5,7-dichloro-oxine and 5,7-dibromo-oxine towards the alkali metals. We could obtain a number of alkali metal complexes having the general formula ML·HL where M = Li, Na, K, Rb or Cs and HL = 5,7-dinitro-oxine (DNHQ), 5,7-dichloro-oxine (DClHQ) and 5,7-dibromo-oxine (DBrHQ) and L = respective anions of (HL) ligands.

EXPERIMENTAL

The ligands DNHQ, DClHQ and DBrHQ were prepared by the procedure described by Dicshoorn[5], Ghosh *et al.*[6] and Gutzeit and Monnier[7] respectively.

Preparation of Complexes

1:1 Stoichiometric ratios of alkali metal hydroxide and ligand (HL) were taken in absolute ethanol in a conical flask. The suspension mixture was refluxed on a magnetic stirrer for 2–3 h. On cooling alkali metal salts of respective ligands precipitated out. These were filtered, washed with ethanol and dried at 80°C.

Again equimolar ratios of the alkali metal salts of respective ligands were taken in absolute ethanol and subjected to the above procedure. The precipitates so formed were filtered, washed with absolute ethanol and dried at 80°C.

RESULTS AND DISCUSSION

Table 1 lists the physical properties of the ligand and the new neutral

complexes. Almost all the alkali metal salts and their respective complexes were found to be stable in dry air but stability decreased on exposure to moisture leading ultimately to decomposition, hence all the salts and complexes made were kept in a desiccator over solid anhydrous calcium chloride. From the results it was evident that almost all the alkali metal complexes undergo a transformation at temperatures which were considerably higher than the melting points of the ligands with a few exceptions, indicating their greater stability. Most of the complexes were soluble in polar solvents, such as ethanol, methanol etc., but insoluble in non-polar solvents like benzene, ether etc.

TABLE 1
ANALYTICAL DATA OF LIGANDS AND THEIR METAL COMPLEXES

Compound (Colour)	M.P. decomp./ Trans. temp. (°C)	% Found (Calcd.)			
		C	H	N	M
DNHQ (Greenish yellow)	315 m	45.86 (45.95)	2.10 (2.12)	17.85 (17.87)	—
LiDNQ·DNHQ (Yellow)	350 d	46.28 (45.37)	1.92 (1.89)	16.50 (17.60)	1.40 (1.47)
NaDNQ·DNHQ (Yellow)	290 t	44.25 (43.90)	1.85 (1.82)	16.80 (17.07)	4.60 (4.60)
KDNQ·DNHQ (Yellow)	275 t	41.75 (42.51)	1.87 (1.77)	15.95 (16.50)	7.70 (7.76)
RbDNQ·DNHQ (Yellow)	260 t	40.28 (38.95)	1.80 (1.60)	15.20 (15.14)	14.38 (15.42)
CsDNQ·DNHQ (Yellow)	250 md	34.12 (35.88)	1.52 (1.49)	13.65 (13.95)	21.80 (22.09)
DClHQ (White)	179 m	50.42 (50.46)	2.30 (2.33)	6.50 (6.54)	—
LiDClQ·DClHQ (Cream)	280 t	48.90 (49.76)	2.00 (2.07)	6.50 (6.49)	1.50 (1.61)
NaDClQ·DClHQ (Cream)	265 t	47.50 (48.00)	1.58 (2.00)	6.25 (6.22)	5.20 (5.11)
K DClQ·DClHQ (Cream)	250 t	45.85 (46.35)	1.90 (1.93)	6.02 (6.00)	8.35 (8.36)
RbDClQ·DClHQ (Cream)	270 d	41.80 (42.14)	1.78 (1.75)	5.40 (5.46)	15.90 (16.67)
CsDClQ·DClHQ (Cream)	240 d	36.95 (38.57)	1.62 (1.60)	4.98 (5.00)	22.50 (23.73)
DBrHQ (Yellow)	195 m	35.60 (35.64)	1.62 (1.65)	4.60 (4.62)	—
RbDBrQ·DBrHQ (Brownish yellow)	240 d	29.98 (31.30)	1.32 (1.30)	4.10 (4.05)	12.00 (12.38)
CsDBrQ·DBrHQ (Brownish yellow)	225 t	28.25 (29.28)	1.25 (1.22)	3.80 (3.79)	17.50 (18.02)

Infrared measurements for the title ligands and their hitherto unknown neutral alkali metal complexes were made between 4000 to 650 cm^{-1} in KBr phase. Pertinent IR data for these compounds were recorded in Table 2.

TABLE 2
PERTINENT IR DATA (cm^{-1}) FOR LIGANDS AND THEIR NEUTRAL COMPLEXES WITH ALKALI METALS.

Compound	ν(OH)	ν(NO_2)	ν(C=N)
DNHQ	3200–2800 br 1950 br, 1900–1800 br	1650 s	1590 s
LiDNQ.DNHQ	3100–2900 br, 2010 br, 1950 br	1650 s	1580 s
NaDNQ.DNHQ	3100 br	1652 s	1570 m
K DNQ.DNHQ	3100–2900 br	1648 m	1575 s
RbDNQ.DNHQ	3150 br	1655 m	1570 m
CsDNQ.DNHQ	3120 br	1650 s	1580 m
DClHQ	3300–2900 br		1620 m
NaDClQ.DClHQ	—		1610 m
KDClQ.DClHQ	—		1600 m
RbDClQ.DClHQ	—		1605 m
CsDClQ.DClHQ	—		1590 m
DBrHQ	3380 br		1630 m
RbDBrQ.DBrHQ	—		1590 m
CsDBrQ.DBrHQ	—		1600 m

The spectra of 5,7-dinitro-oxine shows variable multiple medium absorption bands over a wide range (*i.e.*, 3100–1800 cm^{-1}), while the spectra of 5,7-dichloro-oxine and 5,7-dibromo-oxine show broad bands in the region 3300–2900 cm^{-1} and at 3380 cm^{-1} respectively. The presence of absorption features in this region points out to the presence of strong intramolecular hydrogen bonding involving the hydroxyl hydrogen atom and nitrogen atom of quinoline ring.

The spectra of all the neutral complexes of 5,7-dinitro-oxine differ from that of the ligand by the absence of a variable medium broad hydrogen bonded —OH stretching absorption bands in the region (3100–1800 cm^{-1}). In the spectra of the salt, this band has disappeared, whereas in those of its neutral complexes this shows negative shift. The spectra of all the complexes exhibit a new broad band of medium intensity in the region 3100–2900 cm^{-1}. In the case of the neutral complexes of lithium, in addition to 3100–2900 cm^{-1}, two other broad bands are also observed, which can be attributed to medium to strong hydrogen bonding. The presence of these bands between 3100–1900 cm^{-1} may be due to N - - -H - - -O bond, and this seems to suggest a structure in the *trans* position.

The spectra of all the neutral complexes of 5,7-dichloro-oxine and 5,7-dibromo-oxine differ from the ligand molecule by the absence of a broad O—H stretching frequency absorption above 3000 cm^{-1}. The most probable explanation would be the formation of a strong H-bond.

No bands characteristic of N - - - H - - - O are observed in the region 3100–2050 cm^{-1} and the absence of N - - - H bands suggests again that the

H-bond is between two oxygen atoms and the ligands must therefore be in a *cis* configuration.

The bands at 1590 cm^{-1}, 1620 cm^{-1} and 1630 cm^{-1} in the ligand, 5,7-dinitro-oxine, 5,7-dichloro-oxine and 5,7-dibromo-oxine are assigned to ν(C=N) of quinoline ring. In the spectra of the neutral complexes, these bands are shifted down by 10–30 cm^{-1}. These shiftings of the bands of the ligands suggest coordination of the nitrogen atom of the C=N of the quinoline ring with the central metal atom.

Molar conductivities of all the complexes were measured in methanol at 25°C at a concentration of 10^{-3} M. The low values of molar conductivities (4.5–10.2 $ohm^{-1}\ cm^2\ mole^{-1}$) of these neutral complexes suggest them to be non-electrolytes.[8]

On the basis of elemental analysis, the general molecular formula of the neutral complexes of DNHQ, DClHQ and DBrHQ comes out to be ML·HL where M = Li, Na, K, Rb and Cs, HL = DNHQ, DClHQ and DBrHQ. Their IR spectra suggest that the coordination of the ligand with alkali metals has taken place through oxygen atom of the –OH group and the second coordinating atom is the N atom of quinoline ring. The IR spectra of the complexes also indicate the presence of H-bonding and *trans* structure for the complexes of DNHQ and *cis* structure or configuration of the complexes of DClHQ and DBrHQ.

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