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Homobinuclear Mixed Ligand Complexes of Alkali Metal Salts of Some Organic Compounds with Bis(8-Hydroxy-5-Quinolyl) Methane

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A number of complexes of the composition $(ML)_2 \cdot H_2L'$, where M = Li, Na or K, L = deprotonated 2,4-dinitrophenol, 2,4,6-trinitrophenol, 5,7-dinitro-oxine, 5,7-dichloro-oxine, 5,7-dibromo-oxine and 2-methyl-oxine and H_2L' = bis(8-hydroxy-5-quinolyl) methane, have been synthesised and characterised on the basis of elemental analysis, conductance and infrared spectral data.

INTRODUCTION

In continuation of our earlier study[1,2] we report some novel mixed ligand complexes of alkali metals, representing a model system to explore the mechanism of selective absorption of alkali metal ions by plants. This ligand behaves as a quadridentate ligand and has been shown to form stable complexes[3–7] with a number of transition metals. It, however, appears from literature survey that no alkali metal complex with bis(8-hydroxy-5-quinolyl)methane has yet been reported. It was, therefore, decided to examine this ligand for possible complex formation with alkali metals.

EXPERIMENTAL

The ligand bis(8-hydroxy-5-quinolyl)methane was prepared by the method of Horowitz and Perros[5]. The alkali metal salts of 2,4-dinitrophenol (DNP), 2,4,6-trinitrophenol (TNP), 5,7-dichloro-oxine (DClL), 5,7-dibromo-oxine (DBrL), 5,7-dinitro-oxine (DNL) and 2-methyl-oxine (MeL) were prepared by reported method[2].

Preparation of mixed ligand complex

A mixture of bis(8-hydroxy-5-quinolyl)methane and an alkali metal salt of ligand first (HL) was refluxed in DMF in mole ratio 1 : 2 at 120°C for 4–5 h with constant stirring. The coloured solution so obtained was cooled. On addition of solvent ether to it, the coloured adduct came apart almost instantaneously. It was filtered out, washed with solvent ether and dried in an electric oven at 80°C.

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RESULTS AND DISCUSSION

Some physical properties of the second ligand and the new mixed complexes $(ML)_2 \cdot H_2L'$ obtained are listed in Table 1. All the mixed complexes are coloured. They are partially soluble in polar solvents and are insoluble in non-polar solvents, namely, benzene, ether, etc. All these complexes are stable in air under dry condition for reasonably long period of time. They were stored in corked sample tubes over anhydrous $CaCl_2$ in desiccator. They are hygroscopic in nature. They either decompose or undergo a transformation at temperatures which are considerably higher than the melting point of the corresponding ligand, indicating thereby their greater stability. But in some cases, no conclusion can be drawn from an examination of the action of heat on complexes which appear to decompose at a temperature slightly lower than the melting point of the second ligand (H_2L'),

TABLE 1

Compound/Colour	m.p./decomp./ transition temp. (°C)	% Analysis Found (Calcd.)			
		C	H	N	M
Bis(8-hydroxy-5-quinolylmethane) (H_2L') (White)	280 m	75.8 (75.5)	4.80 (4.64)	9.25 (9.26)	—
$(LiDNP)_2 \cdot H_2L'$ (Yellow)	220 d	52.95 (54.54)	2.95 (2.93)	11.98 (12.31)	1.88 (2.05)
$(NaDNP)_2 \cdot H_2L'$ (Yellow)	270 d	51.58 (52.10)	2.82 (2.80)	11.70 (11.76)	6.30 (6.44)
$(KDNP)_2 \cdot H_2L'$ (Yellow)	250 d	(49.50) (49.59)	2.65 (2.68)	11.20 (11.26)	10.40 (10.45)
$(NaTNP)_2 \cdot H_2L'$ (Yellow)	300 d	45.95 (46.26)	2.29 (2.23)	13.88 (13.93)	5.68 (5.72)
$(KTNP)_2 \cdot H_2L'$ (Yellow)	270 d	45.20 (44.49)	2.30 (2.15)	12.95 (13.93)	9.10 (9.35)
$(NaDClL)_2 \cdot H_2L'$ (Pale brown)	298 d	56.86 (57.35)	2.91 (2.84)	7.01 (7.23)	5.69 (5.94)
$(KDClL)_2 \cdot H_2L'$ (Pale brown)	290 d	54.01 (55.08)	2.93 (2.72)	6.84 (6.94)	9.52 (9.67)
$(NaDBrL)_2 \cdot H_2L'$ (Brownish yellow)	300 d	44.84 (45.19)	2.55 (2.23)	5.60 (5.69)	4.42 (4.69)
$(KDBrL)_2 \cdot H_2L'$ (Brownish yellow)	295 d	42.86 (43.90)	2.36 (2.16)	5.42 (5.51)	7.42 (7.67)
$(NaDNL)_2 \cdot H_2L'$ (Deep yellow)	290 d	52.72 (54.41)	3.05 (2.69)	13.42 (13.82)	5.45 (5.73)
$(LiMeL)_2 \cdot H_2L'$ (Grey)	295 d	73.72 (74.05)	4.90 (4.74)	8.62 (8.86)	2.10 (2.21)
$(NaMeL)_2 \cdot H_2L'$ (Grey)	260 d	68.75 (70.48)	4.83 (4.51)	8.45 (8.43)	6.80 (6.92)
$(KMeL)_2 \cdot H_2L'$ (Light brown)	230 d	66.20 (67.04)	4.53 (4.29)	8.10 (8.02)	11.50 (11.46)

Molar conductivities of some complexes were measured in DMF at 30°C at a concentration of 10^{-3}M. Significantly low values of molar conductivities (8.9–12.36 ohm^{-1} cm^2 $mole^{-1}$) of these mixed complexes suggest them to non-electrolytes[8].

The selected absorption bands of the ligand as well as of the complexes are given in Table 2. The absorption band of principal interest in the infrared spectra of bis(8-hydroxy-5-quinolyl)methane are 3335, 1580 and 1420 cm^{-1}. The moderately strong band at 3335 cm^{-1} in the spectrum of H_2L' is attributed to the stretching —OH vibration frequency, while the strong band at 1420 cm^{-1} in its spectrum is, in all probability, due to the bending —OH frequency[5]. The absorption band in the region 1580 cm^{-1} has been assigned to the vibration νC=N group in the quinoline ring[9].

It is evident that the spectrum of the ligand contains a moderately strong band at 3335 cm^{-1}; this band has virtually disappeared (or with its appreciable shifts of about 35 to 180 cm^{-1}) in the complexes, indicating that coordination has taken place owing to intrinsicality of the oxygen atom of the —OH group of the ligand.

In the IR spectra of these complexes, the 1580 cm^{-1} band of the ligand (assigned to νC=N) has appeared as split band at 1575–1620 cm^{-1} and 1560–1590 cm^{-1}. It is evident from Table 2 that one of the split bands has appeared towards higher frequency side, while the other has appeared towards lower frequency side. Most probable explanation for this splitting seems to be the presence of $—NO_2$ group in the various alkali metal anions of organic acid (*i.e.* first ligand) or to be the simultaneous presence of two quinoline ring —C=N— moiety of the ligand molecule in the complexes. These splittings and shifting of the 1580 cm^{-1} band of the ligand suggest the coordination of N— atom of the C=N group of the quinoline ring with central metal atom.

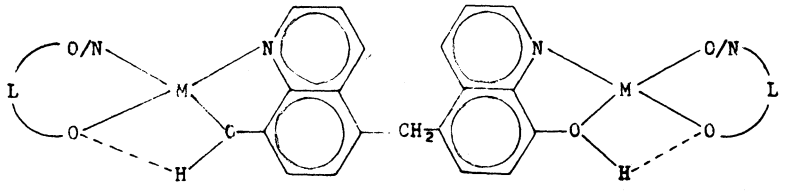
TABLE 2
PERTINENT IR DATA (cm^{-1}) FOR H_2L' AND ITS MIXED COMPLEXES

Compound	ν—OH	νC=N	ν—OH
H_2L'	3335 m	1580 s	1420 s
$(LiDNP)_2 \cdot H_2L'$	3090 w, 2350 br, 2150 br	1600 m, 1590 m	1395 s
$(KDNP)_2 \cdot H_2L'$	3100 br, 2600 br	1600 m, 1570 m	1400 m
$(NaTNP)_2 \cdot H_2L'$	3300 m, 2200 br, 1950 br	1610 sh, 1570 m	1405 m
$(KTNP)_2 \cdot H_2L'$	3050 w, 2350 br, 1900–1800 br	1590 s, 1570 sh	1400 s
$(NaDClL)_2 \cdot H_2L'$	3300 br	1610 sh, 1580 m	1400 m
$(KDClL)_2 \cdot H_2L'$	3050 br	1600 s, 1570 s	1400 m
$(NaDBrL)_2 \cdot H_2L'$	3090 br	1590 sh, 1570 m	1410 m
$(KDBrL)_2 \cdot H_2L'$	3250 br	1620 m, 1575 m	1400 w
$(LiMeL)_2 \cdot H_2L'$	2850 br, 1950 br	1600 sh, 1580 m	1400 m
$(NaMeL)_2 \cdot H_2L'$	2650 br	1575 sh, 1560 m	1405 w

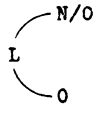
None of the complexes has a band at 1420 cm^{-1}. Rather the spectra of these complexes show a reduced absorption band in the region 1410–1395 cm^{-1}, indicating the chelation of oxygen atom of the —OH group of the ligand. The new bands of reduced frequency are weak and poorly resolved.

A new broad band of weak to medium intensity in the region 3100–1800 cm^{-1} is exhibited by some complexes. This band could be assigned O H- - - O/N - - - H - - - O absorption and suggests that hydrogen bending may be regarded to be an essential feature of these complexes.

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



where M = Li, Na or K



= deprotonated DNP, TNP, DClL, DBrL, DNL or MeL

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