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Alkali Metal Complexes: Homo-Binuclear Complexes of Alkali Metal Salts of Quinizarin with Some Oxygen Donor Ligands

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A series of novel homo-binuclear complexes of the general formula $M_2L \cdot nHL'$ (where M = Li, Na and K; L = quinizarin and HL′ = acetylacetone, benzoylacetone, saclicylaldehyde, *o*-hydroxy acetophenone, *o*-hydroxynaphthaldehyde, ethyl acetoacetate and ethyl malonate; and n = 2 or 4) have been synthesised and characterised on the basis of chemical analysis, conductance and infrared spectral studies. IR spectral data indicate the presence of hydrogen bonding in the complexes, which may be one of the essential features for the stability of these complexes. Low value of the molecular conductivity suggests the covalent nature of bonds in these complexes.

INTRODUCTION

The study of the coordination chemistry of alkali metals[1,2] would be interesting and useful, as the subject remained neglected and received very little attention until recently. We have taken up the study of the coordination chemistry of alkali metals because of their importance in the metabolism of plants. In recent years, much interest exists in the synthesis of polynuclear complexes, which can hold metal centres in close proximity.

In an attempt to explore the mechanism of selective absorption of alkali metal ions by plants, with the assumption that a knowledge of coordination chemistry of alkali metals would facilitate fuller understanding of the mechanism, our attention has been drawn to the naturally occurring ligand hydroxyquinone i.e. quinizarin[3] (1 : 4 dihydroxy anthraquinone).

In view of the above information, it was decided to extend the investigation by a systematic examination of alkali metal salts of quinizarin with oxygen donor ligands *e.g.* acetyl acetone, benzyl acetone, ethyl acetoacetate, *o*-hydroxy acetophenone and 2-hydroxy-1-napthaldehyde. Coordination sites in all these second ligands are only oxygen atoms and they act as a bidentate ligand. All these secondary ligands are expected to form 6-membered chelates.

We could obtain a number of homo-binuclear complexes of alkali metal salts of quinizarin with oxygen donor ligands; they have the general formula

$M_2L{\cdot}nHL'$, where M = Li, Na or K; L = quinizarin; n = 2 or 4 and HL' = acetyl acetone, benzoylacetone, ethyl acetoacetate, ethyl malonate, *o*-hydroxy acetophenone and 2-hydroxy-1-naphthaldehyde. We have also prepared the known mixed complexes of quinizarin[4] (*i.e.* alkali metal salts of quinizarin with salicylaldehyde) for comparative study.

EXPERIMENTAL

Quinizarin, acetylacetone, benzoylacetone, ethyl acetoacetate, ethyl malonate, salicylaldehyde and *o*-hydroxy acetophenone of AnalaR grade were used as such. 2-Hydroxy-1-naphthaldehyde was prepared from β-naphthol as described in the literature[5].

Preparation of alkali metal salts of quinizarin

Molar proportions of alkali metal hydroxide and quinizarin (2 : 1) were refluxed in 95% ethanol on a water bath for *ca.* 1 hr. The solution was filtered, concentrated and cooled when the alkali metal salts precipitated out. It was filtered, washed with the solvent (ethanol) and dried in an electric oven at 80°C.

Preparation of homobinuclear complexes of alkali metal salts of quinizarin with oxygen donor ligands

To the suspension of alkali metal salts of quinizarin (M_2L) in absolute ethanol, oxygen donor ligands e.g. acetyl acetone, benzylacetone, ethyl acetoacetate, ethyl malonate, salicylaldehyde and *o*-hydroxyacetophenone were added in the mole ratio of 1 : 3. On refluxing with continuous stirring on a hot plate for 2 to 4 hrs., the content went into solution. It was concentrated and cooled, when brown adduct of alkali metals came apart. It was filtered, washed with absolute ethanol or ether and dried in an electric oven at 80°C.

These complexes of quinizarin with acetylacetone have also been prepared as given below.

Alkali metal salts of quinizarin and acetyl acetone (mole ratio 1 : 3) were taken in a conical flask and refluxed with continuous stirring on hot plate at 120°C for 2 hrs. In this reaction acetyl acetone itself acts as a solvent. After filtration, the brownish pink solution was allowed to cool. After several hours, the salmon pink solid which formed was filtered off, washed with ether and dried in an anhydrous calcium chloride desiccator.

RESULTS AND DISCUSSION

Quinizarin forms deep red needles, it is insoluble in water but soluble in alcohol, benzene and acetone etc. Its salts are purple violet in colour. They are slightly soluble in water but more soluble in organic solvents like ethanol, acetone, methanol, dimethylformamide and N-methyl-2-pyrrolidone etc. and insoluble in non-polar solvents like benzene, carbon tetrachloride, *p*-xylene etc. Unlike the salts, the mixed complexes are generally brown and in some cases salmon pink in colour. They are appreciably soluble in methanol, dimethylformamide and acetone etc., but they are insoluble in non-polar solvents.

The complexes are stable under dry condition, e.g. over anhydrous calcium chloride in a desiccator. They show no change in stoichiometry or in physical properteis even after 2 years, but the complexes are unstable in moist air, in the presence of which they appear to decompose giving pale brown solids of indeterminate composition. The order of stability is Li > Na > K.

From Table 1, it is apparent that except in some cases of lithium complex, all other complexes undergo a transformation at a temperature higher than the melting or boiling point of the second ligands indicating thereby their greater stability.

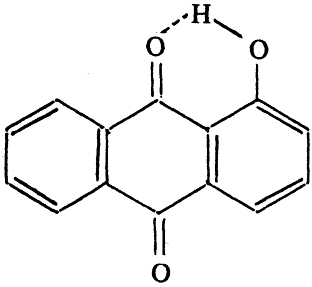
The colours, the decomposition transition temperatures, conductivity values as well as the analytical data of these complexes are listed in Table 1.

Spectra of first ligand (*i.e.* quinizarin) and its salts

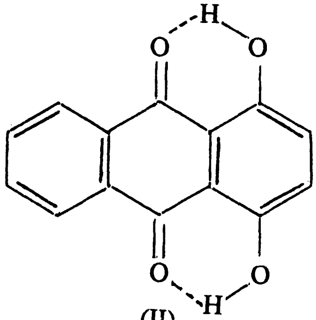
Pertinent IR data for these compounds are recorded in Table 2.

The absorption bands of our interest in the infrared spectrum of quinizarin are 1635 and 1280 cm^{-1}.

The absence of –OH absorption band in the region 3500–1800 cm^{-1} suggests that there is strong hydrogen bonding[6].



(I)



(II)

The monohydroxy anthraquinone (I) shows two bands: the normal carbonyl band at 1675 cm^{-1} and another at 1635 cm^{-1} due to the carbonyl group participating in the hydrogen bonding. Only the latter band appears in the dihydroxyanthraquinone (II) (quinizarin) since both carbonyl groups are involved in the hydrogen bonding.

In the spectra of dialkali metal salts, the O–H absorption band is also missing because both of the hydrogen atoms of phenolic groups in quinizarin are replaced by two alkali metals. The hydrogen bonded C=O band at 1635 cm^{-1} is shifted down by 25 cm^{-1} in the spectra of dialkali metal salts of quinizarin.

TABLE 1

Compound	Colour	M.pt./decomp./ transition temp (°C)	Conductivity (ohm^{-1} cm^{2} mole^{-1})	(%) Found			(%) Calculated		
				C	H	M	C	H	M
Quiniz.	Dark red	198 m	—						
Li_2 Quiniz.	Reddish purple	300 d	5.0	66.50	2.35		66.66	2.38	—
Na_2 Quiniz.	Deep blue purple	300 d	8.5	58.60	2.10	16.00	59.15	2.11	16.19
K_2 Quiniz.	Deep blue purple	300 d	12.5	53.00	2.00	24.00	53.16	1.89	24.68
Li_2 Quiniz. $(acac)_2$	Salmon pink	160 d	4.0	62.90	4.90	—	63.71	4.86	—
Li_2 Quiniz. $(EM)_2$	Brownish pink	165 d	6.5	58.55	5.25	—	58.74	5.24	—
Li_2 Quiniz. $(Bzac)_2$	Brownish orange	145 $\overline{\text{m}}$d	6.5	70.50	4.50	—	70.83	4.51	—
Na_2 Quiniz. $(Bzac)_2$	Deep brown	280 d	10.0	66.20	4.29	7.60	67.10	4.27	7.56
Li_2 Quiniz. $(EAA)_2$	Reddish brown	230 d	7.5	58.20	5.50	—	60.93	5.07	—
Li_2 Quiniz. $(SalH)_2$	Brown	120 $\overline{\text{m}}$d	6.2	67.58	3.61	—	67.74	3.62	—
Na_2 Quiniz. $(SalH)_2$	Brownish pink	240 d	8.8	65.20	3.85	6.00	65.28	3.88	5.95
K_2 Quiniz. $(SalH)_2$	Reddish brown	220 $\overline{\text{m}}$d	13.5	61.50	3.75	9.64	62.64	3.72	9.70
Li_2 Quiniz. $(OHA)_2$	Bluish violet	280 d	7.5	68.50	4.20	—	68.70	4.19	—
Na_2 Quiniz. $(OHA)_4$	Purple	225 t	9.0	65.80	4.50	5.50	66.66	4.58	5.55
Li_2 Quiniz. $(NHaph)_2$	Orange red	165 $\overline{\text{m}}$d	4.5	71.95	3.72	—	72.48	3.69	—
Na_2 Quiniz. $(NHaph)_4$	Brown	180 $\overline{\text{m}}$d	8.2	69.68	4.20	4.80	71.60	3.90	4.73
K_2 Quiniz. $(NHaph)_2$	Dark brown	150 $\overline{\text{m}}$d	14.0	67.20	3.80	8.00	69.32	3.78	7.76

Molar conductivity of 10^{-3} M solutions in methanol.

TABLE 2
PERTINENT IR BANDS IN cm^{-1}

Compound	νO-H...O	νC=O/C=C	νC–O
Quiniz.		1635 m	1280 m
Li_2 Quiniz.		1610 m	1290 m
Na_2 Quiniz.		1610 sh	1310 m
K_2 Quiniz.		1610 sh	1290 m
Li_2 Quiniz. $(acac)_2$	2700–2500 br 2000–1800 br	1620 sh, 1580 s, 1560 sh	1310 m
Li_2 Quiniz. $(EAA)_2$		1680 br, 1610 s 1575 m, 1550 w	1280 m
Li_2 Quiniz. $(EM)_2$		1715 s, 1600 s, 1580 m	1290 m
Li_2 Quiniz. $(Bzac)_2$	2700–2600 br	1630 s, 1590 s, 1570 w	1315 m
Na_2 Quiniz. $(Bzac)_2$	2700–2500 br	1610 sh, 1580 sh, 1560 m	1310 w
Li_2 Quiniz. $(SalH)_2$	2700–2500 br	1668 m, 1650 w, 1580 w	1290 w
Na_2 Quiniz. $(SalH)_2$	2750 br	1670 s, 1630 sh, 1590 m	1315 m
K_2 Quiniz. $(SalH)_4$	2700 br	1660 sh, 1620 s, 1585 s	1310 s 1280 w
Li_2 Quiniz. $(OHA)_2$	2700–2500 br	1620 sh, 1600 s, 1580 s 1550 w	1305 w 1280 m
Na_2 Quiniz. $(OHA)_4$	2700 br	1610 sh, 1590 m, 1560 w	1310 w
Li_2 Quiniz. $(NHaph)_2$	2700–2600 br	1625 s, 1585 s	1315 m
K_2 Quiniz. $(NHaph)_2$	2700–2500 br 2000–1800 br	1630 m, 1585 m, 1560 w	1310 sh 1290 w

If the alkali metal salts of quinizarin had a purely ionic structure, the C=O peak in these compounds would have been at a higher frequency, very near to that of free ketone of anthraquinone i.e. 1690–1660 cm^{-1}; instead, the absorption occurs at 1610 cm^{-1}.

The close similarity of the spectra of alkali metal salts[7–9] of quinizarin to those of transition methyl acetyl-acetonates clearly indicates that these are primarily chelated or they are covalent compounds.

Spectra of mixed ligand complexes

We are discussing the IR spectra of mixed complexes of alkali metal salts of quinizarin with different oxygen donor ligands. In general, the IR spectra of mixed complexes are very complex; so it is very difficult to interpret the mixed complexes of alkali metals because both ligands (first and second ligands) contain C=O, C=C and C–O groups.

On complexation of alkali metal salts of quinizarin with acetyl acetone and benzoyl acetone, the enolic form of C=O bands split into three. One of the split bands is due to the presence of C=O band in the dialkali metal salts of quinizarin and other bands appear due to the chelated enolic form of C=O and C=C stretching bands. This splitting and shifting the enolated C=O band suggests that the coordination has taken place through oxygen atom of the enolated carbonyl group.

In addition to those described above, a new broad band of medium intensity appears in the 2700–1800 cm^{-1} in the complexes. The band is absent in the spectra of either the metal salt or the second ligand and could be assigned to O—H . . . O absorption. This suggests hydrogen bonding to be an essential features of these complexes.

In the mixed ligand complexes of alkali metal salts of quinizarin with salicylaldehyde, *o*-hydroxy acetophenone and 2-hydroxy-1-naphthaldehyde, the C=O bands split into two or three. One of the split bands is due to the preence of C=O band of aldehyde group and other two bands appear due to primary chelated carbonyl bands of dialkali metal salts of quinizarin and C=C stretching bands. These splittings in the carbonyl band suggest that the coordination has taken place through oxygen atom of carbonyl group. The (C–O) stretching band is observed in salicylaldehyde, *o*-hydroxyacetophenone and 2-hydroxy-1-naphthaldehyde in the region between 1280–1275 cm^{-1}. On complexation, these bands are either split or shifted to higher frequency by 10–25 cm^{-1}, suggesting that these phenolic C–O bonds attained some double bond character. Besides this, a new broad band of weak to medium intensity in the region 2700–1800 cm^{-1} in spectra of mixed complexes could be attributed to O—H . . . O absorption. The spectra of mixed ligand complexes of ethyl acetoacetate and ethyl malonate are different from acetylacetone, salicylaldehyde, benzoylacetone, *o*-hydroxy-acetophenone and 2-hydroxy-1-naphthaldehyde. The 1720 cm^{-1} band which appears as a strong intensity band in the spectrum of ethyl acetoacetate has shifted to lower frequency by 40 cm^{-1}. Ethyl malonate exhibits strong absorption band at 1720 cm^{-1}. On complexation, there is no appreciable change in carbonyl band. It is interesting to note that there is no absorption around 1650 cm^{-1}, which is the expected region for the carbonyl band of the enolic form and points to the latter's absence in the keto-enol mixture. None of the spectra shows broad bands near 2700–1800 cm^{-1}.

Conductivities

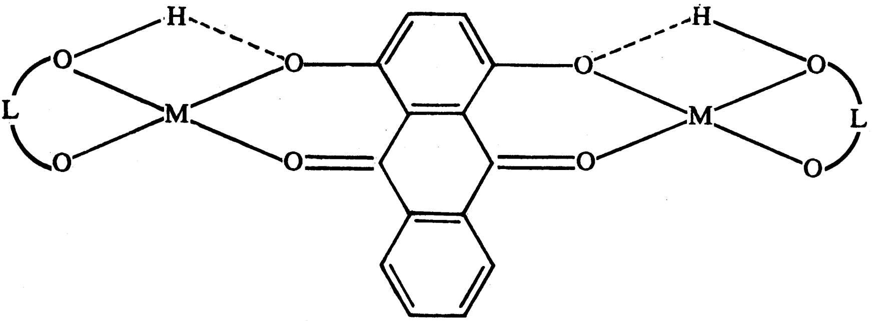
Molar conductivities of all the complexes were measured in methanol at 25°C at a concentration of 10^{-3} M.

A value of *ca.* 35–40 $ohm^{-1} cm^{2} mole^{-1}$ appears characteristic of 1 : 1 electrolyte. Fairly low values of molar conductivities of lithium, sodium and potassium salts of quanizarin suggest the ion-pair formation and the consequent preliminary chelation in them. The order of molar conductivities of these salts is Li < Na < K. This is in conformity with the observation of Banerjee *et al.*[10] that the smaller cations form stronger ion-pairs than the larger ones.

From the results, it is evident that the molar conductivities of none of the complexes approach either ideal or 1 : 1 electrolyte. However, significantly low values of molar conductivities of these mixed complexes suggest them to be non-electrolytes. The higher values of molar conductivities of potassium complex may be due to its dissociation in the solvent used.

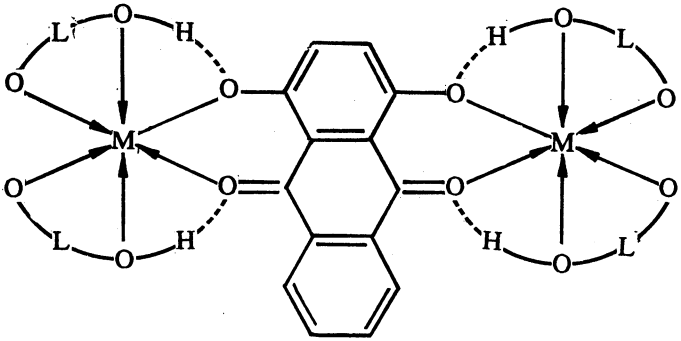
Structure and Bonding

On the basis of elemental analysis, the general formula of the alkali metal complexes described above comes out to be $M_2L \cdot nHL'$ where M = Li, Na or K; L = quinizarin; n = 2 or 4; and HL' = acetyl acetone, benzoylacetone, ethylacetoacetate, ethyl malonate, salicylaldehyde, *o*-hydroxyacetophenone and 2-hydroxy-1-naphthaldehyde. The IR spectra of all these complexes suggest the coordination of alkali metals with the ligand through oxygen atoms of the carbonyl group and enolic form of ketone or phenolic group. The IR spectra of these complexes also point to the presence of hydrogen bonding except in few cases. The significantly low values of molar conductivities of these complexes suggest them to be non-electrolyte. These facts suggest the following structures (IV) and (V) for these complexes.



(M = Li, Na or K)

(IV)



(V)

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REFERENCES

1. D. Prakash and S.P. Singh, *Polyhedron*, **3**, 243 (1984).
2. D. Prakash and S.P. Singh, *Polyhedroen*, **7**, 1 (1988).
3. E.H. Rodd, Chemistry of Carbon Compounds, Vol. III B, p. 1320 (1956).
4. N.V. Sidgwick and F.M. Brewer, *J. Chem. Soc.*, **127**, 2379 (1925).
5. E.C. Horning, Organic Synthesis, collective volume III, p. 463 (1955).
6. M. Stc. Flett, *J. Chem. Soc.,* 1441 (1948).
7. R. West and R. Riley, *J. Inorg. Nucl. Chem.*, **5**, 295 (1958).
8. E.J. Bellamy and R.F. Branch, *J. Chem. Soc.*, 4653 (1952).
9. ________, *J. Chem. Soc.*, 4487, 4491 (1954).
10. A.K. Banerjee, A.J. Layton, R.S. Nyholm and M.R. Truter, *J. Chem. Soc.(A)*, 2536 (1969).

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