

Homobinuclear Complexes of Alkali metal salts of Organic Acids with Quinizarin

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Homobinuclear complexes of alkali metal salts of organic acids with quinizarin of type $(ML)_2 H_2L'$, have been synthesised and characterised by elemental analysis and infrared spectral data. Their infrared spectra suggest that the coordination of the ligand has taken place through hydroxy oxygen atom of the phenolic group as well as through oxygen atom of the quinone group. The IR spectra of the complexes also indicate the presence of hydrogen bond in them which is one of the dominant factor for stability of the complexes.

INTRODUCTION

In continuation of our previous work^{1, 2} some more alkali metal complexes of organic acids having oxygen and nitrogen donor atoms with quinizarin of the general formula $(ML)_2 H_2L'$, where M = Li, Na or K, L = acetyl acetone (acac), salicylaldehyde (salH), 8-hydroxy quinoline (8HQ), 1-nitroso-2-naphthol (1N2N), H_2L' = quinizarin have been synthesised. The hydroxy anthraquinones are of practical interest³ and importance on account of their occurrence in nature, their extensive use in technology as mordant dyes and dyes intermediates. These complexes are likely to be important as models for metallo-enzyme substrate complexes and also as component of the multi-metal-multi ligand systems in biological fluids.

EXPERIMENTAL

Preparation of alkali metal salts of quinizarin and various organic acids: Quinizarin of Analar grade used for complexation and the alkali metal salts of it and organic acids are prepared as follows—Equimolar proportion of metal hydroxide and organic acids (AcAc, SalH, 1N2N, 8HQ) or quinizarin were refluxed in 95% ethanol for 0.5 h. The solution was filtered, concentrated and cooled, when the alkali metal salts precipitated out. It was filtered, washed with 95% ethanol and dried in an electric oven at 80°C.

Preparation of the complexes: 2 : 1 stoichiometric amount of alkali metal salts of (AcAc, SalH, 8HQ) and quinizarin were used in benzene or absolute ethanolic medium with constant stirring and heating for *ca.* 1 h, which on concentration and cooling of the solution led to the separation of coloured adducts of respective complexes. The precipitates were filtered, washed with benzene or absolute ethanol and dried in electric oven at 80°C.

RESULTS AND DISCUSSION

Some physical properties of the ligand, its alkali metal salts and the new complexes are listed in Table 1.

TABLE-1

Compounds	Colour	Melting/Decomp. temp. (°C)	Analysis% (Found/Calcd.)			
			C	H	N	M
Quinizarin	Dark red	198 m	69.94 (70.00)	3.30 (3.33)	–	–
Li ₂ Quiniz	Reddish purple	300 d	66.50 (66.66)	3.35 (2.38)	–	2.80 (2.83)
Na ₂ Quiniz	Deepblue purple	300d	58.60 (59.15)	2.10 (2.11)	–	16.00 (16.19)
K ₂ Quiniz	Deepblue purple	300 d	53.00 (53.16)	2.00 (1.89)	–	24.00 (24.08)
(LiAcAc) ₂ Quiniz	Brownish purple	275 d	63.70 (63.72)	4.85 (4.87)	–	3.00 (3.09)
(NaAcAc) ₂ Quiniz	Dark brown	240 d	59.40 (59.50)	4.52 (4.55)	–	9.00 (9.50)
(LiSa1H) Quiniz	Dark brown	262 d	67.70 (67.74)	3.61 (3.63)	–	2.30 (2.82)
(NaSa1H) ₂ Quiniz	Deep violet	285 md	63.60 (63.64)	3.40 (3.41)	–	8.00 (8.71)
(KSa1H) ₂ Quiniz	Blackish brown	293 m	59.98 (60.00)	3.20 (3.21)	–	13.00 (13.93)
(Li1N2N) ₂ Quiniz	Dark brown	255 d	68.20 (68.22)	3.30 (3.34)	4.65 (4.68)	2.30 (2.34)
(Na1N2N) ₂ Quiniz	Chocolate	281 md	64.72 (64.76)	3.10 (3.17)	4.40 (4.44)	7.00 (7.30)
(K1N2N) ₂ Quiniz	Yellowish brown	261 md	61.62 (61.65)	3.00 (3.02)	4.20 (4.23)	11.10 (11.78)
(Li8HQ) ₂ Quiniz	Dark brown	267 md	68.20 (68.22)	3.30 (3.34)	4.65 (4.68)	2.21 (2.34)
(Na8HQ) ₂ Quiniz	Deep brown	243 md	66.86 (66.89)	3.45 (3.48)	4.85 (4.88)	7.90 (8.01)
(K8HQ) ₂ Quiniz	Blackish brown	289 md	63.32 (63.36)	3.29 (3.30)	4.60 (4.62)	12.50 (12.87)

Quinizarin, its salts and complexes are having characteristic colours, soluble in alcohol, dimethyl formamide and acetone but insoluble in non-polar solvents. The complexes are stable under dry conditions but unstable in moisture, in the presence of which they appear to decompose giving pale brown solids of intermediate composition. From the result, it is apparent that all the complexes undergo a transformation at a temperature higher than the melting point of the ligand (quinizarin), indicating their greater thermal stability.

INFRARED SPECTRA

Infrared spectra of the ligand, its alkali metal salts and the complexes have been recorded in the region 4000–650 cm^{-1} .

Pertinent IR data for these compounds are shown in Table 2. The absorption band of our interest in the infrared spectrum of quinizarin is 1635 cm^{-1} . The absence of O—H absorption band in the region 3500–1800 cm^{-1} suggests that there is strong hydrogen bonding. Anthraquinone shows the usual carbonyl absorption band at 1675 cm^{-1} . The 1-hydroxy anthraquinone shows two bands: the normal carbonyl band at 1675 cm^{-1} and another at 1635 cm^{-1} due to carbonyl group participating in the hydrogen bonding. Only the latter band appears in the 1, 4-dihydroxy anthraquinone (i.e. quinizarin) since both carbonyl groups are involved in the hydrogen bonding⁴. 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. They hydrogen bonded $>C=O$ at 1635 cm^{-1} is shifted down by 25 cm^{-1} in the spectra of dialkali metal salts of quinizarin. If the alkali metal salts of quinizarin had a purely ionic structure, the carbonyl 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 dialkali metal salts of quinizarin to those of other metal acetyl acetonates^{5, 6} clearly indicates that these are primarily chelated or they are covalent in nature.

Compounds	$\nu\text{O—H} \dots \text{O}$	$\nu(\text{C}=\text{O})$
Quinizarin	—	1635 m
Li_2 Quiniz	—	1610 m
Na_2 Quiniz	—	1610 m
K_2 Quiniz	—	1610 m
$(\text{LiAcAc})_2$ Quiniz	2720–2600 br	1680 w, 1600 s.
$(\text{NaAcAc})_2$ Quiniz	2720–2600 br	1720 m, 1630 s, 1590 s
(LiSa1N) Quiniz	2700–2600 br	1660 m, 1610 m
$(\text{NaSa1H})_2$ Quiniz	2700–2600br	1690 m, 1630 s, 1585 m
$(\text{Na1N2N})_2$ Quiniz	2720–2650 br	1625 s,s 1585 s
$(\text{K1N2N})_2$ Quiniz	2720–2600 br	1625 s,s 1590 s
$(\text{Li8HQ})_2$ Quiniz	2720–2550 br	1610 w, 1570 w
$(\text{Na8HQ})_2$ Quiniz	2720–2600 br	1590 m, 1570 m
$(\text{K8HQ})_2$ Quiniz	2720 wbr	1610 m, 1580 m.

The IR spectra of homobinuclear mixed ligand complexes are very complex. The O—H stretching frequency is also missing in the complexes. A new broad band of weak to medium intensity in the region 2720–2550 cm^{-1} observed in all these mixed complexes may be attributed to O—H...O absorption⁷⁻⁹. This suggests the hydrogen bonding to be an essential feature of these complexes.

None of these complexes show anomalous broad absorption band between $1100\text{--}700\text{ cm}^{-1}$ as such the acid salt structure with very short $\text{O}\text{--}\text{H}\dots\text{O}$ ($= 2.7\text{ \AA}$) is most improbable. The $\text{C}=\text{O}$ stretching frequency of the complexes splits into two or three, one of the split band is due to the presence of $\text{C}=\text{O}$, $\text{N}=\text{O}$, $\text{C}=\text{N}$ or $\text{C}=\text{C}$ which is present in alkali metal salts of acetyl acetone, salicylaldehyde, 1-introso-2-naphthol, 8-hydroxy quinoline. These spitting and shifting in the $\text{C}=\text{O}$ band suggest that the coordination has taken place through oxygen atom of carbonyl group.

The probable structure on the basis of above studies can be produced and schematically as given below:

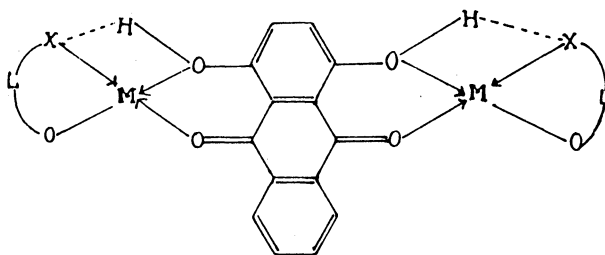


Fig. 1

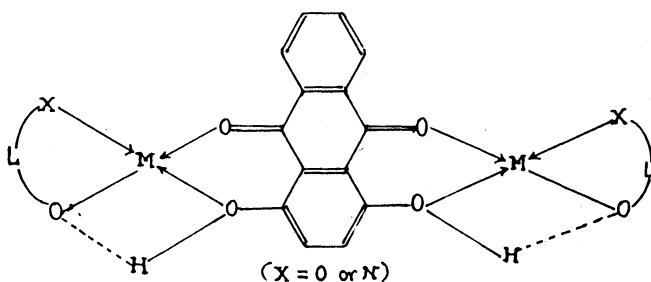


Fig. 2

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