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Alkaline Earth Metal Complexes: Mixed Ligand Complexes of Alkaline Earth Metal Salts of Some Organic Acids with Naturally Occurring Substrate

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Mixed ligand complexes of alkaline earth metal salts of organic acid viz. *o*-nitrophenol, 1-nitroso-2-naphthol, 8-hydroxyquinoline, *o*-aminobenzoic acid, salicylic acid, salicylaldehyde and acetylacetone with 5-hydroxy-1,4-naphthaquinone (Juglone) have been synthesised and characterised on the basis of elemental analysis, conductivity measurement and infrared spectral data. The probable structure has also been assigned.

INTRODUCTION

5-Hydroxy-1,4-naphthaquinone (Juglone) is a bioactive compound and found in most of the plant systems[1]. Complexes of 5-hydroxy-1,4-naphthaquinone with transition metals have been reported earlier[2]. Neutral complexes of alkaline earth metals with this ligand have been studied and reported[3]. In this communication we have taken the above mentioned ligand to investigate the coordination behaviour towards various alkaline earth metal salts of organic acids.

EXPERIMENTAL

5-Hydroxy-1,4-naphthaquinone was prepared by reported method[4], while other chemicals used in this study were AnalaR grade.

The $ML_2 \cdot HL'$ type mixed ligand complexes were prepared by mixing absolute ethanolic solution of alkaline earth metal salts of *o*-nitrophenol (ONP), 1-nitroso-2-naphthol (1N2N), 8-hydroxyquinoline (8HQ), *o*-aminobenzoic acid (OABA), salicylic acid (SalA), salicylaldehyde (SalH) and acetylacetone (acac) with absolute ethanolic solution of 5-hydroxy-1,4-naphthaquinone (HL′) in 1 : 1 molar ratio, respectively. The resulting mixtures were refluxed with stirring for 2–3 h; after concentrating and cooling the adduct got separated which was filtered, washed with absolute ethanol and dried in electric oven at 100°C.

RESULTS AND DISCUSSION

Some physical properties of the ligand and newly formed mixed ligand complexes are listed in Table-1. All the complexes are coloured and stable under dry condition. They show no change in stoichiometry or in physical properties even after a long time. In general the complexes are slightly soluble in methyl alcohol, ethyl alcohol, benzene etc. but insoluble in water. All these complexes undergo a transformation at temperatures which are considerably higher than the melting point of the ligand. This indicates their greater thermal stability. The molar conductivities of all the complexes were measured in DMF at 23°C. The lower values (9.7–13.4 ohm^{-1} cm^2 $mole^{-1}$) of molar conductivities of the complexes suggest the non-electrolytic nature of the complexes.

TABLE-1
ANALYTICAL DATA OF METAL COMPLEXES

Compound (Colour)	m.p./decomp./ tran./temp. (°C)	Analysis % Found (Calcd.)			
		C	H	N	M
Juglone(HL′)	185 m.p.	68.80	3.47	—	—
(yellow)		(68.96)	(3.44)	—	—
$Mg(OABA)_2 \cdot HL'$	280 t	60.50	4.00	6.05	5.40
(brown)		(61.28)	(3.83)	(5.96)	(5.11)
$Ca(OABA)_2 \cdot HL'$	265 t	58.40	3.75	5.70	7.85
(brown)		(59.25)	(3.70)	(5.76)	(8.23)
$Mg(ONP)_2 \cdot HL'$	290 t	55.30	2.97	5.82	4.84
(brownish yellow)		(55.69)	(2.95)	(5.90)	(5.06)
$Ca(ONP)_2 \cdot HL'$	282 t	53.80	2.86	5.68	8.00
(brownish yellow)		(53.87)	(2.85)	(5.71)	(8.16)
$Sr(ONP)_2 \cdot HL'$	275 t	48.50	2.55	5.15	16.25
(brownish yellow)		(49.11)	(2.60)	(5.21)	(16.29)
$Ba(ONP)_2 \cdot HL'$	260 d	43.25	2.40	4.60	22.85
(brownish yellow)		(44.95)	(2.38)	(4.77)	(23.28)
$Mg(1N2N)_2 \cdot HL'$	265 d	64.80	3.40	4.90	4.35
(brown)		(66.42)	(3.32)	(5.17)	(4.43)
$Ca(1N2N)_2 \cdot HL'$	270 d	63.82	3.20	4.90	7.05
(brown)		(64.51)	(3.22)	(5.01)	(7.16)
$Sr(1N2N)_2 \cdot HL'$	280 d	58.90	2.90	4.50	13.95
(brown)		(59.45)	(2.97)	(4.62)	(14.46)
$Ba(1N2N)_2 \cdot HL'$	300	52.55	2.65	4.10	18.95
(brown)		(54.96)	(2.75)	(4.27)	(20.91)
$Mg(oxin)_2 \cdot HL'$	295 d	68.28	3.72	5.70	4.85
(reddish brown)		(69.13)	(3.70)	(5.76)	(4.93)
$Ca(oxin)_2 \cdot HL'$	300	66.25	3.55	5.50	7.80
(reddish brown)		(66.93)	(3.59)	(5.58)	(7.97)
$Sr(oxin)_2 \cdot HL'$	280 d	62.50	3.35	5.15	14.35
(reddish brown)		(61.14)	(3.28)	(5.09)	(15.94)
$Ba(oxin)_2 \cdot HL'$	290 d	55.42	3.20	4.78	23.52
(dark brown)		(56.06)	(3.00)	(4.76)	(22.92)
$Ca(SalA)_2 \cdot HL'$	250 t	58.40	3.45	—	8.25
(yellowish brown)		(59.01)	(3.28)	—	(8.20)
$Sr(SalA)_2 \cdot HL'$	260 t	52.90	2.60	—	16.25
(yellowish brown)		(53.77)	(2.99)	—	(16.36)
$Mg(SalH)_2 \cdot HL'$	300	63.85	3.55	—	5.40
(brown)		(65.45)	(3.63)	—	(5.45)
$Ca(SalH)_2 \cdot HL'$	300	61.90	3.45	—	8.70
(reddish brown)		(63.15)	(3.50)	—	(8.77)
$Sr(SalH)_2 \cdot HL'$	290 d	(57.25)	3.18	—	17.42
(light brown)		(57.14)	(3.17)	—	(17.46)

Compound (Colour)	m.p./decomp./ tran./temp. (°C)	Analysis % Found (Calcd.)			
		C	H	N	M
$Ba(SalH)_2 \cdot HL'$	280 d	51.68	2.86	—	23.95
(brown)		(52.07)	(2.89)	—	(24.77)
$Mg(acac)_2 \cdot HL'$	295 t	59.65	5.10	—	6.00
(reddish brown)		(60.60)	(5.05)	—	(6.06)
$Ca(acac)_2 \cdot HL'$	280 t	56.84	4.89	—	9.62
(brown)		(58.25)	(4.85)	—	(9.70)
$Ba(acac)_2 \cdot HL'$	275 t	46.25	3.95	—	26.20
(deep brown)		(47.15)	(3.92)	—	(26.96)

The key IR bands (cm^{-1}) for these compounds are presented 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 ν(C=O) indicates very marked weakening of the —OH and C=O bond frequencies. The band is attributed to the chelated hydoxyl group of quinoline (C=O---H---O) and indicates the presence of intramolecular hydrogen bonding in the juglone.

TABLE-2

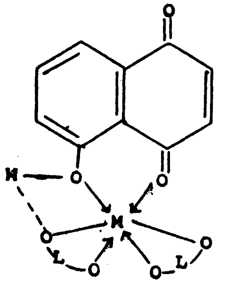
PERTINENT IR DATA (cm^{-1}) FOR MIXED LIGAND COMPLEXES OF JUGLONE (5-HYDROXY-1,4-NAPHTHAQUINONE)

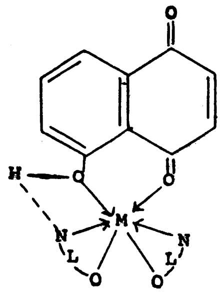
Compounds	ν(OH)/ ν(NH)	O—H---O	ν(C=O)	ν(C=O)/ ν(C=C)	ν(C—O)
Juglone (HL′)	—	—	1663 m	1635 m	1300 m
$Mg(OABA)_2 \cdot HL'$	3320 s, 3140 m	—	1660 m	1620m, 1605 m	1295 m
$Mg(SalH)_2 \cdot HL'$	—	—	1700 m, 1660 m	1620 m, 1595 m	1290 m
$Sr(SalH)_2 \cdot HL'$	—	—	1720 m, 1660 sh	1625 m, 1605 w	1300 w
$Mg(ONP)_2 \cdot HL'$	—	—	1660 sh	1620 m, 1600 m	1295 m
$Sr(ONP)_2 \cdot HL'$	—	1900–1800 br	1660 m	1620 s, 1600 m	1290 m
$Mg(acac)_2 \cdot HL'$	—	—	1700 w, 1660 w	1625 m, 1600 br	1295 m
$Ba(acac)_2 \cdot HL'$	—	1900 br	1720 m, 1658 w	1620 m, 1595 m	1255 w
$Mg(IN2N)_2 \cdot HL'$	—	—	1665 m, 1640 m	1620 m, 1605 w	1295 m
$Ba(IN2N)_2 \cdot HL'$	—	1950 br	1660 m, 1640 m	1620 m, 1605 w	1290 m
$Mg(oxin)_2 \cdot HL'$	—	—	1665 m	1630 s, 1595 m	1290 m
$Sr(oxin)_2 \cdot HL'$	—	1900 br	1665 sh	1630 m, 1600 w	1290 w
$Ca(SalA)_2 \cdot HL'$	—	—	1660 m	1625 m, 1595 m	1295 m

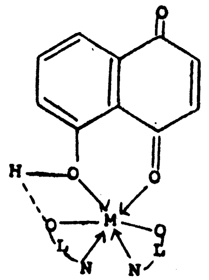
The ν(OH) is also missing in some mixed ligand alkaline earth metal complexes of juglone. But in some cases a new broad band of weak to medium intensity in the region 1900–1800 cm^{-1} is observed. The absence of —OH band and new broad band in the region 1900–1800 cm^{-1} suggests that there is strong hydrogen bonding[6–8] in these complexes. 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 carbonyl and hydrogen bonded carbonyl are assigned to 1663 cm^{-1} and 1635 cm^{-1} respectively. In the spectra of mixed ligand complexes of alkaline earth metals, the free C═O band at 1663 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 NO_2, N═O, —COOH, C═N or C═C groups which are present in the alkaline earth metal drivatives of *o*-nitrophenol, 1-nitroso-2-naphthol, salicylic acid or 8-hydroxyquinoline and the other bands appear due to chelation of C═O group. But the mixed ligand complexes of acetyl acetone and salicylaldehyde show extra band at 1700 cm^{-1}. This band is due to the presence of C═O group in alkaline earth metal derivatives of salicylaldehyde and acetylacetone. In all cases, the shifting of the hydrogen bonded carbonyl absorption peak is appreciable (*i.e.* shifted down by 10–40 cm^{-1}). This splitting and shifting in the carbonyl band suggests that the coordination has taken place through oxygen atom of carbonyl group. The strong band at 1300 cm^{-1} in the spectrum of juglone is, in all probability, due to the C—O (phenolic) stretching vibration. On complexation, there is slight appreciable change in C—O band.

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







= salicylic acid, salicyladehyde and acetylacetone.

= *o*-aminobenzoic acid.

= *o*-nitrophenol, 1-nitroso-2-naphthol and 8-hydroxyquinoline.

(M = Mg, Ca, Sr or Ba)

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