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Alkaline-Earth Metal Complexes: Mixed Ligand Complexes of Alkaline-Earth Metal Salts of Some Organic Acids with 2-Methyl-Oxine

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A number of mixed ligand complexes of alkaline-earth metal salts of some organic acids like 1-nitroso-2-naphthol (1N2N), *o*-nitrophenol (ONP), 2,4-dinitrophenol (DNP), salicylaldehyde (Sal·H) and salicylic acid (Sal·A) with 2-methyl-oxine have been synthesized and characterized by elemental analysis, conductivity measurement and FTIR-spectral studies.

Key words: Mixed complexes, alkaline-earth metals, 2-methyl-oxine, spectra.

INTRODUCTION

In continuation of our previous work[1–4] we have synthesized and characterized some more complexes of alkaline-earth metal salts of some organic acids with 2-methyl-oxine. 2-Methyl-oxine has been well investigated for its possible use in analytical determination of metal ions[5–7]. Its complexes with transition metals as well as rare-earth metals and alkali metals are well investigated[8–11]. However, it appeared from the literature survey that no mixed ligant complexes of alkaline-earth metal salts of organic acids like 1-nitroso-2-naphthol (1N2N), *o*-nitrophenol (ONP), 2,4-dinitrophenol (DNP), salicylaldehyde (Sal·H) and salicylic acid (Sal·A) with 2-methyl-oxine have been synthesized. The present work is an attempt in this direction.

We have synthesized and characterized a number of mixed ligand complexes having the general formula $ML_2 \cdot HL'$, where M = Mg, Ca, Sr or Ba; L = deprotonated 1N2N , ONP , DNP , Sal·H and Sal·A and HL′ = 2-methyl-oxine.

EXPERIMENTAL

The ligand 2-methyl-oxine and the organic acids, *i.e.*, 1-nitroso-2-naphthol (1N2N), *o*-nitrophenol (ONP), 2,4-dinitrophenol (DNP), salicylaldehyde (Sal·H) and salicylic acid (Sal·A) of AnalaR grade were used.

Alkaline earth metal salts of the organic acids were prepared by the method described earlier[4].

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Preparation of Complexes

The complexes were prepared by taking equimolecular proportions of the alkaline earth metal salt and the ligand 2-methyl-oxine in absolute ethanol in a conical flask. It was refluxed for 2–3 h with continuous stirring when the complex was formed. It was cooled, filtered, washed with absolute ethanol and dried in an electric oven at 80°C.

RESULTS AND DISCUSSION

The physical properties and analytical data of the ligand 2-methyl-oxine and its newly prepared mixed ligand complexes are listed in Table-1. All these complexes are coloured and stable in dry condition, *e.g.*, over anhydrous calcium chloride in a desiccator for reasonably long period of time. They are highly resistant to temperature and all of them show no change up to 300°C. This indicates their greater thermal stability.

These complexes are either insoluble, sparingly soluble or partially soluble in solvents like methanol, ether, benzene, nitrobenzene, acetone, chloroform and carbon tetrachloride but completely soluble, giving a clear solution, in N,N-dimethylformamide, dimethyl sulphoxide and N-methyl-2-pyrolidone.

Conductivities of the ligand 2-methyl-oxine and its mixed ligand complexes were measured on Systronics Digital Direct Reading Conductivity meter 304 at 30°C in 10^{-3} M solution in N,N-dimethylformamide. The negligible values of conductivity suggest the non-electrolyte and covalent nature of the complexes.

FTIR measurements of 2-methyl oxime and its mixed ligand alkaline earth metal complexes of the type $ML_2 \cdot HL'$, where, M = Mg, Ca, Sr or Ba, L = deprotonated 1N2N, ONP, DNP, Sal·H or Sal·A and HL′ = 2-methyl-oxine, were recorded in the region between 4000–400 cm^{-1} in KBr phase with the help of Testscan Shimadzu FTIR 8000 series spectrophotometer. The pertinent FTIR data for these compounds are recorded in Table-2. The spectra of 2-methyl-oxine show a medium broad absorption band at 3400 cm^{-1} and a medium band at 1605 cm^{-1} which are attributed to stretching –OH vibration frequency and characteristic C═N frequency respectively.

The presence of absorption band in the region 3400 cm^{-1} points out to the presence of hydrogen bonding.

This band of the ligand 2-methyl-oxine has virtually disappeared or shitted towards higher frequency upto 40 cm^{-1}, *i.e.*, in the range of 3440 to 3400 cm^{-1} and towards lower frequency at 3247 to 1950 cm^{-1}. This over all shifting indicates the coordination of the ligand to metal through oxygen atom of the —OH group. The shifting towards lower frequency also suggests that there exists a strong hydrogen bonding in the complexes.

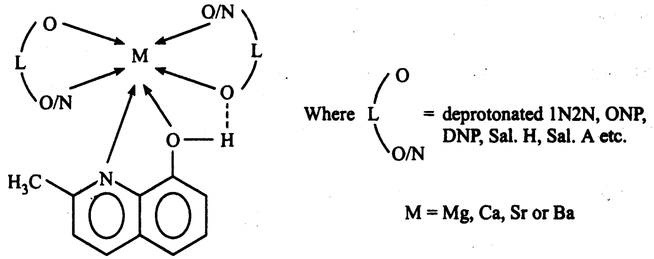
In all these mixed ligand complexes, characteristic absorption band of the ligand at 1605 cm^{-1} also shifted towards the lower frequency up to 54 cm^{-1}. This shifting in the characteristic absorption band of C═N suggests that there is a coordination of alkaline-earth metals to ligand through N-atom of quinoline ring.

TABLE-1
ANALYTICAL DATA OF COMPLEXES OF ALKALINE-EARTH METAL SALTS OF SOME ORGANIC ACIDS WITH 2-METHYL-OXINE

Compound (Colour)	m.p./decomp./ trans temp. (°C)	% analysis, found (calcd.)				Conductivity (μmho)
		C	H	N	M	
MeHQ	74 m					
(white)						
Mg(1N2N)$_2$·MeHQ	> 300	66.25	3.65	7.21	4.22	11.7
(brownish green)		(68.31)	(3.98)	(7.97)	(4.55)	
Ca(1N2N)$_2$·MeHQ	> 300	63.86	3.50	7.25	6.98	11.6
(light green)		(66.30)	(3.87)	(7.73)	(7.37)	
Sr(1N2N)$_2$·MeHQ	> 300	58.72	3.25	6.89	13.89	24.0
(light brown)		(60.96)	(3.56)	(7.11)	(14.82)	
Ba(1N2N)$_2$·MeHQ	> 300	53.55	3.01	6.12	20.14	13.7
(brown)		(56.21)	(3.28)	(6.56)	(21.47)	
Mg(ONP)$_2$·MeHQ	> 300	54.89	3.57	8.72	4.98	13.3
(yellow)		(57.52)	(3.70)	(9.15)	(5.23)	
Ca(ONP)$_2$·MeHQ	> 300	53.28	3.60	8.11	8.00	12.5
(pale yellow)		(55.58)	(3.58)	(8.84)	(8.42)	
Sr(ONP)$_2$·MeHQ	> 300	48.27	3.31	7.79	16.17	9.0
(pale yellow)		(50.53)	(3.25)	(8.04)	(16.75)	
Ba(ONP)$_2$·MeHQ	> 300	43.33	2.80	6.65	23.17	28.0
(brownish yellow)		(46.11)	(2.97)	(7.34)	(24.02)	
Mg(DNP)$_2$·MeHQ	> 300	46.27	2.80	12.73	4.34	13.9
(brownish yellow)		(48.09)	(2.73)	(12.75)	(4.37)	
Ca(DNP)$_2$·MeHQ	> 300	46.69	2.63	11.45	6.35	8.1
(pale yellow)		(46.72)	(2.65)	(12.39)	(7.08)	
Sr(DNP)$_2$·MeHQ	> 300	41.74	2.32	10.82	14.02	96.0
(yellowish brown)		(43.10)	(2.45)	(11.43)	(14.28)	
Ba(DNP)$_2$·MeHQ	> 300	39.14	2.15	10.16	19.98	—
(yellowish brown)		(39.85)	(2.26)	(10.57)	(20.75)	
Mg(Sal·H)$_2$·MeHQ	> 300	71.59	3.64	2.65	4.58	8.4
(light yellow)		(73.70)	(3.65)	(2.69)	(4.61)	
Ca(Sal·H)$_2$·MeHQ	> 300	71.80	3.57	2.58	7.42	—
(light yellow)		(71.51)	(3.54)	(2.61)	(7.45)	
Sr(Sal·H)$_2$·MeHQ	> 300	65.92	3.30	2.37	14.79	—
(sandal wood)		(65.70)	(3.25)	(2.39)	(14.97)	
Ba(Sal·H)$_2$·MeHQ	> 300	60.51	2.82	2.00	19.53	—
(olive green)		(60.52)	(2.77)	(2.04)	(20.09)	
Mg(Sal·A)$_2$·MeHQ	> 300	64.19	4.15	3.00	5.21	—
(broken white)		(63.02)	(4.16)	(3.06)	(5.25)	
Mg(Sal·A)$_2$·MeHQ	> 300	60.19	4.00	2.75	8.02	103.0
(white)		(60.89)	(4.02)	(2.96)	(8.46)	
Mg(Sal·A)$_2$·MeHQ	> 300	54.01	3.55	2.42	16.21	—
(white)		(55.33)	(3.65)	(2.69)	(16.81)	
Mg(Sal·A)$_2$·MeHQ	> 300	48.65	3.31	2.42	23.74	—
(white)		(50.48)	(3.33)	(2.45)	(24.10)	

Some of the mixed ligand complexes also show new absorption bands in the region 1600 cm^{-1} which may be attributed to the presence of different groups like —CHO, —COOH, NO_2, NO, etc.

Structure and Bonding: On the basis of elemental analysis, the molecular formula of the present mixed ligand complexes is found to be $ML_2 \cdot HL'$, where M = Mg, Ca, Sr or Ba; L = deprotonated 1-nitroso-2-naphthol, *o*-nitrophenol, 2,4-dinitro-phenol, salicylaldehyde or salicylic acid and HL′ = 2-methyl-oxine. The FTIR data suggest that the alkaline-earth metal is bonded to oxygen atom of hydroxy group and nitrogen atom of quinoline ring. A strong hydrogen bond is also present in the complexes. The probable structure is shown in Fig. 1.



= deprotonated 1N2N, ONP, DNP, Sal. H, Sal. A etc.

M = Mg, Ca, Sr or Ba

Fig. 1. Probable structures of the metal complexes

TABLE-2
SELECTED ABSORPTION BANDS (cm^{-1}) OF THE METAL COMPLEXES

Compound	ν(–OH)	ν(C═N)
MeHQ	3400 br	1605 m
$Mg(1N2N)_2 \cdot MeHQ$	3440 br, 3044 m, 2170 br, 1950 m	1595 sh, 1565 s
$Sr(1N2N)_2 \cdot MeHQ$	3315 br, 3051 m, 1890 m, 1800 m	1595 s, 1570 s
$Ca(ONP)_2 \cdot MeHQ$	3433 br, 3042 m, 2300 w, 1950 w	1597 m, 1560 s
$Ba(ONP)_2 \cdot MeHQ$	3427 br, 3049 m, 2000 w	1605 s, 1553 s
$Mg(DNP)_2 \cdot MeHQ$	3398 br, 3041 m	1600 m, 1504 s
$Ca(DNP)_2 \cdot MeHQ$	3400 br, 3040 m	1595 m. 1560 s
$Mg(Sal \cdot H)_2 \cdot MeHQ$	3429 br, 3049 w, 2040 br	1647 s, 1607 w, 1570 w
$Ca(Sal \cdot H)_2 \cdot MeHQ$	3433 br, 3041 m	1597 m, 1560 s
$Mg(Sal \cdot A)_2 \cdot MeHQ$	3047 m, 1925 br	1605 sh, 1572 s
$Ca(Sal \cdot A)_2 \cdot MeHQ$	3437 br, 3247 wbr	1600 w, 1551 s

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