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Alkaline Earth Metal Complexes: Mixed Ligand Complexes of Alkaline-Earth Metal Salts of Some Organic Acids with 5,7-Dichloro 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 5,7-dichloro-oxine have been synthesized and characterized by elemental analysis, conductivity measurement and IR-spectral studies.

INTRODUCTION

In recent years the formation of complexes containing two different ligands has been of special interest of coordination chemists and formation constants of these complexes have been determined[1]. Mixed complexes are likely to be important as models for metalloenzyme substrate complexes and also as components of the multi-metal multi-ligand system in biological fluids. The study of complexes, whether neutral or mixed, are mostly concentrated on transition and rare earth metals. Very little attention has been given to the complexing ability of alkali and alkaline earth metals though the complexes of these metals are important for the living body. We are well familar with the vital role of these metals in biological system[2]. Like some non-metals and a few metals Ca, K, Na and Mg are the functionally important elements found in the cells[3]. These elements are present as the complex biomolecules and the mechanism of the transportation and storage of these elements are highly complicated. In order to have some assistance in understanding and unfolding the mechanism of transportation and storage of metal cations in animals and plants with the assumption that a knowledge of coordiantion chemistry of the alkaline-earth metals would facilitate some idea of the mechanism, our attention has been drawn towards the ligand 5,7-dichloro-oxine. The ligand 5,7-dichloro-oxine has been extensively investigated for its possible use in analytical determination of metal ions[4–6]. Its complexes with transition metals as well as rare earths and alkali metals are well investigated[7–11]. However, it appeared from the literature survey that no mixed ligand complexes of alkaline-earth metal salts of organic acids like 1-nitroso-2-naphthol, *o*-nitrophenol, 2,4-dinitrophenol, salicylaldehyde and salicylic acid with

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5,7-dichloro 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′ = 5,7-dichloro-oxine.

EXPERIMENTAL

The ligand 5,7-dichloro-oxine was prepared by the method as described in literature[12]. 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 as follows: To the suspension of metal hydroxide in 95% ethanol was added alcoholic solution of organic acids. The resulting mixture was refluxed for 2–3 h with constant stirring. The content was allowed to cool, filtered, washed with absolute ethanol and dried in an electric oven at 100°C.

Preparation of complexes

The complexes were prepared by taking equimolecular proportions of the alkaline-earth metal salt and the ligand 5,7-dichloro-oxine in absolute ethanol in a conical flask. It was refluxed for 3–4 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 propoerties and analytical data of the ligand 5,7-dichloro 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. Some of them show no change up to 300°C and some of them show transformation at greater temperatures than the melting point of the ligand (HL′) indicating the greater thermal stability of the complexes. These complexes are either insoluble 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 (DMF), dimethyl sulphoxide (DMSO) and N-methyl-2-pyrolidone.

Conductivity of the ligand 5,7-dichloro-oxine and its mixed ligand complexes were measured on Systronics Digital Direct Reading Conductivity meter-304 at 30°C in 10^{-3} M solution inN-N-dimethyl formamide (DMF). The negligible values of conductivity suggest the covalent nature of the complexes.

Infrared measurements for the title ligand and hitherto unknown 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, salicylaldehyde or salicylic acid and

HL′ = 5,7-dichloro oxine were recorded in the region between 4000–400 cm^{-1} in KBr phase with the help of spectrophotometer. Pertinent IR data for these compounds were recorded in Table-2.

TABLE-1
ANALYTICAL DATA OF ALKALINE-EARTH METAL COMPLEXES

Compound (colour)	m.p./decomp./ trans. temp. °C	% analysis, found (calcd.)				conductivity in μmho
		C	H	N	M	
DClHQ (cream)	179 m	50.42 (50.46)	2.30 (2.33)	6.50 (6.54)	–	8.6
$Mg(1N2N)_2\cdot DClHQ$ (yellowish green)	> 300	65.00 (65.22)	3.24 (3.26)	7.57 (7.61)	6.50 (6.52)	15
$Ca(1N2N)_2\cdot DClHQ$ (brown)	235 d	61.45 (62.50)	3.10 (3.13)	7.25 (7.29)	10.40 (10.42)	15
$Sr(1N2N)_2\cdot DClHQ$ (brownish red)	230 d	55.55 (55.61)	2.76 (2.78)	6.47 (6.49)	20.26 (20.30)	20
$Ba(1N2N)_2\cdot DClHQ$ (greenish brown)	255 d	49.80 (49.86)	2.48 (2.49)	5.79 (5.82)	28.51 (28.54)	–
$Mg(ONP)_2\cdot DClHQ$ (light yellow)	290 t	47.49 (48.00)	2.64 (2.66)	9.29 (9.33)	7.98 (8.00)	12
$Ca(ONP)_2\cdot DClHQ$ (yellow)	> 290	45.81 (45.86)	2.52 (2.53)	8.84 (8.86)	12.64 (12.66)	11
$Sr(ONP)_2\cdot DClHQ$ (yellowish white)	> 280	39.10 (39.60)	2.19 (2.20)	7.65 (7.70)	23.82 (24.09)	17.3
$Ba(ONP)_2\cdot DClHQ$ (yellow)	280 d	32.06 (33.88)	1.59 (1.85)	6.35 (6.49)	31.60 (31.84)	–
$Mg(DNP)_2\cdot DClHQ$ (yellowish white)	> 300	36.86 (36.92)	1.53 (1.54)	14.30 (14.36)	6.00 (6.15)	–
$Ca(DNP)_2\cdot DClHQ$ (greyish white)	> 300	35.11 (35.47)	1.47 (1.48)	13.55 (13.80)	9.65 (9.85)	–
$Sr(DNP)_2\cdot DClHQ$ (greyish yellow)	355 t	31.34 (31.72)	1.31 (1.32)	12.05 (12.33)	18.98 (19.38)	–
$Ba(DNP)_2\cdot DClHQ$ (brownish yellow)	300 t	28.42 (28.63)	1.18 (1.19)	11.10 (11.13)	26.98 (27.24)	15
$Mg(Sal.H)_2\cdot DClHQ$ (creamy yellow)	> 300	63.14 (63.16)	3.66 (3.76)	–	9.00 (9.02)	22
$Ca(Sal.H)_2\cdot DClHQ$ (silver grey)	> 300	64.22 (64.12)	3.80 (3.82)	–	15.08 (15.27)	13.5
$Sr(Sal.H)_2\cdot DClHQ$ (grey)	> 300	53.85 (54.26)	3.20 (3.23)	–	27.89 (28.29)	17.3
$Mg(Sal.A)_2\cdot DClHQ$ (light green)	> 300	55.78 (56.38)	3.34 (3.36)	–	7.75 (8.05)	20
$Ca(Sal.A)_2\cdot DClHQ$ (greenish yellow)	> 300	53.35 (53.50)	3.10 (3.18)	–	12.64 (12.74)	172

TABLE-2

PERTINENT IR DATA FOR THE LIGAND AND THE COMPLEXES (cm^{-1})

Compounds	ν(—OH)	ν(C=C/C=N)	ν(—OH)	ν(C—O)
DClHQ	3075 br	1615 m, 1580 m	1400 s	1140 m
$Mg(1N2N)_2 \cdot DClHQ$	3280 br	1680 sh, 1570 m, 1550 m	1445 s	1110 m
$Ba(1N2N)_2 \cdot DClHQ$	3400 br	1650 m, 1580 w, 1545 m	1440 m	1115 sh
$Mg(ONP)_2 \cdot DClHQ$	3300 br	—, 1695 m, 1560 s	1450 s	1110 m
$Ca(ONP)_2 \cdot DClHQ$	3400 br	1595 w, 1565 sh, 1550 m	1445 s	1100 m
$Ba(ONP)_2 \cdot DClHQ$	3390 br	1620 w, 1560 sh, 1550 m	1440 s	1100 m
$Ca(DNP)_2 \cdot DClHQ$	3350 br	1595 w, 1565 sh, 1535 m	1440 s	1100 m
$Ba(DNP)_2 \cdot DClHQ$	3400 br	1610 wbr, 1550 sh, 1535 m	1440 s	1120 m
$Ca(Sal.H)_2 \cdot DClHQ$	3400 br	1645 w, 1570 sh, 1540 m	1440 s	1105 m
$Sr(Sal.H)_2 \cdot DClHQ$	3400 br	—, 1585 sh, 1565 m	1440 s	1100 m
$Mg(Sal.A)_2 \cdot DClHQ$	3300 br	—, 1585 sh, 1565 m	1450 s	1110 m
$Ca(Sal.A)_2 \cdot DClHQ$	3400 br	1640 m, 1580 sh, 1550 m	1450 m	1110 m

The absorption bands of principal interest in the infrared spectra of 5,7-dichloro-oxine are 3075, 1615, 1580, 1400 and 1140 cm^{-1}.

The broad band at 3075 cm^{-1} is due to the stretching —OH vibration. This band also points out the presence of intramolecular hydrogen bonding involving the hydroxy hydrogen atom and the nitrogen atom of the quinoline ring.

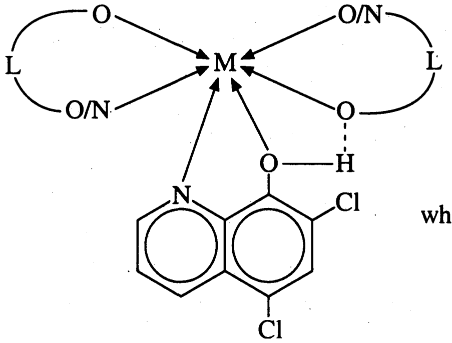
In all the mixed ligand complexes this —OH vibration band disappears and reappears as a broad band by its shift of 205–325 cm^{-1}, *i.e.*, at 3350–3400 cm^{-1} with reduced intensity indicating that the metal is coordinated through hydroxy oxygen atom.

The broadness of the —OH stretching absorption band in all the complexes also shows that there exists hydrogen bonding.

The absorption bands at 1615 and 1580 cm^{-1} are assigned to C=C/C=N groups. In all the mixed ligand complexes these bands have been shifted between 1680–1595 cm^{-1} and 1580–1535 cm^{-1}. This shifting in the stretching vibration frequency of C=C/C=N groups suggests the coordination of the ligand with metal through nitrogen atom of quinoline ring. The absorption band at 1400 cm^{-1} is the characteristic of —OH bending frequency. This bending vibration frequency has also shifted towards the higher frequency range by 40–50 cm^{-1} in all the mixed ligand complexes supporting the coordination of metal through hydroxy oxygen atom. The absorption band at 1140 cm^{-1} is due to the C—O stretching vibration. In all the mixed ligand complexes this band has shifted towards lower frequency by 20–40 cm^{-1}. This also supports the coordination of metal through hydroxy oxygen atom.

Structure and Bonding

On the basis of elemental analysis, the molecular formula of the mixed ligand complexes of alkaline-earth metal salts of some organic acids with 5,7-dichloro oxine 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, salicylic acid and HL′ = 5,7-dichloro oxine. The IR data of the alkaline-earth metal salts of different organic acids suggest that the metal is covalently bonded to the oxygen atom of hydroxy group and coordinated to the N-atom or O-atom of the groups like NO, NO_2, —CHO, —COOH, etc. These alkaline-earth metal salts combine with second ligand, *i.e.*, 5,7-dichloro-oxine through coordination with the hydroxy oxygen as well as the nitrogen atom of the quinoline ring. Probable structure of the complexes is shown in Fig. 1.



where L = deprotonated 1N2N, ONP DNP, Sal. H, Sal. A etc. (L bonded through O/N and O)

M = Mg, Ca, Sr or Ba

Fig. 1

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