Asian Journal of Chemistry Vol. 14, No. 2 (2002), 637–642

Alkaline-Earth Metal Complexes: Mixed Ligand Complexes of Alkaline-Earth Metal Salts of Some Organic Acids with 5,7-Dinitro-oxine

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A number of mixed ligand complexes of alkaline-earth metal salts of some 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-dinitro-oxine have been synthesized and characterized by elemental analysis, conductivity measurement and FTIR-spectral studies.

Key words: Mixed complexes, Alkaline-earth metals, 5,7-Dinitro-oxine, FTIR-spectral studies.

INTRODUCTION

Alkali and alkaline-earth metals play a vital role in biological systems[1–24]. It is obvious from the studies and researches that alkali and alkaline-earth metals are an essential constituent of plant and animal kingdom. Both of them take it through food and store it into their different parts according to their requirements. The mechanism of this intake, its transportation and storage are the subject of understanding and chelation may be one of the important factors for it. Keeping this in mind we have synthesized and characterized several complexes[25, 26] of alkaline-earth metals with oxine derivative ligands. Different oxine derivatives have successfully formed complexes with many transition and rare-earth metals[27–40] as alkali[41–44] and alkaline-earth[25, 26] metals. Since the major objective behind the study of alkaline-earth metal complexes has been to study their role in plant metabolism as well as in biological system, hence it is useful to prepare and study more and more number of mixed ligand complexes of alkaline-earth metals as they are likely to serve as models for metallo-enznyme-substrate complexes and also as components of the multimetal-multiligand system in biological fluids. In the light of above facts attention has been drawn towards the ligand 5,7-dinitro-oxine which has been investigated by several workers[34, 35, 45–52]. However, literature survey has revealed that this ligand has not been investigated for the complex formation with alkaline-earth metals. 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^{2+}, Ca^{2+}, Sr^{2+} or Ba^{2+}; L = deprotonated 1N2N , ONP , DNP , Sal.H and Sal.A and HL′ = 5,7-dinitro-oxine.

EXPERIMENTAL

The ligand 5,7-dinitro-oxine was prepared by the method as described in

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literature[51]. 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[26].

Preparation of Complexes

The complexes were prepared by taking equimolecular proportions of the alkaline-earth metal salt and the ligand 5,7-dinitro-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 properties and analytical data of the ligand 5,7-dinitro-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 a reasonably long period of time. They are highly resistant to temperature; some of them show no change up to 300°C. This indicates their greater thermal stability. 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, dimethyl sulphoxide and N-methyl-2-pyrrolidone.

Conductivity: Conductivity of the ligand 5,7-dinitro-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-electrolytes[53–55] and the covalent nature of the complexes.

Spectral Studies: FTIR measurements for the title ligand and hitherto unknown mixed ligand alkaline-earth metal complexes of the type $ML_2 \cdot HL'$, where M = Mg^{2+}, Ca^{2+}, Sr^{2+} or Ba^{2+}, L = deprotonated 1N2N, ONP, DNP, Sal.H or Sal.A and HL′ = 5,7-dinitro-oxine, were recorded in the region 4000–400 cm^{-1} in KBr phase with the help of Testscan Shimadzu FTIR 8000 series spectrophotometer. Pertinent FTIR data for these compounds are recorded in Table-2.

The spectra of 5,7-dinitro-oxine show a medium broad absorption band over a wide range of 3650–3250 cm^{-1}. The presence of absorption features in this region points out to the presence of strong intramolecular hydrogen bonding involving hydroxy hydrogen atom and nitrogen atom of the quinoline ring.

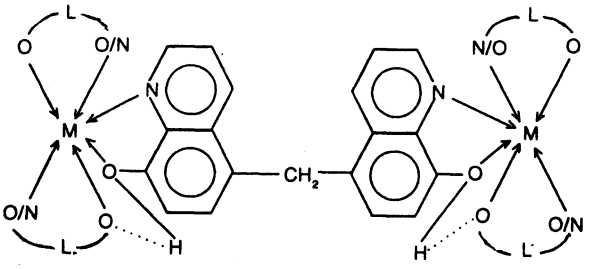
The different bands between 2925 to 1875 cm^{-1} in the spectra are attributed to the C—H stretching vibrations and N.....H hydrogen bonding. For weak hydrogen bonding the bands appear above 2800 cm^{-1} and for strong hydrogen bonding the bands appear between 2800–1800 cm^{-1}.

The bands at 1645, 1585, 1405 and 1110 cm^{-1} are respectively assigned to NO_2, C=C/C=N bending, —OH and C—O stretching vibrations of the 5,7-dinitro-oxine ligand.

In all the mixed ligand complexes the stretching —OH vibration bands appeared in the range of 3465 to 3075 cm^{-1} which clearly indicate the complexation of metal through the hydroxy oxygen atom. The different bands between 3075 and 1850 cm^{-1} are due to the strong hydrogen bonding. The NO_2 group frequencies in all the mixed ligand complexes remain almost unchanged. The characteristic C=C/C=N absorption band at 1585 cm^{-1} has shifted towards lower frequency up to 10 cm^{-1} in almost all the mixed ligand complexes indicating that the complexation has taken place through N-atom of quinoline ring. After complexation the C=C and C=N frequencies have separated and the C=C frequencies of the complexes have appeared between 1600 to 1590 cm^{-1} as a medium to weak band. The —OH bending absorption band at 1405 cm^{-1} of 5,7-dinitro-oxine has shifted towards lower frequency by 5–25 cm^{-1} in all the complexes supporting the complexation of metal through hydroxy oxygen atom. The C—O stretching frequency of ligand at 1110 cm^{-1} has also shifted up to 10 cm^{-1} which also supports the complexation of metal through oxygen of —OH group.

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-dinitro-oxine is found to be $ML_2 \cdot HL'$, where $M = Mg^{2+}$, Ca^{2+}, Sr^{2+} or Ba^{2+}; L = deprotonated 1-nitroso-2-naphthol, *o*-nitrophenol, 2,4-dinitro-phenol, salicylaldehyde or salicylic acid and 5,7-dinitro-oxine. The FTIR data of the alkaline-earth metal salts of different organic acids suggests 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-dinitro-oxine through coordination with the hydroxy oxygen atom as well as the nitrogen atom of the quinoline ring. Probable structures of the complexes are shown in Fig. 1.



Where M = Mg, Ca,

L = deprotonated 1N2N, ONP, DNP, Sal.H and Sal.A.

Fig. 1

TABLE-1
ANALYTICAL DATA OF ALKALINE-EARTH METAL COMPLEXES

Compound (Colour)	M.P./decomp./ trans. temp. (°C)	% analysis, found (calcd.)				Conductivity (μmho)
		C	H	N	M	
DNHQ (greenish yellow)	295d	45.89 (45.95)	2.10 (2.12)	17.84 (17.87)	—	—
$Mg(1N2N)_2$.DNHQ (light green)	> 300	56.62 (57.71)	2.75 (2.82)	10.85 (11.61)	3.65 (3.98)	35
$Ca(1N2N)_2$.DNHQ (brownish green)	> 300	55.15 (56.22)	2.68 (2.75)	10.84 (11.31)	6.26 (6.46)	39
$Sr(1N2N)_2$.DNHQ (olive green)	> 300	50.55 (52.21)	2.45 (2.55)	9.98 (10.50)	12.78 (13.13)	87
$Ba(1N2N)_2$.DNHQ (brownish green)	> 300	46.52 (48.57)	2.29 (2.37)	8.97 (9.77)	18.25 (19.19)	98
$Mg(ONP)_2$.DNHQ (light yellow)	> 300	45.79 (47.10)	2.38 (2.43)	12.75 (13.08)	4.23 (4.48)	29
$Ca(ONP)_2$.DNHQ (yellow)	> 300	44.16 (45.73)	2.30 (2.36)	10.98 (12.70)	6.96 (7.26)	29
$Sr(ONP)_2$.DNHQ (yellow)	> 300	40.35 (42.10)	2.12 (2.17)	10.78 (11.69)	14.12 (14.62)	62
$Ba(ONP)_2$.DNHQ (light yellow)	> 300	37.78 (38.86)	1.97 (2.00)	10.23 (10.79)	20.25 (21.20)	88
$Mg(DNP)_2$.DNHQ (yellow)	290d	39.65 (40.32)	1.70 (1.76)	14.88 (15.68)	3.68 (3.84)	41
$Ca(DNP)_2$.DNHQ (yellow)	> 300	38.66 (39.31)	1.66 (1.72)	14.65 (15.29)	5.55 (6.24)	32
$Sr(DNP)_2$.DNHQ (yellow)	300d	34.86 (36.60)	1.52 (1.60)	13.12 (14.23)	11.61 (12.71)	40
$Ba(DNP)_2$.DNHQ (yellow)	300d	32.84 (34.12)	1.42 (1.49)	12.25 (13.27)	17.86 (18.62)	71
$Mg(Sal.H)_2$.DNHQ (yellow)	280d	53.29 (55.09)	2.78 (2.99)	7.65 (8.38)	4.61 (4.79)	51
$Ca(Sal.H)_2$.DNHQ (yellow)	280d	51.65 (53.38)	2.68 (2.90)	7.04 (8.12)	7.12 (7.74)	53
$Sr(Sal.H)_2$.DNHQ (yellow)	295d	47.23 (48.89)	2.42 (2.66)	6.69 (7.44)	14.70 (15.50)	55
$Ba(Sal.H)_2$.DNHQ (yellow)	300d	43.35 (44.91)	2.02 (2.44)	6.06 (6.83)	21.57 (23.37)	96
$Mg(Sal.A)_2$.DNHQ (yellow)	> 300	50.27 (51.78)	2.61 (2.81)	7.12 (7.88)	4.29 (4.50)	35
$Ca(Sal.A)_2$.DNHQ (yellow)	> 300	48.35 (50.27)	2.66 (2.73)	7.15 (7.65)	6.98 (7.28)	39
$Sr(Sal.A)_2$.DNHQ (yellow)	> 300	43.58 (46.27)	2.32 (2.51)	6.78 (7.04)	13.82 (14.67)	--
$Ba(Sal.A)_2$.DNHQ (yellow)	> 300	40.15 (42.69)	2.11 (2.32)	5.95 (6.50)	20.03 (21.27)	—

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

Compound	ν(OH)	ν(NO_2)	ν(C=C)/ (C=N)	δ(—OH)	ν(C—O)
DNHQ	3650–3250 mbr, 2918 s, 1955 wbr, 1875 wbr	1645 s	1585 s	1405 m	1110 m
Mg(1N2N)$_2$.DNHQ	3465 s, 3210 w, 2918 w, 2137 w	1640 w	1595 m, 1575 s	1380 w	1120 m
Ca(1N2N)$_2$.DNHQ	3405 s, 2925 m, 2808 w	1650 w	1600 m, 1575 s	1400 m	1115 m
Mg(ONP)$_2$.DNHQ	3450 s, 3178 wbr, 3075 w, 2340 w	1640 w	1600 m, 1575 s	1380 w	1120 m
Ca(ONP)$_2$.DNHQ	3420 br, 3110 w, 2925 w, 2340 w	—	1600 m, 1575 s	1400 m	1115 m
Mg(DNP)$_2$.DNHQ	3455 s, 2940 br, 1950 w, 1875 w	1640 m	—, 1585 s	1400 m	1115 m
Ba(DNP)$_2$.DNHQ	3415 br, 2920 mbr, 2045 m, 1950 m	1640 s	1595 m, 1580 m	1400 m	1110 m
Mg(Sal.A)$_2$.DNHQ	3460 s, 3188 wbr, 3078 w, 2250 wbr, 1975 w, 1850 w	1640 w	1590 w, 1575 s	1400 w	1120 m
Ca(Sal.A)$_2$.DNHQ	3435 br , 3107 w, 2365 m	—	1600 m, 1575 s	1400 w	1115 m

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(*Received*: 3 October 2001; *Accepted*: 16 January 2001) AJC-2564