

Synthesis and characterization of complexes of Calcium salts of some organic acids with 2-Methyl-5,7-dichloro-oxine

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Abstract: Five complexes of calcium salts of some organic acids with 2-Methyl-5,7-dichloro-oxine having the general formula $\text{CaL}_2\text{HL}'$, where L = deprotonated 1N2N, ONP, DNP, SalH or SalA were prepared with the assumption that these complexes may serve as models to understand and unfold the highly complicated mechanism of calcium uptake, storage and function in human metabolism and plant system. Characterization of these newly prepared complexes were made by melting point measurement, elemental analysis and spectroscopic studies.

(Key words: 8-Hydroxyquinoline, spectroscopic studies).

Introduction

Calcium is found in plants, animals, and in many marine life forms. It is essential for several biological processes.^{1,2} Numerous important physiological and biochemical activities, including enzymatic reactions, muscular contraction, blood coagulation, etc. are regulated by calcium. It is essential for preserving membrane integrity and imparting stiffness. The skeleton of vertebrates contains the bulk of calcium. An adult human body contains 1.0 to 1.5 kg in the bones and some few grams in the other parts of the body. This comparatively minute quantities present in bodily fluids and cells have immense significance in several aspects. It performs activity like balancing the pH of the blood, causing the release of hormones, regulating cell division, and managing the activity of muscles and nerves.³⁻¹¹

8-Hydroxyquinoline (8-HQ) is one of the most well-known and useful organic compound whose derivatives are used in a wide range of products, including pharmaceuticals, and fluorescent chemo sensors for metal ions. 8-hydroxyquinoline derivatives have been used in medicine as insecticides, antibacterial, antifungal, neuroprotective, and anti-HIV medicines. Moreover, derivatives of 8-hydroxyquinoline have found several uses in fluorescence sensing of biologically and ecologically significant metal ions including Zn^{2+} and Al^{3+} owing to their propensity to chelate toward a wide variety of metal cations. The 8-hydroxyquinoline ligand is an effective reagent for gravimetric analysis to extract metal ions. It has been utilized for analytical purposes and separation processes. The fluorescence emission of 8-hydroxyquinoline is greatly enhanced by its interaction with chelating metal ions. The weak fluorescence of 8-hydroxyquinoline is attributed to the intermolecular proton transfer from the OH-proton functions to the N of the pyridine moiety in its excited state. This rise in emission seems to be mostly the effect of the molecule's enhanced stiffness.^{12,13}

Thus, with the hypothesis that complexes of calcium with biologically potential ligands may serve as models to understand the mechanism of uptake, storage and function of calcium in animals and plants, we have synthesized and characterized several complexes of calcium with 2-Methyl-5,7-dichlorooxine a derivative of 8-hydroxyquinoline.

Experimental:

Organic acids i.e. 1-nitroso-2-naphthol (1N2N), o-nitrophenol (ONP), dinitrophenol (DNP), salicylaldehyde (Sal.H) and salicylic acid (Sal.A) of Anal. R. grade were used. Salts of calcium with organic acids were prepared as follows:

Alcoholic solution of calcium hydroxide and organic acids viz. 1-nitroso-2-naphthol (1N2N), o-nitrophenol (ONP), dinitrophenol (DNP), salicylaldehyde (Sal.H) and salicylic acid (Sal.A) taken in the 1:2 molar ratio in a conical flask was refluxed with constant stirring with the help of a magnetic stirrer at 60-70° C temperature for 3-4 hours, with the help of magnetic heater. During stirring and heating, the colour changed of the solution was noticed. Solution was cooled, filtered, washed with absolute ethanol. The precipitate was dried at about 80°C and stored within a desiccator to prevent moisture absorption. The ligand 2-Methyl-5,7-dichloro-oxine was prepared by the method described in literature.¹³⁵

Preparation of complexes: Complexes were prepared by taking equimolecular ratios of calcium salts of organic acids and the ligand 2-methyl-5,7-dichloro-oxine in absolute ethanol in a conical flask. It was refluxed for 3-4 hours with

continuous stirring till the formation of complex. It was cooled, filtered, washed with absolute ethanol and dried in an electric oven at 100°C.

Results and Discussion:**Physical Properties**

The physical properties of the ligands 2-methyl-5,7-dichloro-oxine and its newly and remain stable in dry conditions e.g., over anhydrous calcium chloride in a desiccator for a reasonable time. All complexes are resistant to high temperature and show no any change up to about 300°C and hence the complexes have greater thermal stability. All 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, dimethylsulphoxide and N-methyl-2-pyrrolidone.

Conductivity of the ligand 2-methyl-5,7-dichloro-oxine and its complexes of calcium salts of different organic acids were measured on Systronics Digital Direct Reading Conductivitymeter-304 at 25°C in 10⁻³M N,N-dimethylformamide solution. The conductivity values are given in Table 4.1. The negligible values of conductivity suggested the maximum covalency in the complexes.

Table- 1: Analytical data of the complexes

Compound (Mol. Formula)	Colour	m.p./decomp./ trans. temp.°C	% analysis, found(calcd)				Conductivity μ Mho
			C	H	N	M	
MeDCIHQ (C ₁₀ H ₇ Cl ₂ NO)	Yellow	220m	52.60 (52.63)	3.04 (3.07)	6.10 (6.14)	-	0.7
[Ca(1N2N) ₂ .MeDCIHQ] CaC ₃₀ H ₁₉ Cl ₂ N ₃ O ₅	Brown	250d	58.80 (58.82)	3.10 (3.10)	6.81 (6.86)	6.51 (6.54)	5.0
[Ca(ONP) ₂ .MeDCIHQ] CaC ₂₃ H ₁₅ Cl ₂ N ₃ O ₇	Yellow	>300	48.50 (48.53)	2.74 (2.76)	7.70 (7.72)	7.30 (7.35)	6.0
[Ca(DNP) ₂ .MeDCIHQ] CaC ₂₂ H ₁₃ Cl ₂ N ₃ O ₁₁	Greenish white	>300	41.60 (41.64)	3.43 (3.47)	11.00 (11.04)	6.29 (6.31)	4.4
[Ca(Sal.H) ₂ .MeDCIHQ] CaC ₂₄ H ₁₇ Cl ₂ NO ₅	Silvery grey	>300	56.42 (56.47)	3.30 (3.33)	2.70 (2.74)	7.80 (7.84)	10.3
[Ca(Sal.A) ₂ .MeDCIHQ] CaC ₂₄ H ₁₇ Cl ₂ NO ₇	Greenish Yellow	>300	53.10 (53.14)	3.10 (3.14)	2.53 (2.58)	7.34 (7.38)	12.2

Spectroscopic studies: Infrared measurement of the ligand 2-methyl-5,7-dichloro-oxine and its complexes with calcium salts of some organic acid (1-nitroso-2-naphthol, o-nitrophenol, 2,4-dinitrophenol, salicylaldehyde and Salicylic acid) were recorded in the region between 4000-440 cm^{-1} in KBr phase with the help of spectrophotometer. Selected absorption bands for the ligand and complexes are recorded in Table 4.2.

As mentioned in the table 4.2 the infrared absorption band of principal interest in the ligand 2-methyl-5,7-dichloro-oxine are 3340, 1620, 1570, 1400 and 1140 cm^{-1} . The broad band at 3340 cm^{-1} in the infrared spectra of ligand is assigned to -OH stretching vibration frequency. This band also points out to the presence of intramolecular hydrogen bonding involving the hydroxy hydrogen atom and the oxygen atom of the organic acids.

In all the newly prepared mixed ligand complexes this broad band at 3340 cm^{-1} has shifted to higher frequency by 70 cm^{-1} and appeared as a broad band at 3410 cm^{-1} except only in the case of $\text{Mg}(\text{DNP})_2 \cdot \text{MeDCIHQ}$ in which the band has shifted towards higher frequency by 60 cm^{-1} . This shifting of frequency in all the mixed ligand complexes suggested the coordination of calcium metal to the hydroxy

oxygen atom. The broadness of the -OH absorption band in all the mixed ligand complexes also suggested that there exists hydrogen bonding in the complexes.

The medium band at 1620 cm^{-1} and 1570 cm^{-1} in the ligand are assigned to $\nu\text{C}=\text{C}/\text{C}=\text{N}$ frequency. In all the complexes these bands have shifted between 1580 to 1640 cm^{-1} and 1520 to 1560 cm^{-1} . Shifting in these frequencies suggest the coordination of the calcium metal with nitrogen atom of the quinoline ring.

The medium broad band at 1400 cm^{-1} in the infrared spectrum of the ligand is assigned to bending -OH frequency. In all the complexes this band has shifted by 20 cm^{-1} and appeared at 1420 cm^{-1} . This shifting in the bending -OH frequency also suggests the coordination of the ligand to calcium metal through hydroxy oxygen atom.

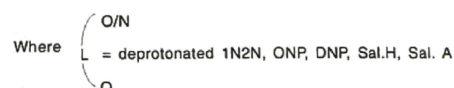
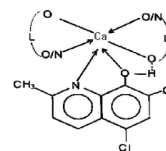
The medium band at 1140 cm^{-1} is attributed to the stretching C-O frequency. This band has shifted towards a lower frequency by 40 cm^{-1} in all the complexes except only in the case of $\text{Ca}(\text{DNP})_2 \cdot \text{MeDCIHQ}$ in which the band has shifted towards lower frequency by 25 cm^{-1} . This also supports the bonding of calcium metal to ligand through hydroxy oxygen atom of the ligand.

TABLE 4.2
Selected IR absorption bands for the ligand and the complexes in cm^{-1} .

Compounds	νOH	$\nu\text{C}=\text{C}/\nu\text{C}=\text{N}$	$\delta\text{-OH}$	$\nu\text{C-O}$
MeDCIHQ	3340 br	1620m, 1570m	1400 m	1140m
$\text{Ca}(\text{1N2N})_2 \cdot \text{MeDCIHQ}$	3410br	1580w, 1560sh, 1540m	1420 m	1100m
$\text{Ca}(\text{ONP})_2 \cdot \text{MeDCIHQ}$	3410 br	1580w, 1560sh, 1520m	1420m	1100m
$\text{Ca}(\text{DNP})_2 \cdot \text{MeDCIHQ}$	3400 br	1620m, 1570sh, 1540m	1420s	1115m
$\text{Ca}(\text{Sal.H})_2 \cdot \text{MeDCIHQ}$	3410 br	1640w, 1560sh, 1520m	1420m	1100m
$\text{Ca}(\text{Sal.A})_2 \cdot \text{MeDCIHQ}$	3410br	1640m, 1560sh, 1520m	1420m	1100m

Structure and Bonding

On the basis of elemental analysis, the general molecular formula of the mixed ligand complexes was found to be $\text{CaL}_2\cdot\text{HL}'$ where, L=deprotonated 1-nitroso-2-naphthol (1N2N), o-nitrophenol (ONP), 2,4- dinitrophenol (DNP), salicylaldehyde (Sal.H), salicylic acid (sal.A) and $\text{HL}' = 2\text{-Methyl-5,7-dichloro-oxine}$. The IR data of the calcium salts of different organic acids suggest that the metal is bonded to the acid through oxygen atom of hydroxy group and coordinated to the O/N atom of the groups like NO, NO₂, CHO, COOH etc. This calcium metal salts combine with ligand i.e. 2-Methyl-5,7-dichloro-oxine through coordination with the hydroxy oxygen atom and the nitrogen atom of the quinoline ring. Probable structure of the complexes are shown in Fig.1.



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