

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

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Abstract: Five complexes of calcium salts of some organic acids with 2-Methyl-5,7-dibromo-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 magnesium uptake, storage and function in human metabolism and plant system. Characterization of these newly prepared complexes were done by melting point measurements, elemental analysis and spectroscopic studies etc.

(Key words: 8-Hydroxyquinoline, infrared measurements).

Introduction

In our previous paper we have reported the preparation and characterization of some complexes of calcium salts of some organic acids with 2-Methyl-5,7-dichloro-oxine. In the present paper, we are reporting the synthesis and characterization of some complexes of calcium salts of some organic acids with 2-Methyl-5,7-dibromo-oxine.

Experimental:

Organic acids i.e. 1-nitroso-2-naphthol (1N2N), o-nitrophenol (ONP), dinitrophenol (DNP), salicylaldehyde (Sal.H) and salicylicacid (Sal.A) of Anal. R. grade were used. Salts of calcium with organic acids were prepared as follows: Calcium hydroxide and organic acids viz. 1-nitroso-2-naphthol (1N2N), o-nitrophenol (ONP), Dinitrophenol (DNP), Salicylaldehyde (Sal.H) or Salicylicacid (Sal.A) were taken in 1:2 molar ratio in a conical flask and added

requisite amount of absolute alcohol to dissolve. The solution was refluxed for 3-4 hours with continuous stirring with the help of magnetic heater. During refluxing, the temperature was maintained at 60-70°C. During stirring and heating, the colour changed of the solution was noticed. After refluxing, the solution was cooled. It was filtered with the help of normal filter paper. Precipitate so obtained was washed with alcohol, dried at about 80°C in an electric oven. The precipitate so obtained was kept in a desiccators for further use.

2-Methyl-5,7-dibromo-oxine was prepared by the method described in literature²².

Preparation of complexes: Complexes were prepared by taking equimolecular ratios of calcium salt of organic acid and the ligand 2-methyl-5,7-dibromo-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: Some of the physical properties of the ligand and complexes of calcium salts of some organic acids are listed in Table 1. All these complexes are coloured and remain stable in dry conditions e.g., over anhydrous calcium chloride in a desiccator for a reasonable time. These complexes are highly resistant to temperature and show no any change upto 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, N-dimethylformamide, dimethylsulphoxide and chloroform and carbon tetrachloride but N-methyl-2-pyrrolidone. completely soluble giving a clear solution in N,

Table- 1 Analytical data of the complexes

Compound (Mol. Formula)	Colour	m.p./decomp./ trans. temp.°C	% analysis				Conductivity μ Mho
			C	H	N	M	
MeDBrHQ (C ₁₀ H ₇ Br ₂ NO)	Yellow	195	37.81 (37.85)	2.18 (2.21)	4.40 (4.42)	-	0.8
Mg(1N2N) ₂ .MeDBrHQ (MgC ₃₀ H ₁₉ Br ₂ N ₃ O ₅)	Yellowish Red	240d	52.51 (52.55)	2.74 (2.77)	6.10 (6.13)	3.47 (3.50)	5.0
Mg(ONP) ₂ .MeDBrHQ (MgC ₂₂ H ₁₃ Br ₂ N ₃ O ₇)	Yellowish Grey	>300	42.75 (42.79)	2.40 (2.43)	6.77 (6.81)	3.84 (3.89)	7.0
Mg(DNP) ₂ .MeDBrHQ (MgC ₂₂ H ₁₃ Br ₂ N ₅ O ₁₁)	Yellow	>300	37.30 (37.34)	1.81 (1.85)	9.86 (9.90)	3.35 (3.39)	4.5
Mg(Sal.H) ₂ .MeDBrHQ (MgC ₂₄ H ₁₇ Br ₂ NO ₅)	Yellowish Brown	>300	49.37 (49.40)	2.87 (2.91)	2.37 (2.40)	4.10 (4.12)	11.0
Mg(Sal.A) ₂ .MeDBrHQ (MgC ₂₄ H ₁₇ Br ₂ NO ₇)	Light Yellow	>300	46.80 (46.83)	2.73 (2.76)	2.25 (2.28)	3.86 (3.90)	12.2

Conductivity of the ligand 2-methyl-5,7-dibromo-oxine and its complexes of calcium salts of different organic acids were measured on Systronics Digital Direct Reading Conductivitymeter-304 at 25°C in 10⁻³ M N,N-dimethylformamide solution. The conductivity values are given in Table 1. The negligible values of conductivity suggested the maximum covalency in the complexes.

Infrared Spectra:

Infrared measurement of the ligand 2-methyl-5,7-dibromo-oxine and its complexes with calcium salts of some organic acids (1N2N, ONP, DNP, Sal.H and Sal.A) were recorded in the region between 4000-400 cm⁻¹ in KBr phase with the help of spectrophotometer. Selected absorption bands for the ligand and complexes are recorded in Table 2.

**Table-2
Selected IR absorption bands for the ligand and the complexes in cm⁻¹.**

Compounds	ν OH	ν C=C/ ν C=N	δ -OH	ν C-O
MeDBrHQ	3370br	1620m, 1580m	1410mbr	1140m
Ca(1N2N) ₂ .MeDBrHQ	3400br	1600m, 1570w	1430 m	1115sh
Ca(ONP) ₂ .MeDBrHQ	3400br	1590w, 1560sh, 1540m	1430s	1100m
Ca(DNP) ₂ .MeDBrHQ	3390br	1590w, 1560sh, 1530m	1430s	1100m
Ca(Sal.H) ₂ .MeDBrHQ	3400br	1600w, 1560sh, 1540m	1430m	1100m
Ca(Sal.A) ₂ .MeDBrHQ	3400br	1600w, 1570sh, 1540m	1430m	1100m

As mentioned in the table 2 the infrared absorption band of principal interest in the ligand 5,7-dibromo-oxine are 3370, 1620, 1580, 1410 and 1140 cm^{-1} .

The broad band at 3370 cm^{-1} in the infrared spectra of ligand is assigned to -OH stretching vibration frequency. This band also point out to the presence of intramolecular hydrogen bonding involving the hydroxyl hydrogen atom and the oxygen atom of the organic acid.

In all the newly prepared mixed ligand complexes this broad band at 3370 cm^{-1} has shifted to higher frequency by 30 cm^{-1} and appeared as a broad band at 3400 cm^{-1} except only in the complex $\text{Ca}(\text{DNP})_2 \cdot \text{MeDBrHQ}$ where this band has shifted towards higher frequency by 20 cm^{-1} and appeared at 3390 cm^{-1} . This shifting of frequency in all the complexes suggested the coordination of calcium metal to the hydroxyl oxygen atom.

The medium band at 1620 cm^{-1} and 1580 cm^{-1} in the ligand are assigned to $\nu\text{C}=\text{C}/\nu\text{C}=\text{N}$ frequency. In all the complexes these bands shifted between 1560-1600 cm^{-1} and 1530 to 1540 cm^{-1} . Shifting in these frequencies suggests the coordination of the calcium metal with nitrogen of the quinoline ring.

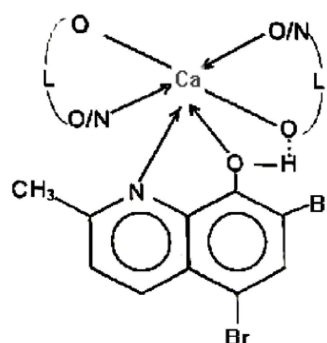
The medium broad band at 1410 cm^{-1} in the infrared spectrum of the ligand is assigned to bending -OH frequency. In all the complexes this band has shifted by 20 cm^{-1} and appeared at 1430 cm^{-1} . This shifting in the bending -OH frequency also suggest the coordination of the ligand to calcium metal through hydroxyl oxygen atom.

The medium band at 1140 cm^{-1} is attributed to the stretching C-O frequency. This band has also shifted towards a lower frequency by 25-40 cm^{-1} in all the complexes. This also support the bonding of metal to ligand through hydroxyl oxygen atom of the ligand.

Structure and Bonding: On the basis of elemental analysis, the general molecular formula of the calcium complexes are found to be Ca_2HL^* where, $\text{L} =$ deprotonated 1N2N, ONP, DNP, Sal.H and Sal.A and $\text{HL}^* = \text{MeDBrHQ}$. The IR data of the calcium metal salts of defferent organic acids suggest that the metal is bonded to the acid through oxygen atom of hydroxyl group and carboxylic acid group in the case of salicylic acid and coordinated to the O/N atom of the groups like NO, NO_2 , CHO, COOH etc. This calcium metal salts combine with ligand i.e. 2-methyl-5,7-dibromo-oxine through coordination with the hydroxy oxygen atom and the nitrogen atom of the quinolone ring. Probable structure of the complexes are shown in Fig. 1

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Conflict of Interest: The authors declare no conflict of interest.



Where $\begin{matrix} \text{O/N} \\ \text{L} \\ \text{O} \end{matrix} = \text{deprotonated 1N2N, ONP, DNP, Sal.H, Sal. A}$

References

1. DM Huber, JB Jones. *Plant and soil*. Jul; 368:73 (2013)
2. MF Al-Mudhaffer, MA Nattiq, MA Jaber. *Archives of Applied Science Research*. ;4(4):1731 (2012)
3. H. Bakr. *Journal Homepage*: <http://ijmr.net>. in. Jun;8(6) (2021)
4. BO Wells, M. Kannan. Krishnan: Fundamentals and Applications of Magnetic Materials 1st Edition: Oxford University Press ; ISBN-10: 0199570442; ISBN-13: 978-0199570447 (2016)
5. E. Aghion, B. Bronfin. In Materials Science Forum (Vol. 350, pp. 19-30). Trans Tech Publications Ltd. (2000)
6. DW Shu, IR Ahmad. In Advanced Materials Research (Vol. 168, pp. 1631-1635). *Trans Tech Publications Ltd.* (2011)
7. Magnesium alloy as a lighter alternative to aluminum alloy, Phys.org, November 29th 2017
8. EL Dreizin, CH Berman, EP Vicenzi. *Combustion and Flame*. Jul 1;122(1-2):30 (2000).
9. RF Dorr. *Zenith Press* Sep 15 (2012).
10. G. Davies. Materials for automobile bodies. Elsevier; Apr 4 (2012)
11. MK Kulekci. *The International Journal of Advanced Manufacturing Technology*. Nov;39:851 (2008)
12. AA Luo, BR Powell. *Magnesium Technology* Feb 1:137 (2001)
13. Yang W, Wang J, Xu D, Li J, Chen T. *Surface and Coatings Technology*. 5 Dec 15;283:281 (2015)
14. Palkowski H, Wondraczek L. Direct strip casting of magnesium. *International Journal of Materials Research*. 2022 Feb 5;95(12):1080-6.
15. R. Vineel, S. Dixit S. *Journal of Water, Energy and Environment*. 6:38 (2010)
16. Khan N, Dollimore D, Alexander K, Wilburn FW. The origin of the exothermic peak in the thermal decomposition of basic magnesium carbonate. *Thermochimica Acta*. Mar 8;367:321 (2001)
17. Ata MA. Evaluation of serum levels of C-reactive protein and Magnesium in Type II Diabetes patients. *Northwest Journal of Medical Sciences*. (2017).
18. R. Vilar Astrid Sigel, Helmut Sigel, Roland KO Sigel (eds): Interplay between metal ions and nucleic acids.
19. Firoz M, Graber M. *Magnesium research*. Dec 1;14(4):257 (2001)
20. Rbaa M, Benhiba F, Abousalem AS, Galai M, Rouifi Z, Oudda H, Lakhri B, Warad I, Zarrouk A. *Journal of Molecular Structure*. Aug 5;1213:128155. (2020)
21. Gawne P, Man F, Fonslet J, Radia R, Bordoloi J, Cleveland M, Jimenez-Royo P, Gabizon A, Blower PJ, Long N, de Rosales RT. *Dalton Transactions*. 47(28):9283 (2018)
22. R. G. W. HOLLINGSHED, Oxine and its derivatives, Vol. III, Page No.-777-778, Butterworth Scientific Publication (1956).