

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

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Abstract: Five complexes of magnesium salts of some organic acids with 2-Methyl-5,7-dichloro-oxine having the general formula MgL_2HL' , 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 m.p. measurement, elemental analysis and spectroscopic studies etc.

(Keywords : 8-Hydroxyquinoline, gastrointestinal absorption and renal excretion)

Introduction

A typical adult's body contains 22-26 grams of Mg, of which 60% is found in the skeleton, 39% is found within cells (20% in skeletal muscle), and 1% is found outside of cells¹. The processes for regulating gastrointestinal absorption and renal excretion are what keep the serum magnesium level stable. There is a relationship between intracellular magnesium and potassium. Depending on the starting level, increased magnesium may either avoid hypercalcemia or lead to hypocalcemia by lowering calcium². The quantity of phosphate, phytate, and fat in the stomach, as well as situations with low or high protein consumption, all prevent the absorption of magnesium. Magnesium from food is expelled in feces when it is not absorbed; it is eliminated via urine and perspiration afterwards³.

Magnesium is necessary for plants to produce chlorophyll, which is crucial for photosynthesis. Like how Fe works in the core

of the porphyrin ring in heme, Mg does the same thing in the center of the porphyrin ring in chlorophyll. Epsom salts, which quickly leached from the soil, or crushed dolomitic limestone may be used to treat magnesium shortage in plants, which results in late-season yellowing between leaf veins, particularly in older leaves⁴. Thus it is obvious that magnesium play a crucial role in human metabolism and in plant system. In fact, the mechanism of magnesium uptake, storage and function is highly complicated which may be understood by developing the models of magnesium complexes. Besides these, there are also several uses of magnesium as metal and compounds in various fields.⁵⁻²²

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 use 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 and may be used 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^{23,24}.

Thus, with the hypothesis that complexes of magnesium with biologically potential ligands may serve as model to understand the mechanism of uptake, storage and function, we have synthesized and characterized several complexes of magnesium 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 salicylicacid (Sal.A) of Anal. R. grade were used. Salts of magnesium with organic acids were prepared as follows:

Alcoholic solution of magnesium hydroxide and organic acids viz. 1-nitroso-2-naphthol (1N2N), o-nitrophenol (ONP),

Dinitrophenol (DNP), Salicylaldehyde (Sal.H) and Salicylicacid (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.

2-Methyl-5,7-dichloro-oxine was prepared by the method described in literature²⁵. The elemental composition was found as given in table-1.

Preparation of complexes: Complexes were prepared by taking equimolecular ratios of magnesium salt of organic acid 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:

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
[Mg(1N2N) ₂ .MeDCIHQ] MgC ₃₀ H ₁₉ Cl ₂ N ₃ O ₅	Yellow	>300	60.40 (60.42)	3.19 (3.21)	7.04 (7.08)	4.00 (4.04)	5.0
[Mg(ONP) ₂ .MeDCIHQ] MgC ₂₂ H ₁₃ Cl ₂ N ₃ O ₇	Yellow	>300	49.98 (50.00)	2.80 (2.84)	7.92 (7.95)	4.52 (4.55)	6.0
[Mg(DNP) ₂ .MeDCIHQ] MgC ₂₂ H ₁₃ Cl ₂ N ₅ O ₁₁	Light Yellow	>300	42.70 (42.72)	2.07 (2.10)	11.30 (11.33)	3.85 (3.88)	4.4
[Mg(Sal.H) ₂ .MeDCIHQ] MgC ₂₄ H ₁₇ Cl ₂ NO ₅	Yellowish brown	>300	58.27 (58.30)	3.40 (3.44)	2.80 (2.83)	4.83 (4.86)	10.3
[Mg(Sal.A) ₂ .MeDCIHQ] MgC ₂₄ H ₁₇ Cl ₂ NO ₇	Bright Yellow	>300	54.71 (54.75)	3.20 (3.23)	2.62 (2.66)	4.52 (4.56)	12.2

Physical Properties

Some of the physical properties of the ligand 2-methyl-5,7-dichloro-oxine and its newly prepared complexes of Magnesium 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 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, nitrobenene, 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 magnesium salts of different organic acids were measured on Systronics Digital Direct Reading Conductivitymeter-304 at 25°C in 103M N,N-dimethylformamide solution. The negligible values of conductivity suggested the maximum covalency in the complexes.

Spectroscopic studies: Infrared measurement of the ligand 2-methyl-5,7-dichloro-oxine and its complexes with magnesium salts of some organic acid (1-nitroso-2- naphthol, o-nitrophenol, 2,4-dinitrophenol, salicylaldehyde and Salicylic acid) were recorded in the region between 4000-400 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	νOH	$\nu\text{C}=\text{C}/\nu\text{C}=\text{N}$	$\delta\text{-OH}$	$\nu\text{C-O}$
MeDCIHQ	3330 br	1610m,1560m	1390 m	1130m
Mg(1N2N) ₂ . MeDCIHQ	3400br	1570w, 1550sh,1530m	1410 m	1090m
Mg(ONP) ₂ . MeDCIHQ	3400 br	1570w, 1550sh,1510m	1410m	1090m
Mg(DNP) ₂ . MeDCIHQ	3390 br	1590m, 1560sh,1530m	1410s	1105m
Mg(Sal.H) ₂ . MeDCIHQ	3400 br	1580w, 1550sh,1510m	1410m	1090m
Mg(Sal.A) ₂ . MeDCIHQ	3400br	1590m, 1550sh,1510m	1410m	1090m

As mentioned in the table 2 the infrared absorption band of principal interest in the ligand 2-methyl-5,7-dichloro-oxine are 3330, 1610, 1560, 1390 and 1130 cm^{-1} . The broad band at 3330 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 hydroxy hydrogen atom and the nitrogen atom of the quinoline ring.

In all the newly prepared mixed ligand complexes this broad band at 3330 cm^{-1} has

shifted to higher frequency by 70 cm^{-1} and appeared as a broad band at 3400 cm^{-1} except only in the case of Mg(DNP)₂.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 Magnesium metal to the hydroxy oxygen atom. The broadness of the -OH absorption band in all the mixed ligand complexes also suggest that there exists hydrogen bonding in the complexes. The medium band at 1610 cm^{-1} and 1560 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 1590 to 1510 cm^{-1} . Shifting in these frequencies suggested the coordination of the magnesium metal with nitrogen atom of the quinoline ring. The medium broad band at 1390 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 1410 cm^{-1} . This shifting in the bending -OH frequency also suggest the coordination of the ligand to magnesium metal through hydroxy oxygen atom. The medium band at 1130 cm^{-1} is attributed to the stretching C-O frequency. This band has also shifted towards a lower frequency by 40 cm^{-1} in all the complexes except only in the case of $\text{Mg}(\text{DNP})_2 \cdot \text{MeDCIHQ}$ in which the band has shifted towards lower frequency only by 25 cm^{-1} . This also supports the bonding of magnesium metal to ligand through hydroxy oxygen atom of the ligand.

Structure and Bonding

On the basis of elemental analysis, the general molecular formula of the mixed ligand complexes are found to be $\text{MgL} \cdot \text{HL}'$ where, L=deprotonated 1-nitroso-2-naphthol (1N2N), o-nitrophenol (ONP), 2,4- dinitrophenonl (DNP), salicylaldehyde (Sal.H), salicylic acid (sal.A) and $\text{HL}' = 2\text{-Methyl-5,7-chloro-oxine}$. The IR data of the magnesium salts of different organic acids suggest that the metal is bonded to the acid through oxygen atom of hydroxy group and carboxylic group in the case of salicylic acid and coordinated to the O/N atom of the groups like

NO, NO₂, , CHO, COOH etc. This magnesium metal salts combine with ligand i.e. 2-Methyl-5,7-chloro-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.

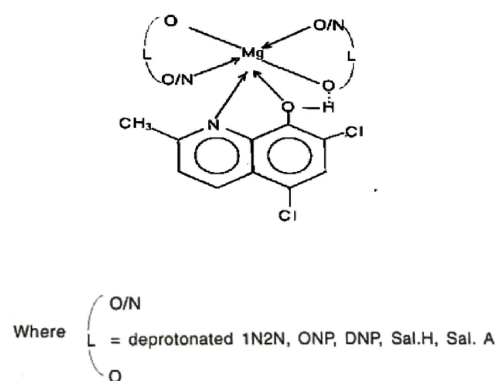


Fig. – 1

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References

1. NE Saris, E. Mervaala, H. Karppanen, JA A. Khawaja, *Clinica chimica acta*. Apr 1;294(1-2):1-26 (2000).
2. MENEZES EG, Oliveira ER, Carvalho GR, Guimaraes IC, Queiroz F. *Food Science and Technology*. Jun 27;39:662-72 .
3. T. Dyckner, P.O. Wester. *The American journal of medicine*. Mar 20;82(3):11 (1987)
4. DM Huber, J.B. Jones JB. *Plant and soil*. Jul ; 368:73 (2013)
5. MF Al-Mudhaffer, MA Nattiq, MA Jaber *Archives of Applied Science Research*. 4(4):1731 (2012)
6. H. Bakr *Journal Homepage*: <http://ijmr.net>. in. Jun; 8(6) (2021).
7. BO Wells, M. Kannan, Krishnan: *Fundamentals and Applications of Magnetic*

- Materials 1st Edition: Oxford University Press ISBN-10: 0199570442; ISBN-13: 978-0199570447 (2016).
8. E. Aghion, B. Bronfin, In *Materials Science Forum* Vol. 350, pp. 19-30). *Trans Tech Publications Ltd.* (2000)
 9. DW Shu, IR Ahmad. In *Advanced Materials Research* 1 (Vol. 168, pp. 1631-1635). *Trans Tech Publications Ltd.* (2011)
 10. Magnesium alloy as a lighter alternative to aluminum alloy, Phys.org, November 29th 2017
 11. Dreizin EL, Berman CH, Vicenzi EP. *Combustion and Flame*. Jul 1; 122(1-2):30 (2000)
 12. RF Dorr. Mission to Tokyo: The American Airmen who Took the War to the Heart of Japan. Zenith Press Sep 15 (2012).
 13. G. Davies Materials for automobile bodies. Elsevier; Apr 4 (2012).
 14. M.K. Kulekci *The International Journal of Advanced Manufacturing Technology*. **39** : 851 Nov; (2008)
 15. Luo AA, Powell BR. Tensile and Compressive Creep of Magnesium Aluminum Calcium Based Alloys. *Magnesium Technology* 2001. Feb 1:137 (2001)
 16. Yang W, Wang J, Xu D, Li J, Chen T. Characterization and formation mechanism of grey micro-arc oxidation coatings on magnesium alloy. *Surface and Coatings Technology*. Dec 15;283:281-5 (2015).
 17. Palkowski H, Wondraczek L. Direct strip casting of magnesium. *International Journal of Materials Research*. Feb 5;95(12):1080 (2022)
 18. R. Vineel, S. Dixit *Journal of Water, Energy and Environment*. 6, 38 (2010).
 19. N. Khan, D. Dollimore, K. Alexander, FW Wilburn, *Thermochimica Acta*. 8; 367 :321 (Mar 2001).
 20. M.A. Ata, *Northwest Journal of Medical Sciences*. (2017).
 21. R. Vilar Astrid Sigel, Helmut Sigel, Roland KO Sigel (eds): Interplay between metal ions and nucleic acids.
 22. M. Firoz, M. Graber. *Magnesium research*. **1**;14(4):257 (2001 Dec)
 23. M. Rbaa, F. Benhiba, AS Abousalem, M. Galai, Z. Rouifi, H. Oudda, B. Lakhrissi, I. Warad, A. Zarrouk *Journal of Molecular Structure*. **5**;1213:128155 (2020 Aug).
 24. P. Gawne, F. Man, J. Fonslet, R. Radia, J. Bordoloi, M. Cleveland, P. Jimenez-Royo, A. Gabizon, PJ Blower, N. Long, de Rosales RT. *Dalton Transactions*. ;47(28):9283 (2018)
 25. R.G.W. Hollingshead, oxine and its derivatives, Vol. (3), 777-778 butterworth Scientific Publications, London (1956).

