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# Synthesis and characterization of Mg (II) and Ca (II) complexes with 2-hydroxy-1,4-naphthoquinone dioxime

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## Abstract

Oxime derivatives of 2-hydroxy-1,4-naphthoquinone ( Lawsone) which include, 2-hydroxy- 1,4-naphthoquinone-1-oxime ( Lawsone monoxime) and 2-hydroxy 1,4-naphthoquinone-2-oxime ( Lawsone dioxime) are of special interest in coordination and structural inorganic chemistry due to the natural occurrence of their parent compound i.e. Lawsone. Their characteristic features include (a) enhanced chelating ability (b) comparative aspects between O-N donor system and N-N donor system and (c) powerful antimicrobial activities. Therefore 2- hydroxy-1,4-naphthoquinone dioximates of Ca(II) and Mg(II) was synthesized and structural investigations have been carried out through elemental analysis, thermal analysis, IR and UV spectroscopy. The Ca (II) and Mg (II) 2-hydroxy- 1,4-naphthoquinone dioximes are brown in color and their molecular composition being  $ML_2 \cdot 2H_2O$ .

**Keywords:** - Synthesis, characterization, Ca(II) & Mg(II), 2-hydroxy-1, 4- naphthoquinone dioxime

**1.1 Introduction:** -It is well known that oximes are better ligands as compared to the parent compound from which they are derived. To study the **effect of oximation** on Complexing ability of hydroxy derivatives, some monoxime derivatives of 2-hydroxy-1,4-naphthoquinone studied in our laboratory are given below.

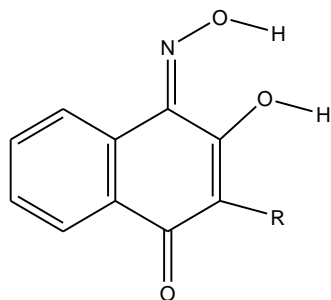


Fig.1 Lawsone monoxime

R	Compound
H	Lawsone monoxime
CH <sub>3</sub>	Phthicol monoxime
Cl	3-chloro lawsone monoxime
Br	3-bromolawsone monoxime
NO <sub>2</sub>	3-nitro lawsone monoxime
NH <sub>2</sub>	3-amino lawsone monoxime

Table: 1 Derivatives of 2-hydroxy-1, 4-naphthoquinone

The study of monoxime derivatives shows that on changing O-O donor to O-N donor on formation of monoxime of 2-hydroxy-1, 4-naphthoquinone complexation ability is increased. Therefore it is expected that on formation of dioxime derivative O-N donor system changes to N-N donor system, so that there should be more enhance in complexing ability. To study this, in present work we have synthesized dioxime of 2-hydroxy-1, 4-naphthoquinone and their complexes with Ca (II) and Mg (II). The biological role of Mg (II) is well through natural chelate "Chlorophyll" and Ca (II). structural role.

## 2.0 Experimental:-

### 2.1 Synthesis of 2-hydroxy-1,4-naphhoquine dioxime [ligand]

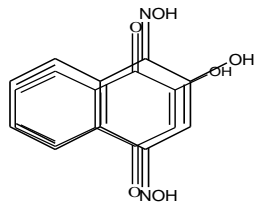


Fig. 2 2-hydroxy-1,4-naphhoquine

[Lawsone]

Fig. 3 2-hydroxy-1,4-naphhoquine dioxime

[Lawsone dioxime]

The solution of lawsone was prepared by dissolving 1.0 mmole (1.741 g. of lawsone) in about 25 ml 2M sodium hydroxide. This solution was mixed with hydroxylamine hydrochloride (2.0892g, 3.0 mmole) dissolved in about 25 ml distilled water. The mixture was warmed on water bath to 50-60 °C for about one hour. After cooling the mixture to room temperature it was further diluted with about 50ml ice- cold water. The mixture was then neutralized by using 2M hydrochloric acid till complete precipitation of lawsone dioxime in the form of dark brown colour. It was cooled in ice bath, filtered under suction, washed repeatedly with ice cold water and dried in vacuum over fused calcium chloride. It was recrystallized from ethanol. Melting point of lawsone dioxime was 210 °C. The purity of it was checked by thin layer chromatography using acetone-water (1:1) as developing solvent.

### 2.2 Synthesis of complexes of Mg (II) and Ca(II) with 2-hydroxy-1, 4-naphhoquinone dioxime

The 2.25 mmole solution of lawsone dioxime was prepared in about 20 ml methanol to which 1 mmole aqueous about 20 ml of metal chloride was added drop-wise with stirring. Adjust pH to 4 to 5 by using sodium acetate buffer and reflux mixture for about three hours. The brown colour complex is formed, filter it and wash with hot water followed by methanol. Dry complex in vacuum over fused calcium chloride and record yield.

## 3.0 Instrumentation:-

The synthesized 2-hydroxy-1, 4-naphhoquinone dioxime (Lawsonedioxime) and their complexes with Mg (II) and Ca (II) were characterized by using following techniques-

**3.1 Elemental Analysis-** The synthesized ligand and their complexes were analyzed for the percentage of carbon, hydrogen and metal oxide residue with the help of Hosli - Holland C, H –Microanalyser while the percentage of nitrogen was obtained by using Microdumas Hosli apparatus. The results obtained are given in the following table 2

Table 2. Elemental Analysis:-

Complex	Colour	Yield %	Wt. %			Molecular composition
			C	H	Residue	
Mg-LwDiox	Brown	64	51.46 (51.47)	3.85 (3.88)	12.02 (12.00)	ML <sub>2</sub> .2H <sub>2</sub> O
Ca-LwDiox	Brown	65	49.77 (49.79)	3.69 (3.76)	8.29 (8.30)	ML <sub>2</sub> .2H <sub>2</sub> O

(Figures in parenthesis indicate theoretical values)

**3.2 Thermogravimetry:** - Thermo gravimetric analysis of the ligand and their complexes has been carried out on Perkin-Elmer Delta series Model TGA-7 thermal analyzer provided with a chromel-alumel thermocouple in oxygen atmosphere. The results obtained are given in the following table 3 and 4

Table 3 Thermogravimetric analysis data of lawsonedioxime and Mg (II) & Ca (II) complexes

Compound	Stage of decomp.	Temp. Range (°C)	Total % weight loss	Tentative assignment
LwDiox	I	60-100	10.8	Oxidative decomposition of ligand
	II	110-200	30.9	
	III	200-550	100	
Mg (II)-LwDiox	I	80-190	22.0	Loss of two coordinated water molecules along with partial decomposition of ligand
	II	190-230	83.2	Oxidative decomposition of remaining ligand
	III	260-500		
Ca (II)-LwDiox	I	80-160	35.0	Loss of two coordinated water molecules along with partial decomposition of ligand
	II	180-270	84.0	Oxidative decomposition of remaining ligand
	III	270-450		

Table 4. Differential Thermal analysis data of 2-hydroxy 1,4-naphthoquinone dioxime and its complexes

Compound/ Chelate	Temperature range (°C)	Peak Temperature(°C)	Reaction type
LwDiox	80-120	107.5	Endo
	185-195	194.4	Endo
	510-550	539.4	Endo
Mg(II)-LwDiox	140-160	152.2	Endo
	210-230	215.0	Endo
	260-300	294.5	Endo
Ca(II)-LwDiox	140-160	155	Endo
	210-230	220.0	Endo
	300-330	320.0	Endo

**3.3 Infrared Spectra:** IR spectra of ligands and their complexes were recorded in nujol mulls on Perkin –Elmer IR spectrophotometer Model No 1600 in the range of 4000-450  $\text{cm}^{-1}$ . Considering our principle object of present work to throw light on molecular structure of complex, the IR spectra of 2-hydroxy-1,4-naphthoquinone dioxime and their complexes with Mg (II) and Ca (II) are analyzed for those specific frequencies which are directly or indirectly involved in the process of complex formation. These includes (O-H) stretching frequency, (C=N) stretching frequency, (C-O) stretching frequency, (N-O) stretching frequency, Relevant IR frequencies in  $\text{cm}^{-1}$  of ligands and Mg (II) and Ca(II) complexes are given in table no.5

**Table 5- The significant IR frequencies of 2-hydroxy 1,4-naphthoquinone dioxime and its complexes (in  $\text{cm}^{-1}$ )**

Ligand /complex	O-H	C=N		C-O	N-O	M-O
		Free	Chelated			
LwDiox	3508 3124	1627	1576	1210	1094 1047	--
Mg- LwDiox	3640	1580	1511	1248	1030	577
Ca- LwDiox	3655	1587	1537	1211	1010	573

### 3.4 Electronic Spectra

Electronic spectra of ligand and their complexes were recorded in the range of 200-800 nm on Shimadzu UV -300 spectrophotometer using 1 cm matched quartz cell in solvents methanol, acetonitrile, DMSO and DMF. The Electronic spectra of 2-hydroxy-1,4- naphthoquinone dioxime and their complexes are analyzed on the basis of benzenoid electron transfer (BET) Quinonoid Electron Transfer (QET) and  $n \rightarrow \pi^*$  transition as proposed by Scott.[A. J Scott “ Interpretation of Ultraviolet Spectra in Natural Products”, Mc Millan, New York (1968).The significant absorption maxima (in nm) for ligands and Mg (II) and Ca(II) complexes are given in table no.6.

Table 6. Significant absorption maxima in nm

Compound	Solvent				Assignment
	Methanol	Acetonitrile	DMF	DMSO	
LwDiox	209	--	--	--	B.E.T.
	287	280	286	283	Q.E.T
	--	345	382	--	n→π*
Mg (II)-LwDiox	236	--	--	--	B.E.T.
	285	--	--	--	Q.E.T
	345	--	--	--	n→π*
Ca (II)-LwDiox	225	--	--	--	B.E.T.
	270	--	--	--	Q.E.T
	370	--	--	--	n→π*

#### 4.0 Results and Conclusions–

The elemental analysis shows molecular composition of Mg (II) and Ca(II) complexes with of 2-hydroxy 1,4-naphthoquinone dioxime as  $ML_2 \cdot 2H_2O$ , which is also confirmed by Thermal analysis.

IR studies shows that two bands at 3508 and 3124  $cm^{-1}$  indicate two types of hydroxy groups present in ligand, one attached to oximino group and other phenolic group. For hydrated chelate, stretching frequency observed in the range at 3640 to 3655  $cm^{-1}$  is due to coordinated water. In lawsone dioxime both C=O bonds being replaced by oxime groups hence (C=O) stretching frequency is not observed as per expectation. In the lawsone dioxime there are two distinct bands at 1627  $cm^{-1}$  and 1576  $cm^{-1}$  due to (C=N) bonds out which one bond involved in chelation while other remain as free. On chelation this stretching frequency shifted to lower frequency region (red shift) indicating that there is a decrease in the bond order (reduction in double bond character of C=N bond) and involvement of oximino nitrogen in chelation with formation of five membered chelate. The (C-O) stretching frequency was at 1210  $cm^{-1}$  for lawsone dioxime which was shifted towards higher frequency region (1211-1248  $cm^{-1}$ ) in their chelates indicating the (C-O) bond strengthen on chelation as it directly involved in chelation. There are two distinct peaks at 1094 and 1047  $cm^{-1}$  which is due to two (N-OH) groups. On chelation with metal ion second band is shifted to lower frequency region in range of 1010 to 1030  $cm^{-1}$ . This red shift is due to delocalization of electrons from (N-OH) bond to the metal ion. In the chelates of lawsone dioxime this stretching frequency is observed in the region 573-577  $cm^{-1}$ .

As expected this BET is the first intense band observed in the region 200-240 nm. The BET bands observed in only methanol while it is absent in other solvents for ligand as well as both complexes. It is observed that QET bands occurs in narrow region 270 to 285nm.. These QET bands are found to sensitive to solvent as its red shift is larger in coordinating solvent as compared to polar solvent in case of 2-hydroxy 1,4-naphthoquinone dioxime. The  $n \rightarrow \pi^*$  bands occurs at about 345-382 nm.. These bands show less pronounced solvent effect.

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