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Alkaline Earth Metal Chelates of 3-Halolawsonemonoximes

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Metal chelates of 3-halolawsonemonoximes with beryllium (II), magnesium (II), calcium (II), strontium (II) and barium (II) were synthesized. The structural investigations were carried out using infrared spectra and electronic spectra. The molecular composition of all the chelates corresponds to $[ML_2 \cdot (H_2O)_2]$ except for beryllium (II) chelate in which it is $[ML(OH)]_2 \cdot 2H_2O$. A dimeric structure for tetrahedrally surrounded metal ion with bridging hydroxo group is proposed for beryllium (II) chelates, while *trans*-octahedral structure is suggested for all remaining chelates.

Key Words: Synthesis, Spectral, Chelates, Beryllium(II), Magnesium(II), Calcium(II), Strontium(II), Barium(II), 3-Halolawsonemonoximes.

INTRODUCTION

3-Halolawsonemonoxime [I] which is C-3 halo substituted derivative of lawsonemonoxime (X = Cl, Br, I) is found to be better chelating agent which can form stable complexes with many non-transition[1, 2] as well as transition metals[3, 4]. It is also used as an analytical reagent[5, 6]. Kosttanecki and Zincke[7] synthesized 3-chlorolawsonemonoxime from 3-chlorolawsone long back and isolated it as golden yellow needles from aqueous ethanol. 3-Bromolawsonemonoxime is prepared by Kulkarni and Sonawane[8]. Kehrmann[9] has obtained 3-iodolawsonemonoxime derivative from an alkaline solution of 3-iodo-2-hydroxy-1,4-naphthoquinone on treatment with one mole of hydroxylamine hydrochloride.

The NMR spectrum of 3-halolawsonemonoxime was analyzed by Khan[10] on the basis of which the *syn* and *amphi* isomers were detected by studying the ^1H NMR spectrum. The quantitization of these isomers was also done on the basis of this spectrum indicating that the composition of *syn* and *amphi* isomers is in 50 : 50 proportion. The evidence of this agreement with the predominance of *amphi* form indicated by near infrared spectra. Therefore, a systematic and detail study of the alkaline earth metal chelates of 3-halolawsonemonoximes [II] has been undertaken in our laboratory.

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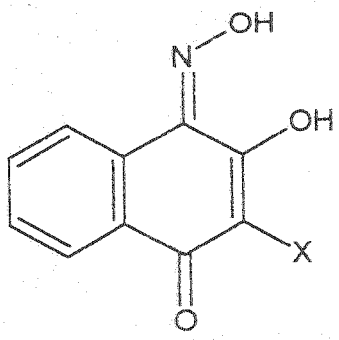
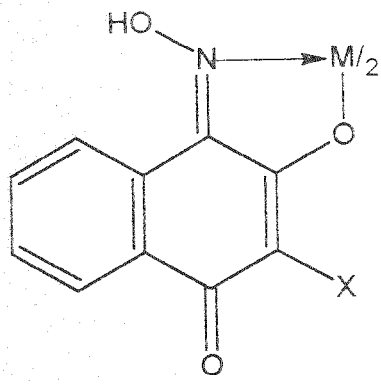


[I]
(X: Cl, Br, I)



[II]
(M: Be, Mg, Ca, Sr, Ba; X: Cl, Br, I)

In the present work, the study of metal chelates of 3-halolawsonemonoximes with beryllium (II), magnesium (II), calcium (II), strontium (II) and barium (II) is reported.

EXPERIMENTAL

All reagents, chemicals and solvents used were of AR grade.

3-Halolawsonemonoximes have been prepared from 3-halolawsones[11]. 3-Halolawsone was synthesized by using the method suggested by Kulkarni and Sonawane[4, 8]. 3-Halolawsonemonoxime was prepared from it using hydroxylamine hydrochloride as per the method developed in our laboratory[1]. The crude product was recrystallized from hot water and its purity was checked by m.p., TLC and elemental analysis.

The appropriate quantities of the metal acetate in ethanol : water solution (80 : 20) corresponding to 1 mmol concentration were prepared.

The 3-halolawsonemonoxime is partially soluble in water, but is completely soluble in 80 : 20 ethanol : water. Therefore, its solution corresponding to 2 mmol concentration was prepared in 80 : 20 ethanol : water by dissolving the necessary quantity of the recrystallized sample.

All the metal chelates were prepared by mixing the respective metal ion solution and ligand solution in 1 : 2 (with a slight excess of ligand solution) proportion slowly by keeping the mixture under nitrogen atmosphere with constant stirring using magnetic stirrer. The pH (6–8) was adjusted with the solution of sodium acetate (2 M). After complete precipitation the chelates were filtered under suction, washed with acetone and finally dried carefully.

The chelates were analyzed micro analytically using the Hosli-Holland analyzer for obtaining the percentage of carbon, hydrogen and residue (as metal oxide MO). The thermograms of all the chelates were recorded on NETZSCH simultaneous thermoanalyzer STA 409 model with the platinum thermocups. For each run about 25 mg of the sample was taken. The solid state infrared spectra were recorded in nujol mull on Perkin Elemer model-337 in the range 4000–400 cm^{-1}. Electronic spectra of all solutions of the chelates were recorded in spectroscopic methanol in the range 200–800 nm on Shimadzu UV-160 spectrophotometer.

RESULTS AND DISCUSSION

Molecular composition has been established on the basis of elemental analysis and is supported by infrared spectra (for presence of water molecule) and thermogravimetry and their general physical properties are given in Table-1.

TABLE-1
ANALYTICAL DATA

Compound	X	Colour	Elemental analysis: Found (Calculated)		
			C	H	M (as MO)
$[Be(OH)L]_2 \cdot 2H_2O$	Cl	Dark Brown	44.22 (44.75)	3.04 (2.90)	3.27 (3.10)
	Br	Red	38.74 (38.50)	2.60 (2.48)	2.91 (2.74)
	I	Yellow	33.64 (33.44)	2.26 (2.24)	2.52 (2.44)
$[MgL_2 \cdot (H_2O)_2]$	Cl	Red	47.71 (46.54)	2.80 (3.97)	4.83 (4.20)
	Br	Yellowish Brown	40.55 (39.01)	2.38 (3.35)	4.10 (3.41)
	I	Yellow Orange	35.00 (34.47)	2.06 (1.84)	3.53 (3.44)
$[CaL_2 \cdot (H_2O)_2]$	Cl	Yellowish Brown	46.26 (45.96)	2.72 (2.48)	7.72 (7.25)
	Br	Orange	39.50 (38.84)	2.32 (2.22)	6.59 (5.88)
	I	Reddish Orange	34.21 (33.88)	2.01 (1.87)	5.67 (5.54)
$[SrL_2 \cdot (H_2O)_2]$	Cl	Reddish Brown	42.38 (41.75)	2.49 (2.08)	15.46 (14.79)
	Br	Orange	36.63 (36.44)	2.15 (2.00)	13.36 (12.44)
	I	Pale Brown	32.04 (31.84)	1.88 (1.84)	11.69 (10.44)
$[BaL_2 \cdot (H_2O)_2]$	Cl	Brown	38.96 (37.98)	2.29 (1.97)	22.27 (26.38)
	Br	Yellowish Brown	34.05 (34.43)	2.00 (1.74)	19.46 (18.44)
	I	Orange	30.05 (29.16)	1.76 (1.28)	17.18 (16.68)

L = ligand = 3-X-Lwox and X = Cl, Br, I.

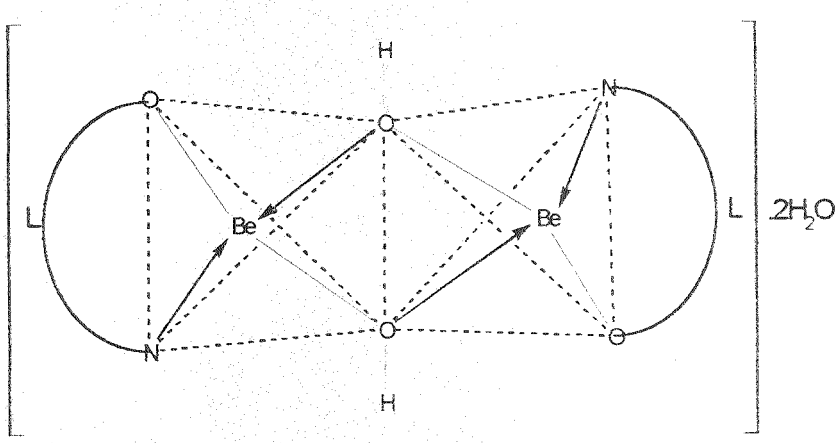
From the result of the elemental analysis it can be concluded that the molecular composition for Be (II) chelate corresponding to $[ML(OH)]_2 \cdot 2H_2O$, while that for all the remaining chelates is $[ML_2 \cdot (H_2O)_2]$, where M represents the metal ion and L represents the ligand.

All the chelates are coloured possessing the shades ranging from yellow to yellow red. The presence of water molecule in the aquated chelates has been proved by thermogravimetry.

Beryllium(II) chelate

Elemental analysis for this chelate close to the composition $[ML(OH)]_2 \cdot 2H_2O$. Considering the small size of the Be(II), its coordinating number four is

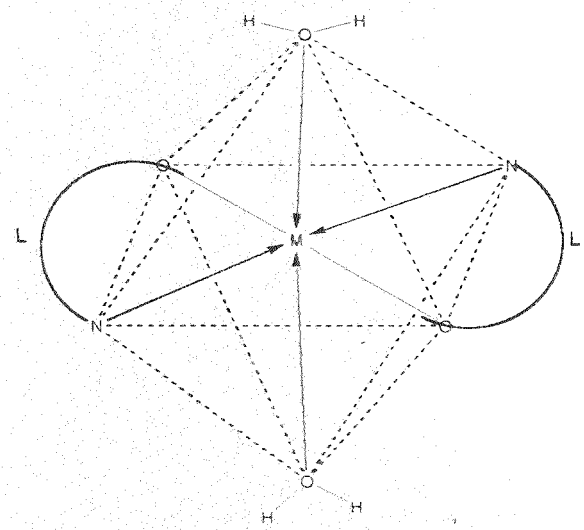
more probable and hence we propose a dimeric structure for tetrahedrally surrounded Be(II) ions with bridging hydroxo groups and two molecules of lattice water [III]. Possibility of such geometry for Be(II) chelate is given by Everest[12] while discussing the chemistry of beryllium. Hydroxy bridged chelates of Be (II) are recently reported by Mhaske[13].



[III]
(L: Ligand)

Other Metal Chelates

In the case of other metal chelates the results of the elemental analysis match with the composition $[ML_2 \cdot (H_2O)_2]$, the two water molecules acting as ligand for acquiring coordination number six. We therefore, propose a *trans*-octahedral structure for all the chelates [IV]. Similar octahedral structures for the alkaline earth metal chelates of the acetylacetone have been reported[14] earlier.



[IV]
(L: Lgand)

The significant IR peaks of the ligand and its chelates are shown in Table-2.

TABLE-2
KEY IR BANDS (cm^{-1})

Compound	X	ν(O—H)	ν(C=O)	ν(C—O)	ν(N—O)	ν(C=N)	ν(M—O)	ν(C—X)
3-X-Lwoxs	Cl	3100 b, 3500 b	1200 s	1610 s	1045 s	1550 m	—	700 s
	Br	3100 b, 3500 b	1200 m	1630 s	1050 s	1590 s	—	670 m
	I	3250 b, 3400 b	1205 s	1650 s	1050 s	1600 m	—	600 s
$[Be(OH)L]_2 \cdot 2H_2O$	Cl	3450 b	1225 b	1610 s	1440 w	1550 b	460 w	700 w,sh
	Br	3150 b	1200 s	1610 m	1035 w	1550 b	490 w	665 s
	I	3400 b	1220 s	1625 w	1030 w	1600 s	480 w	600 w
$[MgL_2 \cdot (H_2O)_2]$	Cl	3350 b	1190 b	1600 w	1040 m	1500 s	450 sh	700 s
	Br	3300 b	1190 b	1640 m	1040 w	1570 w	500 w,b	680 sh
	I	3300 b	1205 w,sh	1650 b	1040 m	1600 w	470 w	595 w
$[CaL_2 \cdot (H_2O)_2]$	Cl	3150 w,b	1210 b	1600 w	1040 b	1500 m,sh	460 sh	700 w
	Br	3150 b	1210 s	1600 s	1045 s	1520 s	460 sh	675 s
	I	3150 b	1205 w,sh	1625 w,sh	1040 m	1600 s	460 s	605 w
$[SrL_2 \cdot (H_2O)_2]$	Cl	3200 w,b	1210 s	1610 s	1040 b	1540 s	440 w	700 m
	Br	3150 b	1200 s	1600 s	1045 m	1510 s	450 sh	690 s
	I	3150 b	1230 w	1610 w,sh	1035 w	1600 m	450 w	540 s
$[BaL_2 \cdot (H_2O)_2]$	Cl	3150 b	1210 s	1610 s	1050 s	1525 b	500 w	700 s
	Br	3100 b	1205 s	1600 s,sh	1045 s	1500 b	490 w	675 m
	I	3350 w	1205 w	1610 w,sh	1035 b	1600 w	450 w	600 w

L = ligand = 3-X-Lwox and X = Cl, Br, I.

(i) These peaks are directly involved in the chelate formation. The infrared spectra of all these chelates indicates a broad band in the region approximately 3700–3100 cm^{-1}, which is due to the (O—H) stretching frequency from coordinated/lattice water.

(ii) The (C=N) frequency of the ligand is lowered in all chelates indicating the weakening of the bond, hence bonding with the metal ion is through this (C=N) bond.

(iii) The (C—O) stretching frequency assigned at 1210 cm^{-1} is shifted towards higher frequency region in the spectra of all the metal chelates with the exception of Mg (II) chelate where the opposite trend is observed there being a red shift and the peak is observed at 1200 cm^{-1}.

(iv) The (N—O) stretching frequency is shifted towards lower frequency region indicating weakening of the bond.

(v) The (M—O) stretching frequencies are assigned in the region 500–400 cm^{-1}.

Electronic spectra

Electronic spectra of several lawsone derivatives of 3-halolawsonemonoximes and their metal chelates have been previously analyzed in our laboratory[1] and their spectra involve mainly the following types of bands: benzenoid electron transfer bands (B.E.T.), quinonoid electron transfer bands (Q.E.T.) and n→π* transition bands.

When the electronic spectra of the chelates in ethanol are compared with the parent ligand, in general it is observed that the spectra of ligand (*viz.* 3-Halolawsonemonoximes) itself with slight modifications due to chelation. The major absorption peaks are given in Table-3.

TABLE-3
SIGNIFICANT ABSORPTION MAXIMA (nm) IN METHANOL AND DIOXANE

Compound	X	Absorption maxima λ_{max} (nm)					
		Methanol			Dioxane		
		B.E.T.	Q.E.T.	n→π*	B.E.T.	Q.E.T.	n→π*
3-X-Lwox	Cl	221	273	415	211 248	287	—
	Br	232	287	—	239	287	450 612
	I	230	291	—	244	289	488
$[Be(OH)L]_2 \cdot 2H_2O$	Cl	221	270	346	212 245	284	—
	Br	231	273	466	252	282	329
	I	238	299	346	243	290	391
$[MgL_2 \cdot (H_2O)_2]$	Cl	226	272	426	212 244	284	757
	Br	234	283	—	244	286	—
	I	240	291	406	243	286	—
$[CaL_2 \cdot (H_2O)_2]$	Cl	225	272	—	212	244	278
	Br	233	274	416	249	283	450
	I	241	291	404	244	288	754
$[SrL_2 \cdot (H_2O)_2]$	Cl	222	272	450	252	281	—
	Br	234	281	413	212	251	286
	I	240	290	403	244	—	—
$[BaL_2 \cdot (H_2O)_2]$	Cl	225	273	—	251	278	—
	Br	232	274	435	211	252	281
	I	240	291	—	244	—	—

L = ligand = 3-X-Lwox and X = Cl, Br, I.

(i) In general, this solution spectrum consist of three major bands observed in the regions 210–250 nm, 280–300 nm and 373-470 nm. These are respectively assigned to B.E.T., Q.E.T. and n→π* transitions in methanol and dioxane.

(ii) In methanol, the spectrum of the chelates shows close resemblances among themselves but shows remarkable differences from the ligand spectrum. Thus, (a) there is a weak but distinct and sharp band at 222 nm in the spectrum of all chelates this band was not resolved in 3-halolawsonemonoximes due to B.E.T., (b) there is most dominant band in the region approximately 288–297 nm involving Q.E.T. invariably of the similar nature in all spectra. The band at 289 nm is most characteristic band expect in Be (II) spectrum and it is at 297 nm, (c) the characteristic $n\rightarrow\pi^*$ transition band expected in the spectra of chelates is observed but it is very broad it is about 373–456 nm without any trend so the nature of alkaline earth although influence this band, the trend is quite arbitrary.

(iii) In dioxane, (a) four bands recorded in 3-halolawsonemonoximes spectra (instead of two as recorded in methanol). These are at 212 and 246 nm (both due to B.E.T.), at 285 nm (Q.E.T.) and at 451 nm ($n\rightarrow\pi^*$ transition), (b) the weak band at 212 nm is absent in all the 3-halolawsonemonoximes except Be (II). The second band at 246 nm is a dominant band in the spectra of all chelates. Similarly, the third band at 285 nm is also present in all chelates but it is most dominant band in Be (II) and Mg (II), (c) The other two bands, one in the region 445–451 nm and the other in 608–612 nm is observed in the spectra of the chelates it is not resolved. The $n\rightarrow\pi^*$ transition are thus suppressed in dioxane.

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