

Synthesis and Characterization of Alkaline Earth Metal Chelates of Phthiocolmonoxime

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Metal chelates of phthiocolmonoxime with beryllium(II), magnesium(II), calcium(II), strontium(II) and barium(II) were synthesized and their chemical identities were established on the basis of elemental analysis. 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 other chelates.

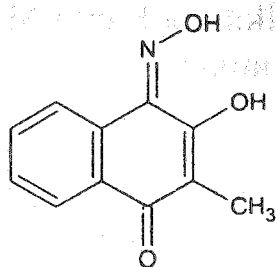
Key Words: Synthesis, Spectral studies, Chelates, Alkaline earth metals, Phthiocolmonoxime.

INTRODUCTION

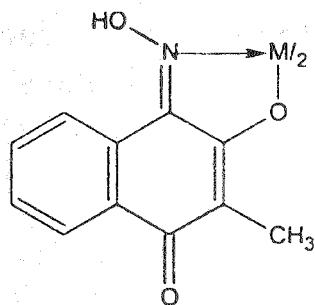
Phthiocolmonoxime (I) is found to be a better chelating agent which can form stable complexes with many non-transition¹ as well as transition metals^{2, 3}. Rane⁴ was the first to study phthiocolmonoxime both from structural as well as analytical point of view, while detailed coordination and analytical studies were done by Kulkarni³ and Khan^{5, 6}. On the basis of near infrared spectra in carbon tetrachloride in the region 1–3.5 micron, Kadam⁷ proposed *v*-form or *amphi* form in which the O—H group associated with oxime is more free and the O—H group has very weak intramolecular hydrogen bonding with nitrogen. The presence of —CH₃ group at C-3 position has been found to play a significant role in the molecular structure due to which the intramolecular hydrogen bonding becomes weak.

The NMR spectrum of phthiocolmonoxime was analyzed by Khan⁴ on the basis of which the “*syn*” and “*amphi*” isomers were detected by studying the ¹H NMR spectrum. The quantization of these isomers was also done on the basis of this spectrum indicating that the composition of “*syn*” and “*amphi*” isomers is in 30 : 70 proportion. The evidence of this agreement with the predominance of *amphi* form indicated by near infrared spectra. Therefore, a systematic and detailed study of the alkaline earth metal chelates of phthiocolmonoxime (2) has been undertaken.

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(1)



(M: Be, Mg, Ca, Sr, Ba)

(2)

EXPERIMENTAL

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

Synthesis of ligand: Phthiocolmonoxime has been prepared from phthiocol. Phthiocol⁷ was synthesized by using the reported method⁸. Phthiocolmonoxime was prepared from it using hydroxylamine hydrochloride. The crude product was recrystallized from ethanol and its purity was checked by m.p., TLC and elemental analysis.

The phthiocolmonoxime 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.

Synthesis of metal chelates: Metal chelates of all the five metal ions were prepared by mixing the metal ion solution and ligand solution in 1:2 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 platinum thermocups. For each run about 25 mg of the sample was taken. Infrared spectra were recorded in nujol mull on Perkin-Elmer model-337 in the range 4000–400 cm^{-1} . Electronic spectra of all 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 and thermogravimetry and their general physical properties are given in Table-1.

From the result of the elemental analysis, it can be concluded that the molecular composition for Be(II) chelate corresponds to $[\text{ML}(\text{OH})]_2 \cdot 2\text{H}_2\text{O}$ while that for all the other chelates is $[\text{ML}_2 \cdot (\text{H}_2\text{O})_2]$, where M represents the metal ion and L represents the ligand.

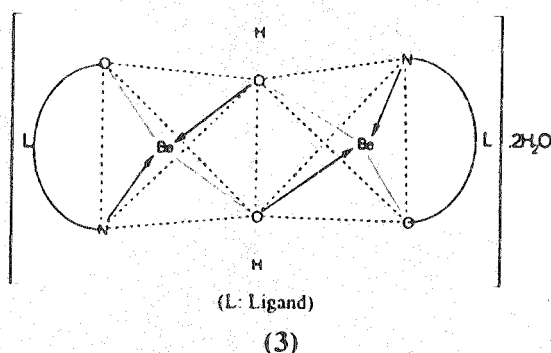
All the chelates are coloured possessing the shades ranging from yellow to yellow red. The presence of water molecule in the aquated chelates has been proved by thermogravimetry.

TABLE-I
ANALYTICAL DATA

S. No.	Compound	Yield (%)	Colour	Elemental analysis: Found (Calcd.) (%)		
				C	H	M
1.	[Be(OH)(Phox)] ₂ ·2H ₂ O	82	Yellowish green	53.64 (52.04)	4.50 (4.94)	3.70 (3.62)
2.	[Mg(Phox) ₂ ·(H ₂ O) ₂]	73	Brown	56.89 (49.78)	3.45 (5.43)	5.23 (5.18)
3.	[Ca(Phox) ₂ ·(H ₂ O) ₂]	65	Brownish yellow	55.00 (56.04)	3.33 (4.11)	8.34 (8.22)
4.	[Sr(Phox) ₂ ·(H ₂ O) ₂]	67	Dark yellow	50.00 (48.89)	3.03 (3.58)	16.59 (15.94)
5.	[Ba(Phox) ₂ ·(H ₂ O) ₂]	58	Yellowish brown	46.48 (47.14)	2.82 (3.43)	23.77 (22.79)

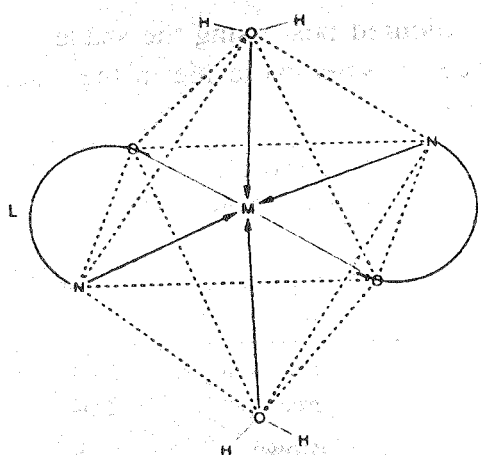
[(Phox) = Phthiocolmonoxime]

Beryllium(II) chelate: Elemental analysis for this chelate does not match neutral composition like $ML_2 \cdot 4H_2O$ or $[ML(H_2O)CH_3COO]$ or $[ML(OH)_2]$. It is, however, close to the composition $[ML(OH)]_2 \cdot 2H_2O$. Considering the small size of Be(II), its coordinating number four is more probable and hence a dimeric structure for tetrahedrally surrounded Be(II) ions with bridging hydroxo groups and two molecules of lattice water (3) is proposed. Possibility of such geometry for Be(II) chelate is given by Everest⁹ while discussing the chemistry of beryllium. Similar hydroxy bridged chelates of Be(II) are recently reported by Mhaske¹⁰ and Kulkarni *et al.*¹¹



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. Therefore, a *trans*-octahedral structure for all the chelates (4) is proposed. Similar octahedral structure for the alkaline earth metal chelates of the acetylacetonone have been reported¹² earlier.



[M = Mg(II), Ca(II), Sr(II) and Ba(II)]

(4)

Infrared Spectra

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

TABLE-2
SIGNIFICANT IR PEAKS (cm^{-1})

S. No.	Compound	$\nu(\text{O—H})$	$\nu(\text{C=O})$	$\nu(\text{C—O})$	$\nu(\text{N—O})$	$\nu(\text{C=N})$	$\nu(\text{M—O})$
1.	Phthalocolmonoxime (Phox)	3350 (s)	1640 (s)	1210 (sh)	1060 (s)	1560 (b)	—
2.	$[\text{Be}(\text{OH})(\text{Phox})]_2 \cdot 2\text{H}_2\text{O}$	3350 (b)	1600 (w)	1220 (s)	1040 (b)	1525 (b)	500 (w)
3.	$[\text{Mg}(\text{Phox})_2 \cdot (\text{H}_2\text{O})_2]$	3250 (b)	1590 (w)	1200 (b)	1055 (b)	1500 (sh)	450 (b)
4.	$[\text{Ca}(\text{Phox})_2 \cdot (\text{H}_2\text{O})_2]$	3150 (b)	1600 (s)	1210 (s)	1030 (b)	1525 (b)	470 (b)
					1055 (s)		
5.	$[\text{Sr}(\text{Phox})_2 \cdot (\text{H}_2\text{O})_2]$	3125 (w)	1590 (s)	1210 (s)	1030 (b)	1550 (w)	450 (b)
					1055 (s)		
6.	$[\text{Ba}(\text{Phox})_2 \cdot (\text{H}_2\text{O})_2]$	3100 (b)	1580 (s)	1210 (s)	1030 (sh)	1500 (s)	465 (b)

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

(ii) The $\nu(\text{C=N})$ 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 $\nu(\text{C—O})$ 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 $\nu(\text{N—O})$ stretching frequency is shifted towards lower frequency region indicating weakening of the bond.

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

Electronic Spectra

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.* phthiocolmonoxime) 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

S. No.	Compound	Absorption maxima λ_{\max} (nm)					
		Methanol			Dioxane		
		B.E.T.	Q.E.T.	$n \rightarrow \pi^*$	B.E.T.	Q.E.T.	$n \rightarrow \pi^*$
1.	Phthiocolmonoxime (Phox)	240	289	—	212 246	285	451
2.	[Be(OH)(Phox)] ₂ ·2H ₂ O	222	297	373	213 244	285	446 608
3.	[Mg(Phox) ₂ (H ₂ O) ₂]	222 249	289	443	245	285	449 612
4.	[Ca(Phox) ₂ (H ₂ O) ₂]	222 245	289	373	244	284	—
5.	[Sr(Phox) ₂ (H ₂ O) ₂]	222	288	456	246	284	451
6.	[Ba(Phox) ₂ (H ₂ O) ₂]	222	289	429	245	284	451

(i) In general, this solution spectrum consists 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 $n \rightarrow \pi^*$ transitions in methanol and dioxane.

(ii) In methanol, the spectra of the chelates show close resemblances among themselves but show remarkable differences from the ligand spectrum. (a) Thus there is a weak but distinct and sharp band at 222 nm in the spectrum of all chelates; this band was not resolved in phthiocolmonoxime due to B.E.T.. (b) There is the most dominant band in the region approximately 288–297 nm involving Q.E.T. invariably of similar nature in all spectra. The band at 289 nm is the most characteristic band except 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 influences this band, the trend is quite arbitrary.

(iii) In dioxane: (a) Four bands are recorded in phthiocolmonoxime spectra (instead of two as recorded in methanol). These are at 212 nm 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 phthiocolmonoximates 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 the 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 $n \rightarrow \pi^*$ transitions are thus suppressed in dioxane.

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