

Mixed ligand complexes of 8-hydroxyquinolates of Ca(II) with some bidentate ligand

Poonam Ojha*, D.N. Thakur** and Richa Sharma***

Department of Chemistry, Patna University, Patna-800005

Email : akhileshwart8@gmail.com

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Abstract: A number of complexes of 8-hydroxyquinoline using Ca as central metal cation and benzil, benzoin and benzoin oxime as secondary ligands have been prepared and characterised on the basis of microanalytical, conductivity and infrared spectral studies. Their probable structures have been proposed on the basis of physicochemical analysis.

(Key words : Complexes, 8-hydroxyquinolates, benzil, benzoin and benzoinoxime, Ca metal).

Introduction

The complexes of alkaline earth metals particularly Calcium is very interesting. There appears to exist a preferential assimilation for Ca and Na over Mg and K in the animal system, the reverse being true in the case of plants^{1,2}. As the chemistry of these metals are very similar, this apparent discrepancy in the behaviour could be due to electro negativity, size or even because of the coordinating ability of different elements and their environmental setting within the bio system.

Calcium and magnesium are essential for muscle contraction³. If the concentration of both the ions are below 10^{-7} M, contraction and actomyosin -ATPase activity ceases. In the presence of ATP, if the concentration of either Mg or Ca alone is raised, it has no restorative effect. But in the presence of minimal Mg ions, increasing the Ca ion concentration to 3×10^{-6} M restores ATPase activity and permits contraction. When the Ca ion concentration is kept at 3×10^{-6}

M and then the Mg ion concentration raised to 10^{-2} M once again ATPase activity ceases. This inhibitory action can be countered with Ca ion concentration at about 4×10^{-4} M⁴⁻⁵ under these conditions of ATP concentration.

So the role of high concentration of Mg ions on actomyosin - ATPase activity is of great interest. Calcium is an important mineral mainly found in bones and teeth. It is widely distributed in food substances such as milk, cheese, egg, yolk, beans, lentils, nuts, figs and cabbage. The daily requirement of calcium is about 700-800 mg for adults.

The total calcium content of the body is 100g - 170 g. About 99% of this exists as carbonates or phosphates of calcium in bones, 0.5% in soft tissues and 0.1% in ECF⁶. The normal level of plasma calcium is 9 - 11 mg/dl⁷ in adult human beings. Ionized calcium is physiologically active form of Ca. It is also an important factor for blood coagulation⁷ as conversion of prothrombin into thrombin is dependent on its presence. Calcium acts as a second messenger releasing neurotransmitter after receiving a nervous impulse either at neuromuscular junction⁸ or at synapses. The same role is played by calcium in releasing adrenaline from adrenal medulla⁹. Calcium is also associated with the contraction of muscles¹⁰.

The semipermeable membranes maintain their integrity¹¹ in the presence of calcium and become porous and leaky in its absence. Calcium

*Corresponding author, Flate No. D/2, TVR, Buddha Colony, Patna – 800 001

**Head, Department of Chemistry, Patna University, Patna-5.

*** Chandra Niketan, Law College Road, Patna. E-mail: akhileshwart8@gmail.com

is essential for the calcification of tissues¹² by getting accumulated in the mitochondria and being released on demand. It has also been noticed in the traces in endoplasmic reticulum¹³.

Bones are made up of calcium phosphate. A calcium rich fluid maintains the integrity of the cementing material by converting it into a nondispersible complex. Edathamil calcium disodium (versene) a cyclic complex of calcium is used as a detoxifying agent in lead poisoning because of its chelating property¹⁴. Versene is the mono calcium disodium salt of ethylenediamine tetra acetic acid (EDTA). In the blood, versene replaces its calcium for a more stable Pb ion. The Pb complex formed is water soluble, thus helps in rapid excretion of stored Pb from the body. Similarly heavy metal poisoning can also be cured.

Experimental

Equimolar proportion (0.01 mole) of the oxinate complex $[\text{Ca}(\text{8HQ})_2 \cdot 2\text{H}_2\text{O}]$ and secondary ligand L (where L = benzil, benzoin and benzoin oxime) were dissolved separately in about 50 ml

of absolute alcohol and then mixed. The resulting solution was refluxed on a steam bath for an hour and half. On cooling the refluxate crystals of mixed ligand complexes separated out gradually. These crystals were filtered, washed with cold ethanol and dried in a desiccator over CaCl_2 .

Results and Discussion

These complexes were analysed and results of elemental analysis, solubility in different solvents and the quantitative electrical conductance value of complexes are listed in Table-I. These complexes were either white or cream coloured. The solubility of complexes have been examined in some organic solvents like methanol, ethanol, benzene and DMF. The complexes were soluble to some extent in ethanol and methanol, poor in benzene but dissolved appreciably in DMF. The methanol or DMF solution of the complex have been found to show negligible electrical conductance value (Table I) suggesting the non- ionic character of complexes.

Table - 1
Results of elemental analysis and quantitative value of solubility and electrical conductance of complexes

Complex	Ca	C	H	N	Qualitative Data of solubility				Molar electrical conductance value (λ_{α}) $\text{ohm}^{-1} \text{mol}^{-1} \text{cm}^2$
	Found (Cal.)	Found (Cal.)	Found (Cal.)	Found (Cal.)	Methanol	Ethanol	Dioxan	DMF	
$\text{Ca}(\text{8HQ})_2 \cdot 2\text{H}_2\text{O}$	10.78 (10.99)	59.53 (59.34)	04.38 (04.40)	07.81 (07.69)	S	S	FS	HS	10
$\text{Ca}(\text{8HQ})_2 \cdot \text{bzI}$	0.79 (0.741)	70.18 (71.11)	04.38 (05.28)	05.28 (05.19)	S	S	FS	HS	5
$\text{Ca}(\text{8HQ})_2 \cdot \text{bn2n}$	07.27 (07.38)	71.05 (70.85)	04.83 (04.80)	05.05 (05.17)	S	S	FS	HS	4
$\text{Ca}(\text{8HQ})_2 \cdot \text{benox}$	07.31 (07.18)	68.73 (68.94)	04.73 (04.85)	07.71 (07.54)	S	S	FS	HS	5

S = Soluble, FS = Fairly Soluble, HS = Highly Soluble

The infrared spectrum of ligands have been recorded as KBr disc on FTIR spectrophotometer at CDRI Lucknow and a few spectrum were recorded on Perkin Elmer - 577 spectrophotometer

as KBr optics at Chemical Laboratory Patna University Patna. The prominent and diagnostic I.R. bands of complexes and ligands are given in Table II.

Table - II
Prominent IR bands of 8-hydroxyquinoline complexes and
their mixed ligand complexes (band in cm⁻¹)

Complexes	$\nu(\text{OH})$ $\nu(\text{H}_2\text{O})$	$\nu(\text{C}=\text{O})$ δ	$\nu(\text{C}=\text{N})$	$\nu(\text{C}-\text{O})$	$\delta(\text{C}-\text{H})$ ring	Ring Deformation Vibration
Ca(8HQ) ₂ .2H ₂ O	3400 br	—	1585	1235	(795) (745)	(680) (645) (590)
Ca(8HQ) ₂ bzl	—	1672 (1688)	1585	1245	780, 760, 742	680, 660, 635, 580, 460
Ca(8HQ) ₂ .bnzn	3300	1662 (1678)	1580	1242	780, 765, 742	682, 645, 625, 580, 461
Ca(8HQ) ₂ .benox	—	1660	1575	1248	780, 755, 745	682, 655, 632, 575

The IR spectra of 8 hydroxyquinone (8HQ) shows $\nu(\text{OH})$ vibration as broad band near 2950 - 2690 cm⁻¹ as strong band but disappears in its complexes. The $\nu(\text{C}=\text{N})$ of free ligand appears as sharp band at 1590 cm⁻¹ which is shifted to lower frequency and observed at 1585- 80 cm⁻¹ indicating coordination of pyridine nitrogen. The $\nu(\text{C}-\text{O})$ phenolic 8 HQ is observed at 1100 cm⁻¹ which gets affected appreciably on co-ordination. The $\nu(\text{C}-\text{O})$ is raised to higher frequencies by 100 - 250 cm⁻¹. The blue shift of $\delta(\text{C}-\text{O})$ band 1200 - 1350 cm⁻¹ in its bis chelates suggested the increase in (C - O) bond order and thus indicates chelate ring formation between metal hydroxyl oxygen on deprotonation. Complexes of Ca (II) with 8 hydroxyquinoline showed the red shift of $\nu(\text{C}=\text{N})$ vibration and blue shift of $\nu(\text{C}-\text{O})$ vibration. The $\nu(\text{OH})$ vibration of phenolic group completely disappear in its bis chelates as well as its mixed ligand complexes.

Benzil (C₆ H₅ - CO - CO - C₆ H₅) is a diketone and oxygen bidentate chelating molecule. The ligand displays prominent IR band at 1688 cm⁻¹ due to $\nu(\text{C}=\text{O})$ vibration which gets affected appreciably while other phenyl rings are not affected substantially supporting the co-ordination of ketonic oxygen in mixed ligand complexes¹⁵. Benzoinoxime is a good chelating ligand and displays $\nu(\text{C}=\text{O})$ band at 1674 cm⁻¹ and $\nu(\text{N}-\text{OH})$ is observed at 3209 cm⁻¹. The (N - OH) group $\nu(\text{O}-\text{H})$ band is retained in mixed

ligand complexes suggesting that the ligand is not deprotonated in complexes. The $\nu(\text{C}-\text{O})$ band of ligand is observed at 987 cm⁻¹ and this is also retained in complex. The benzoin oxime group C = N and $\delta(\text{N}-\text{O})$ bands are observed at lower frequencies in complex indicating the involvement of ligand carboxyl oxygen and oxime (N-OH) nitrogen. The benzoin (C₆ H₅ CO - CHOH - C₆ H₅) display $\nu(\text{C}=\text{O})$ band at 1678 which is affected on complex formation. The hydroxyl $\nu(\text{C}-\text{O})$ vibration is assigned to a band at 1093cm⁻¹ which shifts to higher frequency in complex by 50 - 100 cm⁻¹. Thus ligand appears to co-ordinate as oxygen donor bidentate molecule.

Conclusion and suggested structures

The melting of Ca(oxime)₂.2H₂O and its mixed ligand complexes were recorded. The melting point of mixed complexes were higher than Ca (oxime)₂.2H₂O. Higher MP of the complex as that of pure ligand and its calcium complexes support the bonding of the ligand with metal atom. Thus from IR spectral forms, the bonding sites of these ligand is concluded. 8 hydroxyquinoline is deprotonated and forms bis chelates [Ca(8HQ)₂ H₂O]. The absence of $\nu(\text{OH})$ in complexes suggest the protonation of OH and shift of $\nu(\text{C}-\text{O})$ to higher frequency indicates bonding of oxygen atoms to metal.

In mixed chelates the benzil, benzoin and benzoin oxime are bonded as bidentate molecule forming bonds through both the oxygen atom.

From IR studies and other physicochemical data the probable structure of these complexes are given in Fig.1a, 1b and 1c.

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Structure of $M(8HQ)_2L$ Where $M=Ca^{2+}$, $L=bzl, bnzn, benox$

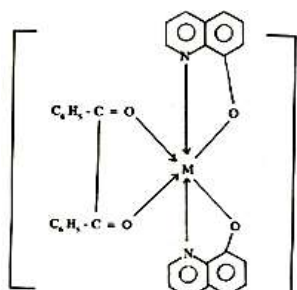


FIG.1a structure of $[M(8HQ)_2(bzl)]$

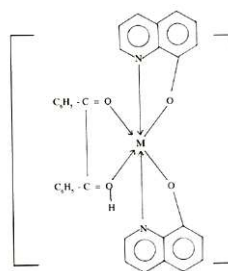


FIG.1b structure of $[M(8HQ)_2(bnzn)]$

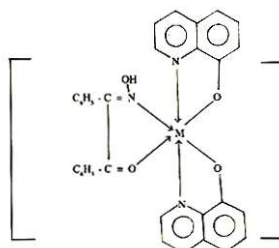


FIG.1c structure of $[M(8HQ)_2(benox)]$

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