

Mixed ligand complexes of 8-hydroxyquinoline of Mg(II) with some bidentate ligand.

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Abstract : The characterization and synthesis of mixed ligand complexes of Mg (II) with 8-hydroxyquinoline as parenting chelating ligand and benzyl, benzoin and benzoinoxime as secondary co-ordinating molecule has been studied and possible structure has been proposed.

(Keywords: Complexes, 8 hydroquinoline, benzil, benzoin and benzoin oxime, Mg metal.)

Introduction

Magnesium is the fourth most abundant and important cation in humans. It is extremely essential for life and is present as intracellular ion in all living cells and tissues. About 2/3 of the magnesium of the body is present in bones, 1% in E.C. fluid and remainder in soft tissues. In plasma 1.5 to 1.8 m Eq/L of Mg ion is present which is vigorously maintained within normal limits. 15% of the total body magnesium is exchangeable with tissues but there is wide variation. Muscles contain 20% of exchangeable magnesium and bones only 2%. In hyperthyroidism the amount of exchangeable magnesium increase remarkably whereas reverse is the case with hypothyroidism. About 1/3 magnesium exists in blood as protein bound metal1 the remainder 2/3 is ionic. Magnesium is excreted from the body in the form of faeces, sweat and urine. Magnesium is a cofactor of all the enzymes involved in phosphate transfer reaction that utilise ATP and other nucleotide triphosphate as substrate.

Magnesium acts as a inhibitor for myosin ATP but stimulates actomyosin activity in muscle contraction. An increased concentration of magnesium in E.C. fluid causes depression of CNS. It also depresses the skeletal muscles. When the concentration of magnesium in E.C. fluid is abnormally low, it leads to increased acetylcholine release resulting in muscle excitability producing tetany. High concentration of magnesium greater than 15 m Eq/L produces cardiac arrest in diastole.

Magnesium deficiency can occur in acute diarrhoea and steatorrhoea or chronic alcoholism. Deficiency of Mg leads to nervousness, retarded growth and irregularity of heart beat.

Magnesium plays equally important role in plant kingdom. It helps in the synthesis of protein containing lipid substance, an important constituent of protein. 5 - 6 % by weight of magnesium is present in chlorophyll. The single atom of Mg is covalently bonded inside the porphyrin ring of plant chlorophyll and in conjugation with light energy it produces green colour. This green plant pigment chlorophyll undergoes photosynthesis.

Chlorophyll



Sunlight

Mg plays a key role in metabolic processes like respiration²⁻⁵ activating enzymes like phosphorylase, hexokinase and dehydrogenase. Magnesium ions play a crucial

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role in protein synthesis by binding the microsomal particles. Deficiency of magnesium in plants result in intervenial chlorosis of leaves leading to defoliation and development of anthocyanin pigment with dead spots. In nature, it is present in low concentration as magnesium silicates, which releases available magnesium on weathering to plants.

Experimental

About 0.1 mole of metal chelate[Mg (8HQ)₂·2H₂O] was dissolved in 50 ml ethanol and treated with 0.1 mole of secondary ligand L (L= Benzil, benzoin and benzoin oxime) dissolved in about 50 ml. of absolute alcohol. The resulting solution was then refluxed on a steam bath for

about 2 hours. A clear solution was obtained. On cooling the solution the adduct separated. It was filtered, washed with 95% ethanol and dried in a desiccator over CaCl₂

Physical Properties

The mixed ligand complexes of Mg (II) were either white or cream coloured. They were highly soluble in DMF, but only slightly in methanol and ethanol. The DMF solution of these complexes showed negligible electrical conductivity. The complexes were quite stable in air but when kept for long in open air, they lost lustre and crystal packing. The results of elemental analysis, solubility in different solvents and the quantitative electrical conductance value of complexes are listed in Table-I.

Table - 1
Results of Elemental Analysis and Qualitative value of solubility and
Eletrical conductance data of complexes

Complex	Mg (Cal.)	C Found (Cal.)	H Found (Cal.)	N Found (Cal.)	Qualitative Data of Solubility				Molar electrical Conductance value (λ_{α}) ohm ⁻¹ mol ⁻¹ cm ²
	Found (Cal.)	Found (Cal.)	Found (Cal.)	Found (Cal.)	Methanol	Ethanol	Dioxan	DMF	
Mg(8HQ) ₂ ·2H ₂ O	06.94 (06.90)	62.24 (62.07)	04.89 (04.60)	08.22 (08.05)	S	S	FS	HS	10
Mg(8HQ) ₂ .bzI	04.34 (04.58)	73.34 (73.28)	04.63 (04.58)	05.47 (05.34)	S	S	FS	HS	3
Mg(8HQ) ₂ .bnzn	04.26 (04.56)	73.09 (73.00)	04.90 (04.94)	05.39 (05.32)	Sts	Sts	FS	HS	4
Mg(8HQ) ₂ .benox	04.57 (04.44)	70.67 (70.98)	04.89 (04.99)	07.49 (07.76)	S	S	FS	HS	3

S = Soluble

FS = Fairly Soluble

HS = Highly Soluble

Sts = Slightly Soluble

Results and Discussion

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.

The IR spectra of complexes of 8-hydroxyquinoline have been investigated widely⁶⁻¹². Hill and Curran¹² reported the i.r. spectra of 8-hydroxyquinoline and its metal complexes mode of bonding of 8HQ. The free ligand (8-HQ) 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

Table -2
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
$\text{Mg}(\text{8HQ})_2 \cdot 2\text{H}_2\text{O}$	2950-2690	—	1585(1590)	1240(1100)	790, 742	675, 625, 580
$\text{Mg}(\text{8HQ})_2 \cdot \text{bzI}$	—	1668	1575	1240	790, 755, 740	675, 650, 625, 570, 462
$\text{Mg}(\text{8HQ})_2 \cdot \text{bnzn}$	3300 (3381)	1662 (1678)	1570	1265	785, 760, 741	678, 652, 635, 581, 450
$\text{Mg}(\text{8HQ})_2 \cdot \text{benox}$	—	1655	1578	1245	785, 760, 735	685, 655, 630, 595

sharp as strong band 1590cm^{-1} which is observed at $1585 - 80\text{cm}^{-1}$ indicating coordination of pyridine nitrogen. The $\nu(\text{C}-\text{O})$ phenolic of 8-HQ is observed at 1100cm^{-1} which is raised to higher frequencies by $100 - 250\text{cm}^{-1}$. It has been found that complexes of Mg(II) with 8 - hydro xyquinoline show 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. The benzil complexes show substantial red shift in $\nu(\text{C}=\text{O})$ vibration. The $\nu(\text{C}=\text{O})$ band of benzil at 1747cm^{-1} shifted to lower frequency and observed near $1664 - 1668\text{cm}^{-1}$ indicating the bonding of benzil carboxyl group with metal atom in complexes. The $\nu(\text{C}=\text{O})$ and $\nu(\text{C}-\text{OH})$ of benzoin observed in free ligand at 1678 and 3381cm^{-1} are observed at lower frequencies and observed near $1660 - 1662$ and $3520 - 3300\text{cm}^{-1}$. The red shift indicated the bonding of benzoin ($\text{C}=\text{O}$) and ($\text{C}-\text{OH}$) oxygen to metal atom. The retention of $\nu(\text{OH})$ indicated that (OH) of benzene is not deprotonated and retained in its mix ligand complexes.

Benzil [$\text{C}_6\text{H}_5\text{-CO-CO-C}_6\text{H}_5$] is a diketone and oxygen donor bidentate chelating molecule.

The ligand displays prominent i.r. bands at 3064 , 1668 , 1589 , $1489(\text{w})$, 1446 , 1321 , 1211 , 1170 , $1097(\text{w})$, 873 , 741 , 719 , 686 , 638 and 463cm^{-1} . The strong band at 1668cm^{-1} is assigned to $\nu(\text{C}=\text{O})$ vibration and strong band at 1589 , 1489 , 1446 and 1321 are attributed to phenyl ring skeletal vibration (Fig.IR.1). The phenyl ($\text{C}-\text{H}$) out-of plane bending bands of ligand are observed at 741 and 719cm^{-1} . The i.r. bands at 1211 , 1170 and 1097cm^{-1} are assigned to $\nu(\text{C}-\text{C})$ vibration of $\nu(\text{C}_6\text{H}_5-\text{C})\nu(\text{CO}-\text{CO})$ and phenyl ring $\nu(\text{C}-\text{C})$ band. In complexes only ($\text{C}=\text{O}$) stretching band is affected appreciably and other phenyl ring vibrations are not affected substantially, supporting the coordination of ketonic oxygen in metal mixed ligand complexes (Fig.IR.2).

The benzoin ($\text{C}_6\text{H}_5\text{CO}-\text{CHOH}-\text{C}_6\text{H}_5$) displays $\nu(\text{O}-\text{H})$ vibration as a strong band at 3373cm^{-1} and aliphatic CH stresses at 2928cm^{-1} . The phenyl ring CH stretches of ligand (Fig.IR 3) is observed at 3060 and 3028cm^{-1} . The ketonic $\nu(\text{C}-\text{O})$ band is located at 1678cm^{-1} which is affected on complex formation. The phenyl ring skeletal vibrations are observed in finger print region at 1589 , 1489 , 1448 , 1390 , 1338 , 1265 and

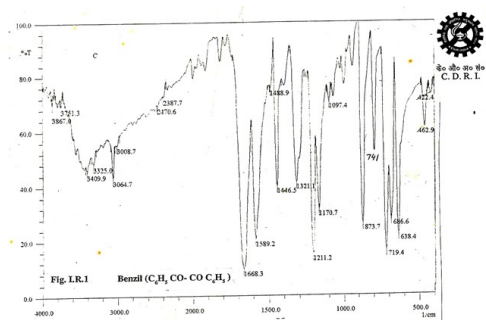
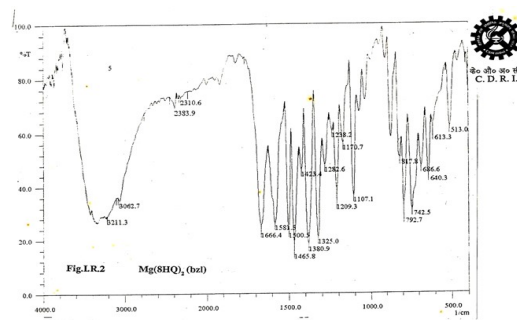
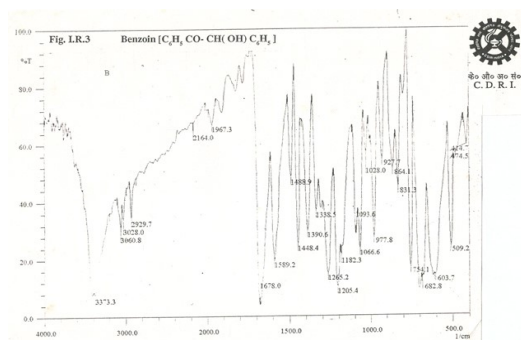
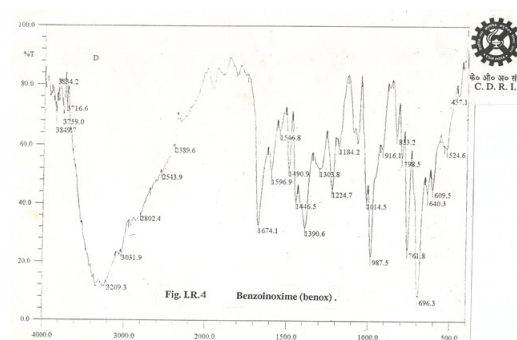
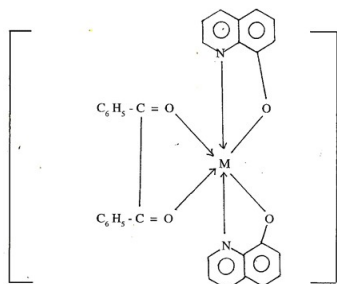
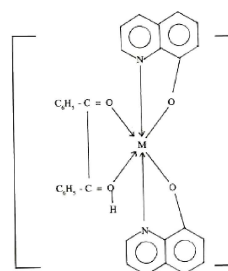
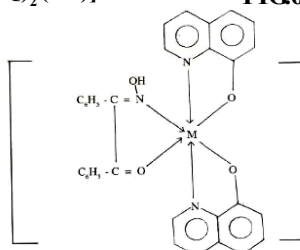
Fig. I.R.1. Benzil ($C_6H_5CO-CO-C_6H_5$)Fig. I.R.2. $Mg(8HQ)_2$ (bzl).Fig. I.R.3. Benzoin [$C_6H_5CO-CH(OH)C_6H_5$].

Fig. I.R.4. Benzoinoxime (benox).

Structure of $M(8HQ)_2$ L Where $M=Mg$, $L=bzl, bnzn, benox$

FIG.5. Structure of $[Mg(8HQ)_2(bzl)]$ FIG.6. Structure of $[Mg(8HQ)_2(bnzn)]$ FIG.7. Structure of $[Mg(8HQ)_2(benox)]$.

1205 cm⁻¹. The hydroxyl $\nu(\text{C}-\text{O})$ vibration is assigned to a band at 1093 cm⁻¹, which shift to higher frequency in complexes by 50-100 cm⁻¹. Thus ligand appears to co-ordinate as oxygen donor bidentate molecule. The i.r. band at 1182, 1066, 1026 and 978 cm⁻¹ are attributed to $\nu(\text{C}-\text{C})$ of (C₆H₅-C), (C-C) and (C₆H₅-CHOH) group. The phenyl ring (C-H) out of plane bending band are observed at 831 and 745 cm⁻¹. The phenyl ring deformation, $\delta(\text{C}-\text{C}=\text{O})$ and $\delta(\text{C}-\text{C}-\text{OH})$ are observed at 682, 603, 509, 474 and 415 cm⁻¹. these i.r. vibrations coupled with other phenyl ring vibration in mixed ligand complexes and some i.r. band are observed as broad band.

Benzoin oxime is good chelating ligand and display $\nu(\text{C}=\text{O})$ band at 1674 cm⁻¹. The $\nu(\text{C}=\text{N})$ and phenyl ring (C-C) band is observed at 1597 cm⁻¹. The $\nu(\text{N}-\text{OH})$ stretch is observed at 3209 cm⁻¹ (Fig. IR-4). 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 complexes. The prominent i.r. bands at 1546, 1491, 1446, 1390, 1224 and 1184 cm⁻¹ are assigned to phenyl ring skeletal vibrations. The (C-H) out-of-plane bending band of ligand is observed at 762 and 798 cm⁻¹. The (C=O) deformation band is located at 698 cm⁻¹ (Fig. IR - 4). The i.r. band at 640, 609, 524 and 457 cm⁻¹ are assigned to ring deformation vibration. The mixed ligand complexes with benzoinoxime shows a number of bands due to benzoinoxime and primary ligand molecules like 8-hydroxyquinoline. The benzoinoxime C=N and $\delta(\text{N}-\text{O})$ bands are observed at lower frequencies in complexes indicating the involvement of ligand carbonyl oxygen and oxime (C=N) nitrogen.

Conclusion and Suggested Structures

Though Mg²⁺ does not have vacant 'd' orbital for accommodation of lone pair of electrons still the outer orbitals are hybridised to form hexa co-ordinated complex. The electrical conductance value measurement of complexes indicated that these complexes are non-ionic. The melting point of complexes were higher than the melting point of pure ligands which supported the bonding of ligand with metal atom.

The i.r. spectral studies of complexes and bonding of ligand molecules in complexes showed the change in intensity and shift in the position of i.r. spectral bands of ligand in complexes from those of free uncoordinated ligand molecules. Thus stoichiometry of metal and ligands in complexes formed the basis for suggesting the structure and I.R. spectral studies decided the bonding sites of ligand molecules. 8-hydroxyquinoline is deprotonated and forms bis chelates [Mg (8HQ)₂ 2H₂O]. The absence of $\nu(\text{OH})$ in complexes suggested the protonation of OH and shift of $\nu(\text{C}-\text{O})$ to higher frequency indicated 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. So on the basis of IR studies and other physicochemical data the probable structure of these complexes are given in Fig.5, 6 and 7.

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