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STUDIES ON BIOLOGICALLY ACTIVE COMPLEXES OF Cu(II) WITH BENZIMIDAZOLE OXIMES

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ABSTRACT:

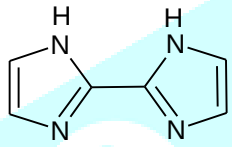
We have study the infra red and electronic spectra in this paper. Widely studies of diffrent carbonic anhydrases [(1)] and alkaline phosphatases[(2)] indicate the presence of a catalytic Cu^{2+} bound to three imidazole residues of enzyme histidines. In the carboxy peptidases [(3)] and in thermolysin [(4)], the critical Cu^{2+} is bound to two imidazoles and a carboxylate group of the enzyme. Inspite of the obvious interest such systems would have few chelating ligands using imidazole rings have been made so far, and none which combine three simple imidazole rings as models for the metal binding sites of carbonic anhydrase.

Keywords- UV, IR, NMR and magnetic susceptibility

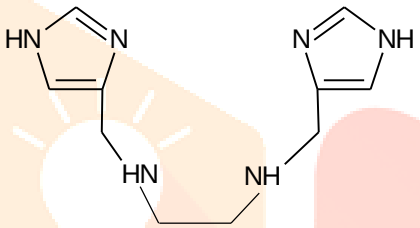
INTRODUCTION:

Widely studies of diffrent carbonic anhydrases[(1)] and alkaline phosphatases[(2)] indicate the presence of a catalytic Cu^{2+} bound to three imidazole residues of enzyme histidines. In the carboxy peptidases [(3)] and in thermolysin[(4)], the critical Cu^{2+} is bound to two imidazoles and a carboxylate group of the enzyme. Inspite of the obvious interest such systems would have few chelating ligands using imidazole rings have been made so far, and none which combine three simple imidazole rings as models for the metal binding sites of carbonic anhydrase.

Holmes et.al [5] have investigated metal binding by 2, 2|–bis (imidazole) (1) while Gruenwedel [6] has studied Cu^{2+} and binding by the tetradentate ligands(2). An important study by Fruton [7] led to the synthesis and metal binding constants for bis [4(5) –imidazolyl] methane(3). Fruton's synthesis from histidine is not adaptable for the preparation of related tris (imidazoles). Thompson et.al [8] have described some metal binding properties of a tris (benzimidazole) ligand system (4). Finally the tris (pyrazolyl) borohydride ligand (5) first reported by Trofimenko [9] but studied by Marks and Ibers [10]. The X–ray studies [11] on carbonic anhydrase show that the three imidazole ligands have distorted tetrahedral coordination to the Cu^{2+}. Molecular models suggested that a similar geometry could be attained with a tris (imidazolyl) methane derivative.



(1)



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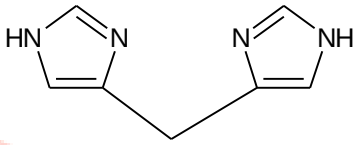
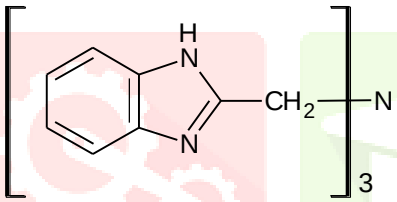


4 - BIM (3)



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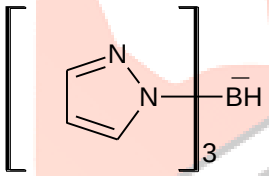


(5)

Benzimidazole complexes of transition metals exhibit interesting spectral and magnetic properties [12–15]. Oxime function located adjacent to another donor atom in an organic molecule, can act as a versatile chelating group and may make the molecule useful in the separation and estimation of metal ions [16–17]. These considerations prompted us to synthesise new polydentate ligands containing both oxime and imidazole functions together. Here we discuss the synthesis and characterization of the complexes of 2–Acetyl–4|–methyl benzimidazole oxime ($ACMBZOXH_2$) or 2–benzoyl–4|–methyl–benzimidazole oxime ($BzMBzOXH_2$) with Cu (II).

EXPERIMENTAL:

Material and Methods: The chemicals used were of AR or equivalent purity, 4−Methyl−2−Acetyl benzimidazole and 4−methyl−2−benzoyl benzimidazole were prepared by the reported methods.[18,19] Their oximes were prepared by refluxing the ketone and hydroxylamine hydrochloride in ethanol in presence of pyridine. The excess of ethanol was removed by distillation or evaporation oximes were purified by recrystallisation from methanol−benzene mixture.

Synthesis of Complexes: To an ethanolic solution of 2−Acetyl benzimidazole oxime (0.005 mol), copper (II) chloride/nitrate/sulphate (0.005 mol) in the same solvent copper (II) acetate in water was added. The resulting mixture was refluxed on a water bath for 2−hour cooled and filtered, washed with ethanol and dried over phosphorous pentoxide.

In the synthesis of 4−methyl−2−benzoyl benzimidazole oxime complexes, the ligand (0.005mol) was dissolved in the minimum quantity of ethanol and copper (II) chloride/acetate (0.005mol) in water was added. The resulting precipitate was refluxed on a water bath for 2−hour cooled, filtered and washed with aqueous ethanol and dried, over phosphorous pentoxide.

Results and Discussion: The elemental analysis of the complexes along with their magnetic moment data are given in table (3.1A). The complexes are insoluble in common organic solvents except in DMF, DMSO and pyridine. The molar conductances of 10^{-3}M DMF−solutions of the complexes were found to be in the range 7−30 mho cm^2 mol^{-1}. The slightly higher values than those of expected for non electrolytes indicate the solvation of the complexes resulting in the displacement of anion from coordination sphere by strong donor DMF molecules. The complexes may be regarded as non electrolytes.

Magnetic Properties:

The copper (II) complexes [Cu ($C_{10}H_{11}N_3O$)] $Cl_2.2H_2O$; [Cu ($C_{10}H_{11}N_3O$)] $SO_4.2H_2O$; [Cu ($C_{15}H_{12}N_3O$)]$Cl.3H_2O$ & [Cu ($C_{10}H_{11}N_3O$)] $(NO_3)_2.2H_2O$ have normal magnetic moments (1.84 − 1.90 B.M.) indicating the presence of one unpaired electron. The slightly higher magnetic moments probably result from the spin−orbit coupling.

The complexes [Cu($C_{10}H_9N_3O$)]H_2O and [Cu($C_{15}H_{11}N_3O$)]H_2O however possess subnormal magnetic moments, possibly due to antiferromagnetic coupling between

neighbouring copper atoms via oximato bridge in a polymeric structure. This type of phenomenon is well known. [22]

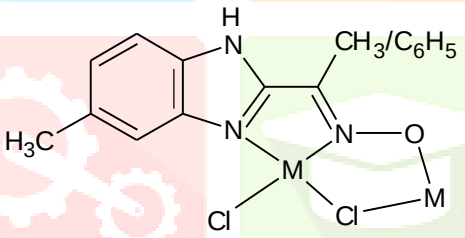
Table (3.1A): Analytical Data of the Complexes

S. No.	Complex	Colour	% Chemical Analysis Found (Calculated)					μ−effective (B.M.)
			C	H	N	M	Anion	
1.	$[Cu(C_{10}H_{11}N_3O)]Cl_2.2H_2O$	Green	33.20(33.37)	4.0(4.17)	11.50(11.68)	17.50(17.67)	19.60(19.74)	1.84
2.	$[Cu(C_{10}H_{11}N_3O)](NO_3)_2.2H_2O$	Dark green	28.90(29.08)	3.50(3.63)	16.80(16.96)	15.30(15.40)	−	1.90
3.	$[Cu(C_{10}H_{11}N_3O)]SO_4.2H_2O$	Green	31.02(31.20)	3.73(3.90)	10.80(10.92)	16.40(16.52)	−	1.88
4.	$[Cu(C_{10}H_9N_3O)]H_2O$	Dark green	44.53(44.68)	3.90(4.09)	15.50(15.64)	23.50(23.66)	−	0.84
5.	$[Cu(C_{15}H_{12}N_3O)]Cl.3H_2O$	Green	44.50(44.60)	4.32(4.46)	10.25(10.40)	15.62(15.74)	8.70(8.80)	1.86
6.	$[Cu(C_{15}H_{11}N_3O)]H_2O$	Green	54.30(54.45)	3.80(3.93)	12.53(12.70)	19.10(19.22)	−	1.44

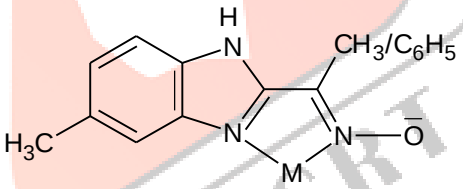
Electronic Spectra:

The electronic spectra of Cu(II) complexes $[Cu(C_{10}H_{11}N_3O)]Cl_2.2H_2O$; $[Cu(C_{10}H_{11}N_3O)](NO_3)_2.2H_2O$; $[Cu(C_{10}H_{11}N_3O)]SO_4.2H_2O$; $[Cu(C_{10}H_9N_3O)].H_2O$ $[Cu(C_{15}H_{12}N_3O)]Cl.3H_2O$ and $[Cu(C_{15}H_{11}N_3O)].H_2O$ were almost similar in pyridine and nujol showed three bands in the regions 31350−26666, ~22220 and 16665 − 14792 cm^{-1}. The comparatively weak low energy band may be assigned as 10Dq band for distorted octahedral configuration [25] of copper (II) corresponding to the transition $^2T_{2g} \leftarrow {}^2E_g$. The band around 22220 cm^{-1} can be attributed to symmetry forbidden ligand → metal charge transfer, from its position and intensity. In some cases it was observed as a shoulder and in other cases it merged with high intensity ligand band occurring in the region 31340−26667 cm^{-1}. In DMF−solution these bands were observed in the regions 31745−27548, 25000−23529 and 14705−12987 cm^{-1}.

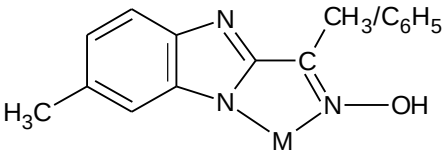
Infrared Spectra: A comparison of the infrared spectra of the ligands and their complexes indicated that the benzimidazole oximes were coordinated to the metal in the present complexes in five different ways (a − e)



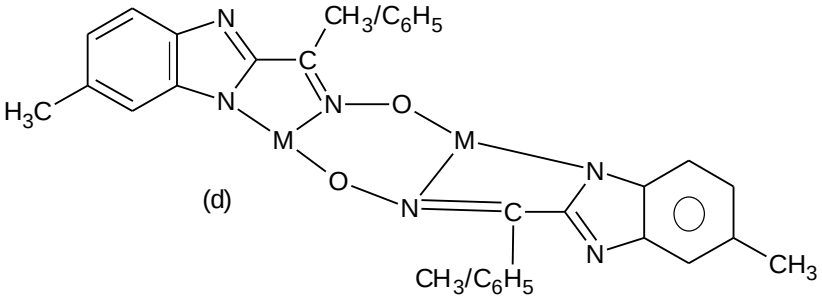
(a)



(b)



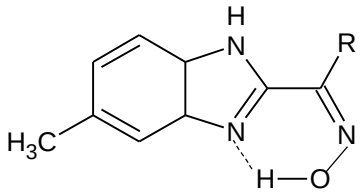
(c)



(d)

In type (a) [Cu $(C_{10}H_{11}N_3O)]$ Cl_2.2H2O; [Cu $(C_{10}H_{11}N_3O)]$ $(NO_3)_2.2H_2O$; [Cu $(C_{10}H_{11}N_3O)]SO_4.2H_2O$ complexes, ligand functions as a neutral bidentate ligand coordinating through the nitrogen of oxime function and the tertiary nitrogen of benzimidazole moiety. Here ν(C=N) (oxime group) is lowered by about 20 cm^{-1} on coordination ν(C=N) (benzimidazole ring) is lowered from its position at 1570−1580 cm^{-1}

in ligands and is probably merged with ν(C=C) band at ~ 1540 cm^{-1}. A band at 3300−3460 cm^{-1} is assigned to ν (OH) of coorinated water. A medium intensity band in the region 3250−3280 cm^{-1} in the ligand is assigned to intramolecularly hydrogen bonded (OH) structure (I, II) of the following type.



(I)

R = CH_3 - (i)

R = C_6H_5 - (ii)

Similar type of hydrogen bonding is reported to be present in pyridine−2−Aldoxime[26].The band due to ν(OH) is expected in these complexes as no deprotonation occurs. In [Cu ($C_{10}H_{11}N_3O$)] $Cl_2.2H_2O$ this band is observed at 3240 and 3280 cm^{-1} respectively. In [Cu($C_{10}H_{11}N_3O$)]$(NO_3)_2$. $2H_2O$ and
[Cu ($C_{10}H_{11}N_3O$)]$SO_4.2H_2O$ this band might have merged with ν(OH) of water. The shift of ν(OH) to higher frequency might be consequence of breaking of the intramolecular hydrogen bonding with the chloride. The band due to pyrrolic NH appears at 3100−3120 cm^{-1} in these complexes.

In type (d) [Cu ($C_{10}H_9N_3O$)] H_2O and [Cu($C_{15}H_{11}N_3O$)] H_2O complexes the ligands function as dibasic tridentate bridging ligands. Bands assignbale to ν (OH) and ν(NH) disappear indicating deprotonation at these sites and replacement of protons by metal. The ligands coordinate to the metal through pyrrolic nitrogen and oxime nitrogen. Tertiary nitrogen of imidazole is free as suggested by the presence of a band at 1580 cm^{-1}.

of ν(C=N), ν(N−O) in the ligands assigned of 935−950 cm^{-1} shifts to higher frequency as a result of coordination through oxime nitrogen.

Presence of nitrate in [Cu ($C_{10}H_{11}N_3O$)]$(NO_3)_2.2H_2O$ is indicated by the bands at 1500, 1395 and 840 cm^{-1}. The difference of 105 cm^{-1} between 1500 and 1395 cm^{-1} bands, the two components of ν_3−band of nitrate suggests unidentate coordination of nitrates [27]. Unidentate coordination of two nitrates leads to octahedral coordination around copper.

Complex [Cu ($C_{10}H_{11}N_3O$)] $SO_4.2H_2O$ shows bands of 1240, 1130, 1040 and 920 cm^{-1} indicating bidentate coordination of sulphate to the metal. These four bands result from ν(S−O) modes of sulphate having C_{2v}−symmetry. The coordination through N− and

O− is further supported by the appearance of new non ligand bands in the region 420−520, [ν(M−N)] and 385−410 cm^{-1} [ν(M−O)] ν(M−Cl) bands are observed as medium intensity bands in the region 280−300 cm^{-1}.

$[Cu(C_{10}H_{11}N_3O)]Cl_2.2H_2O$ showed exothermic mass losses in the temperature ranges 180−350°C (~ 15%) and 200−240°C (~18%) respectively. These mass changes suggest possible interaction of chloride with the acidic hydrogen on the ligand resulting in the elimination of hydrogen chloride.

On further heating, mass loss occurred gradually upto 600°C. This mass loss was accompanied by a strongly exothermic peak on DTA curve. No mass loss occurred beyong 600°C. This must be the result of oxidative decomposition of the ligand leading to the formation of stable metal oxide. The observed masses of the residues suggest the formation of NiO, CuO and CO_3O_4.

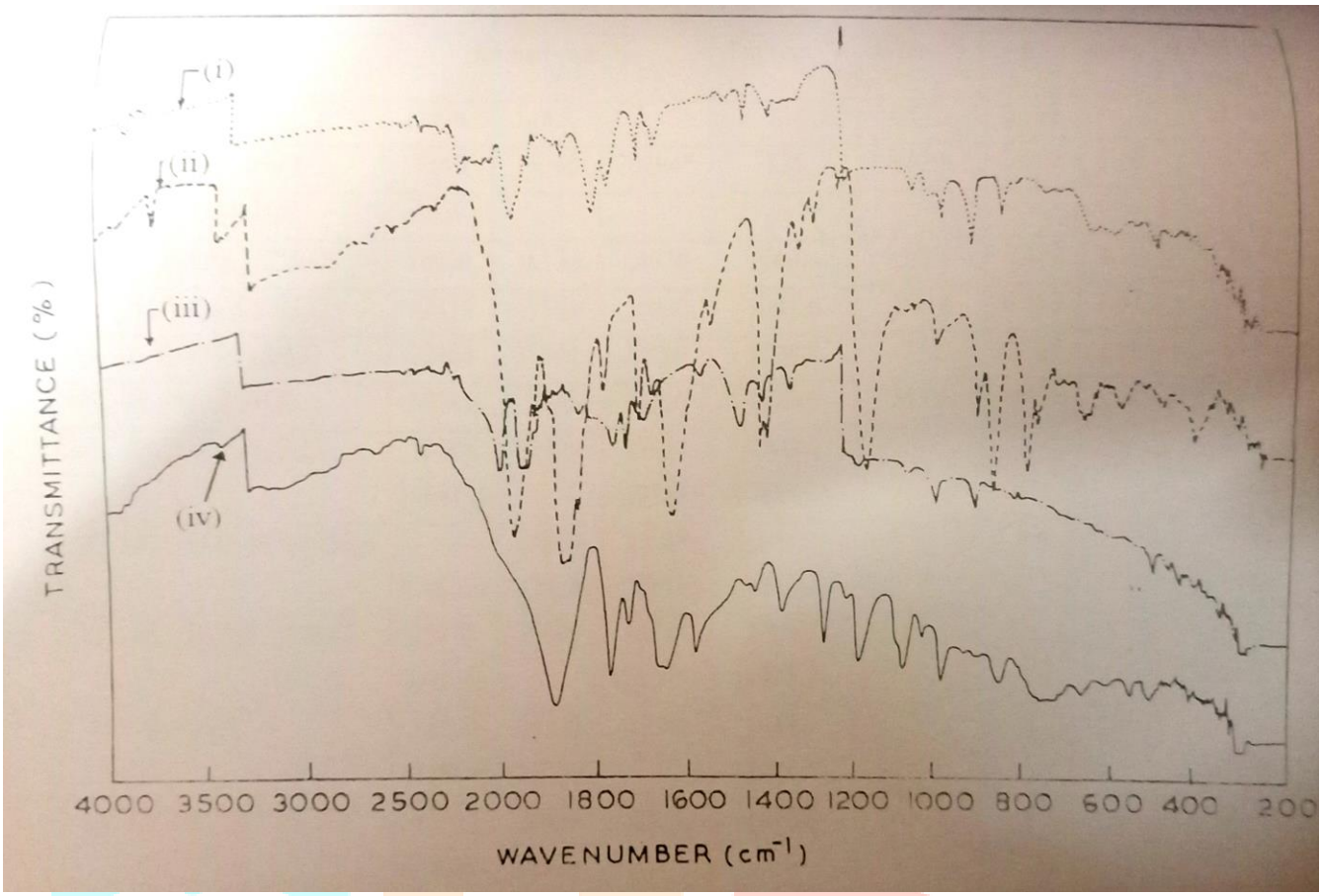
Table (3.2A): Electronic Spectral data and ligand field parameters of the **complexes**

S.No.	Complex	λ−max (cm^{-1})			Dq (cm^{-1})	B (cm^{-1})	β	ν_2/ν_1	LFSE (Kcal mol^{-1})
1.	$[Cu(C_{10}H_{11}N_3O)]Cl_2.2H_2O$	13004 (14815)	23529	27548 (25316)	1300.4 (1481.5)	–	–	–	22.3
2.	$[Cu(C_{10}H_{11}N_3O)](NO_3)_2.2H_2O$	– (18612)	25000 (22026)	31748 (28571)	– (1861.2)	–	–	–	– (31.9)
3.	$[Cu(C_{10}H_{11}N_3O)]SO_4.2H_2O$	13793 (14430)	25000	30769 (28248)	1379.3 (1443.0)	–	–	–	23.6 (24.7)
4.	$[Cu(C_{10}H_9N_3O)]H_2O$	14285 (14815)	23529 (22224)	27548	1428.5 (1481.5)	–	–	–	24.5 (25.4)
5.	$[Cu(C_{15}H_{12}N_3O)]Cl.3H_2O$	14706 (16000)	24691 (22222)	32258	1470.6	–	–	–	25.2 (27.4)
6.	$[Cu(C_{15}H_{11}N_3O)]H_2O$	17391 (15748)	30581 (2777)	–	1739.1 (1574.8)	–	–	–	29.8 (26.9)

* Values in nujol phase are given in parentheses calculated value

Table (3.3A): Infrared Spectral Data (cm^{-1}) of complexes

S. No.	Compounds	ν(OH) water	ν(OH) oxime	ν(NH)	ν(C=N) oxime	ν(C=N) imidazole	ν(C=C)	ν(N−O)	ν(M−N)	ν(M−O)	ν(M−Cl)
Ligands											
1.	4−methyl−2−Acetyl benzimidazole oxime ($MACBZOXH_2$)	–	3280	3160	1625	1570	1520	935	–	–	–
2.	4−methyl−2−benzoyl benzimidazole oxime ($MBZBZOXH_2$)	–	3250	3140	1620	1580	1540	950	–	–	–
Complexes											
1.	$[Cu(C_{10}H_{11}N_3O)]Cl_2.2H_2O$	3460	3280	3120	1595	–	1550	1000	–	–	–
2.	$[Cu(C_{10}H_{11}N_3O)](NO_3)_2.2H_2O$	3350	–	3130	1600	–	1550	995	–	–	–
3.	$[Cu(C_{10}H_{11}N_3O)]SO_4.2H_2O$	3400	–	3120	1600	–	1550	980	–	–	–
4.	$[Cu(C_{10}H_9N_3O)]H_2O$	3350	–	–	1600	1580	1550	995	–	–	–
5.	$[Cu(C_{15}H_{12}N_3O)]Cl.3H_2O$	3380	3290	–	1615	1580	1550	990	–	–	–
6.	$[Cu(C_{15}H_{11}N_3O)]H_2O$	3450	–	–	1610	1580	1540	980	–	–	–


(i)
(ii)
(iii)
(iv)
TRANSMITTANCE (%)
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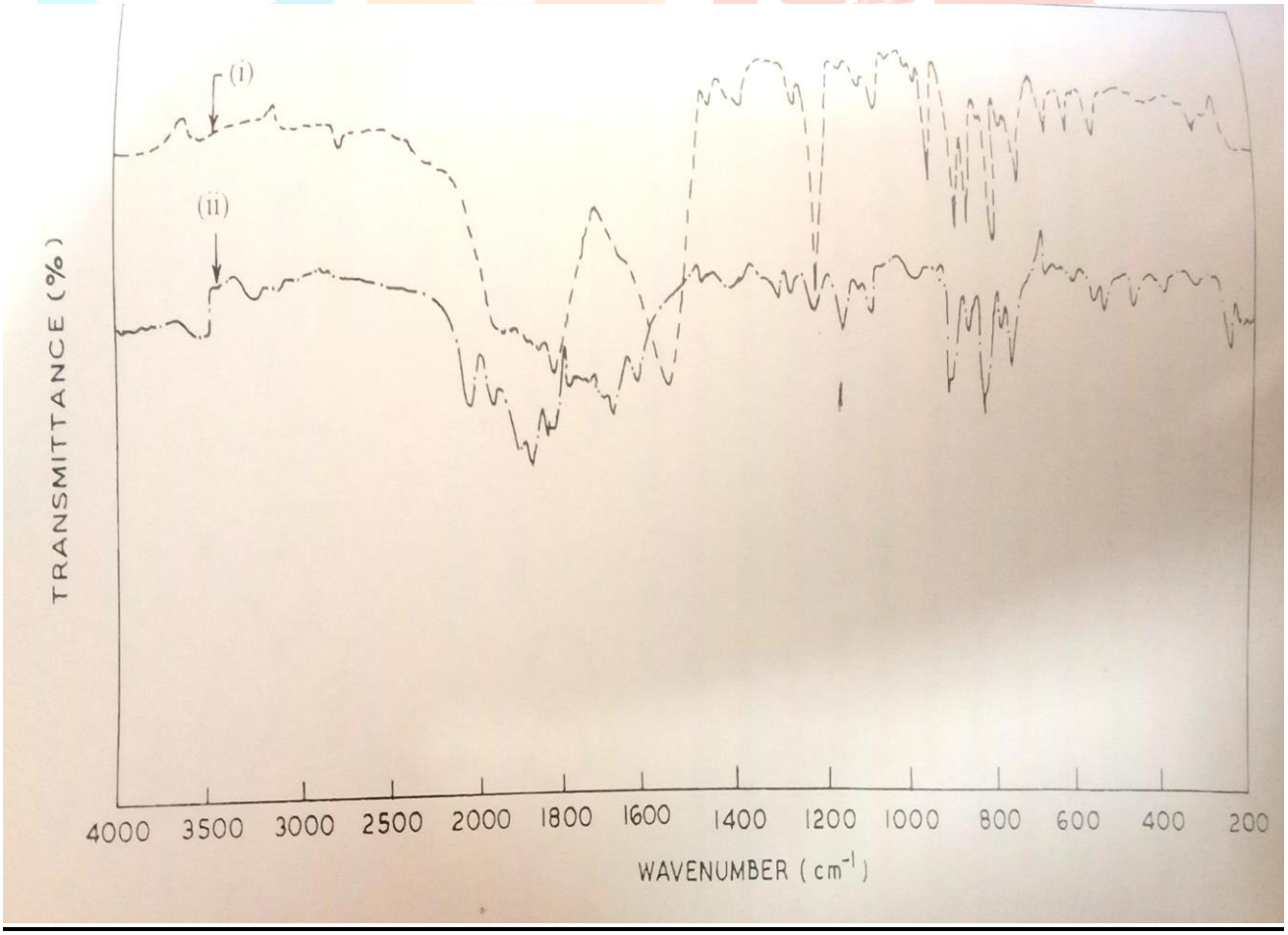
WAVENUMBER (cm⁻¹)


(i)
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TRANSMITTANCE (%)
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WAVENUMBER (cm⁻¹)

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