Ultravoilet and Vibrational Spectral Sudies on Biologically Active Complexes of Cobalt –Ii with Benzimidazole Compound

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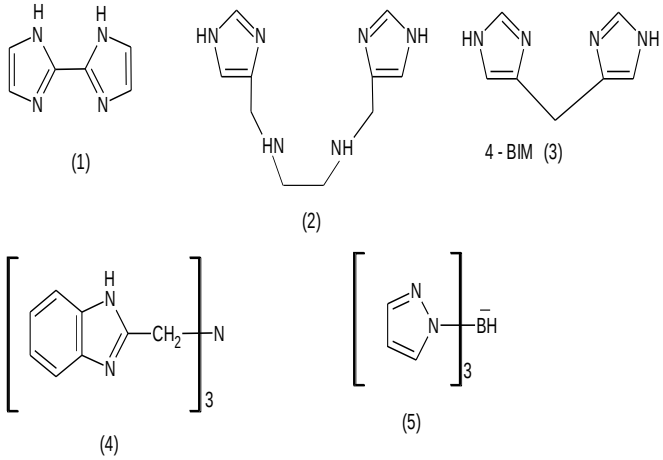
***Abstract*-We have study the vibrational and ultravoilet spectra in this paper. Widely studies of different carbonic anhydrases (1) and alkaline phosphatases (2) indicate the presence of a catalytic Co^{2+} bound to three imidazole residues of enzyme histidines. In the carboxy peptidases (3) and in thermolysin (4), the critical Co^{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: Ultravoilet, Vibrational Spectra, Biological study

INTRODUCTION

Extensive studies of various carbonic anhydrases[(1)] and alkaline phosphatases[(2)] indicate the presence of a catalytic Co^{2+} bound to three imidazole residues of enzyme histidines. In the carboxy peptidases[(3)] and in thermolysin[(4)], the critical Co^{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.

Fruton's[(4)] synthesis from histidine is not adaptable for the preparation of related tris (imidazoles). Thompson et.al[(5)] have described some metal binding properties of a tris (benzimidazole) ligand system(4). Finally the tris (pyrazolyl) borohydride ligand(5) first reported by Trofimenko[(6)] but studied by Marks and Ibers. The X−ray studies[(5)] on carbonic anhydrase show that the three imidazole ligands have distorted tetrahedral coordination to the Co^{2+}. Molecular models suggested that a similar geometry could be attained with a tris (imidazolyl) methane derivate[(7,8)].



Benzimidazole complexes of transition metals exhibit interesting spectral and magnetic properties[(9.10)]. 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[(11)]. 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 Co(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.[(12)] 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), metal (II) chloride/nitrate/sulphate (0.005 mol) in the same solvent or metal(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 (0.005 mol) was dissolved in the minimum quantity of ethanol and metal(II) chloride/acetate (0.005 mol) 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.

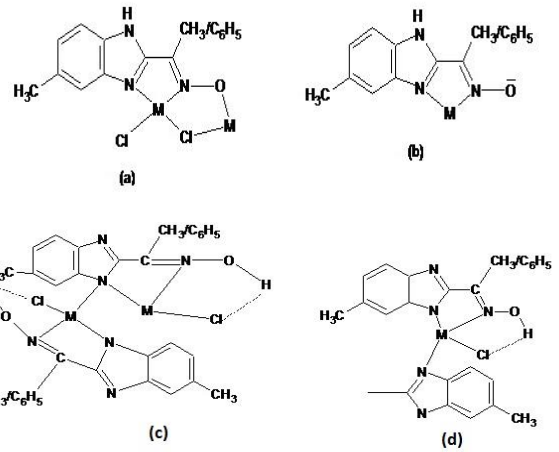
Results and Discussion: The elemental analysis of the complexes along with their magnetic moment data are given in table-1. The complexes are insoluble in common organic solvents except in DMF, DMSO and pyridine. The molar conductances of 10^{-3}M DMF−solutions of the complexes were found to be in the 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 cobalt(II) complexes $[Co(C_{10}H_{10}N_3O)]Cl$ and $[Co(C_{10}H_{10}N_3O)_2]2H_2O$ show moment values of 3.95 and 4.02 B.M. respectively. These are much lower than the values expected for tetrahedral (4.2 − 4.7 B.M.) or octahedral (4.7 − 5.2 B.M.) cobalt(II) complexes. This lowering of magnetic moment may be explained by assuming the co−existence of high spin as well as low spin states of Co(II) ($t_{2g}{}^5e_g{}^2 \rightleftharpoons t_{2g}{}^6 e_g{}^1$) the presence of antiferromagnetism or the polymeric nature of the complexes.[20,21]

The μ−effective value of $[Co(C_{15}H_{12}N_3O)_2].2H_2O$ (4.90 B.M.) agrees very well with the expected value for octahedral cobalt(II).

Ultervoilet Spectra: The electronic spectra of $[Co(C_{10}H_{10}N_3O)]Cl$ showed a multicomponent band at 14815 cm^{-1} which is typical of a tetrahedral cobalt(II) complex. This is assigned to ν_3−band resulting from $^4T_1(P) \leftarrow {}^4A_2$ transition. The band observed at 6896 cm^{-1} may be taken as ν_2 band $^4T_1(F) \leftarrow {}^4A_2$. The spectrum of $[Co(C_{10}H_{10}N_3O)_2]2H_2O$ was quite different from that of $[Co(C_{10}H_{10}N_3O)]Cl$ and showed two bands at 20490 and 7145 cm^{-1}. These are assigned to the transitions $^4T_{1g}(P) \leftarrow {}^4T_{1g}(F)$ and $^4T_{2g} \leftarrow {}^4T_{1g}(F)$ respectively of octahedral Co(II) complex. The ν_2− band, since it involves a two electron transition was not observed. Its position was calculated using konig equation.[13-16] The various ligand field parameters (Dq, B°, β, ν_2/ν_1 and LFSE) have been calculated. The ν_2/ν_1 ratio for $[Co(C_{10}H_{10}N_3O)_2].2H_2O$ is found to be in the range (2.1 −2.2) which is reported for octahedral cobalt(II) complexes.[17-19] Satisfactory electronic spectrum could not be obtained for $[Co(C_{15}H_{12}N_3O)_2].2H_2O$.

Vibrational 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 four different ways
(a − d)



In type (b) $[Co(C_{10}H_{10}N_3O)_2].2H_2O$ and $[Co(C_{15}H_{12}N_3O)_2].2H_2O$ complexes, the ligands behave in a mono basic bidentate manner coordinating through the oxime nitrogen and tertiary imidazole nitrogen. The NOH group is deprotonated as shown by the disappearance of the ligand band at 3250−3280 cm^{-1}. A band at 3360−3450 cm^{-1} is assigned to ν(OH) of coordinated water. The coordination through oxime nitrogen and tertiary nitrogen is suggested from the lowering of ν(C=N) as in type (a) complexes.

In type (c) $[Co(C_{10}H_{10}N_3O)]Cl$ complex the ligand behaves as a monobasic tridentate ligand coordinating through the oxime nitrogen, pyrrole nitrogen and tertiary nitrogen of imidazole moiety thus forming a polymeric complex[19]. N(OH) of oxime function is observed at 3240 cm^{-1} due to hydrogen bonding with chloride. ν(NH) disappears confirming deprotonation and coordination through the nitrogen. The coordination through oxime nitrogen and tertiary nitrogen is suggested by the lowering 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.

CONCLUSION

In conclusion, we have widened a practical and novel procedure for the selective synthesis of cobalt(II) complexes $[Co(C_{10}H_{10}N_3O)]Cl$ and $[Co(C_{10}H_{10}N_3O)_2]2H_2O$ by using infrared and electronic spectra. The present procedure has a several advantage, mild reaction, non harzadous methed, experimental easy and simple workup process, less reaction time to conventional method

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Table-1: Analytical Data of the Complexes

S. No.	Complex	Colour	% Chemical Analysis Found (Calculated)					μ–effective (B.M.)
			C	H	N	M	Anion	
1.	$[Co(C_{10}H_{10}N_3O)]Cl$	Red	42.38 (4.48)	3.40 (3.54)	14.70 (14.87)	20.72 (20.86)	2.41 (2.56)	3.95
2.	$[Co(C_{10}H_{10}N_3O)_2]2H_2O$	Pink	50.80 (50.96)	4.90 (5.09)	17.70 (17.83)	12.40(12.51)	–	4.02
3.	$[Co(C_{15}H_{12}N_3O)_2]2H_2O$	Red	64.30 (64.40)	4.88 (5.0)	14.90 (15.02)	10.40(10.54)	–	4.90

Table-2: 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.	$[Co(C_{10}H_{10}N_3O)]Cl$	6898	14820		404	645.3	0.662	–	13.8
2.	$[Co(C_{10}H_{10}N_3O)_2]2H_2O$	7145	15380	20494*	825	963.6	0.992	2.15	18.9
3.	$[Co(C_{15}H_{12}N_3O)_2]2H_2O$	7830			–	–	–	–	–

Table-3: 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(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											
3.	$[Co(C_{10}H_{10}N_3O)]Cl$	–	3240	–	1600	–	1545	1010	445	–	300
4.	$[Co(C_{10}H_{10}N_3O)_2]2H_2O$	3420	–	3200	1600	–	1540	980	420	385	–
5.	$[Co(C_{15}H_{12}N_3O)_2]2H_2O$	3400	–	3200	1600	–	1550	1020	–	–	–

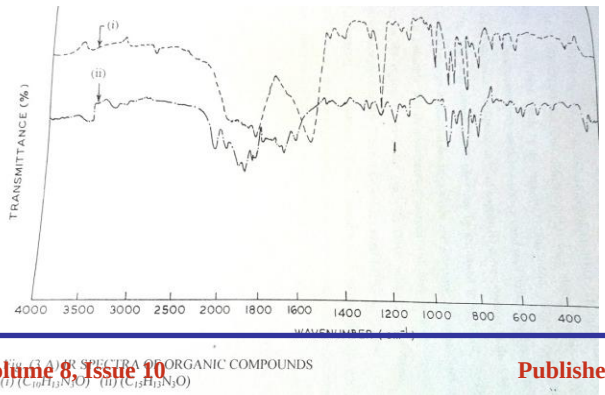

Fig (3.1 A) IR SPECTRA OF ORGANIC COMPOUNDS
(i) $(C_{10}H_{11}N_3O)$ (ii) $(C_{15}H_{13}N_3O)$

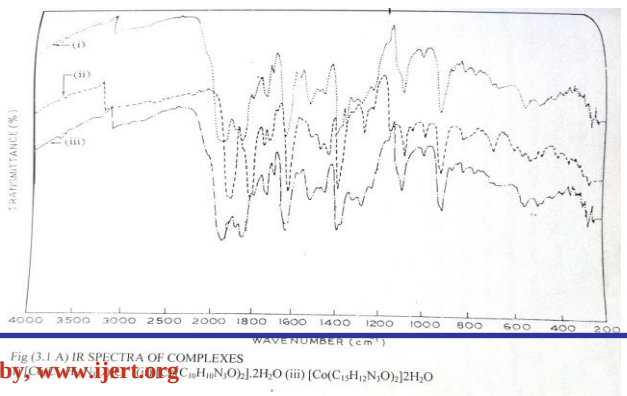

Fig (3.1 A) IR SPECTRA OF COMPLEXES
(i) $[Co(C_{10}H_{10}N_3O)]Cl$ (ii) $[Co(C_{10}H_{10}N_3O)_2].2H_2O$ (iii) $[Co(C_{15}H_{12}N_3O)_2]2H_2O$