



INTERNATIONAL JOURNAL OF CREATIVE RESEARCH THOUGHTS (IJCRT)

An International Open Access, Peer-reviewed, Refereed Journal

ELECTRONIC, IR AND THERMAL STUDIES ON BIOLOGICALLY ACTIVE COMPLEX OF Ni (II) WITH BENZIMIDAZOLE OXIMES

¹Dr. Ishwar Singh, ²Mohit Tyagi, ³Dr. Pradeep Kumar, ⁴Prashant Kumar

^{1,3,4}. Department of Applied Science, Mangalmay Institute of Engineering and Technology, Greater Noida, (U P) 201306

²Greater Noida Institute of Technology, Greater Noida. (U P) 201306

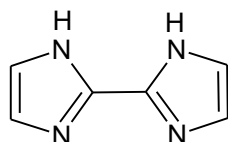
ABSTRACT: The Electronic, IR and Thermal studies on biologically active complexes of Ni (II) has been reported. The bands observed and discussed assuming the molecule under C_s point group symmetry. The IR spectral studies of this compound have been discussed. The thermal study of complex compound has been calculated. The electronic study in nujol phase has been calculated.

Keywords: Electronic Spectra, IR, Thermal studies, EPR and Benzimidazole oxime.

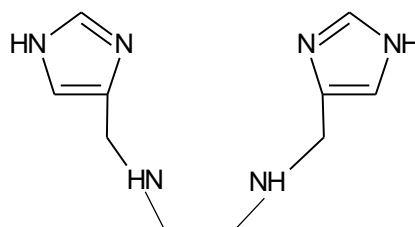
INTRODUCTION:

Extensive studies of various carbonic anhydrases ⁽¹⁾ and alkaline phosphatases ⁽²⁾ indicate the presence of a catalytic Zn^{2+} bound to three imidazole residues of enzyme histidines. In the carboxy peptidases ⁽³⁾ and in thermolysin ⁽⁴⁾, the critical Zn^{2+} is bound to two imidazoles and a carboxylate group of the enzyme. In spite 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.

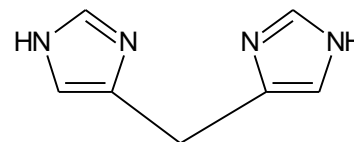
Holmes et.al ⁽⁵⁾ have investigated metal binding by 2, 2'-bis (imidazole) (1) while Gruenwedel ⁽⁶⁾ has studied Zn^{2+} and Co^{2+} binding by the tetradentate ligands (2). An important study by Fruton ⁽⁷⁾ led to the synthesis and metal binding constants for bis [4(5) -imidazolyl] methane (3). Fruton's synthesis from histidine is not adaptable for the preparation of related tris (imidazoles). Thompson et.al ⁽⁸⁾ has 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 Zn^{2+} . Molecular models suggested that a similar geometry could be attained with a tris (imidazolyl) methane derivative.



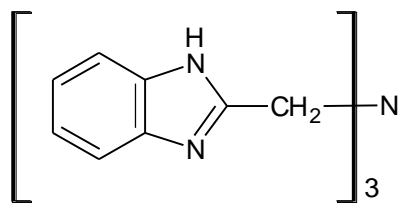
(1)



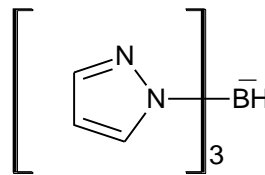
(2)



4 - BIM (3)



(4)



(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 (ACMBZOXH₂) or 2-benzoyl-4-methyl-benzimidazole oxime (BzMBzOXH₂) with Ni (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), Ni (II) chloride/nitrate/sulphate (0.005 mol) in the same solvent or Ni (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 Ni (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-1. The complexes are insoluble in common organic solvents except in DMF, DMSO and pyridine. The molar conductances of 10⁻³M DMF-solutions of the complexes were found to be in the range 7-30 mho cm² 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 nickel (II) complexes [Ni (C₁₀H₁₁N₃O)]Cl₂.2H₂O; [Ni(C₁₀H₁₀N₃O)₂].2H₂O; [Ni(C₁₅H₁₂N₃O)]Cl.3H₂O; [Ni(C₁₅H₁₁N₃O)].3H₂O possess μ-effective value in the range (2.94 – 3.10 B.M.) which are suggestive of octahedral geometry.

Table-1 : Analytical Data of the Complexes

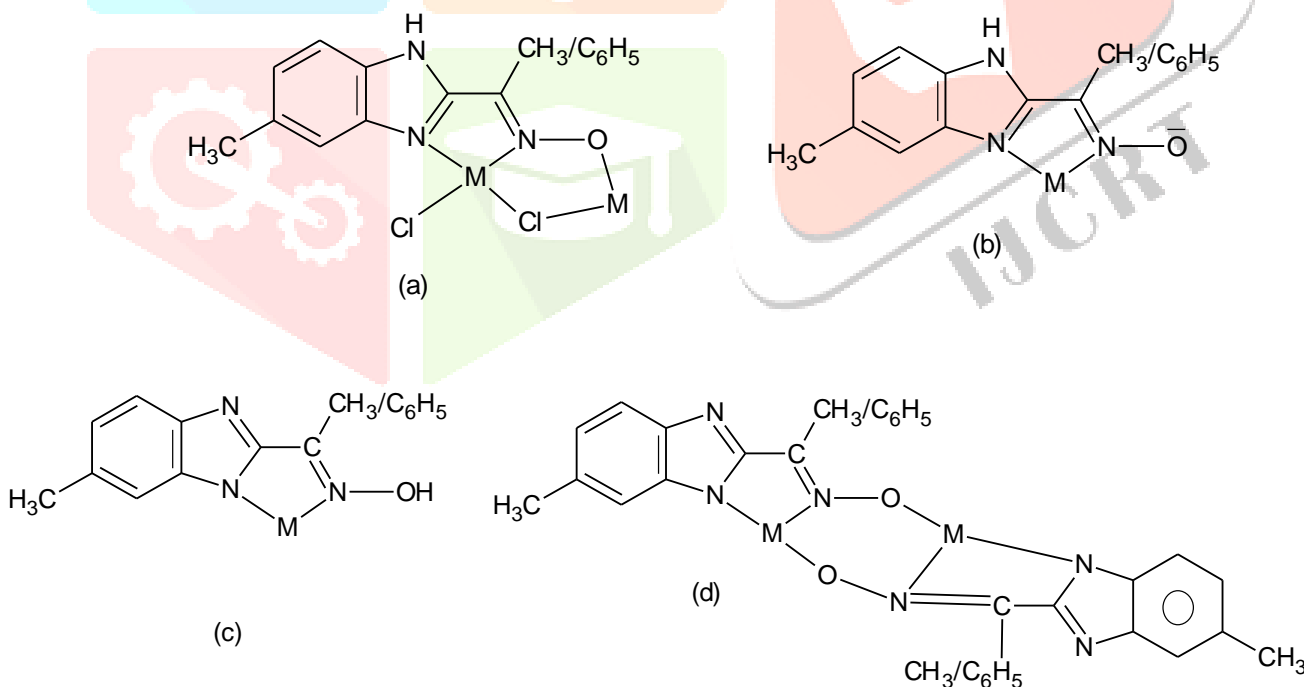
S. No.	Complex	colour	% Chemical Analysis Found (Calculated)					μ-effective (B.M.)
			C	H	N	M	Anion	
1	[Ni(C ₁₀ H ₁₁ N ₃ O)]Cl ₂ .2H ₂ O	Yellowish green	33.70(33.83)	4.10(4.22)	11.70(11.84)	16.40(16.55)	19.90(20.01)	3.04

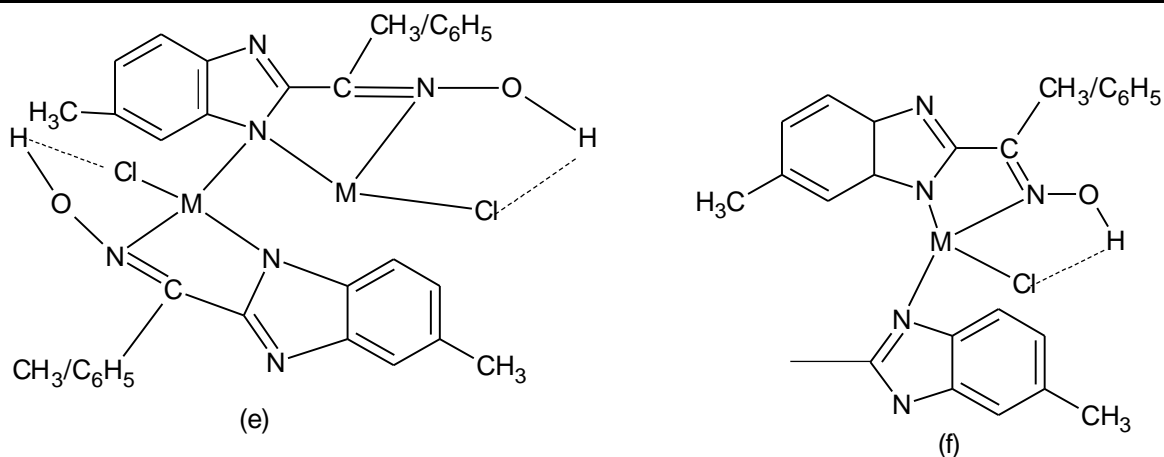
2.	[Ni(C ₁₀ H ₁₀ N ₃ O) ₂]Cl.3H ₂ O	Green	50.82(50.98)	4.90(5.09)	17.70(17.84)	12.30(12.47)	–	2.94
3.	[Ni(C ₁₅ H ₁₂ N ₃ O)]Cl.3H ₂ O	Greening yellow	45.03(45.20)	4.40(4.52)	10.40(10.54)	14.60(14.74)	8.72(8.91)	2.96
4.	[Ni(C ₁₅ H ₁₁ N ₃ O)].3H ₂ O	Yellowish green	49.60(49.76)	4.52(4.69)	11.50(11.61)	16.10(16.23)	–	3.10

Electronic Spectra:

The electronic spectra of Ni (II) complexes [Ni (C₁₀H₁₁N₃O)]Cl₂.2H₂O; [Ni(C₁₀H₁₀N₃)₂].2H₂O; [Ni(C₁₅H₁₂N₃O)]Cl.3H₂O; [Ni(C₁₅H₁₁N₃O)].3H₂O showed three bands in the regions 25920–24692, 17391–16130 and 10638–10205 cm⁻¹. these are assigned to ν₃[³T_{1g}(P) ← ³A_{2g}]; ν₂[³T_{1g}(F) ← ³A_{2g}] and ν₁[³T_{2g} ← ³A_{2g}] transitions respectively, expected for nickel(II) octahedral complexes. One of these the low energy band (ν₁) has been equated to 10Dq. The various spectral parameters have been calculated table-2. The ratio ν₂/ν₁ is close to that required for octahedral geometry⁽²⁴⁾.

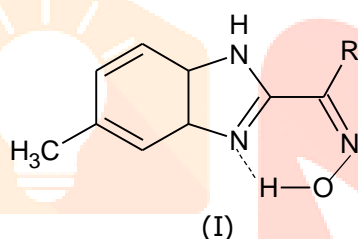
Infrared Spectra: A comparison of the infrared spectra of the ligands and their complexes indicated that the benzimidazole oximes were coordinated to the metal in the present complexes in five different ways (a – d)





In type (a) $[\text{Ni}(\text{C}_{10}\text{H}_{11}\text{N}_3\text{O})]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ and $[\text{Ni}(\text{C}_{10}\text{H}_{11}\text{N}_3\text{O})](\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$;

$[\text{Ni}(\text{C}_{10}\text{H}_{11}\text{N}_3\text{O})]\text{SO}_4 \cdot 2\text{H}_2\text{O}$ complexes, ligand functions as a neutral bidentate ligand coordinating through the nitrogen of oxime function and the tertiary nitrogen of benzimidazole moiety. Here $\nu(\text{C}=\text{N})$ (oxime group) is lowered by about 20 cm^{-1} on coordination $\nu(\text{C}=\text{N})$ (benzimidazole ring) is lowered from its position at $1570\text{--}1580\text{ cm}^{-1}$ in ligands and is probably merged with $\nu(\text{C}=\text{C})$ band at $\sim 1540\text{ cm}^{-1}$. A band at $3300\text{--}3460\text{ cm}^{-1}$ is assigned to $\nu(\text{OH})$ of coordinated water. A medium intensity band in the region $3250\text{--}3280\text{ cm}^{-1}$ in the ligand is assigned to intramolecularly hydrogen bonded (OH) structure (I, II) of the following type.



$\text{R} = \text{CH}_3$ - (i)

$\text{R} = \text{C}_6\text{H}_5$ - (ii)

Similar type of hydrogen bonding is reported to be present in pyridine-2- Aldoxime⁽²⁶⁾. The band due to $\nu(\text{OH})$ is expected in these complexes as no deprotonation occurs. In $[\text{Ni}(\text{C}_{10}\text{H}_{11}\text{N}_3\text{O})]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ this band is observed at 3240 cm^{-1} respectively. The shift of $\nu(\text{OH})$ to higher frequency might be consequence of breaking of the intramolecular hydrogen bonding with the chloride. The band due to pyrrolic NH appears at $3100\text{--}3120\text{ cm}^{-1}$ in these complexes (table-3).

In type $[\text{Ni}(\text{C}_{10}\text{H}_{10}\text{N}_3\text{O}_2)] \cdot 2\text{H}_2\text{O}$ and $[\text{Ni}(\text{C}_{15}\text{H}_{12}\text{N}_3\text{O})]\text{Cl} \cdot 3\text{H}_2\text{O}$ the ligands function in a monobasic bidentate manner, $\nu(\text{OH})$ of oxime function is observed at 3240 cm^{-1} due to hydrogen bonding with chloride/tertiary nitrogen of benzimidazole moiety. $\text{N}(\text{NH})$ disappears confirming deprotonation and coordination through the pyrrolic nitrogen $\nu(\text{C}=\text{N})$ (imidazole) appears at the same frequency as in ligands.

In type $[\text{Ni}(\text{C}_{15}\text{H}_{11}\text{N}_3\text{O})] \cdot 3\text{H}_2\text{O}$; complexes the ligands function as dibasic tridentate bridging ligands. Bands assignable to $\nu(\text{OH})$ and $\nu(\text{NH})$ 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} .

EPR Spectra: EPR-spectra of the $[\text{Ni}(\text{C}_{15}\text{H}_{12}\text{N}_3\text{O})]\text{Cl} \cdot 3\text{H}_2\text{O}$ and $[\text{Ni}(\text{C}_{10}\text{H}_{10}\text{N}_3\text{O}_2)] \cdot 2\text{H}_2\text{O}$ were recorded in polycrystalline samples and in DMF solution, both at room temperature (RT) and liquid nitrogen temperature (LNT). The EPR-parameters computed from spectra are indicative of octahedral or square planar geometry for the complexes.

Thermal Studies: $[\text{Ni}(\text{C}_{10}\text{H}_{10}\text{N}_3\text{O}_2)] \cdot 2\text{H}_2\text{O}$; and $[\text{Ni}(\text{C}_{15}\text{H}_{12}\text{N}_3\text{O})]\text{Cl} \cdot 3\text{H}_2\text{O}$ were examined complexes at high temperature underwent endothermic mass loss in the temperature ranges, $120\text{--}170$; $160\text{--}180$ and $150\text{--}170^\circ\text{C}$ respectively. The mass losses (8.5%), 10.0% and 8.0% respectively agree well with the loss of coordinated water (table-4).

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	v ₂ /v ₁	LFSE (Kcal mol ⁻¹)
1	[Ni(C ₁₀ H ₁₁ N ₃ O)]Cl ₂ .2H ₂ O	10604	16130	24936	1060.4	663.7	0.637	1.59	36.4
2.	[Ni(C ₁₀ H ₁₀ N ₃ O) ₂]Cl.3H ₂ O	10416	17361	25000	1041.6	740.8	0.712	1.67	35.7
3.	[Ni(C ₁₅ H ₁₂ N ₃ O)]Cl.3H ₂ O	10363	17391	24690	1036.7	732	0.702	1.69	35.5
4.	[Ni(C ₁₅ H ₁₁ N ₃ O)].3H ₂ O	10204	1600	25316	1020.4	713.6	0.685	1.57	34.9

* Values in nujol phase are given in parentheses calculated value

Table -3: Infrared Spectral Data (cm⁻¹) of complexes

Compounds	v(OH) water	v(OH) oxime	v(NH)	v(C=N) oxime	v(C=N) imidazole	v(C=C)	v(N-O)	v(M-N)	v(M-O)	v(M-Cl)
Ligands										
4-methyl-2-Acetylbenzimidazoleoxime (MACBZOXH ₂)	-	3280	3160	1625	1570	1520	935	-	-	-
4-methyl-2-benzoylbenzimidazoleoxime (MBZBZOXH ₂)	-	3250	3140	1620	1580	1540	950	-	-	-
Complexes										
[Ni(C ₁₀ H ₁₁ N ₃ O)]Cl ₂ .2H ₂ O	3460	3240	3100	1610	-	1550	1025	480	410	280
[Ni(C ₁₀ H ₁₀ N ₃ O) ₂].2H ₂ O	3360	3270	-	1600	1575	1535	975	-	-	-
[Ni(C ₁₅ H ₁₂ N ₃ O)]Cl.3H ₂ O	3400	3250	-	1605	1580	1560	1020	-	-	-
[Ni(C ₁₅ H ₁₁ N ₃ O)].3H ₂ O	3450	-	-	1610	1580	1540	1000	-	-	-

Table -4: Thermal analysis data on Ni (II) complex

S.No.	Complexes	Decomposition Temperature °C		Decomposition Product	Weight Loss (%)	
		Initial	Final		Found	Calculated
1	[Ni(C ₁₀ H ₁₀ N ₃ O) ₂].2H ₂ O	320	300	[Ni(C ₁₀ H ₁₀ N ₃ O) ₂]	7.08	7.64
		310	440	[NiO]	15.10	15.87

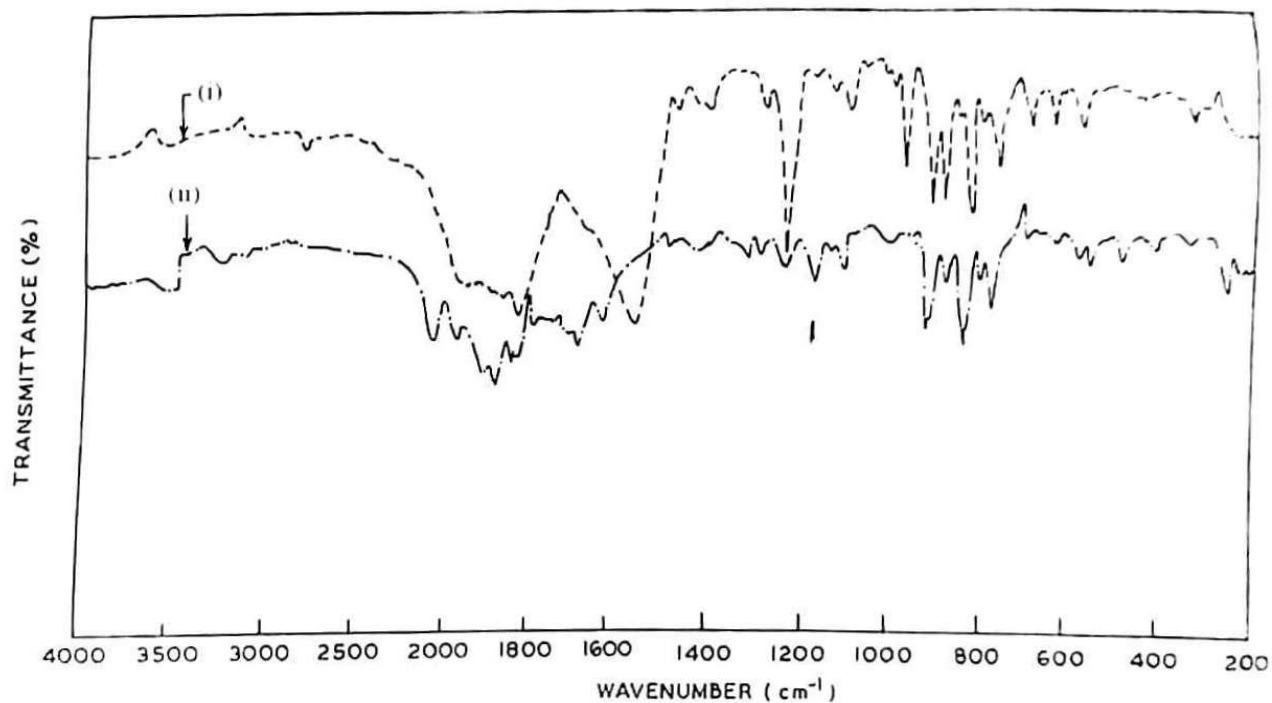


Fig -1 : IR SPECTRA OF ORGANIC COMPOUNDS

(i) $C_{10}H_{13}N_3O$ (ii) $C_{15}H_{13}N_3O$

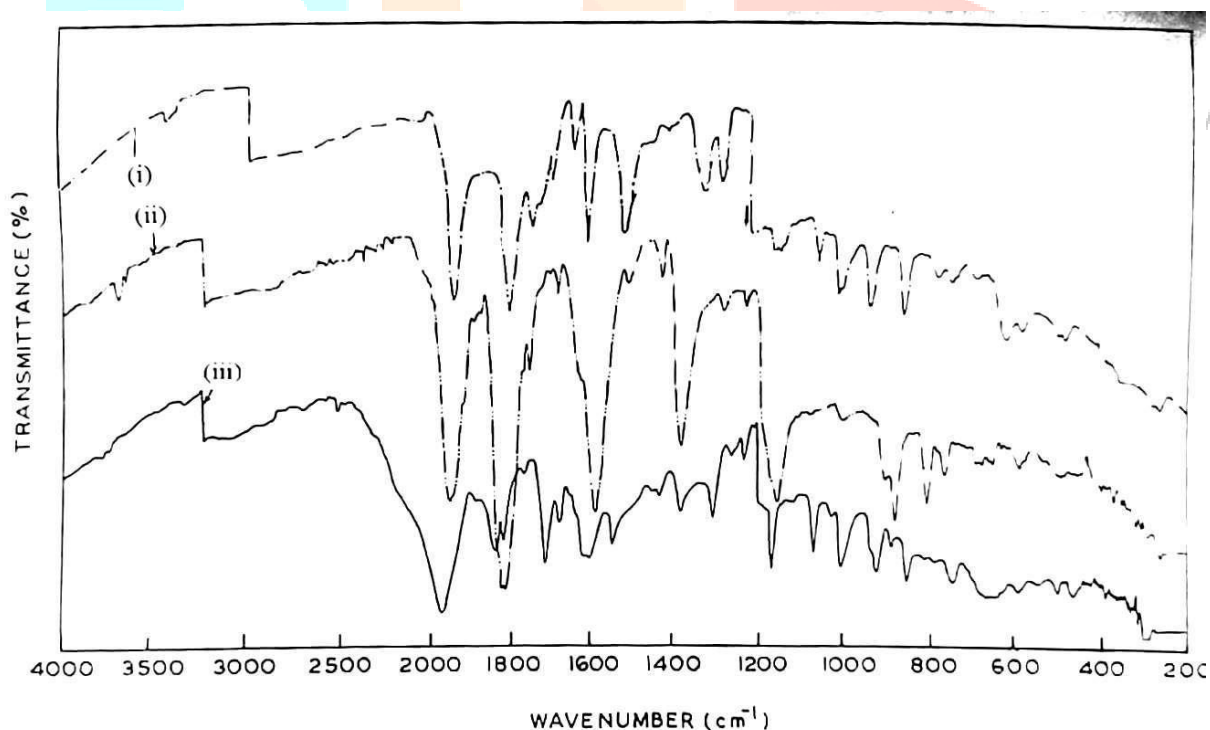


Fig. -2 IR SPECTRA OF COMPLEXES

(i) $[Ni(C_{10}H_{11}N_3O)]Cl_2 \cdot 2H_2O$ (ii) $[Ni(C_{10}H_{11}N_3O)_2] \cdot 2H_2O$ (iii) $[Ni(C_{15}H_{12}N_3O)]Cl \cdot 3H_2O$

REFERENCES

1. J.E. Coleman, *Inorg. Biochem*; 1 (1973) 488.
2. Ishwar, Pradeep and Prashant, *IJCRT* 9(8) 698 (2021)
3. R. Breslow and D.L. Wernick, *Proc. Natl. Acad. Sci. U.S.A.* 74 (1977) 1303.
4. W.R. Kester and B.W. Mathews, *J. Mol. Chem.* 252 (1977) 7704.
5. F. Holmes, K.M. Jones and E.G. Torrible, *J. Chem. Soc.* 4790 (1961).
6. D.W. Gruenwedel, *Inorg. Chem.* 7 (1968) 495.
7. C.N.C. Drey and J.S. Fruton, *Biochemistry* 4 (1965) 1; 4 (1965) 1258.
8. C.K.Thompson, B.S.Ramaswamy & E.A.Seymour, *Can. J.Chem.* 55(1977) 877.
9. S. Trofimenko, *Chem. Rev.* 72 (1972) 497 *Acc. Chem. Res.* 4 (1971) 17.
10. J.S.Thompson,T.J.Marks & J.A.Ibers, *Proc.Natl.Acad.Sci. USA* 74(1977) 3114.
11. K.K. Kanan, B. Nostrand et.al, *Proc. Natl. Acad. Sci. U.S.A.* 72 (1975) 51.
12. M. Goodgame, & F.A. Cotton, *J. Am. Chem. Soc.*; 84 (1964) 1543.
13. N. Shashikala, E.G. Leelamani and G.K.N. Reddy, *Ind. J. Chem.* 21A (1982) 743; *J. Ind. Chem. Soc.* 62 (1985) 928.
14. P.K. Nath, N.C. Mishra, V.Chakravorty & K.C. Dash, *Polyhedron* 6 (1987) 455.
15. L.D. Prabhakar, K.M.M.S. Prakash & M.C. Chowdhary, *Ind. J. Chem.* 26A (1987) 142.
16. C. Keshavolu, R.S. Naidu & R.R. Naidu, *Polyhedron* 4 (1985) 761.
17. Madan Mohan & Munesh Kumar, *Polyhedron* 4 (1985) 1929.
18. B. Egneus, *Talanta* 19 (1972) 387.
19. G.W.H. Cheeseman, *J. Chem. Soc.* (1964) 1387.
20. A. Bistrzycki & G. Przeworski, *Berft. Chem. Ges.* 45 (1912) 3492.
21. D.L. Williams, D.W. Smith, & R.C. Stanfer, *Inorg. Chem.* 6 (1937) 590.
22. D. Datta, S. Baral, & A. Chakravorty, *Ind. J. Chem.*; 16A (1978) 709.
23. E. Konig, *Structure and Bonding*, Vol. 9, Springer, Verlag, Berlin, 1971, 175.
24. A.B.P. Lever, *Inorganic Electronic Spectroscopy*, Elsevier, New York (1968).
25. R.A. Krause, N.B. Colthup & D.H. Busch, *J. Phys. Chem.* 65 (1961) 2216.
26. K. Nakamoto and P.J. Mccarthy, *Spectroscopy and structure of metal chelate compounds*, John Wiley & Sons Inc. New York (1968).
27. S. Chandra, K.B. Pandey and R.P. Singh, *Ind. J. Chem.* 18A (1979) 476.
28. Pradeep, Ishwar and Deepak, *IJCRT* 9(8) 684 (2021)
29. Pradeep, Ishwar, Jyotsna and Deepak, *IJERT ENCADEMS-2020 Conference Proceedings*.