

Synthesis and spectral characterization of Mn(II),Fe(III) and Ni(II) complexes produced from the Template Reaction of Diacetyloxime and 1,2-diaminopropane

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Abstract

A new series of Mn(II) ,Fe(III) and Ni(II) complexes obtained by the template reaction of diacetyloxime and 1.2-diaminopropane with metal ions have been synthesizd and characterized by elemental analysis , IR spectroscopy , u.v –Vis spectroscopy , electrical conductivity and magnetic moment . From the above data , the molecular structure of Mn(II) complexes is tetrahedral , while Fe(III) and Ni(II) complexes were octahedral and square planar structure respectively .

Introduction :-

There is a growing interest in oximes and their coordination compounds caused by their biological activity ⁽¹⁻³⁾. Transition metal complexes of α -dioxime⁽⁴⁻⁷⁾ or vicinal oxime – imine ligands ⁽⁸⁻¹⁰⁾ have revealed several interesting properties related to the ability of the oximato group to coordinate to the metal ion through either the oximino oxygen or the oximino nitrogen atoms .

N.N-ethylene-bis-(isonitrosoacetylacetoneimine)M(II) complex (M=Co(II), Ni(II) and Cu(II)) showed complexes coordinated through both oxygen atoms , both nitrogen atoms or one oxygen and one nitrogen atoms . some interconversion of the isomers was observed ^(11,12)

Experimental:-

Preparation of the metal complexes :

1,2-propylene- bis (diacetyloximeimine) Ni(II) (LNi) :

The ethanolic solution (25 ml) of 1,2- diaminopropane (0.02 mol) was added dropwise to that (25ml) containing diacetyloxime (5.0 g ; 0.04 mol) . The resulting solution was refluxed on a hot plate for 2h . The hot ethanolic solution (25 ml) of Ni (OAc) 2.4H₂O (4.8g ; 0.02 mol) was

added to the reaction mixture . The mixture was refluxed for another 1 h . After cooling the red product was filtered off , washed with EtOH and dried over P₂O₅ (yield = 82%) .

1,2- propylene – bis (diacetyloximeimine) Mn(II) , (HLMnCl) :

This complex was prepared following the method describe above , using diacetyloxime , 1,2- diaminopropane and MnCl₂.2H₂O in the ratio 2:1:1 respectively . The formed yellow complex was filtered off , washed with EtOH and dried over P₂O₅ (yield=86%)

1,2- propylene – bis (diacetyloximeimine) Fe (III) , (LFeCl.H₂O) :

This complex was prepared following the method describe above with the use of FeCl₃.6H₂O instead of MnCl₂.2H₂O. The violet product was filtered off , washed with EtOH and dried over P₂O₅ (yield=80%) . The chemical analyses confirmed the composition inside 0.3% error . Reagent grade chemicals were used .

Physical properties : The IR spectra were measured as Nujol mull using a perkin – Elmer, 681 spectrophotometer (4000-200 cm⁻¹) . Electronic spectra in the region (900-200 nm) were recorded on a perkin – Elmer 550 spectrophotometer . Magnetic susceptibilities were measured at 25C° by the Gouy's method using mercuric titration cyanato cobaltate (II) as a standard . Diamagnetic corrections were estimated from Pascal's constant . The magnetic moments were calculated by $\mu_{eff} = 2.84 \sqrt{XM_{corr.T}}$. Molar conductances were measured with a Bibby conductometer type MCI . The T.L.C of all compounds confirmed their purity .

Results and Discussion

The metal complexes were prepared using a template method . Elemental analyses (Table 1) and spectral data (Table2,3) are compatible with the suggested structures shown in Fig (1)

LNi complex : IR spectrum of this complex (Table 2) (Figure 2) revealed the presence of $\nu(\text{CO})$ at 1652 cm⁻¹ , which is due to the carbonyl group ^(9,10,12) attached to a five – membered chelate ring in the vicinal oxime – imino Ni(II) complexes . This type required the oximato group to be coordinated through the nitrogen atom . The $\nu(\text{NO})$ observed at 1101 cm⁻¹ and 1234 cm⁻¹ produces a NO bond with a larger double bond character . The $\nu(\text{CN})$ (imino) appears at 1550 cm⁻¹ and the band at 1476 cm⁻¹ corresponds to $\nu(\text{CN})$ of N-coordination oximato groups , Which is identical with that reported⁷ for the Ni(II) complexes of camphorquinone dioxime .

The absence of other $\nu(\text{CN})$ bands in this region suggests that , both oximato group have the same N-coordination mode .The magnetic

moment was diamagnetic , indicating a square – planar geometry around the Ni(II) ion¹³ .

The electronic spectrum of this complex (Table 3) (Figuer 3) indicates two intense peaks at 273 nm and 328 nm which is due to the ligand field and charge transfer respectively . The peaks at 380 nm and 555 nm are assigned to (¹A_{1g} – ¹B_{1g}) and (¹A_{1g} – ¹A_{2g}) d-d transitions in square planar geometry ¹⁴ .

[HLMnCl] Complex : IR spectrum of this compex (Table 2) revealed $\nu(\text{CO})$ at 1690 cm^{-1} , this band is located in the $1960\text{-}1670\text{ cm}^{-1}$ region , which was tentatively associated with six – membered chelate ring in the vicival oxime – imine complexes ^(9,10,15) .

The $\nu(\text{OH})$ of the uncoordinated oxime appeared as abroad band at $3450\text{-}3210\text{ cm}^{-1}$, as a result of hydrogen bonding with the chlorine atom .The band at 330 cm^{-1} is assigned to $\nu(\text{MnCl})$ vibration ¹⁵ .

The electronic spectrum (Table 3) exhibits peaks at 440 and 365 nm characteristic of d-d transitions of tetrahedral Mn(II) complex^(14,15) .

The value of molar conductance of this complex in DMF IS $20.0\ \Omega^{-1}\text{ cm}^2\text{ mol}^{-1}$ indicating nonelectrolytic nature ¹⁶ .

[L FeCl(H₂O)] Complex : IR spectrum of this complex is shown in (Table 2) . Vibrational evidence for N-coordination of the oximato groups concerning $\nu(\text{CO})$, $\nu(\text{CN})$) and $\nu(\text{NO})$ are identical with those of Ni(II) complex .

The broad $\nu(\text{OH})$ band at $3600\text{-}3210\text{ cm}^{-1}$ is attributed to the hydrogen bonding of the coordinated water molecule with the oxygen atom of the N- coordinated oximato groups . the $\nu(\text{FeCl})$ band¹⁵ was detected at 352 cm^{-1} .

The electeonc spectrum (Table 3) in CHCl₃ comprised peaks at 290 nm , 410 nm and 570 nm . The peak at 290 nm is due to the ligand field, wherease peaks at 410 nm and 570 nm are assigned to (d-d) transitions which are comparable to those ^(17,18) of the octahedral Fe (acac)₃ (Hacac:actylacetone) whose structure has been determined by X-ray analysis¹⁹ .

Accordingly , an octahedral structure is suggested for this complex . The magnetic moment was 1.71 B-M , indicating monomeric , low spin , Fe (III) complex . The value of molar conductance of this complex in DMF is $35\ \Omega^{-1}\text{ cm}^2\text{ mol}^{-1}$ indicting nonelectrolytic nature ¹⁶ .

Table 1

Results of Elemental Analysis and Physical properties of Metal complexes^a

Empirical Formula	Mwt.	Yield %	M.P.(c°)	Colour	Micro analysis found , (calc.) %			
					C	H	N	Metal
[NiC ₁₃ H ₁₈ O ₄ N ₄]	353	82	230-232 (dec.)	Red	(3.40) 3.66	(0.28) 0.42	(3.96) 3.78	(16.71) 16.23
[MnC ₁₃ H ₁₉ O ₄ N ₄ Cl]	385	86	252-254 (dec.)	Yellow	(3.11) 2.84	(0.26) 0.38	(3.63) 3.24	(14.28) 14.60
[FeC ₁₃ H ₂₀ N ₄ O ₅ Cl]	403	80	241-243 (dec.)	Violet	(2.97) 2.51	(0.24) 0.54	(3.47) 3.14	(13.89) 13.14

(a) (Calc.) : calculated

(dec.) : decomposed

Table(2) IR spectra (cm⁻¹) of metal complexes

Complex	$\nu(\text{OH})$	$\nu(\text{CO})$	$\nu(\text{CN})$ (imine)	$\nu(\text{CN})$ (oxime)	$\nu(\text{NO})$	$\nu(\text{MN})$ (oximo)	$\nu(\text{MN})$ (imine)
[NiL]	-	1652	1550	1476	1224 1101	440	521
[Mn(HL)Cl]	3450-3210	1690	1615	1580	1150	--	650
[Fe(L)Cl(H ₂ O)]	3600-3210	1655	1610	1585	1165	500	602

Table(3) Electronic spectra of metal complexes in CH₃Cl₃ solvent

Complex	λ nm	νcm^{-1}	ϵ_{max} molar ⁻¹ .cm ⁻¹	Electronic transition	Suggested structure
(NiL)	273 328 380 555	36630 30488 26316 18018	1667 1003 800 239	Ligand field Ligand field ¹ A _{1g} → ¹ B _{1g} (d-d) ¹ A _{1g} → ¹ A _{2g} (d-d)	Square – planar
[Mn(HL)Cl]	320 365 440	31250 27397 22727	1217 71 50	Ligand field d-d d-d	Tetrahedral
[Fe(L) Cl (H ₂ O)]	290 410 570	34483 22727 17544	2440 63 49	Ligand field d-d d-d	Octahedral

Table (4) The Molar conductance of the complexes in DMF

Complex	Λ_M (S cm ² mole ⁻¹)
[NiL]	26
[Mn(HL)Cl]	20
[Fe(L)Cl(H ₂ O)]	35

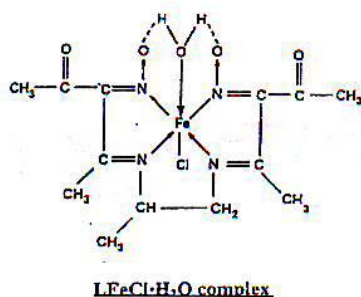
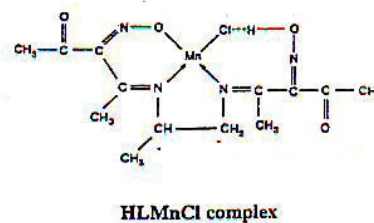
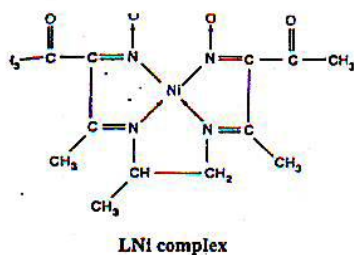


Figure 1

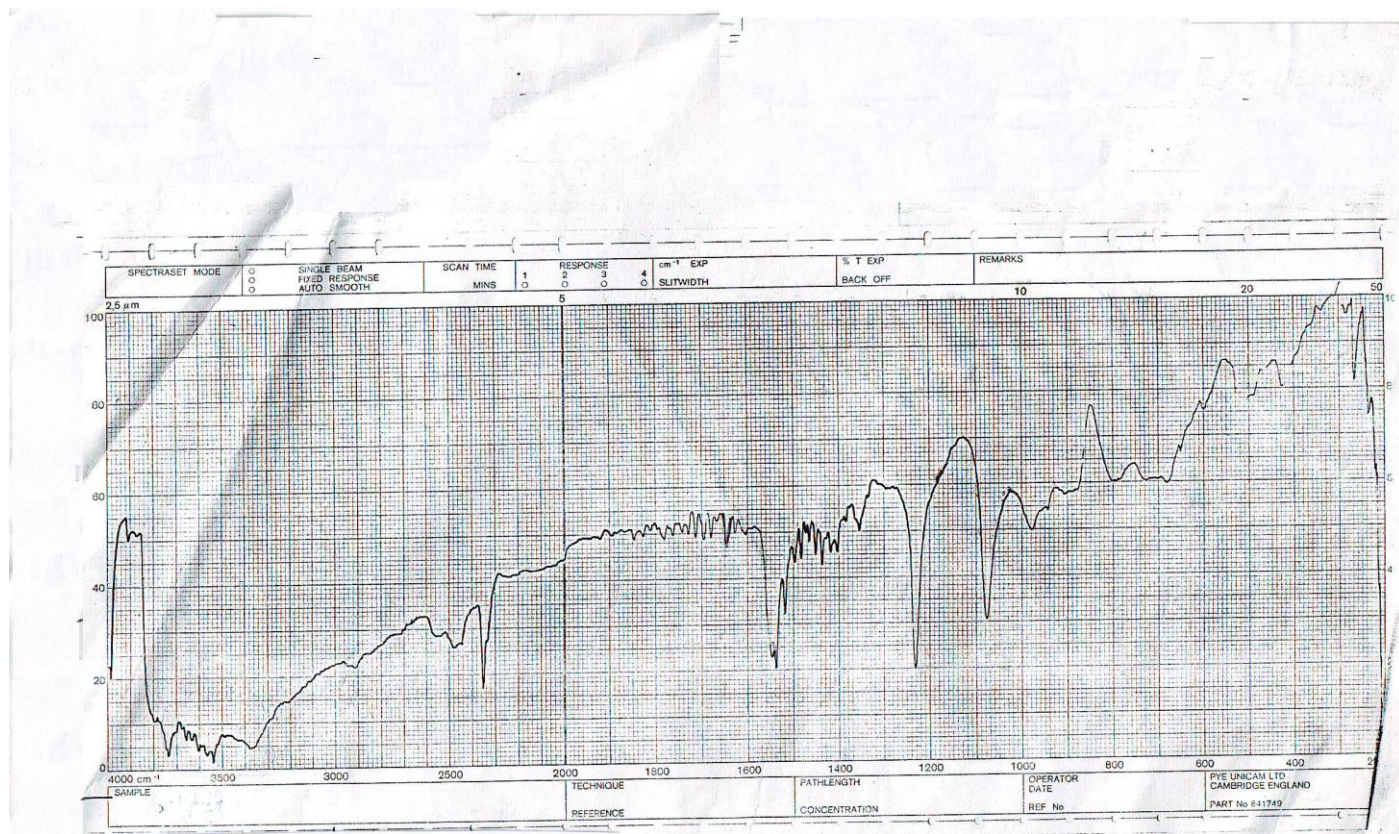


Figure (2) The Infrared Spectrun of [Nil] Complex

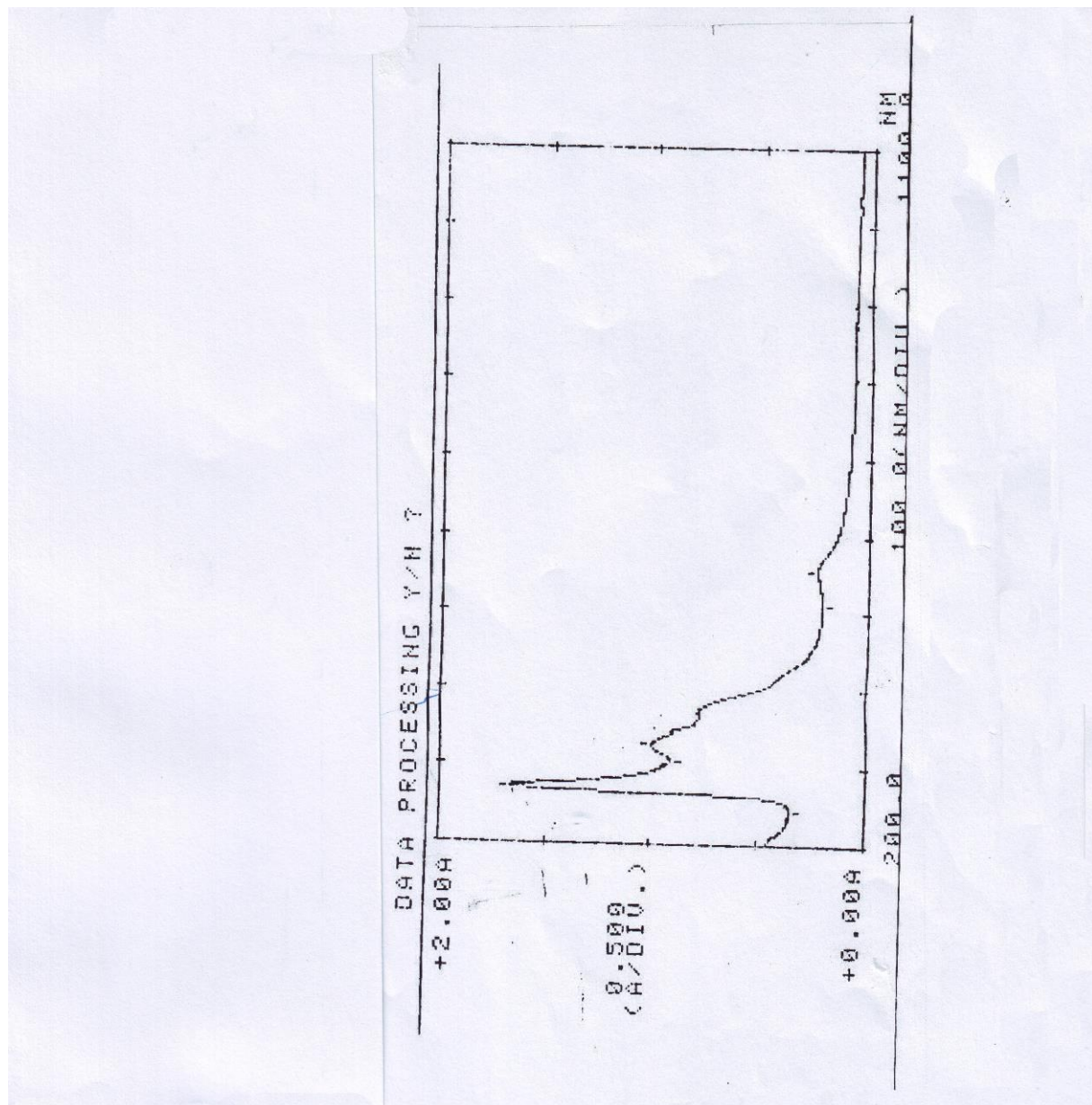


Figure (3) The Electronic Spectrum of [NiL] Complex

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