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STUDIES ON “3d” METAL COMPLEXES OF N^2-ETHOXY THIOCARBONYL-MORPHOLINE-N-THIOHYDRAZIDE

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Abstract:

The dihydrazones of benzil and diacetyl exist in trans configuration. In the presence of the metal ions they attain a cis-configuration rendering the –NH2 groups to come to close proximity.Trans metal complexes involving such vicinal dihydrazones(1-7) have been used as intermediates to prepared macrocyclic metal complexes by template condensation with aldehydes and ketones(8-9).It is reported that the metal complexes of ligands containing electron withdrawing group exhibit unproved biological activity(10).

The sulphur compounds containing NS and NSO donor atoms(11-13) and their 3d metal complexes have been found to exhibit fungicidal,bactericidal,antiviral and antitubercular activities. Studies on metal complexes of 2-hydroxybenzaldehyde-3-thiosemicarbazone or 2-hydroxy benzaldehyde-4-substituted-3-thiosemicarbazone have been reported (14).

Binuclear complexes are of extensive investigation owing to their biological and industrial application(15).Heterobinuclear complexes particularly those comprising of copper(II) and zinc(II) with in the same ligand framework are gaining momentum due to their mimicking behaviour with active centre of copper-zinc super oxide dismutase enzymes(16-17).Heterobimetallic complexes containing copper(II),zinc(II) ions with a series of Schiff bases viz N,N^1-hexylene/heptylene/octylene/dodecaline bis (acetyl acetonimine) containing N_2O_2 donor atoms have been prepared and characterised by elemental analysis,magnetic moments, conductance measurement,IR,electronic and ESR-spectral data.

Hydrazides and hydrazones have interesting ligational properties due to the presence of several potential co-ordination sites and transition metal complexes of these ligands have been studied extensively(18,19) . Although some reports are available on the transition metal complexes of thiohydrazones(21).In view of this and potential biologically active nature of transition metal complexes of thiosemicarbazones,which are structurally very similar to thiohydrazones, we have prepared and characterised the transition metal complexes of N^2-ethoxy thiocarbonyl morpholine-N-Thiohydrazide.

1. Experimental:

Materials and Methods:

The solvents and chemicals used were purified and dried before use by standard techniques. Morpholine-N-thiohydrazide was prepared via the preparation of morpholine dithioacetate by a published method (21) and its subsequent treatment with 85% hydrazine hydrate(22).

Synthesis of N^2-ethoxy thiocarbonyl morpholine-N-Thiohydrazone

(H^2etmth)C_2H_5OC (S)NHNHC(S)N(O)C_4H_8 was prepared byadding an ethanolic solution of morpholine-N-Thiohydrazide(0.16 moles dissolved in 25 ml of ethanol) to a solution of (ethoxy carbonyl) thioacetic(23-24) acid (0.16 moles dissolved in 80 ml of 2N-NaOH) in a ~1:1 molar ratio , adjusting the pH of the reaction mixture between 6.5-7.0 and stirring and refluxing for about two hours. The dirty white product which separated out was suction filtered washed with water and recrystallised from ethanol.Repeated recrystallisation gave white crystals which were dried in vacuo; yield ~50% m.p. 150^0C.

Preparation of Complexes:

The (1:1) complexes were prepared by mixing an aqueous solution of the cobalt acetate, nickel acetate, copper acetate and zinc acetate (0.01 mole of metal (II) acetate in 50 ml of water) and an ethanolic solution of the ligand (0.01 moles of N^2-ethoxy thiocarbonyl morpholine-N-thiohydrazone in 50 ml of ethanol) in 1:1 molar ratio followed by addition of sodium acetate (~ 1.07) and refluxing the solution for about two hour.

The (1:2) complex Mn(Hethnth)$_2$ was prepared by adding the manganese acetate solution (0.005 moles of $Mn(CH_3COO)_2.4H_2O$ in 50 ml of water) to the N2-ethoxy-thiocarbonyl morpholine-N-thiohydrazone in 50 ml ethanol keeping metal salt and ligand in 1:2 molar ratio, followed by addition of sodium acetate (~1.0 g), and refluxing the whole content for two hours on water bath.The Fe(II) complex was prepared by mixing an ethanolic solution of $FeCl_2.4H_2O$ (0.005 moles of metal salt in 50 ml of ethanol) to theN2-ethoxy thiocarbonyl morpholine-N-thiohydrazone solution (0.01 moles of ligand in 50 ml of ethanol) in 1:2 molar ratio.Ethanolic potassium hydroxide(0.01 moles) was then added dropwise to the above reaction Fe(II) to Fe(III) and the whole content refluxed for two hours.

The complexes thus precipitated were digested on a water bath for about five minutes,cooled suction filtered, washed with water to remove any salt and finally with alcohol and ether, and dried in vacuo. The complexes were analysed for their metal contents employing standard procedures,after destroying the organic matter, first with a mixture of nitri acid and hydrochloric acid and then with concentrated sulphuric acid sulphur was determined as $BaSO_4$.Hydrazine was estimated volumetrically using KIO_3, after(25) refluxing the complexes with ~7N-HCl for 2-3 hour.

3. Results and discussions

The results of elemental analysis and magnetic moment data of the complexes are given in table (1). All the complexes are insoluble in water, but soluble in solvents like dimethyl formamide. The complexes are non electrolyte as shown by molar conductance values which lie in the range 8-10 $ohm^{-1}cm^2mol^{-1}$. The chemical analysis and spectral data revealed that the complexes were pure. This was also confirmed by thin layer chromatography. The complexes are coloured.

The analytical data given in table (1) show that Co(II),Cu(II) and Zn(II) form(1:1) complexes by the loss of two and one proton(s), respectively from the ligand N2-ethoxy thiocarbonyl morpholine-N-thiohydrazone according to the following reactions-

$$(CH3COO)_2M + H_2.etmth \xrightarrow{CH_3COONa} M(etmth) + 2CH_3COOH$$

$$(CH3COO)_2M + 2\ H_2.etmth \xrightarrow{CH_3COONa} M(Hetmth)_2 + 2CH_3$$

$$FeCl_2 + 2\ H_2.etmth + 2KOH \longrightarrow Fe(Hetmth)_2 + 2KCl + 2H_2O$$

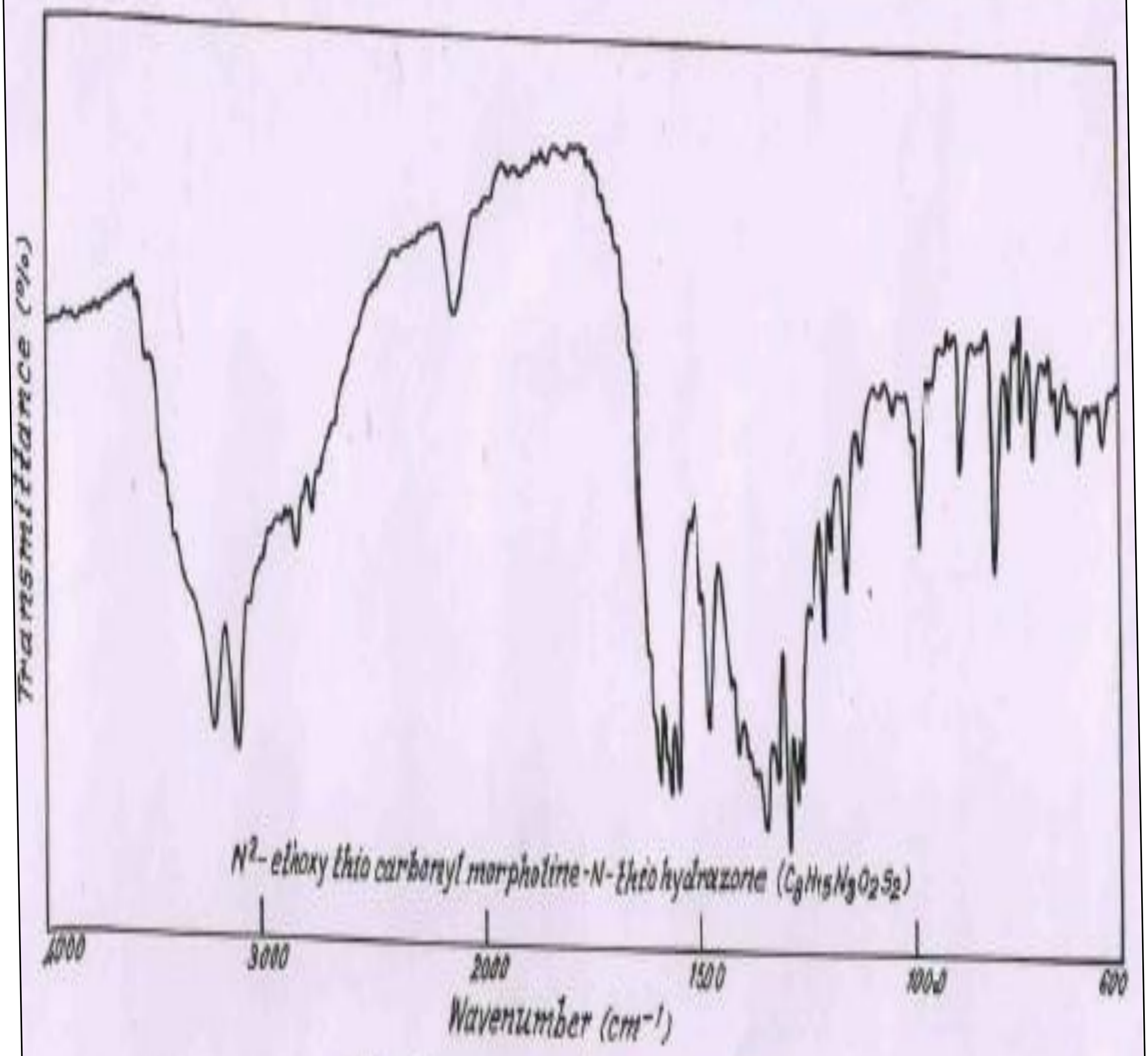


Fig.(F) : I.R. Spectrum of ligand.

TABLE 1-ANALYTICAL DATA OF N^2-ETHOXY THIOCARBONYL MORPHOLINE-N-THIOHYDRAZONE (H_2etmth)

S.N.	Compound	colour	% Anal	Found	(Calculat		χ^1M ×10	μ-eff. (B.M.
			M	N	Hydrazin	S		
1.	Mn(H-etmth)$_2$ Mn$(C_8H_{14}N_3O_2S_2)_2$	Yellow	6.83 (6.95)	10.47 (10.62	7.96 (8.09)	16.03 (16.18)	12590.16	5.5
2.	Fe(H-etmth)$_2$ Fe$(C_8H_{14}N_3O_2S_2)_2$	Yellow	6.94 (7.05)	10.50 (10.60	8.0 (8.08)	16.04 (16.16)	8503.206	4.52
3.	Co(H-etmth)$_2$ Co$(C_8H_{13}N_3O_2S_2)_2$	Green	13.73 (13.84)	9.76 (9.86)	7.38 (7.51)	15.10 (15.20)	8278.956	4.46
4.	Ni(H-etmth)$_2$ Ni$(C_8H_{13}N_3O_2S_2)_2$	Reddish Brown	13.65 (13.79)	9.80 (9.87)	7.40 (7.51)	14.93 (15.03)	149.833	8.60
5.	Cu(H-etmth)$_2$ Cu$(C_8H_{13}N_3O_2S_2)_2$	Violet	14.63 (14.75)	9.65 (9.75)	7.33 (7.43)	14.76 (14.87)	1502.495	1.90
6.	Zn(H-etmth)$_2$ Zn$(C_8H_{13}N_3O_2S_2)_2$	White	15.02 (15.12)	9.60 (9.71)	7.22 (7.40)	14.72 (14.80)	95.893	0.48

$(C_8H_{13}N_3O_2S_2)$-(H_2-etmth)-N^2–ethoxy-thiocarbonyl-morpholine-N-Thiohydrazid

Magnetic Susceptibility Studies:

The magnetic moment of Co(II) chelate is 4.46 B.M. at room temperature. Carline(26) observed amagnetic moment value of 4.73 B.M. for Co(II) complex of ethylene thiourea at room temperature and it is temperature independent and suggested tetrahedral geometry to the Co(II) complex. In the present case magnetic moment value is 4.46. This indicate tetrahedral character of Co(II) chelate.

The magnetic movement of Ni(II) chelate is found to be 0.60 which is unusual and lower than spin only value of two unpaired electrons. Holt et al(27) and others suggested that partial paramagnetic moment of Ni(II) complexes may be attributed to the square planar tetrahedral equilibrium.Therefore a square planar geometry can be suggested for Ni(II) chelate in the present case.

The magnetic moment of 4.52B.M. of the iron (II) complex corresponds to four unpaired electrons. The ground state of Fe(II) in high spin oh-symmetry(29) is $^5T_{2g}$,where as in Td-symmetry, it is 5E.Irrespective of the oh or Td geometry of the Fe(II) complex, the number of unpaired electrons on the iron will be four and in both the cases there will be a certain amount of orbital contribution to the spin only value of the magnetic moment.

In practice,the value of the magnetic moment of tetrahedral and octahedral complex, of Fe(II) has magnetic moment of 5.2 B.M. respectively. The observed value of 4.52B.M. for the complex under discussion suggested the tetrahedral geometry for the Fe(II) complex.

The zinc complex is diamagnetic as expected for d^{10} systems. Hence we suggested a tetrahedral structure for the Zn(II) complex. Cu(II) complex exhibits a magnetic moment of 1.90 B.M. which is in the normal range (1.7- 2.2B.M.) observed for the magnetically dilute Cu(II) complexes(30) . Cu(II) complexes exhibits an asymmetric band at 18500cm^{-1} suggesting the presence of a square planar structure with (Cu NSS) coordination sphere(31) . Mn(II) complexes show magnetic moments which correspond to the presence of five unpaired el ectrons and show spin free complex.

Electronic Spectra:

The UV-spectra of H2etmth shows two bands at 250 nm 40000cm^{-1} and310 nm 32258cm^{-1} which may be assigned to $\pi \rightarrow \pi^*$ transitions of the >C=S chromophore(32) . The various band maxima and their assignments are given in table (8.2)

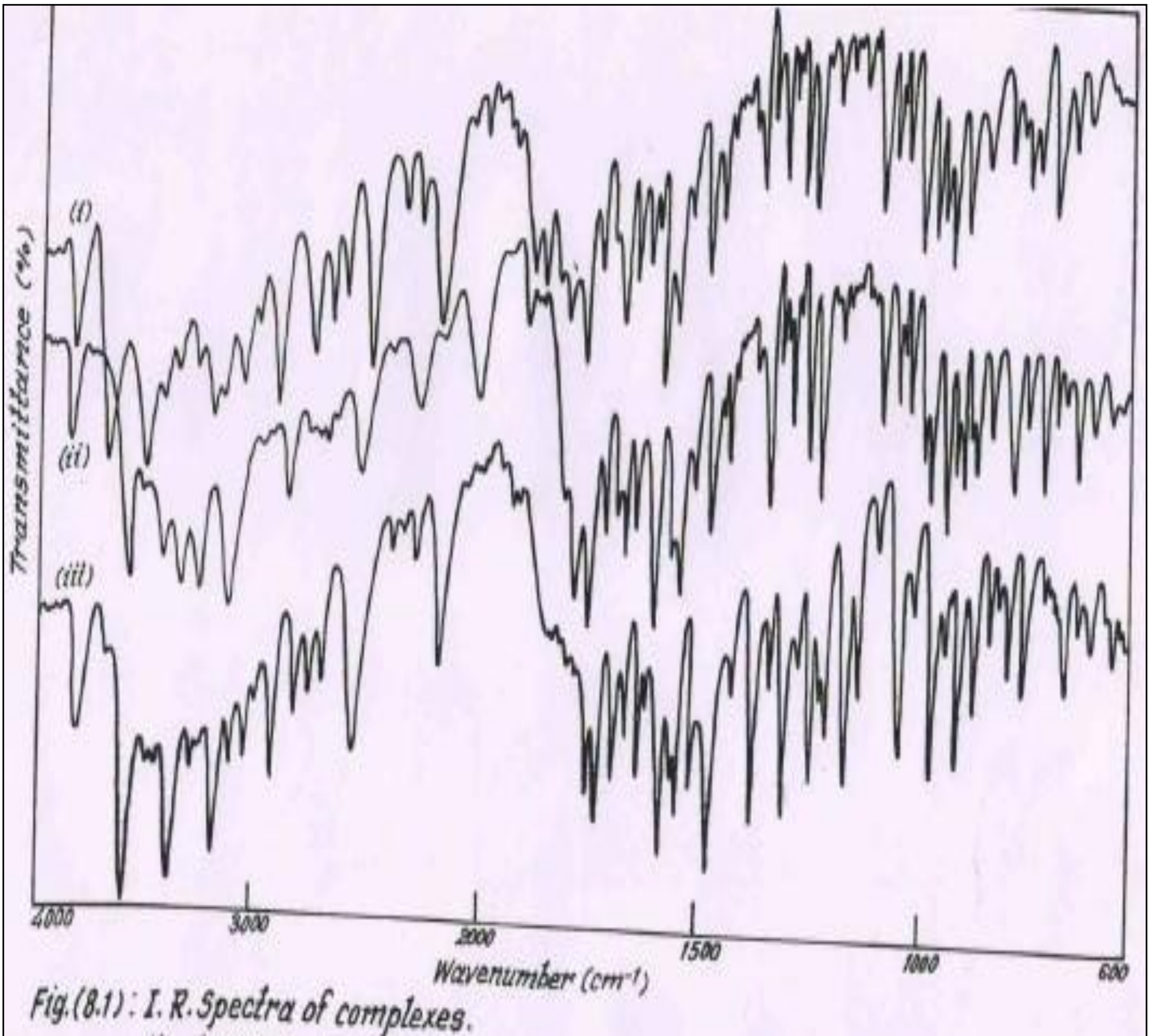


Fig.(8.1): I.R. Spectra of complexes.
(i) [$Mn(C_{18}H_{14}N_3O_2S_2)_2$]
(ii) [$Fe(C_{18}H_{14}N_3O_2S_2)_2$]
(iii) [$Co(C_{18}H_{13}N_3O_2S_2)$]

TABLE 2-ELECTRONIC SPECTRAL DATA AND LIGAND FIELD PARAMETERS OF N^2 – ETHOXY THIOCARBONYL

S.N.	Compound	Band maxima(c	Assignments	10 Dq (cm^{-1})	B (cm^{-1})
1.	Fe(Hetmth)$_2$	15320 22240	$^5T_{2g} \rightarrow {}^5E_g(D)$ $T_{2g} \rightarrow \pi$	15320	-
2.	Co(etmth)	7160 9365 10545 15620	$^4A_2 \rightarrow {}^4T_{1g}(F)(\upsilon_2)$ $^4A_2 \rightarrow {}^4T_{1g}(P)(\upsilon_3)$	6095	558
3.	Ni(etmth)	15400 21070	$^1A_{1g} \rightarrow {}^1B_{1g}$ $^1A_{1g} \rightarrow {}^1B_{3g}$	-	-
4.	Cu(etmth)	19250	Envelope of $^2B_{1g}$ – $^2A_{1g}$; $^2B_{2g}$ and ^2E_g	19250	-
5.	Mn($C_8H_{14}N_3O_2S_2$)	15300 20600 23400	$^6A_{1g} \rightarrow {}^4T_{1g}(G)$ $^6A_{1g} \rightarrow {}^4T_{2g}(G)$ $^6A_{1g} \rightarrow {}^4E_g$	10600	597

(H_2-etmth)($C_8H_{15}N_3O_2S_2$ Co($C_8H_{13}N_3O_2S_2$) shows four bands at 7160,9365,10545,15620 cm^{-1}.The bands occurring in the 7140-10525 cm^{-1} region may be due to $^4A_2 \rightarrow {}^4T_{1g}(F)(\upsilon_2)$ while those in the 7140 – 10525 cm^{-1}region to the $^4A_2 \rightarrow {}^4T_{1g}$ (P)(υ_3) transition in the tetrahedral geometry around Co(II)$^{(33)}$. The value of υ_2- for Co(etmth) has been calculated by the method of Drago$^{(34)}$. The values of Dq and B have been worked out to be 6095 and 558cm^{-1} .

Ni($C_8H_{13}N_3O_2S_2$) shows two bands at 15400 and 21070 cm^{-1} in the visible region which may be assigned to $^1A_{1g} \rightarrow {}^1B_{1g}$ and $^1A_{1g} \rightarrow {}^1B_{3g}$ transitions respectively in the square planar geometry of the complex$^{(35)}$. The single electron parameters Δ_1 and Δ_2 the observed(d-d) transitions as suggested by Gray et al$^{(36)}$, assuming after shupack et al$^{(37)}$ that F_2 = $10F_4$ =800cm^{-1} . The calculated values are 19000 an d 6293 cm^{-1} respectively. The occurance of a band at 19250 cm^{-1} in Cu($C_8H_{13}N_3O_2S_2$) is indicative of a square planar geometry for complex which may be assigned to the envelop of the $^2B_{1g} \rightarrow {}^2A_{1g}$ $^2B_{2g}$ and ^2E_g transitions$^{(38)}$.

The magnetic moment of the Mn(II) complex lie in the range 5.6-5.7 B.M. at room temperature indicating high spin nature of the complex$^{(38)}$. The electronic spectra show three bands in the ranges 15000 – 15600 , 20000 – 20800 , and 23000 - 23500 cm^{-1} which can be assigned to the transitions $^6A_{1g} \rightarrow {}^4T_{1g}$; $^6A_{1g} \rightarrow {}^4T_{2g}$ and $^6A_{1g} \rightarrow {}^4E_g$ respectively in an octahedral field$^{(39)}$. The spectra of octahedral Mn(II) complex has been rationalised by calculating ligand field and nephelauxetic parameters (10 Dq β , C and β) using equations derived from Tanabe –Sugano diagrams$^{(40)}$ .The value of different parameters 10 Dq = 10600 cm^{-1} , B = 597 cm^{-1} and β = 0.62 are comparable with those reported for other octahedral Mn(II) complexes. The low values of β- indicate that the metal-ligand bonds are covalent $^{(41)}$.

The diffuse electronic spectrum of Fe (II) complex exhibits bands at 20410,16000,12200 and 9430 cm^{-1}. The high energy band may be attributed to the spin allowed $^5T_{1g} \rightarrow {}^5E_g$ transition in octahedral stereochemistry. The low energy band at 9430 cm^{-1} is presumed to be due to low symmetry ligand field component $^{(43)}$. B,C and using $\pi = 5/2\ B + C = 18.5\ B$ (assuming C = 4B). Taking10 Dq = π =1600 cm$^{-1(44)}$,the value of B- comes out to 860 cm^{-1}. B- has been evaluated as 0.82 and C as 3460 cm^{-1}. Reduction in the value of B indicates the partial covalent nature of the metal ligand bond.

Infrared spectral studies:

The IR – data given in the table (8.3) show two bands at 3320 and 3160 cm^{-1} for (H_2-etmth) ($C_8H_{15}N_3O_2S_2$) in KBr due to υ(NH) . These bands disappear in the spectra of the (1:1) complexes suggesting the removal of NH – protons via enolisation and thioenolisation .The spectra of 1:2 complexes show only one band in the 3400-3210 cm^{-1}. Region indicating the non involvement of one of the imino nitrogen bonding. These features clearly indicate that one of the > NH- groups of the ligand does not co-ordinate in the (1:2) complexes.

The thioamide bands observed at 1640-1680 cm^{-1} in the ligand disappear in (1:1) metal complexes and a new band due to υ(NCS) appear at ~ 1540 cm^{-1}, suggesting the destruction of the >C = S group through enolisation and its subsequent bonding with metal ions . However the spectra of (1:2) complexes show a significant negative shift of 40-60 cm^{-1} in the above band indicating coordination of the thiocarbonyl sulphur to the metal ions.

The thioamide band (IV) mainly due to υ(C = S) observed at 910 cm^{-1} in ($C_8H_{15}N_3O_2S_2$) (H_2-etmth) is found to be absent in the spectra of all the complexes and new band is found in the 680-730 cm^{-1} region due to the υ(C = S). This indicates the destruction of the > C = S group through thioenolisation and its subsequent bonding with metal ions. The bands occurring in the 1500-1410 , 1310-1220 and 1060-1055 cm^{-1} regions in the ligand due to thioamide I (β-NH) + υ(CN);II (υCN + β-NH) (45-47) and υ(N-H) (48) respectively , show positive shift of (40 - 130 cm^{-1}) , (40 - 90 cm^{-1}) and (70 - 45 cm^{-1}) repectively in the complexes supporting bonding through sulphur and hydrazide nitrogen (s). The absence of bands in the region 2800–2650 cm^{-1} in the free ligand indicates absence of (S – H) grouping in the free ligand(49) . The υ(C = S) in the ligand appears at 850 cm^{-1} . These bands appear on complexion and instead new bands around 660 cm^{-1} , characteristic of υ(C = S). Appear in the complexes. The above facts are compatible with the enplisation of the NH – C = S group in the ligand to N = C – SH in the presence of the metal ions and co-ordination of the metal through the sulphur atom.

In the ligands the bands occurring around 1550,1200,1090 and 775 cm^{-1} are assigned to thioamide bands –I,II,III and IV respectively. These bands are not pure and have contribution from δNH, υ(C = N), υ(C = S) and δ(C – H) vibrations. The first three bands do not show significant changes while the thioamide – IV band, having maximum

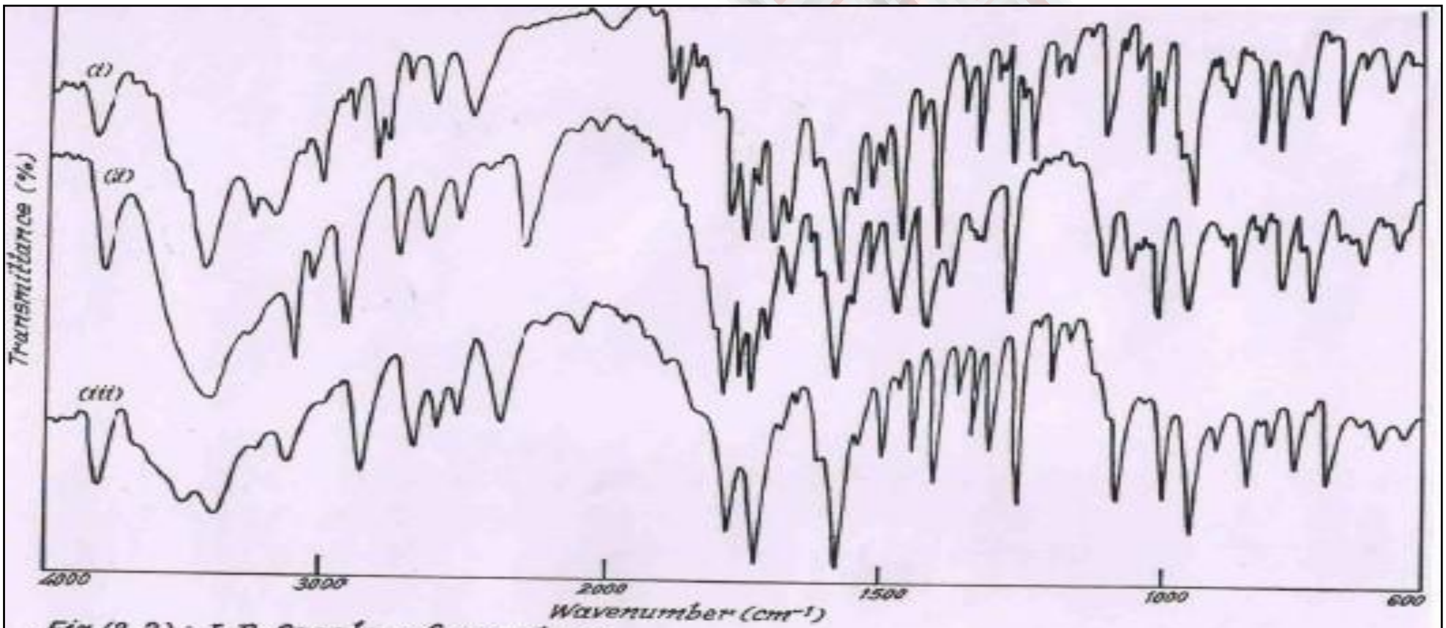


Fig.(8.2) : I.R. Spectra of complexes.
(i) [Ni ($C_{18}H_{13}N_3O_2S_2$)]
(ii) [Cu ($C_{18}H_{13}N_3O_2S_2$)]
(iii) [Zn ($C_{18}H_{13}N_3O_2S_2$)]

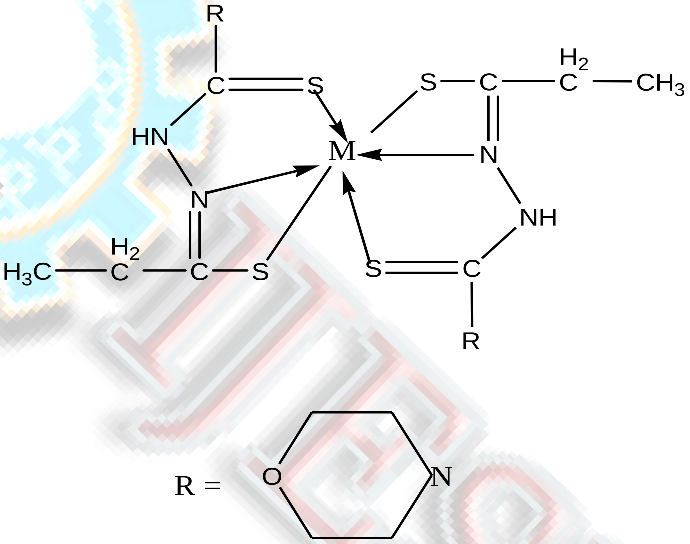
TABLE (3) – IMPORTANT INFRARED SPECTRAL BANDS (cm^{-1}) AND THEIR ASSIGNMENT OF N^2- ETHOXY THIOCARBONYL MORPHOLINE – N – THIOHYDRAZONE (H_2-etmth) ($C_8H_{15}N_3O_2S_2$)

S.N	Compound	υ(NH)	υ(C = S)/ υ(NCS	Thioamide		bands	υ(N - N	υ(M - N	υ(M - S
				I(βNH+ υ	II(υCN+β	III(C			
1.	H_2-etmth($C_8H_{15}N_3O_2S_2$	33205r 31605r	1640s	1500s	1310m	910m	1060m	-	-
2.	Mn($C_8H_{14}N_3O_2S_2$)	3240m	1580s	1540m	1350s	700s	1100m	390m	300m
3.	Fe($C_8H_{14}N_3O_2S_2$)	3210m	1570s	1530m	1340s	680s	1090m	390m	280m
4.	Co($C_8H_{13}N_3O_2S_2$)	-	1520m	1550m	1340m	680s	1090m	385m	310m
5.	Ni($C_8H_{13}N_3O_2S_2$)	-	1510m	1540m	1350s	685m	1110m	390m	310m
6.	Cu($C_8H_{13}N_3O_2S_2$)	-	1520m	1540m	1350m	690m	1130m	390m	320m
7.	Zn($C_8H_{13}N_3O_2S_2$)	-	1525m	1550m	1350m	680s	1100m	390m	320m

S – Strong; M – Medium; W – Weak

(C = S) contribution either splits or appears at lower frequencies (~10 - 25) in the complexes. These changes are consistent with the co-ordination of the sulphur atom of thiocarbonyl group(50-51).
In Co(II) , Ni(II) , Cu(II) and Zn(II) complexes a band around 950 cm^{-1} indicate that the ligand co-ordinate to metal atom through thioenol group involving deprotonation(52-54).
The non ligands bands occurring in the 390-380, 280-320 cm^{-1} region in the spectra of all the complexes may be tentatively assigned to υ(M-N) and υ(M-S) modes respectively(55-60) .

The IR spectral studies indicate that ligand is uninegative tridentate in their 1:2 complexes and binegative tetradentate in (1:1) complexes. Since due to steric reasons, all the four steps cannot be simultaneously involved in bonding to the same metal ions a polymeric structure is proposed for the 1:1 complexes. The polymeric structure for these complexes is consistent with their high melting or decomposition temperatures and insolubility in water or common organic solvents. Based on analytical data, general behaviour and physico chemical studies discussed above suggests the following structures are suggested for the complexes.



M = Mn(II), Fe(II)

Fig: ....

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