STRUCTURAL INVESTIGATIONS OF SOME METAL COMPLEXES OF MALON-DI-(α-NAPHTHYL)AMIDE-OXIME

Abstract

The study investigates the structural properties of Cu(II), Ni(II), Fe(II), Co(III), Zn(II), Cd(II), and Hg(II) complexes with malon-di-(α-naphthyl)amide-oxime (isonitrosomalon-di-(α-naphthyl)amine oxime). It summarizes chemicals, equipment, experimental methods, metal-ligand bonding, stereochemistry, oxidation states, and coordination modes using spectral and magnetic data.

The green Cu(II) complex is dimeric, confirmed by its electronic and reflectance spectra, with a likely square planar structure. Yellow Ni(II) and dark-blue Fe(II) complexes are paramagnetic, suggesting high-spin octahedral geometries. The dark-red Co(III) complex exhibits weak paramagnetism, explained by the Van Vleck term, spectral data, and its diamagnetic nature, indicative of an octahedral structure. Zn(II), Cd(II), and Hg(II) complexes are assigned tetrahedral structures based on magnetic and infrared spectral data.

Keywords: Bleaney-bowers equation; polymeric complexes; freeman and carroll equation; vosburgh and cooper method; job's continuous variation method; yoe and jones mole ratio method; Van Vleck's expression; anti-ferromagnetic behaviour.

1.0 INTRODUCTION

The coordination chemistry of oxime-containing ligands has attracted significant research interest due to its relevance to molecular structure, stability, reactivity, analytical chemistry, and biochemical models (1-4). A comprehensive review (5) explores various oxime types, including simple oximes, VIC dioximes, nitroso phenols, pyridine oximes, azo oximes, aryloximes, hydroxy oximes (e.g., α-acyloin oximes, salicylaldoximes), amine oximes, aldoximes, and Schiff bases of carbonyl oximes or isonitrosoketones. These ligands exhibit diverse bonding modes with metals, forming bidentate, tridentate, tetradentate, and hexadentate complexes (6). Substituted malonic oximes with the -CO-C(=NOH)- moiety have also been reported (7), forming blue complexes with ferrous salts in alkaline media. Such ligands are known to produce complexes in varied colors, including green Cu(II), yellow Ni(II), blue Fe(II), and red Co(III) complexes (8, 9), highlighting their utility as complexing agents.

The present study (6) focuses on the synthesis and characterization of malon-di-(α-naphthyl)amide-oxime (isonitrosomalon-di-(α-naphthyl)amine oxime, abbreviated as HINMANAP) and its complexes with Cu(II), Ni(II), Fe(II), Co(III), Zn(II), Cd(II), and Hg(II). These complexes were prepared in solid form, with solution studies determining the metal-to-ligand ratios. Their structures were analyzed using infrared, electronic, reflectance, ESR, and NMR spectroscopy, along with magnetic measurements.

2.0 EXPERIMENTAL METHODS

All chemicals, including cupric chloride, nickel chloride, cobalt chloride, zinc sulphate, cadmium bromide, ferrous ammonium sulphate, benzene, acetone, chloroform, and pyridine, were of AR or LR grade. LR-grade chemicals were purified prior to use. Double-distilled conductivity water was used throughout. Ethyl alcohol was filtered and fractionally distilled at 77–78 °C over anhydrous calcium oxide; ether was distilled and dried over sodium metal; pyridine was distilled at 114–118 °C over sodium hydroxide pellets; ethyl acetate at 77–78 °C; chloroform at 65 °C over anhydrous calcium chloride; and acetone was distilled. Buffers for solution studies included N/20 potassium hydrogen phthalate (pH 5) and N/100 sodium tetraborate (pH 9.2) for pH meter calibration (10), and sodium acetate-acetic acid buffers for pH 6–7.5. Glass apparatus, including burettes, pipettes, and standard flasks, were calibrated by standard methods (10).

2.1 Equipment used are:

An analytical balance with 0.1 mg sensitivity was calibrated using the method described by Scott (11). Ultraviolet absorption measurements were performed on a Systronic MK II 106 spectrophotometer, calibrated with 0.004% K□CrO□ solution in 0.05M potassium hydroxide and 0.0062% potassium permanganate solution. The observed spectra aligned well with reported literature values (10). Reflectance spectra of solid complexes were recorded using a CZ VSU 2-P spectrophotometer (Germany), calibrated with a standard magnesium carbonate block. Infrared spectra were obtained in KBr using a Beckman IR 20 spectrophotometer (USA). pH measurements were made using a Model LI-10 pH meter (ELICO Pvt Ltd., Hyderabad, India) with glass and calomel electrodes. Conductivity was measured using a Magic Eye conductivity bridge supplied by Toshniwal.

2.2 Preparation of reagent malon-di-(α-naphthyl)amide-oxime (isonitrosomalon-di-(α-naphthyl) amine oxime) abbreviated as HINMANAP:

The reagent HINMANAP was synthesized following the procedure described in the literature (7, 6). Diethyl malonate (48 g, 0.1 M) and α-naphthyl amine (85.8 g, 0.6 M) were refluxed in a round-bottom flask for eight hours. Upon cooling, the solid reaction product was filtered under suction, washed with alcohol, and dried. The product was crushed and suspended in ethyl acetate, and dry nitrosyl chloride was passed through the suspension at 0 °C until a clear solution formed. The solution was evaporated at room temperature in a large dish, yielding crystalline malon-di-(α-naphthyl)amide oxime. The crystals were purified by recrystallization from alcohol and analyzed.

2.3 Preparation of metal complexes:

2.3.1 Copper(II) Complex of reagent HINMANAP

Cupric chloride (1.7 g) and HINMANAP (3.83 g) were separately dissolved in 40:60 acetone:water. The HINMANAP solution was added dropwise to the cupric chloride solution with constant stirring, and the pH was adjusted to 3.75. A bright green copper(II) complex precipitated, which was filtered under suction, washed with water and acetone, and dried at 80 °C. The complex was insoluble in common organic solvents, making crystallization impractical.

2.3.2 Cobalt(III) Complex of reagent HINMANAP

Cobalt(II) chloride (2.38 g) and HINMANAP (11.49 g) were separately dissolved in 40:60 acetone:water. The HINMANAP solution was added dropwise to the cobalt(II) chloride solution. Hydrogen peroxide (25 mL) was added, and air was bubbled through the mixture for 8 hours. An amorphous dark red cobalt(III) complex formed, which was filtered under suction, washed with 1:1 acetone:water, and dried at 80 °C. The product was crystallized from chloroform for analysis.

2.3.3 Nickel(II), Iron(II), Zinc(II), Cadmium(II), and Mercury(II) Complexes of reagent HINMANAP

HINMANAP in 40:60 acetone:water was added to metal salt solutions prepared in the same solvent (except ferrous ammonium sulfate, dissolved in water), maintaining a 2:1 reagent-to-metal molar ratio. The pH was adjusted using dilute ammonium hydroxide to form the respective complexes:Nickel(II) - pH 3.5, bright yellow complex; Iron(II) - pH 7.2, dark blue complex; Zinc(II) - pH 5.5, greenish-yellow complex; Cadmium(II) - pH 4.25, pale yellow complex; Mercury(II) - pH 4.5, pale yellow complex.The complexes were filtered under suction, washed with 1:1 acetone:water, and dried at 80 °C.

2.4 Estimation of Metal Ions, Total Nitrogen, and Magnetic Moment

Quantitative estimation of metal ions was carried out using the following methods: copper and cadmium with dipyridine dithiocyanate, nickel with dimethyl glyoxime, iron and zinc with EDTA, cobalt with tetra pyridine dithiocyanate, and mercury with mercuric sulphide. Total nitrogen in the organic reagent and metal complexes was determined using Kjeldahl's method (10).Magnetic susceptibility measurements were performed at room temperature and over the 77–300 K range using the Faraday method (12), with corrections for □M based on the diamagnetic ligand (13). The HgCo(SCN)□ complex was used as a secondary standard (14), with a χ_g value of 16.44×10^{-6} cm^3/g at 20 °C.

2.5 Composition of Metal Complexes with reagent HINMANAP

The composition of Cu(II), Ni(II), Cd(II), and Hg(II) complexes with HINMANAP was determined in alcoholic solutions using spectral studies. The metal-ligand stoichiometry, pH, and the effects of pH and time on isolating solid-state complexes were investigated. Standard analytical methods were employed, including spectral studies, variation of optical density with pH (10), Vosburgh and Cooper's metal-to-ligand ratio vs absorbance method (15), Job's continuous variation method (16), Yoe and Jones mole ratio method (17), and conductometric analysis (18).

3.0 RESULTS AND DISCUSSION

All metal complexes, except Co(III), were insoluble in common organic solvents, indicating a

polymeric nature that prevented recrystallization. These complexes were washed under suction with appropriate solvents, dried, and analyzed. The Co(III) complex was crystallized from chloroform. The color, pH, probable molecular formula, and elemental analysis of each complex are summarized in Table 1, while their solubility details are presented in Table 1A.

3.1 Composition of Cu(II), Ni(II), Cd(II), and Hg(II) Complexes(See (19) for similar look of data for tables not given here and figures using that data,Fig 1 a-d to 6a-d) are presented.

3.1.1 Spectral Studies in Solution

Upon mixing equimolar solutions of HINMANAP and metal salts (Cu(II), Ni(II), Cd(II), Hg(II)) in ethanol, distinct colors developed rapidly. These were analyzed on a colorimeter at 390 nm. While metal salts of Cu(II) and Ni(II) exhibited negligible absorbance beyond 420 nm, and the reagent did not absorb significantly beyond 500 nm, the resulting complexes absorbed strongly between 340 nm and 600 nm, with maxima at 390 nm.

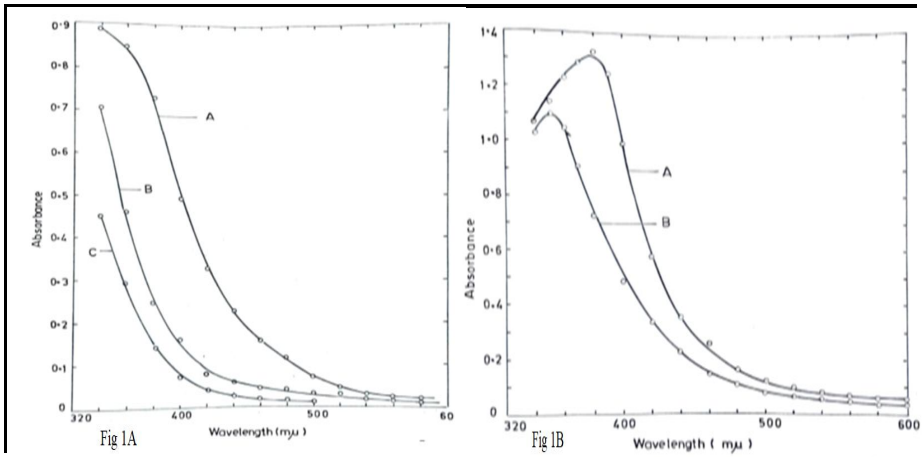


Fig 1A. Absorbance of A – Cu(II)complex = 2 x 10^{-3}M; B – HINMANAP = 1 x 10^{-3}M; C – $CuCl_2$ = 1 x 10^{-3}M in alcohol **Fig 1B.** Absorbance of A – Ni(II)complex = 2 x 10^{-3}M; B – HINMANAP = 1 x 10^{-3}M in alcohol

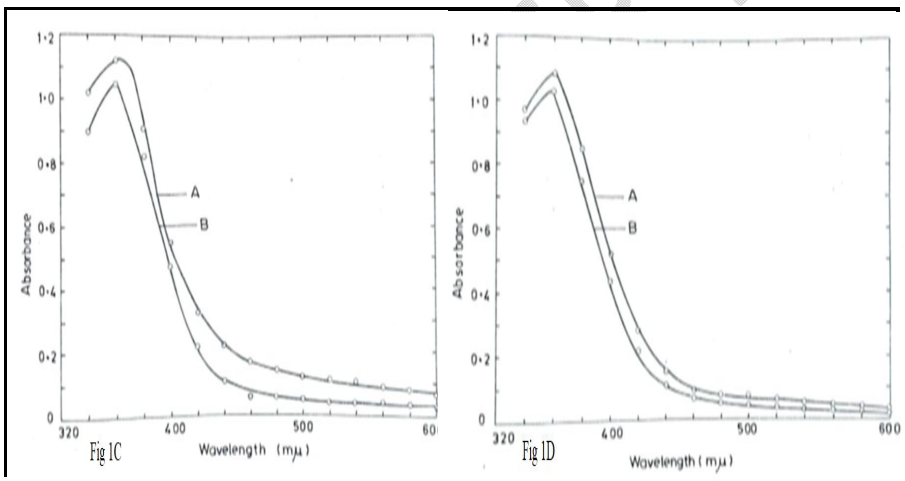


Fig 1C. Absorbance of A – Cd(II)complex = 2 x 10^{-3}M B – HINMANAP = 1 x 10^{-3}M in alcohol;**Fig 1D**. Absorbance of A – Hg(II)complex = 2 x 10^{-3}M B – HINMANAP = 1 x 10^{-3}M in alcohol

3.1.2 Effect of pH and Time

The stability of the complexes in solution was assessed by adjusting the pH with dilute sodium hydroxide while keeping the total volume constant using ethanol. Absorbance at 390 nm was measured for Cu(II), Ni(II), Cd(II), and Hg(II) complexes. The pH ranges over which constant absorbance was observed were:Cu(II) - 3.40–4.15 (mean: 3.75); Ni(II) - 2.5–4.3 (mean: 3.50); Cd(II) - 3.0–5.5 (mean: 4.25); Hg(II) - 3.0–6.0 (mean: 4.50). The observed mean pH was used for isolating the solid-state complexes. The color of the complexes in solution remained stable for over eight hours at 26–40 °C.

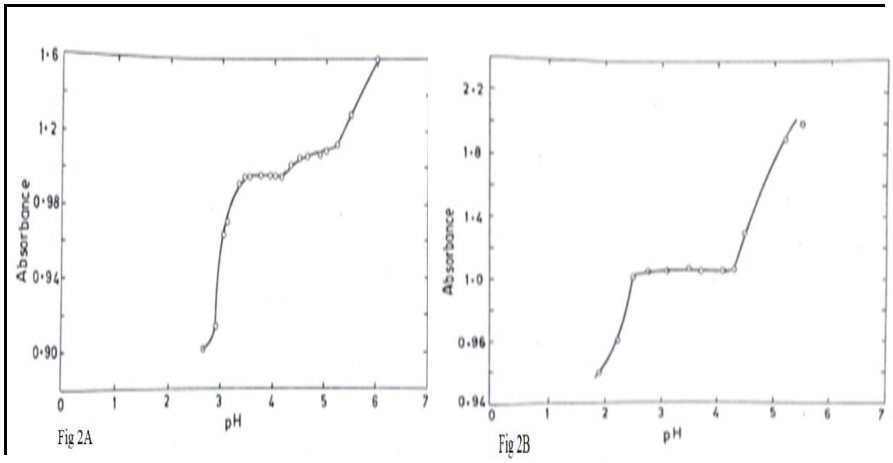


Fig 2A. Effect of pH on absorbance of Cu(II) complex in alcohol at $C_R = C_M = 1 \times 10^{-3}$M

Fig 2B. Effect of pH on absorbance of Ni(II) complex in alcohol at $C_R = C_M = 1 \times 10^{-3}$M

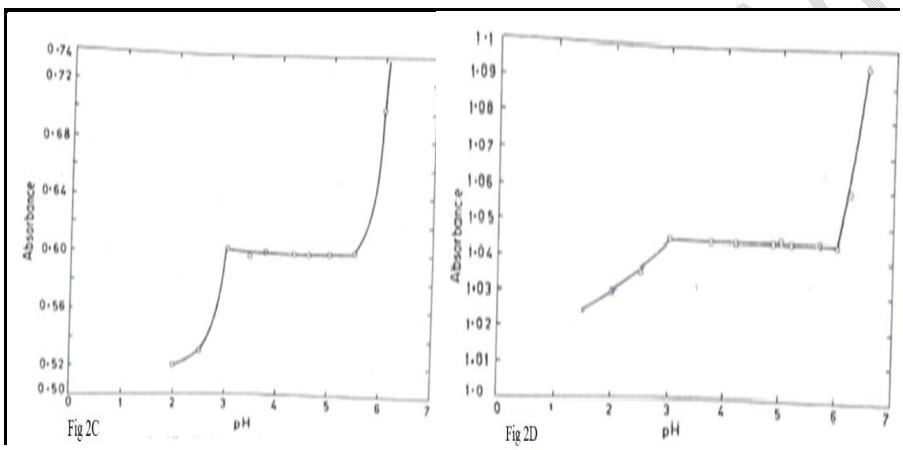


Fig 2C. Effect of pH on absorbance of Cd(II) complex in alcohol at $C_R = C_M = 1 \times 10^{-3}$M

Fig 2D. Effect of pH on absorbance of Hg(II) complex in alcohol at $C_R = C_M = 1 \times 10^{-3}$M

3.1.3 Vosburgh and Cooper Method

Equimolar solutions (1×10^{-3} M) of HINMANAP and metal salts were mixed in 25 ml flasks. The reaction resulted in rapid and stable color development within seconds, which persisted for eight hours. Absorbance measurements across different wavelengths indicated the presence of a single absorbing species in each complex.

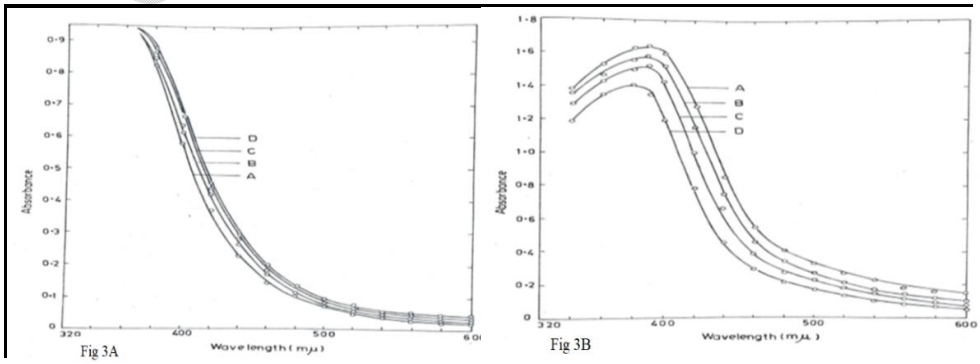


Fig 3A. Method of Vosburgh and Cooper in alcohol: for Cu(II) complex at $C_R = C_M = 1 \times 10^{-3}$M where M:R = A – 1:1; B – 1:2; C – 1:3; D – 1:4; **Fig 3B.** for Ni(II) complex at $C_R = C_M = 2 \times 10^{-3}$M where M:R = D – 1:1; C – 1:2; B – 1:3; A – 1:4

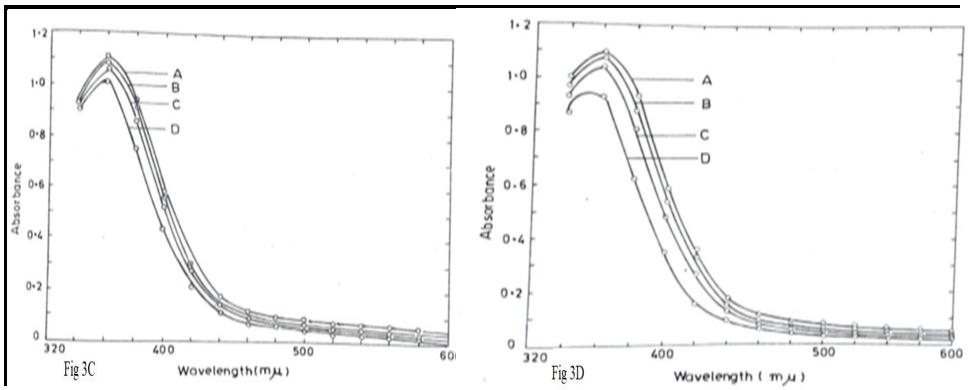


Fig 3C. for Cd(II) complex at $C_R = C_M = 1 \times 10^{-3}$M where M:R = A – 1:4; B – 1:3; C – 1:2; D – 1:1;
Fig 3D. for Hg(II) complex at $C_R = C_M = 1 \times 10^{-3}$M where M:R = D – 1:1; C – 1:2; B – 1:3; A – 1:4

3.1.4 Job's Continuous Variation Method

Absorbance was recorded at 390 nm for mixtures of varying proportions of metal salt and reagent solutions in ethanol (total volume: 10 ml). Cu(II) showed a maximum at an equimolar ratio of 1:1, while Ni(II), Cd(II), and Hg(II) reached maxima at a 1:2 molar ratio of metal to ligand.

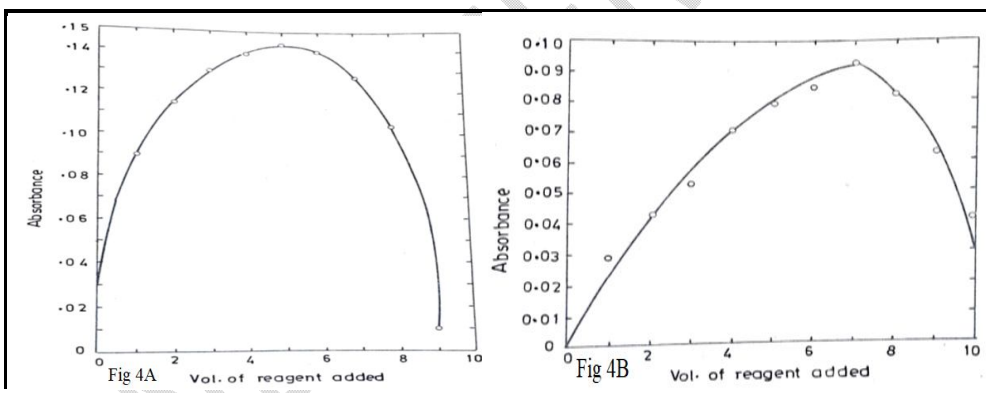


Fig 4A. Composition of Cu(II) complex in alcohol by Job's method at $C_R = C_M = 1 \times 10^{-4}$M;

Fig 4B. Composition of Ni(II) complex in alcohol by Job's method at $C_R = C_M = 1 \times 10^{-4}$M

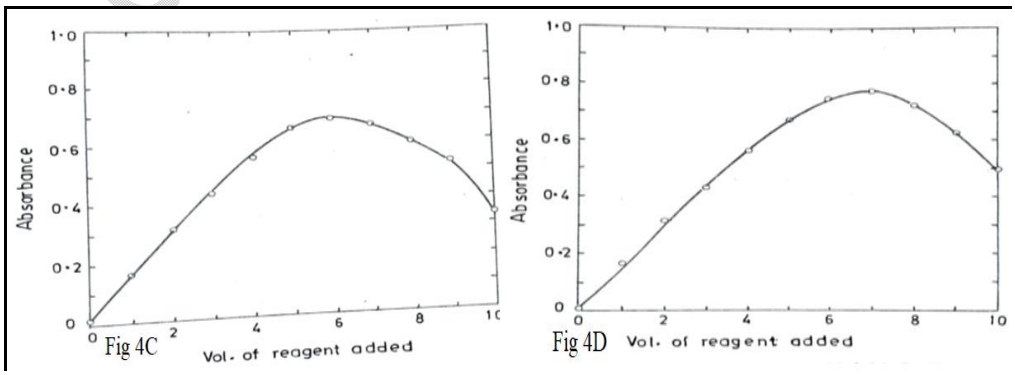


Fig 4C. Composition of Cd(II) complex in alcohol by Job's method at $C_R = C_M = 5 \times 10^{-4}$M

Fig 4D. Composition of Hg(II) complex in alcohol by Job's method at $C_R = C_M = 3 \times 10^{-4}$

3.1.5 Yoe and Jones Mole Ratio Method

Ethanolic solutions of metal salts and the reagent were mixed, maintaining a total volume of 10 ml, and absorbance was measured at 390 nm. The plots showed a distinct intersection: 1:1 for Cu(II) and 2:1 for Ni(II), Cd(II), and Hg(II), indicating the respective stoichiometries.

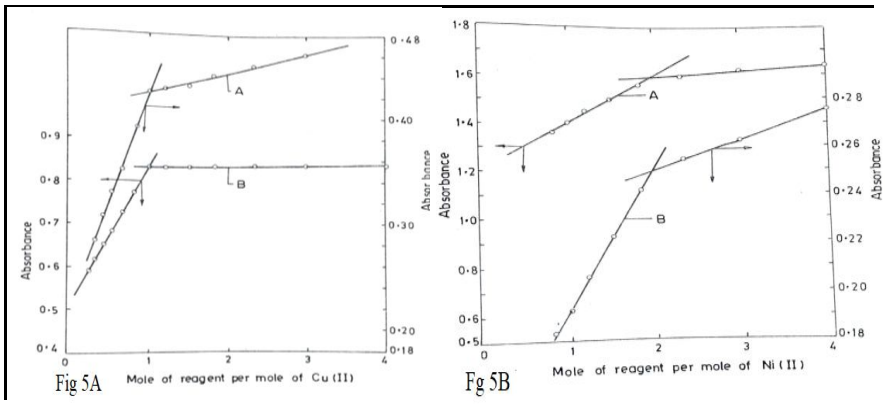


Fig 5A Composition in alcohol by Yoe and Jones Mole Ratio Method of: Cu(II) complex A - $C_R = C_M = 2 \times 10^{-3}$M and B - $C_R = C_M = 1 \times 10^{-4}$M, **Fig 5B** Ni(II) complex, A - $C_R = C_M = 5 \times 10^{-4}$M and B - $C_R = C_M = 3 \times 10^{-4}$M

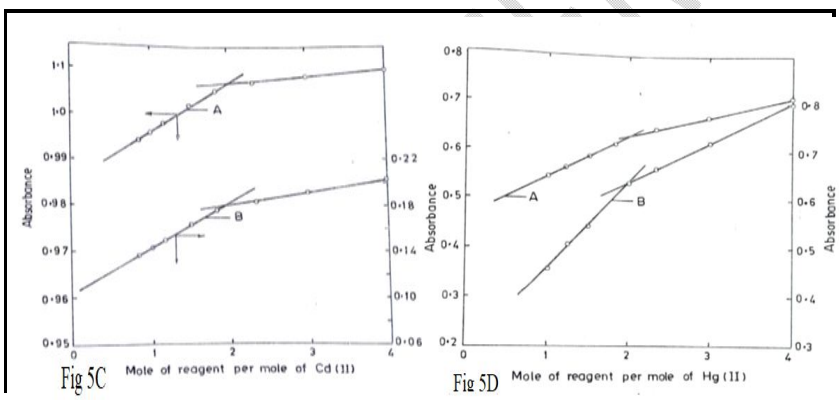


Fig 5C Cd(II) complex, A - $C_R = C_M = 1 \times 10^{-3}$M and B - $C_R = C_M = 1 \times 10^{-4}$M,

Fig 5D Hg(II) complex A - $C_R = C_M = 1 \times 10^{-3}$M and B - $C_R = C_M = 5 \times 10^{-4}$M

3.1.6 Conductometric Method

The conductometric titrations were performed by adding HINMANAP solution incrementallyto metal salt solutions of varying concentrations. Results confirmedto metal salt solutions of varying concentrations.

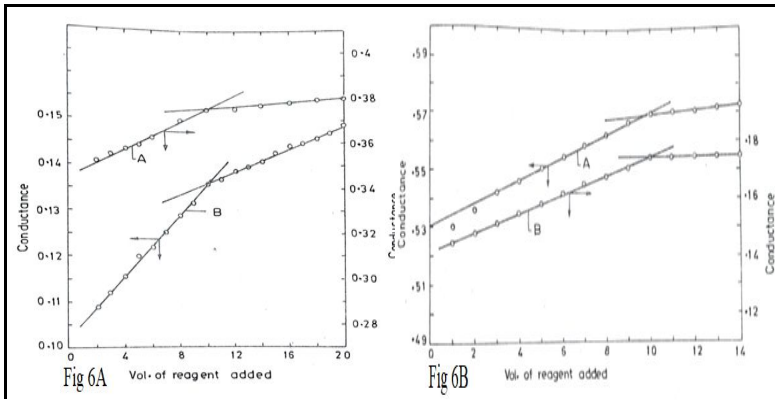


Fig 6A. Composition of Cu(II) complex conductometric titration in alcohol A - C_R -1 x 10^{-2}M, C_M = 2 x 10^{-3}M; B - C_R - 2 x 10^{-3}M, C_M = 4 x 10^{-4}M, **Fig 6B.** Composition of Ni(II) complex: A-C_R= 1 x 10^{-2}M, C_M = 1 x 10^{-3}M; B - C_R = 5 x 10^{-3}M, C_M = 5 x 10^{-4}M

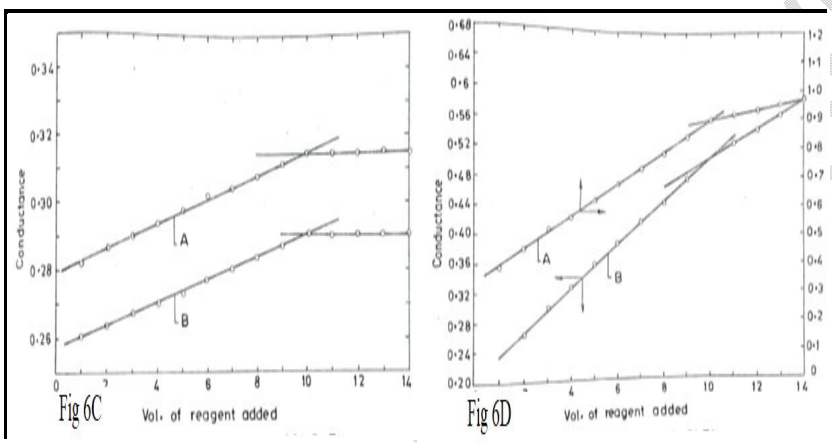


Fig 6C. Composition of Cd(II) complex: A - C_R -1 x 10^{-2}M, C_M = 1 x 10^{-3}M; B - C_R - 5 x 10^{-3}M, C_M = 5 x 10^{-4}M; **Fig 6D.** Composition of Hg(II) complex: A-C_R= 1 x 10^{-2}M, C_M = 1 x 10^{-3}M; B - C_R = 5 x 10^{-3}M, C_M = 5 x 10^{-4}M

The above mentioned solution studies have confirmed the composition as 1:1 for Cu(II) and 1:2 for Ni(II), Cd(II), and Hg(II) salts resulting in Cu(INMANAP)Cl and $M(INMANAP)_2$ complexes respectively.

3.2 Assignment of Geometrical Structure Based on the Complex Formation, Magnetic Moments, Spectra, and Other Properties(See (19) for electronic spectral data, diffuse reflectance data, which are similar data collected absorbance vs wavelength, so are not given here, but the associated figures 7, 14 – 21, 23-24 are given, which cover all the data given in them. Figures from 25-31 for IR spectra, not given here, also are look-alike as in (19) and the ligand IR spectrum in Fig 8, however, the Table 4 gives all the data compiled in it.)

Table 1. Statement showing preparation, formation of Cu(II), Ni(II), Fe(II), Co(III), Zn(II), Cd(II) and Hg(II) complexes, their chemical analysis

S No	Metal salt used	Likely complex formed at		Colour	Metal %		Carbon as C%		Hydrogen as H%		Nitrogen as N%		Chloride as Cl%		Magnetic moment μ, BM	Geometry
		pH	Formula		Expt	Calc	Expt	Calc	Expt	Calc	Expt	Calc	Expt	Calc		
1	Ligand (R) HINMANAP	-	-	Light yellow	-	-	72.40	72.06	3.80	4.38	9.90	10.96	-	-	-	-
2	Cupric(II) chloride	3.75	MRX	Bright green	13.4	13.2	57.1	57.4	3.40	3.32	8.90	8.73	6.90	7.36	1.3	Sq Pl
3	Nickel(II) chloride	3.5	MR_2	Pale yellow	7.91	7.13	67.05	66.30	3.88	3.20	10.21	10.50	-	-	3.3	Oh
4	Ferrous(II) ammonium sulphate	7.2	MR_2	Dark blue	6.80	6.85	66.4	67.3	4.1	3.9	10.8	10.2	-	-	5.2	Oh
5	Cobalt(III) chloride	H_2O_2	MR_2	Dark red	4.61	4.89	68.2	68.7	3.90	3.98	10.4	11.2	-	-	1.4 (Dia)	L S Oh
6	Zinc(II) sulphate	5.5	MR_2	Greenish yellow	7.00	7.88	66.10	66.55	3.60	3.85	9.90	10.11	-	-	Dia	Td
7	Cadmium(II) bromide	4.25	MR_3	Pale yellow	12.10	22.78	62.1	62.9	4.20	3.65	9.10	9.58	-	-	Dia	Td
8	Mercuric(II) chloride	4.5	MR_2	Pale yellow	19.90	20.74	57.6	57.2	2.90	3.31	7.50	8.71	-	-	Dia	Td

Dia – Diamagnetic; Expt – Experimental; Calc – Calculated; Td – Tetrahedral; L S Oh – low spin Octahedral; Oh – Octahedral; Sq Pl – Square Planar

Table 1A. Statement showing the solubilities of complexes of HINMANAP in various solvents (solubilities in g/L)

S No	Solvents	Cu(II) complex	Ni(II) complex	Fe(II) complex	Co(II) complex	Zn(II) complex	Cd(II) complex	Hg(II) complex
1	Acetone	0.591	1.36	1.39	3.00	0.41	0.51	0.59
2	Chloroform	0.618	4.56	4.97	13.31	0.69	1.40	1.60
3	Methanol	0.527	0.46	0.53	2.10	0.13	0.26	0.30
4	Ethanol	0.581	0.60	0.71	2.40	0.24	0.27	0.32
5	Benzene	0.128	1.26	1.43	3.20	0.42	0.56	0.61

3.2.1 Ligand HINMANAP

Ligand characterization was confirmed via CHN analysis (Table 1), UV electronic spectral analysis in methanol (Fig. 7), infrared spectra in KBr (Fig. 8), and PMR spectra in DMSO (Fig. 9).

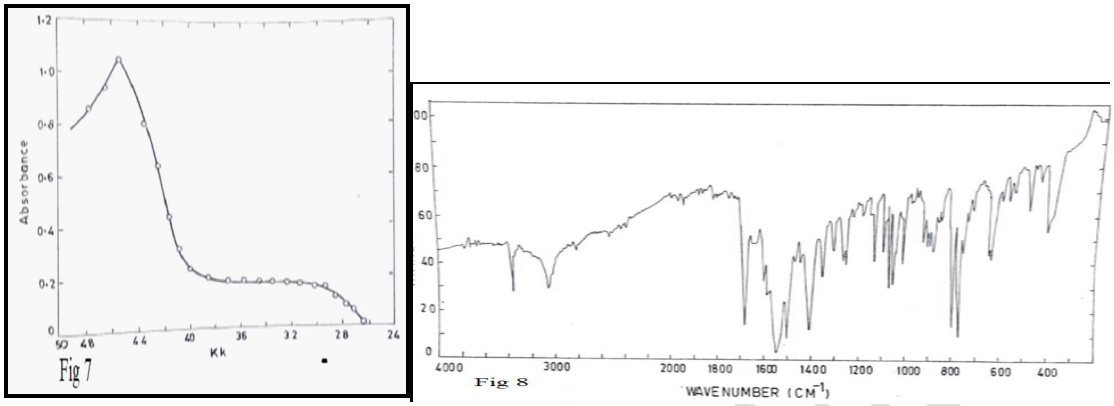


Fig 7. Electronic spectra in methanol and Fig 8. Infrared spectra in KBr of HINMANAP

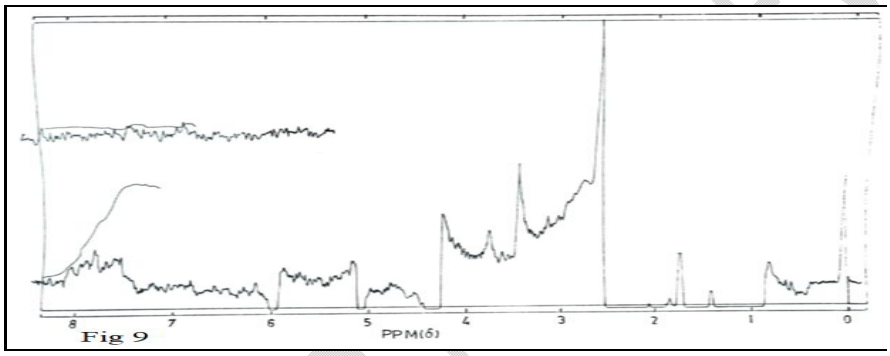


Fig 9. NMR spectra of HINMANAP in DMSO

3.2.2 Cu(INMANAP)Cl – Bright Green Complex

Magnetic Properties: Solution studies and elemental analysis suggest the formula Cu(INMANAP)Cl. The complex is feebly paramagnetic at room temperature, with a magnetic moment μ=1.3 BM. The variation of μwith temperature (77–293 K) is summarized in Table 2 and Fig. 10. Calculations of μ_{eff}were done using the expression:

$$\mu_{eff}=2.828 \text{ sqrt } [(\chi M - N\alpha)\cdot T] \quad (1)$$

where χM is the molar magnetic susceptibility (corrected for diamagnetic contributions using Pascal's constants, and Nα accounts for temperature-independent paramagnetism(20, 21).

The low μ (22), which decreases with temperature, suggests strong antiferromagnetic interactions, consistent with binuclear Cu(II) systems (23–28). The plot of χM vs. T (Fig. 11,12) indicates the presence of oxygen-bridged Cu atoms(29–30), similar to binuclear Cu(II) complexes (31–32). Binuclear structures about ten in number with various reagent orientations and possibilities for coordination are proposed for this complex, are not given here, but are similar to proposed in (19), not given here but are discussed and ruled out based on data.

Table 2. Magnetic behaviour of Cu(INMANAP)Cl complex at low temperature (Fig 10, 11, 12)

Temp ^{o}C	χ_g x 10^{-6} cgs units	χ_M x 10^{-6} cgs units	χ^{-1}_{M}corr μ_{eff} = 2.828	(χ^{-1}_{M} – N) x T	1/χ^{-1}_{M}
77.0	3.96	1904.7	2161.7	1.137	462.7
85.5	3.171	1525.2	1782	1.0851	561.1
102.3	2.260	1087.0	1344	1.025	744.0
118.4	1.925	925.9	1183	1.031	845.3
134.1	1.704	819.6	1076	1.043	929.3
152.4	1.551	746.0	1003	1.072	997.0
171.4	1.432	688.7	945.7	1.101	1057.4
193.3	1.331	640.10	897.19	1.137	1114.4
214.2	1.254	603.16	860.16	1.170	1162.6
235.3	1.182	566.3	825.5	1.200	1211.0
254.6	1.127	542.0	799.0	1.226	1251.5
273.6	1.0725	515.6	722.6	1.248	1294.3
293.3	1.012	486.76	743.76	1.266	1344.4

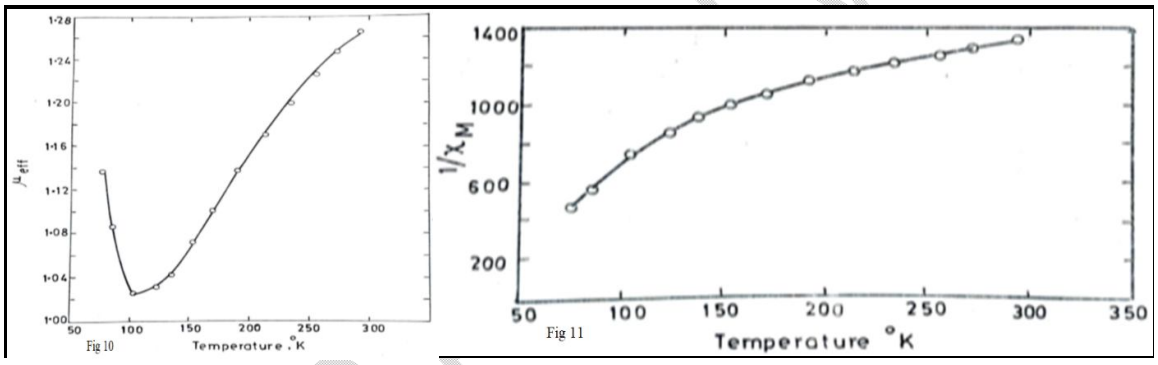


Fig 10. Magnetic behaviour of Cu(INMANAP)Cl at low temperatures,μ_{eff} vs T.

Fig 11. Magnetic behaviour of Cu(INMANAP)Cl complex at low temperatures, 1/χ^{-1}_{M} vs T

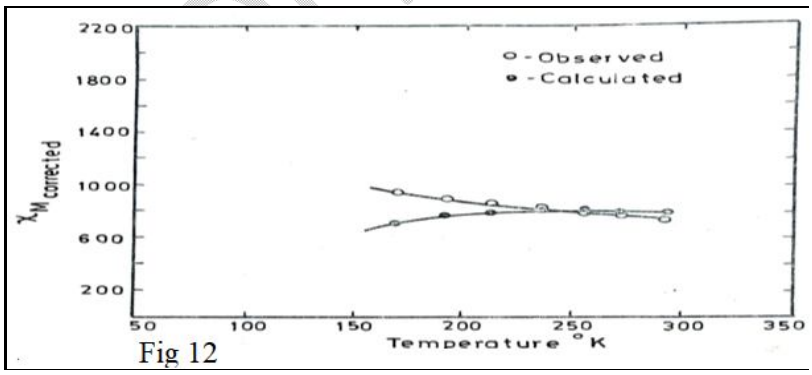


Fig 12. Magnetic susceptibility of Cu(INMANAP)Cl complex in various temperature, χ^{-1}_{M}corrvs T

Bleaney-Bowers Equation Analysis: Magnetic susceptibility of binuclear Cu(II) complexes follows the Bleaney-Bowers equation (33):|

Using ESR data (Fig. 13), the gyromagnetic constant g=2.0084was determined via:

$h\nu = g\beta H$…….(3)

where h is Planck's constant, β is the Bohr magneton, ν is microwave frequency, and H is the field strength. The value of 2J=280 was calculated as the best-fit parameter. Agreement between experimental and calculated χM values (Table 3) confirms Bleaney-Bowers applicability in the 190–300 K range (34-37).

Table 3. Calculations of $\square^1_M$ using Bleaney Bowers equation for Cu(INMANAP)Cl complex–

$2J = 280$; $g = 2.008$ (ESR); $N\beta^2g^2/3K = 0.4970$; $\square^1_M = N\beta^2g^2/3K\ 1 + 1/3\ 3^{-25}/KT + N_\alpha$

Temp ^oC	KT x 2.303	25/ KT x 2.303	$e^{2J/KT}$	$e^{2J/KT}/3 +1$	$B^{B.T.}$	A/BT x 10^{-6}	$\square^1_M$ x 10^{-6} + N_α
77.0	123.2	2.2720	168.9	57.30	4412.1	112.6	172.6
85.5	136.8	2.0467	111.2	38.06	3254.1	152.7	212.7
102.3	163.7	1.7104	51.34	18.11	1852.6	268.2	328.2
118.4	189.5	1.4775	30.03	11.01	1303.5	381.2	441.2
134.1	214.6	1.3047	20.17	7.723	1035.6	479.9	539.9
152.4	243.9	1.1480	14.06	5.686	866.5	573.5	633.5
171.4	274.3	1.0207	10.49	4.496	770.6	644.9	704.9
193.3	309.3	0.9052	8.039	3.679	7111	698.9	758.9
214.2	342.8	0.8168	6.568	3.189	683.0	727.6	787.6
235.3	376.9	0.7429	5.533	2.844	669.1	742.0	802.0
254.6	407.5	0.6871	4.865	2.621	667.3	744.7	804.7
273.6	437.9	0.6394	4.359	2.453	671.1	740.5	800.5
293.3	469.45	0.5964	3.949	2.316	679.2	731.7	791.7

Electronic and Reflectance Spectra: The electronic spectrum in pyridine solution (Fig. 14) exhibits two bands at 27,780 and 15,620 cm^{-1}, with an extinction coefficient ratio of 2.15, consistent with the literature (28, 43). The diffuse reflectance spectrum (Fig. 15) shows similar bands at 25,640 and 15,640 cm^{-1}, with an optical density ratio of 2:1.

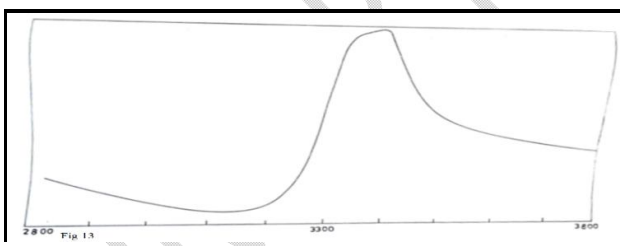


Fig 13. ESR spectra of Cu(INMANAP)Cl complex (dimethyl sulfoxide)

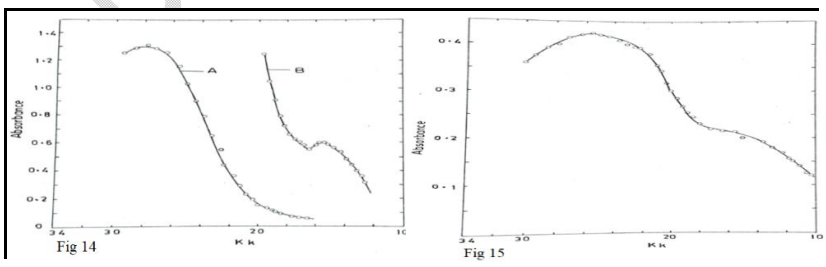
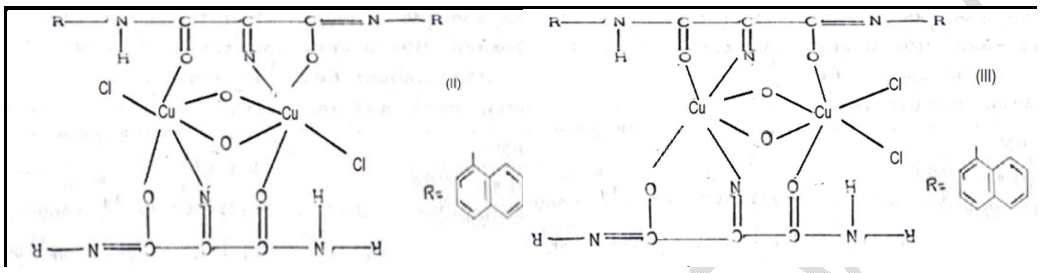


Fig 14. Electronic spectra of Cu(INMANAP)Cl in $C_A = 2.5 \times 10^{-4}M$, $C_B = 2.5 \times 10^{-3}M$

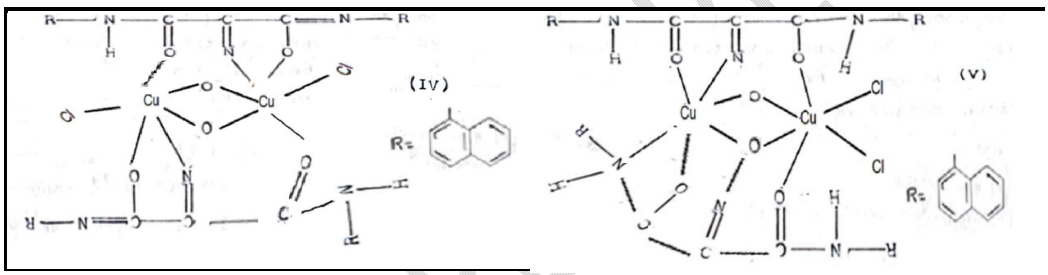
Fig 15. Diffuse reflectance spectra of Cu(INMANAP)Cl pyridine

Structural Assignment: Strong antiferromagnetism, applicability of the Bleaney-Bowers equation, and electronic spectra suggest a binuclear Cu(II) complex with oxygen bridges. Structures proposed with O- bridge, involving nitronic oxygen coordination, are most likely,with similar cis-trans systems considered (38-41). The pyramidal five coordinated structure (42-45) are also ruled outwhich involve chlorine bridges, are ruled out due to weaker magnetic interactions observed in due to significant disparity.The dimeric structure likely involves superexchange magnetism via nitronic oxygen bridges, consistent with other dimeric Cu(II) complexes.

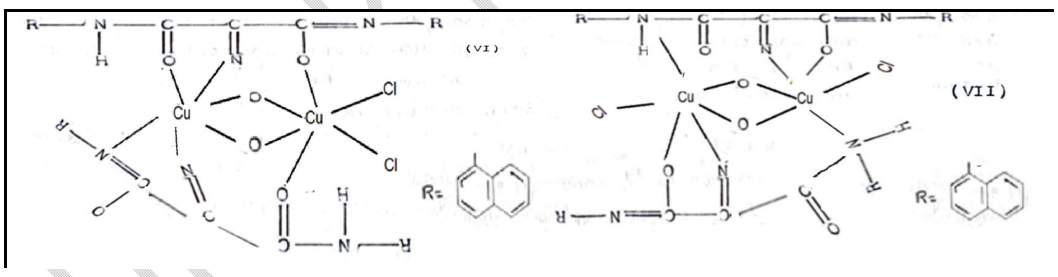
Structure II **Structure III**



Structure IV **Structure V**

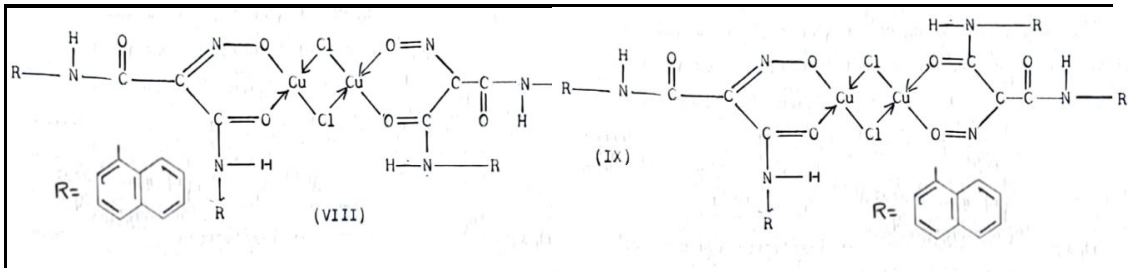


Structure VI **Structure VII**

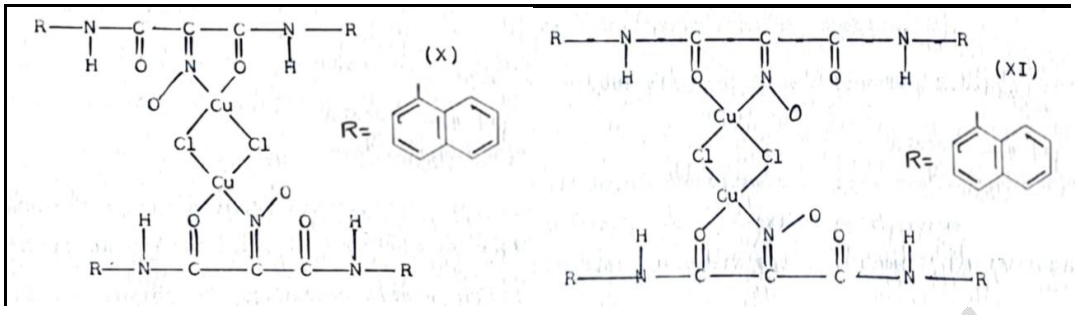


Possible structures with chlorine bridge between copper ions

Structure VIII **Structure IX**



Structure X **Structure XI**



3.2.3 Nickel(II) Complex (Pale Yellow) – Ni(INMANAP)□

The results of solution studies and chemical analysis suggest the composition of the pale yellow complex as Ni(INMANAP)□. Solubility data (Table 1A) indicates that the complex is insoluble in water and most organic solvents. The complex exhibits paramagnetic behavior with a magnetic moment (μ) of 3.3 BM at 295 K, consistent with two unpaired electrons. This μ value aligns with typical Oh or distorted Oh Ni(II) complexes, which usually show μ between 2.92–3.4 BM (47).

The electronic absorption spectrum (Fig 16) reveals a strong band at 23,260 cm^{-1}, assigned to π-π* transitions. The observed π-π* transition differs from that of the ligand (Fig 7), indicating significant alteration in the π-electron energy state upon complex formation. A shoulder around 18,520 cm^{-1} corresponds to the first d-d transition, while the band at 11,110 cm^{-1} represents the second d-d transition. These spectral features and the observed magnetic moment suggest an Oh structure for the yellow complex.

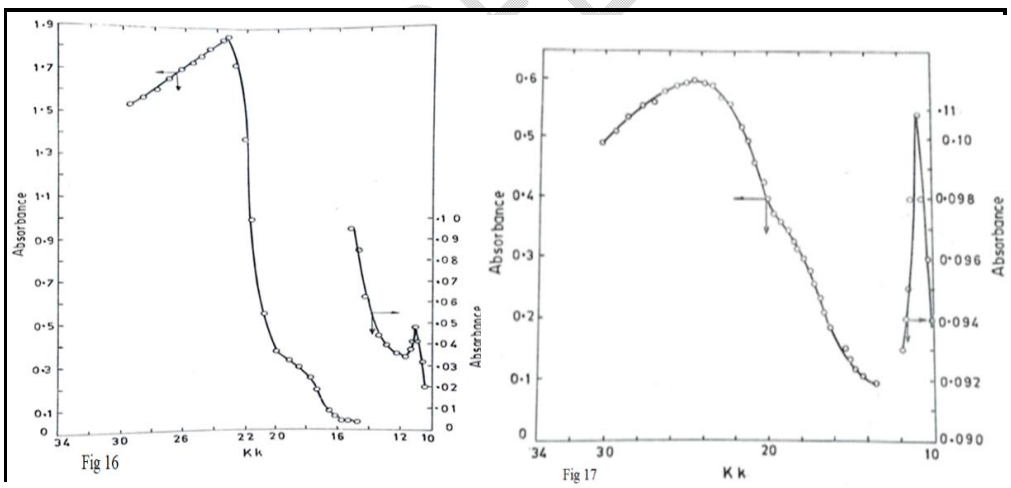
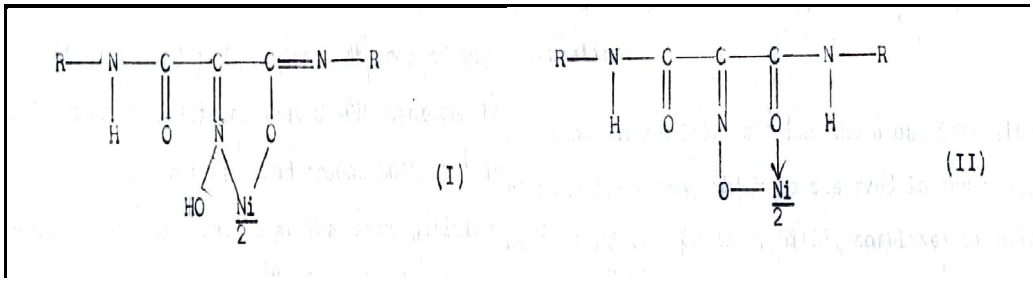


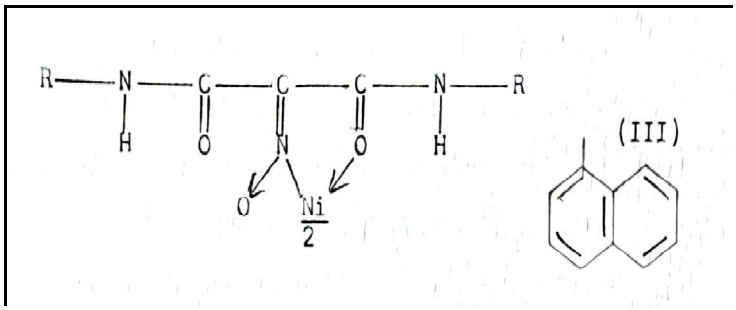
Fig 16. Electronic spectra of $Ni(R)_2$ in Chloroform Fig 17. Diffuse reflectance spectra of $Ni(R)_2$ complex

The diffuse reflectance spectrum (Fig 17) corroborates these findings, showing three bands: a π-π* transition at 24,390 cm^{-1}, a shoulder at 19,230 cm^{-1}, and a d-d transition band at 10,640 cm^{-1}. Based on these observations, the yellow complex is likely to adopt one of the three probable structures proposed.

Structure I **Structure II**



Structure III



3.2.4 Iron(II) Complex (Dark Blue) – Fe(INMANAP)□

The dark blue Fe(II) complex, Fe(INMANAP)□, is paramagnetic with a magnetic moment (μ) of 5.2 BM at room temperature, characteristic of a high-spin octahedral (Oh) configuration (48). This high-spin state suggests that the ligand field strength of INMANAP is insufficient to induce spin pairing in the Fe(II) electrons during complex formation (45).Electronic Spectrum (Fig 18): In chloroform, the complex shows a strong band at 30,300 cm^{-1} corresponds to a π-π* transitionand a weaker band at 16,670 cm band can be attributed to a d-d transition.Diffuse Reflectance Spectrum (Fig 19): In the solid state, the complex exhibits a broad band at 28,570 cm^{-1} and a strong band at 16,130 cm^{-1} assigned to π-π* and d-d transitions, respectively.

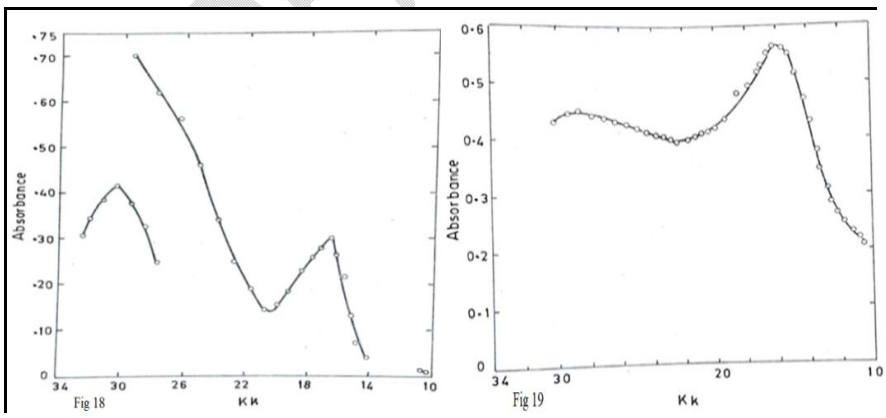
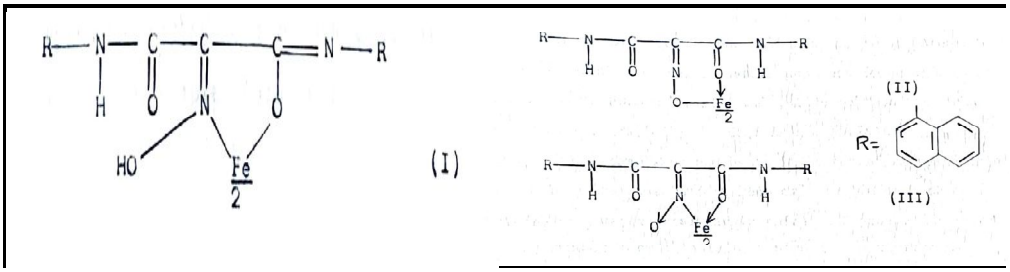


Fig 18. Electronic spectra of $Fe(R)_2$ in chloroform; Fig 19. Diffuse reflectance spectra of $Fe(R)_2$ complex

The $Fe(INMANAP)_2$ complex, based on its magnetic and spectral properties, is likely a high-spin octahedral complex. Three probable structures are proposed.

Structure I **Structure II and Structure III**



3.2.5 Cobalt(III) Complex: Co(INMANAP)□ (Dark Red)

The cobalt(III) complex exhibits a dark red color and is feebly paramagnetic, with a magnetic moment (μ) of 1.4 BM at room temperature. This aligns with the electronic configuration of Co(III) (3d□), which favors d^2sp^3 hybridization (49). Feeble paramagnetism in this complex may arise due to two mechanisms (49–52):

1. Temperature-independent contribution from high-frequency terms in Van Vleck's formula, ▪ M = ▪ d + ▪ p, typically reported for Co(III) complexes as 200 × 10^{-6} CGS units.
2. Temperature-dependent susceptibility from a thermally accessible state near the magnetically inert ground state.

For $Co(INMANAP)_3$, ▪ M was measured as 825.2 × 10^{-6} CGS units, suggesting temperature-independent paramagnetism and classifying the complex as effectively diamagnetic.The electronic spectrum (Fig 20) of the complex displays three bands:A strong band at 22,730 cm^{-1},a band at 19,230 cm^{-1}, anda weak band at 10,870 cm^{-1}.These observations suggest a low-symmetry ligand field, where the splitting of the $^1A_1$ g → $^1T_1$ g band into two transitions ($^1A_1$ g → ^{1}Eag and $^1A_1$ g → $^1A_2$ g) occurs due to symmetry lowering (53). The transitions can be assigned to $^1A_1$ g → ^{1}Eag, $^1A_1$ g → $^1A_2$ g, and $^1A_1$ g → $^1T_2$ g, characteristic of octahedral Co(III) complexes (54).The diffuse reflectance spectrum (Fig 21) supports these findings, showing:a band at 22,220 cm^{-1} (charge transfer),a shoulder at 18,520 cm^{-1}, anda band at 11,630 cm^{-1} (d-d transitions).

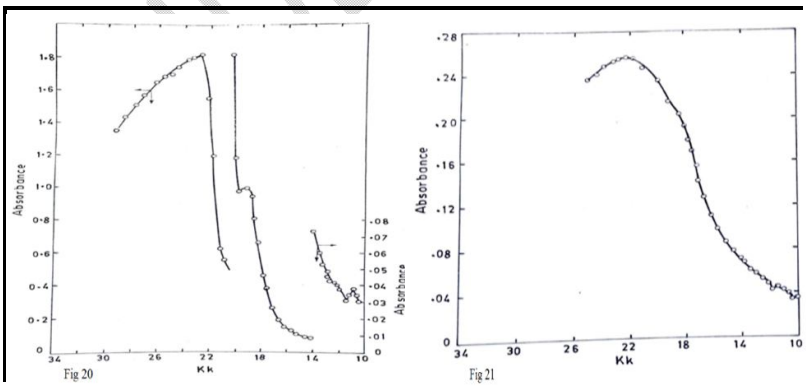


Fig 20. Electronic spectra of $Co(R)_3$ in chloroform Fig 21. Diffuse reflectance spectra of $Co(R)_3$ complex

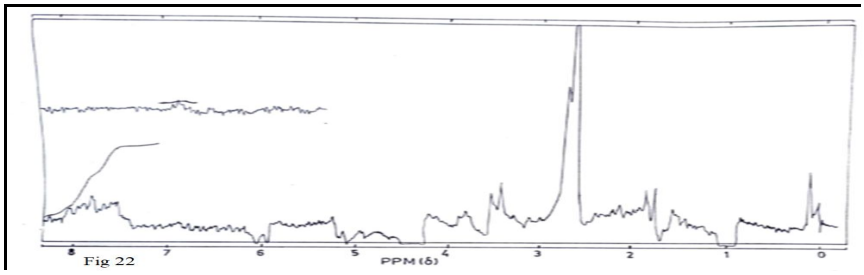
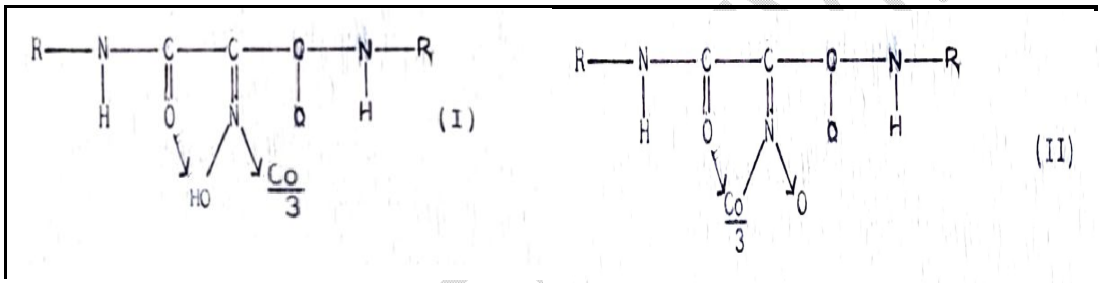


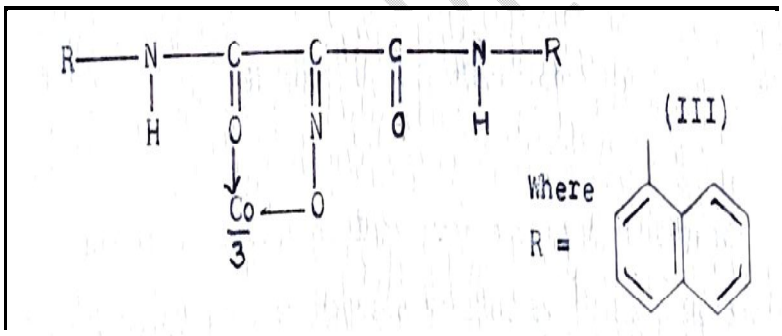
Fig 22. NMR spectra of $Co(INMANAP)_3$ in DMSO

Proton magnetic resonance (PMR) of the ligand in DMSO (Fig 9) shows a peak at δ = 2.5ppm, attributed to the =NOH group. However, PMR of the complex (Fig 22) lacks this peak, indicating the involvement of the =NOH group in complex formation through proton displacement by cobalt ions. Based on magnetic, spectral, and structural data, probable four structures are proposed for Co(INMANAP)□.

Structure I **Structure II**



Structure III



3.2.6 Zinc(II), Cadmium(II), and Mercury(II) Complexes

Analytical data indicates that Zn(II), Cd(II), and Hg(II) complexes can be represented as M(INMANAP)□, where $INMANAP^-$ denotes the anion of the ligand HINMANAP. These complexes are insoluble in common organic solvents and exhibit high decomposition temperatures of 290°C (Zn), 310°C (Cd), and 325°C (Hg), suggesting their polymeric nature.

The electronic spectra of the Zn(II), Cd(II), and Hg(II) complexes in chloroform (Fig. 23) display single bands at 26,320 cm^{-1}, 25,640 cm^{-1}, and 24,390 cm^{-1}, respectively, which are assigned to π-π* transitions arising from complex formation. The diffuse reflectance spectra of the solid complexes (Fig. 24) exhibit bands at 27,030 cm^{-1} for Zn(II) and Cd(II) and at 23,260 cm^{-1} for Hg(II), also corresponding to π-π* transitions, confirming the same.

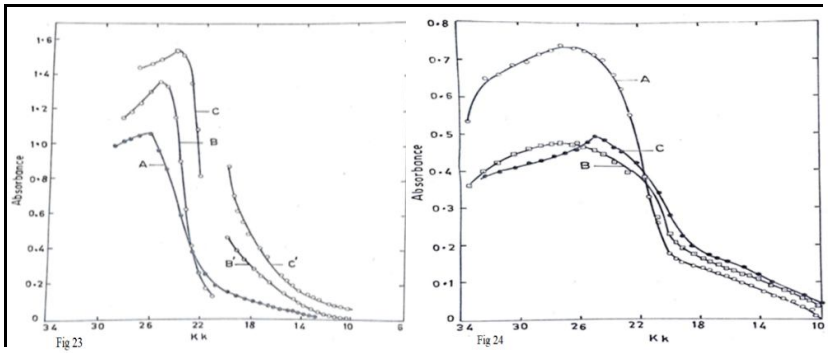
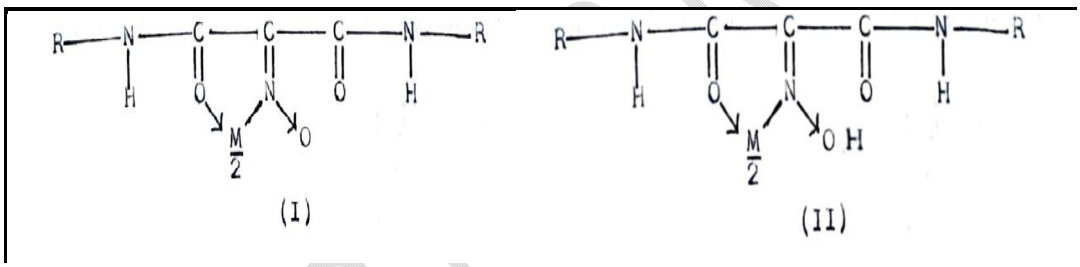


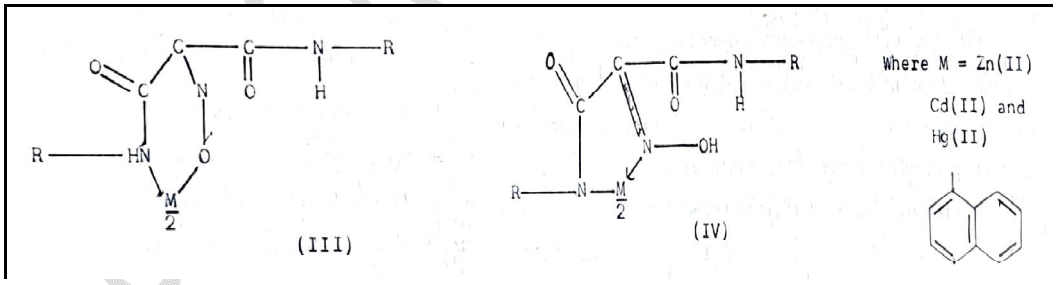
Fig 23. Electronic spectra of A – Zn(II) complex B & B' – Cd(II) complex C-C' – Hg(II) complex;
Fig 24. Diffuse reflectance spectra of A – Zn(II) complex; B – Cd(II) complex; C – Hg(II) complex in chloroform

These complexes are diamagnetic, with molar magnetic susceptibilities deviating from Pascal's additivity law (55). The diamagnetic nature and the lack of significant distinguishing bands in their electronic and reflectance spectra render the stereochemistry of these complexes indeterminate. Based on the available data, fourstructuresare proposed as the most probable representations of these complexes.

Structure I **Structure II**



Structure III **Structure IV**



3.3 Interpretation, Structure finalization, and Conclusion based on Infrared Spectra

General Observations from Ligand (Table 4, Fig 8)

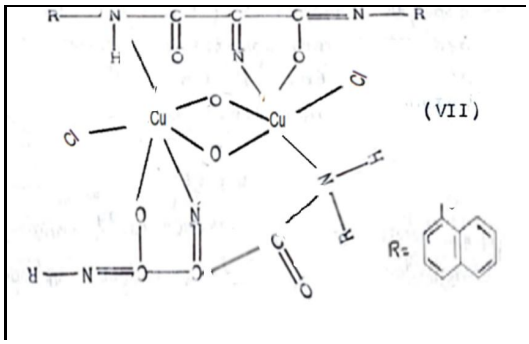
The ligand's IR spectrum shows a sharp band at 3360 cm^{-1} (-OH group) and a broad band at 3040 cm^{-1} (-NH group). The disappearance of the 3360 cm^{-1} band in all complexes confirms that the oxime proton (=NOH) is replaced by metal ions. The -NH band at 3040 cm^{-1} remains unchanged, indicating its non-involvement in complexation (55,56).Shifts in the strong 1660 cm^{-1} band (free -C=O group) and the 1295 cm^{-1} band (-N-oxide linkage)

after complexation suggest metal-ligand interactions. Additionally, metal-nitrogen (M-N) linkages are identified through bands between 600-400 cm^{-1}, absent in the ligand's spectrum.

3.3.1 Cu(II) Complex (Table 4)

The spectrum shows: bands at 1680, 1650, and 1595 cm^{-1} (C=O and perturbed C=N/-NH); a shift in the N-O stretching frequency from 1295 cm^{-1} (ligand) to 1265 cm^{-1} indicates oxygen bridging and a strong band at 600 cm^{-1} confirms Cu-N vibrations (46, 57-63).

The Cu(II) complex forms a binuclear molecule, $[CuRCl]_2$, with oxygen-bridged copper atoms in a square planar configuration. It exists predominantly as the trans-isomer (Structure VII), consistent with its stability and spectral features.

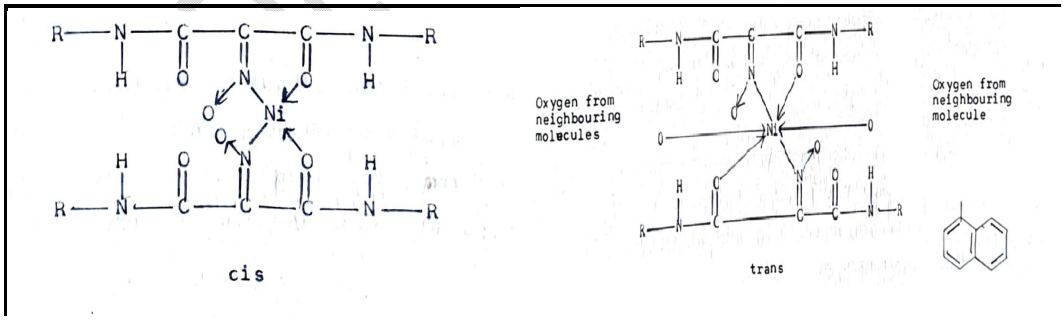


3.3.2 Ni(II) Complex (Table 4)

The IR spectrum reveals: a strong band around 1660 cm^{-1} (C=O group) and perturbed frequencies at 1630 and 1595 cm^{-1} (C=N/-NH).The absence of an N-O stretching band around 3400 cm^{-1} rules out Structure I.The band at 1285 cm^{-1} is attributed to an N-oxide linkage, while the 590 cm^{-1} band indicates Ni-N vibrations (64-66).

$Ni(INMANAP)_2$ achieves Oh configuration through ligand oxygen sharing, represented by a trans-isomer of structure is proposed.

Cis structure **Trans structure**



3.3.3 Fe(II) Complex (Table 4)

Key spectral features include:Strong bands at 1660 cm^{-1} (C=O) and 1550 cm^{-1} (perturbed C=N/-NH).A band at 1285 cm^{-1} suggests an N-oxide linkage, and a band at 595 cm^{-1} indicates Fe-N vibrations (67-68).

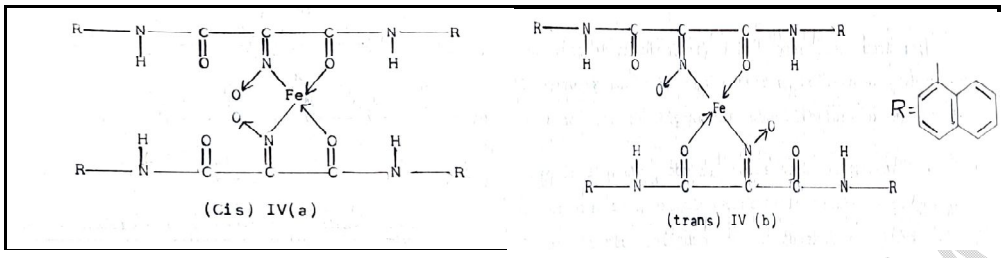
Table 4: Infrared spectral bands of ligand and metal complexes in the region 4000 cm^{-1} to 400 cm^{-1} in KBr medium (Fig 8, 25- 31)

S No	Ligand, HINMANAP Bands cm^{-1}	$Cu(R)_2$ complex cm^{-1}	$Ni(R)_2$ complex cm^{-1}	$Fe(R)_2$ complex cm^{-1}	$Co(R)_3$ complex cm^{-1}	$Zn(R)_2$ complex cm^{-1}	$Cd(R)_2$ complex cm^{-1}	$Hg(R)_2$ complex cm^{-1}	Assignments	Basis of interpretation	Reference
1	3360 (sh)	Absent	Absent	Absent	Absent	Absent	Absent	Absent	Stretching vibration of group C=NOH oxime	Not participated	
2	3040 (b), (str)	3040 (b), (str)	3040 (b), (str)	3040 (b), (str)	3040 (b), (str)	3040 (b), (str)	3040 (b), (str)	3040 (b), (str)	NH group	unchanged	55,56
3	1660	1680	1660	1665	1660	1600	1600	1600	C=O stretching	-O- coordinated, frequency shift	48,60,62, 65,70,
4		1650	1630 (str)	1620 (str)	1630 (str)	1630 (str)	1630 (str)	1630 (str)	Perturbed C=N stretching frequency or =NH bending	New frequencies	
		1595 (str)	1595 (str)	1595 (str)	1595 (str)	1595 (str)	1595 (str)	1595 (str)			
5		1560	1550-1540 (b)	1550-1540 (b)	1550-1540 (b)	1550	1550	1550	Free C=O, C=N and/or C=O perturbed	New frequencies	60,65
6	1295	1265 (str)	1285 (str)	1285 (str)	1250 (b)	1285 (b)	1285 (b)	1285 (b)	N-Oxide linkage	Frequency shift	48,60,62,66, 67
7		600	590	595	595	600	605	600	M=N/M-O vibration	New frequencies	48,46-65, 57,58,68,69

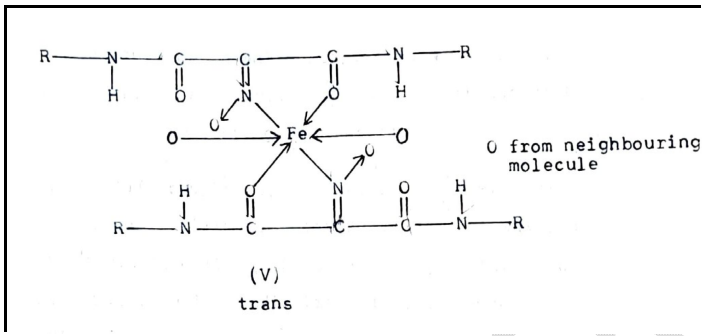
R = INMANAP, (b) – broad, (str) – strong, (sh) - sharp

The absence of an -OH stretching band around 3400 cm^{-1} rules out two proposed structures. $Fe(INMANAP)_2$ adopts three proposed structures, but represented as a trans-configuration (Structure V), supported by magnetic and spectral data.

Structure IVA – cis **Structure IVB – trans**



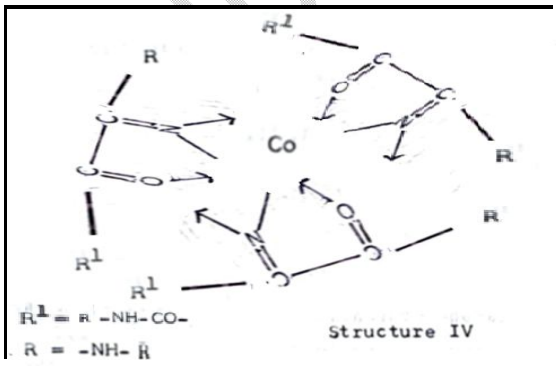
Structure V – trans



3.3.4 Co(III) Complex (Table 4)

The absence of the sharp 3360 cm^{-1} band confirms the replacement of the =NOH proton by cobalt.Strong bands are observed at 1660 cm^{-1} (C=O) and 1595 cm^{-1} (perturbed C=N/-NH).A shift in the 1295 cm^{-1} band (N-oxide linkage) and the appearance of a new band at 595 cm^{-1} (Co-N vibration) further confirm complexation, three proposed structures are ruled out) (69-70).The Co(III) complex is a low-spin Oh, tris-chelate complex, represented by Structure IV.

Structure IV



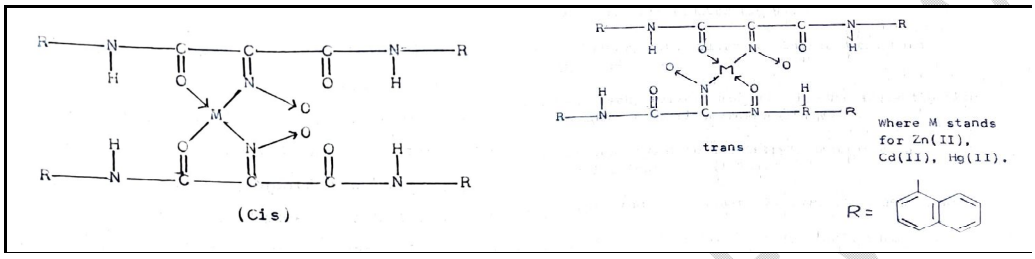
IR spectral analysis confirms complex formation via oxime and N-oxide groups, with significant shifts in C=O and M-N bands.Cu(II), Ni(II), and Fe(II) complexes form cis or trans configurations, while Co(III) adopts unique stereochemistries.Proposed structures satisfactorily explain all observed spectral and magnetic properties.

3.3.5 Zn(II), Cd(II), and Hg(II) Complexes (Table 4)

These complexes exhibit identical spectral features, indicating isostructurality:The C=O band at 1660 cm^{-1} shifts to ~1600 cm^{-1}, suggesting oxygen coordination.Bands at 1630 cm^{-1} and 1595 cm^{-1} correspond to perturbed C=N/-NH.The 1285 cm^{-1} band signifies N-oxide linkage, while bands at 600–605 cm^{-1} confirm M-N vibrations.

Their Td geometry involves sp^3 orbital hybridization, forming covalent bonds between metal ions and the ligand (69-70). The observed deviation in molar magnetic susceptibility supports this stereochemistry, which is represented by the trans-isomer.

Structure – cis **Structure – trans**



4.0 CONCLUSION

Whitley (7) reported the preparation of mesoximes, including malon-di-(α-naphthyl)amide-oxime (isonitrosomalon-di-(α-naphthyl) amine oxime), but their reactions with metals remain unexplored. This study investigates reactions of HINMANAP with various metal salts, yielding solid-state complexes.

Chemical analysis shows that Ni(II), Fe(II), Zn(II), Cd(II), and Hg(II) form $M(INMANAP)_2$ complexes, Cu(II) forms Cu(INMANAP)Cl, and Co(III) forms $Co(INMANAP)_3$. HINMANAP acts as an oxime anion ($INMANAP^-$) after losing a proton.Solution studies using methods like Job's and Yoe-Jones mole ratio reveal structural insights, supported by magnetic and spectral data (infrared, electronic, reflectance, ESR, and PMR). Cu(II) exhibits antiferromagnetic behavior with a subnormal magnetic moment (1.3 BM), suggesting a polymeric structure. Ni(II) (3.3 BM) is paramagnetic, likely polymeric and octahedral. Fe(II) (5.2 BM) is high-spin, sparingly soluble, and Oh. Co(III) (1.4 BM) is temperature-independent paramagnetic, likely diamagnetic. Zn(II), Cd(II), and Hg(II) are diamagnetic with Td structures, deviating from Pascal's additivity law and sharing isostructural characteristics.

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