Structural Investigations of Some Metal Complexes of Malon-Di-(α-Naphthyl) Amide-Oxime

Mukesh Shrivastava [a,b*], G. Swarnabala [a,b*], S. B. Khatavkar [b], G. S. Sadana [b] and Anahita Bharadwaj [a,c*]

[a] *Swaram Biochem, Hyderabad, India.*
[b] *Research Laboratory, Chemistry Department, G. N. Khalsa College, Mumbai– 400019, India.*
[c] *Department of Agricultural and Biological Engineering, Penn State College, Pennsylvania, USA.*

Authors' contributions

This work was carried out in collaboration among all authors. All authors read and approved the final manuscript.

Original Research Article

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 (isonitroso malon-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. Solution studies done with reagent and metal salts assisted in predicting geometry for these complexes, to finalize the M:L ratios and have allowed the pH to be established to separate the complex formed in solid state. The green Cu(II) complex is dimeric, confirmed by its electronic and reflectance spectra, with a likely square planar structure, Bleaney-Bower's equation helped to finalize the dimeric complex formation. 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. From the dark colours of the complexes obtained, they may be utilized as complexing agents like the well-known oxime containing ligands.

1. 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 (Morgan & Drew, 1920; Godycki & Rundle, 1953; Fox et al., 1962; Diehl, 1937). A Russian review (Mikhaleva et al., 2006) details on oximes as reagents and mentions them as selective ligands for transition metal cations and also the components of highly efficient palladium catalysts. However, a most recent review (Ranjan, 2019)classifies and summarizes a decade long advancement in metal-mediated and metal-catalyzed reactions of oximes. Their diverse reactions applied for syntheses of metal complexes & cage-compounds, oxime functionalizations, and the synthesis of new class of organic species, particularly spanning a wide variety of heterocyclic systems ranging from small 3-membered ring systems to macro-heterocycles. Most recent review mentions oxime derivatives as valid pharmacophores in medicinal chemistry (Chandran et al, 2024). A comprehensive review (Chakravorty, 1974) 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 (Shrivastava, 1981). Substituted malonic oximes with the -CO-C(=NOH)- moiety have also been reported (Whiteley, 1903), 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 (Desai, 1975; Deshpande, 1976), highlighting their utility as complexing agents.

The study (Shrivastava, 1981) focuses on the synthesis and characterization of malon-di-(α-naphthyl)amide-oxime (isonitroso malon-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 PMR spectroscopy, along with magnetic measurements.

2. EXPERIMENTALS 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 (Vogel, 1975).

2.1 Equipment Used Are

An analytical balance with 0.1 mg sensitivity was calibrated using the method described by Scott, (1939). Ultraviolet absorption measurements were performed on a Systronic MK II 106 spectrophotometer, calibrated with 0.004% K_2CrO_4 solution in 0.05M potassium hydroxide and 0.0062% potassium permanganate solution.

The observed spectra aligned well with reported literature values (Vogel, 1975). 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 (Isonitroso Malon-di-(α-naphthyl) Amine Oxime) Abbreviated as HINMANAP

The reagent HINMANAP was synthesized following the procedure described in the literature (Whiteley, 1903; Shrivastava, 1981). 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.
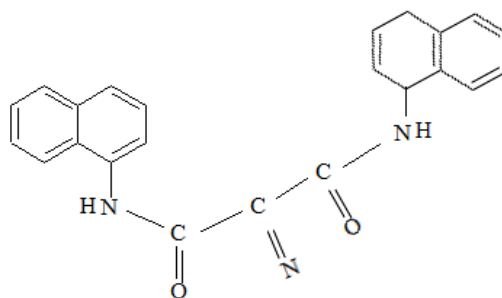
REAGENT - HINMANAP

Structure I. Structure of reagent HINMANAP

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 (Vogel, 1975). Magnetic susceptibility measurements were performed at room temperature and over the 77–300 K range using the Faraday method (Mulay, 1972) with corrections for χM based on the diamagnetic ligand (Figgis & Martin, 1960). The $HgCo(SCN)_4$ complex was used as a secondary standard (Figgis & Nyholm, 1958, 1959; Marathe 1966); Dunne & Cotton, 1963), with a χ_g value of 16.44×10^{-6} cm³/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 (Vosburgh & Cooper, 1941), Job's continuous variation method (Job, 1928), Yoe and Jones mole ratio method (1944), and conductometric analysis (Gupta et al, 1966).

3. 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 and PMR could be recorded. 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 (Swarnabala et al, 2022) for similar look of data for tables not given here and figures using that data, Figs. 1 a-d to 6 a-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.
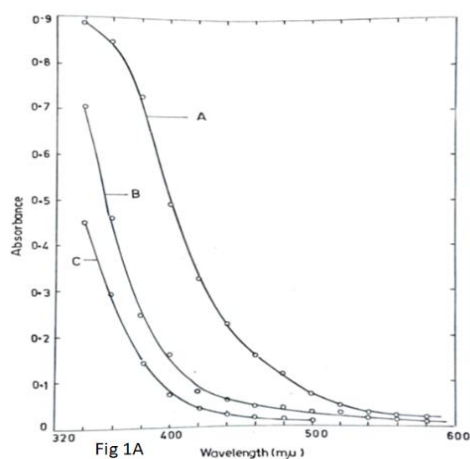

Fig. 1A. Absorbance of A – Cu(II)complex = 2 x 10⁻³M; B – HINMANAP = 1 x 10⁻³M; C – CuCl₂ = 1 x 10⁻³M in alcohol
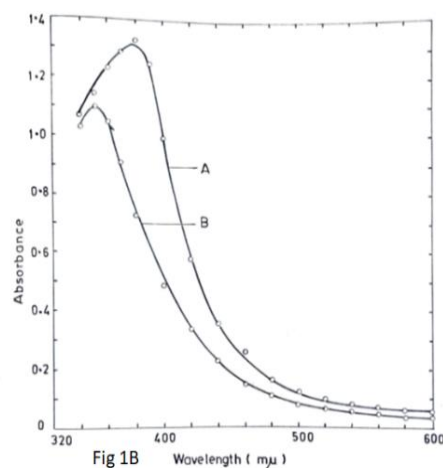
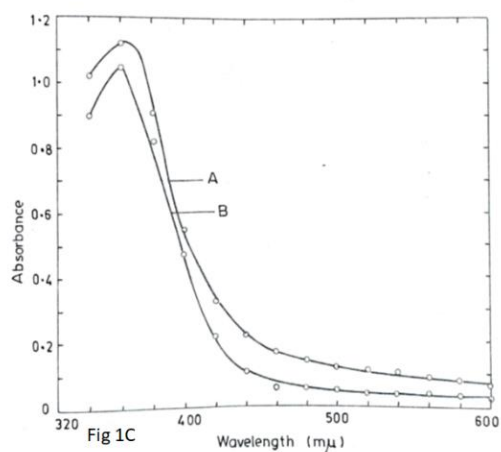**Fig. 1B. Absorbance of A – Ni(II)complex = 2 x 10⁻³M; B – HINMANAP = 1 x 10⁻³M in alcohol**

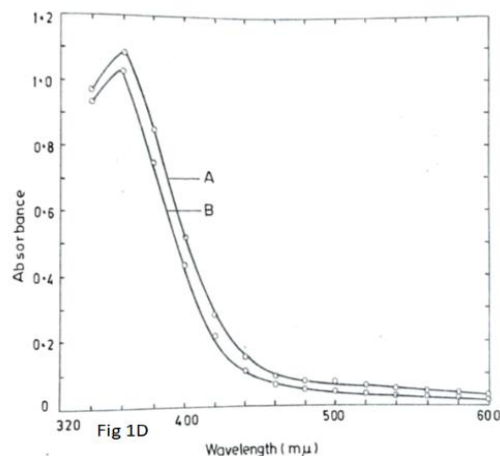**Fig. 1C. Absorbance of A – Cd(II)complex = 2 x 10^{-3}M B – HINMANAP = 1 x 10^{-3}M in alcohol**

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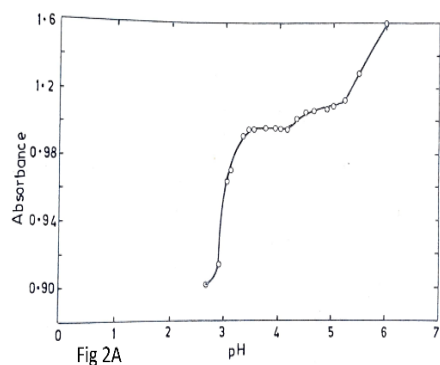

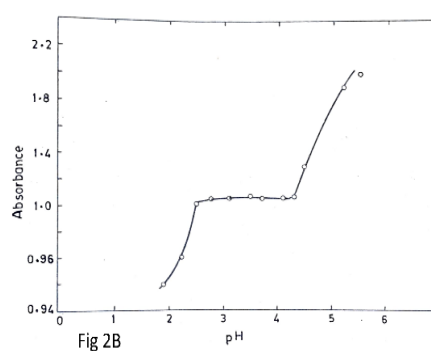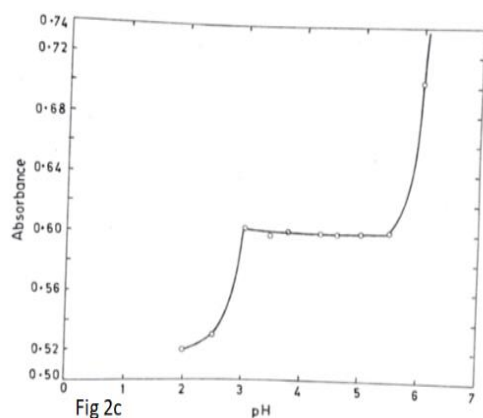**Fig. 2A. Effect of pH on absorbance of Cu(II) complex in alcohol at $C_R = C_M = 1$ x 10^{-3}M**

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

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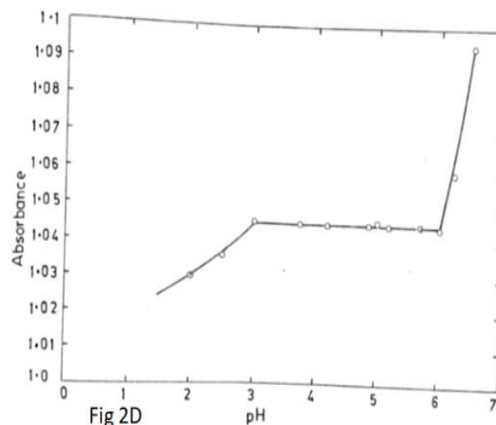

Fig 2D. Effect of pH on absorbance of Hg(II) complex in alcohol at $C_R = C_M = 1$ x 10^{-3}M

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.

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.

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.

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.

3.1.6 Conductometric method

The conductometric titrations were performed by adding HINMANAP solution incrementally to metal salt solutions of varying concentrations. Results confirmed to metal salt solutions of varying concentrations.

3.2 Assignment of Geometrical Structure Based on the Complex Formation, Magnetic Moments, Spectra, and Other Properties

(See (Swarnabala et al, 2022) for electronic spectral data, diffuse reflectance data, which are similar data collected absorbance vs wavelength, so are not given here, but the associated Figs. 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 (Swarnabala et al, 2022) and the ligand IR

spectrum in Fig. 8, however, the Table 4 gives all the data compiled in it.).

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.

3.2.1 Ligand HINMANAP

Ligand characterization was confirmed via CHN analysis (Table 1), UV electronic spectral analysis in methanol (Fig. 7) data were collected wavelength in KK vs absorbance and are plotted showing a strong band at 45,450 cm^{-1} assigned to π-π* transition which is found shifted to lower wave numbers with complex formation, infrared spectra in KBr (Fig. 8), Proton magnetic resonance (PMR) of the ligand in DMSO (Fig. 9) shows a peak at δ = 2.5ppm, attributed to the =NOH group, along with the routine standard peak for TMS (tetramethylsilane) at zero. This peak is not found in the representative PMR spectrum for Co(III) complex, confirming the complexation at this group, which is seconded by the absence of infrared peak for this group in all complexes as discussed below.

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 μ with temperature (77–293 K) is summarized in Table 2 and Fig. 10. Calculations of μ$_{eff}$ were done using the expression:

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

where χM is the molar magnetic susceptibility (corrected for diamagnetic contributions using Pascal's constants, and Nα accounts for temperature-independent paramagnetism (Selwood, 1956; Figgis & Martin, 1956; Gruber et al., 1968).

The low μ (Kato et al., 1964), which decreases with temperature, suggests strong antiferromagnetic interactions, consistent with binuclear Cu(II) systems (Figgis & Nyholm, 1959); Hatfield & Whyman, 1969; Whiteley, 1907;Martin & Waterman, 1968; Harris et al, 1959; Kalia & Chakravorty, 1970; Chakravorty, 1971). The plot of χM vs. T (Figs. 11,12)

indicates the presence of oxygen-bridged Cu atoms (Martin & Waterman, 1959; Kokot & Martin, 1964) similar to binuclear Cu(II) complexes (Harris et al., 1959). (Sinn & Harris, 1969) 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 (Swarnabala et al, 2022), not given here but are discussed and ruled out based on data.

Bleaney-Bowers Equation Analysis: Magnetic susceptibility of binuclear Cu(II) complexes follows the Bleaney-Bowers equation (Bleaney & Bowers, 1952).

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

$$hv = g\beta H \qquad (2)$$

where h is Planck's constant, β is the Bohr magneton, v 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 (Fanning & Jonassen, 1963), Starr et al, 1940; Tokii et al, 1973; Figgis, & Martin, 1972).
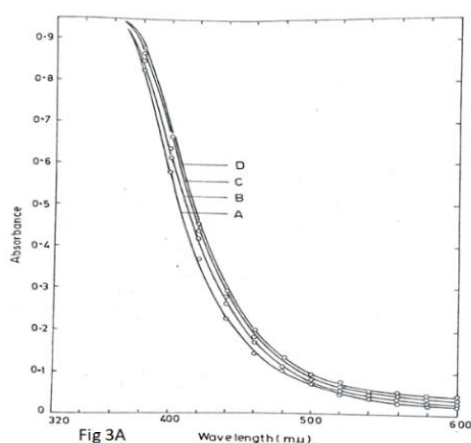
Fig. 3A. Method of Vosburgh and Cooper in alcohol: for Cu(II) complex at $C_R = C_M = 1 \times 10^{-3}$M where M:R = A – 1:1; B – 1:2; C – 1:3; D – 1:4
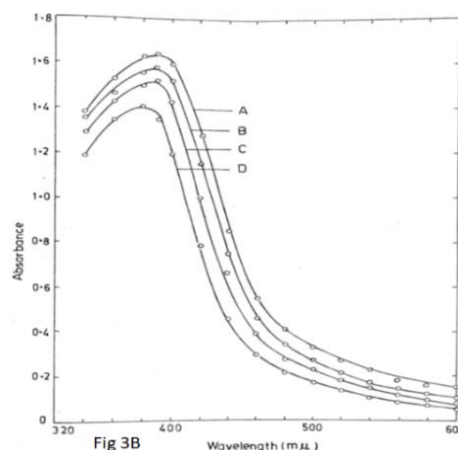
Fig. 3B. for Ni(II) complex at $C_R = C_M = 2 \times 10^{-3}$M where M:R = D – 1:1; C – 1:2; B – 1:3; A – 1:4
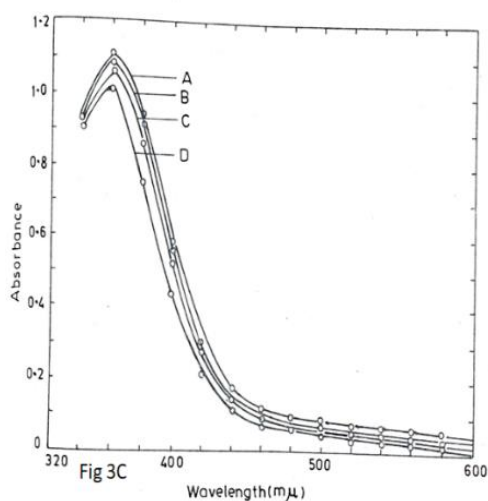

Fig. 3C. for Cd(II) complex at $C_R = C_M = 1 \times 10^{-3}$M where M:R = A – 1:4; B – 1:3; C – 1:2; D – 1:1
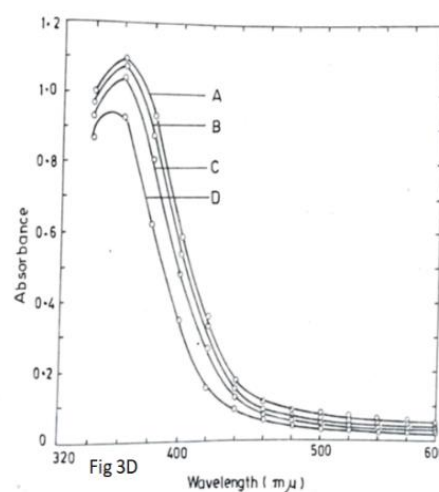

Fig. 3D. for Hg(II) complex at $C_R = C_M = 1 \times 10^{-3}$M where M:R = D – 1:1; C – 1:2; B – 1:3; A – 1:4
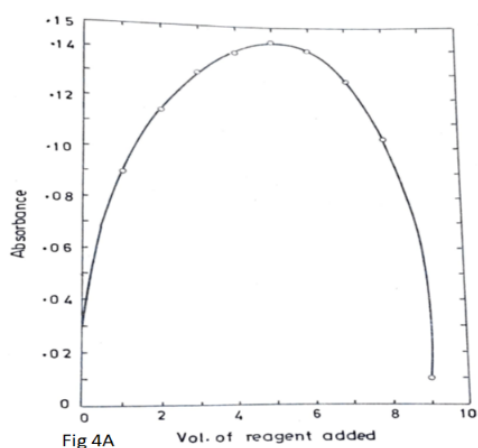
Fig. 4A. Composition of Cu(II) complex in alcohol by Job's method at $C_R = C_M = 1 \times 10^{-4}$M
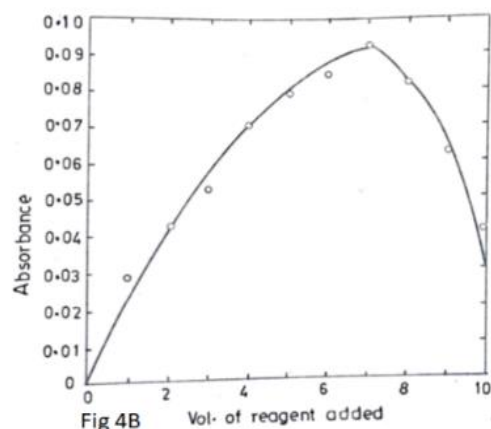
Fig. 4B. Composition of Ni(II) complex in alcohol by Job's method at $C_R = C_M = 1 \times 10^{-4}$M
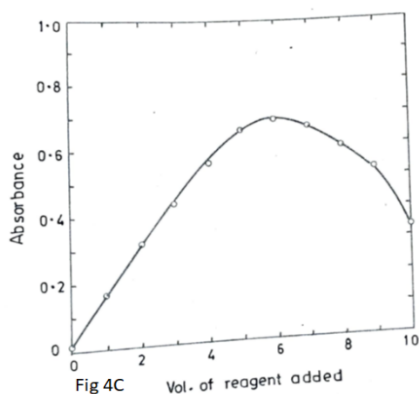
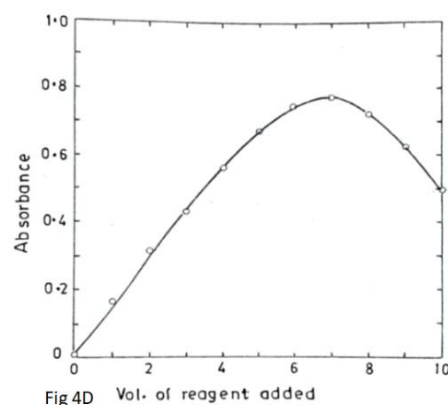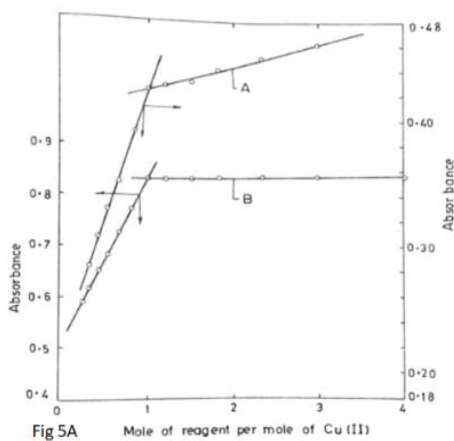**Fig. 4C. Composition of Cd(II) complex in alcohol by Job's method at $C_R = C_M = 5 \times 10^{-4}$M**

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

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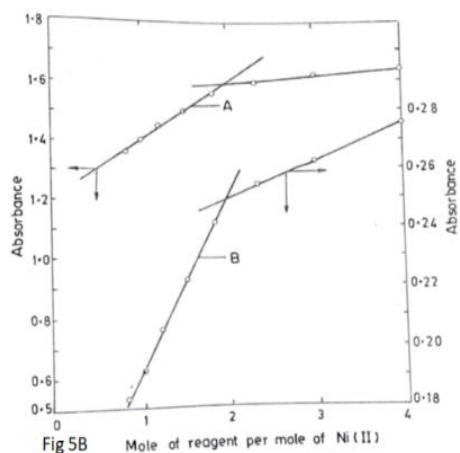
Fig. 5B. Ni(II) complex, A - $C_R = C_M = 5 \times 10^{-4}$M and B - $C_R = C_M = 3 \times 10^{-4}$M
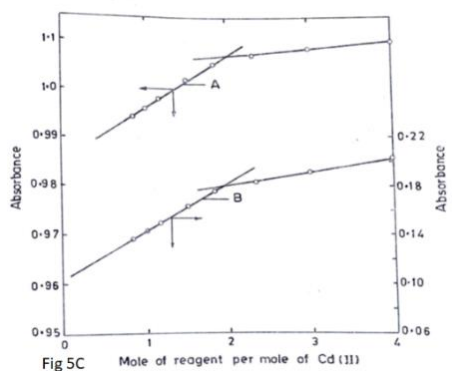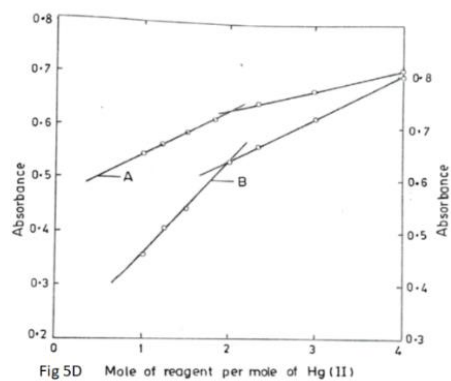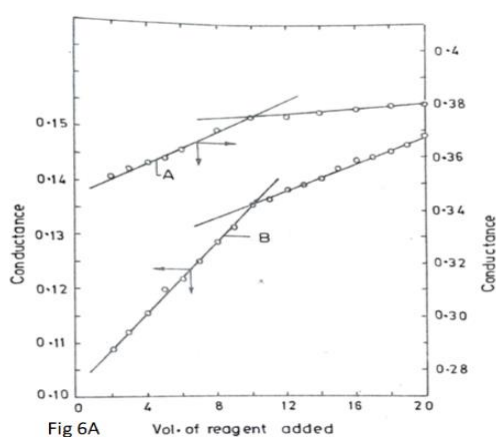
Fig. 5C. Cd(II) complex, A - C_R = C_M = 1 x 10^{-3}M and B - C_R = C_M = 1 x 10^{-4}M

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

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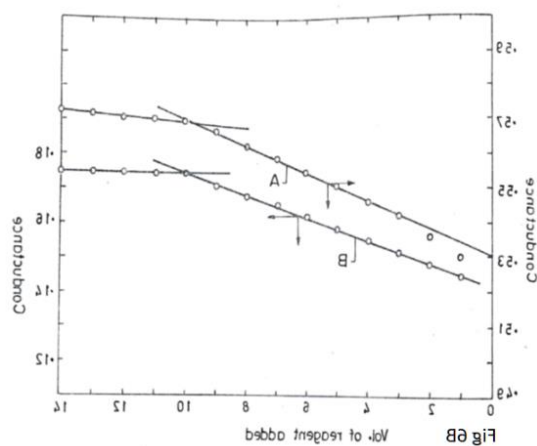
Fig. 6B. Composition of Ni(II) complex: A- C_R= 1 x 10^{-2}M, C_M = 1 x 10^{-3}M; B - C_R = 5 x 10^{-3}M, C_M = 5 x 10^{-4}M
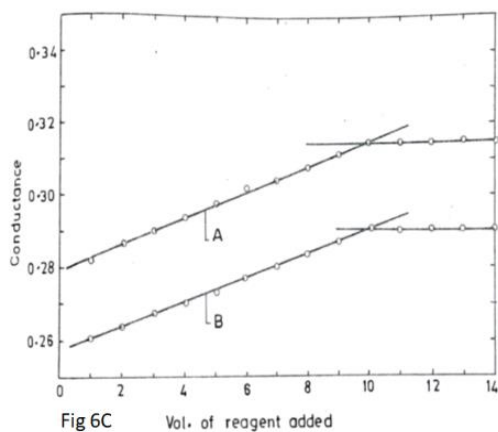
Fig. 6C. Composition of Cd(II) complex: A - C_R -1 x 10^{-2}M, C_M = 1 x 10^{-3}M; B - C_R - 5 x 10^{-3}M, C_M = 5 x 10^{-4}M
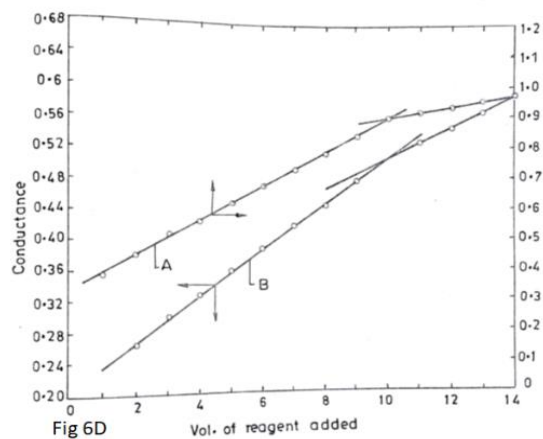
Fig. 6D. Composition of Hg(II) complex: A-C_R= 1 x 10^{-2}M, C_M = 1 x 10^{-3}M; B - C_R = 5 x 10^{-3}M, C_M = 5 x 10^{-4}M

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)

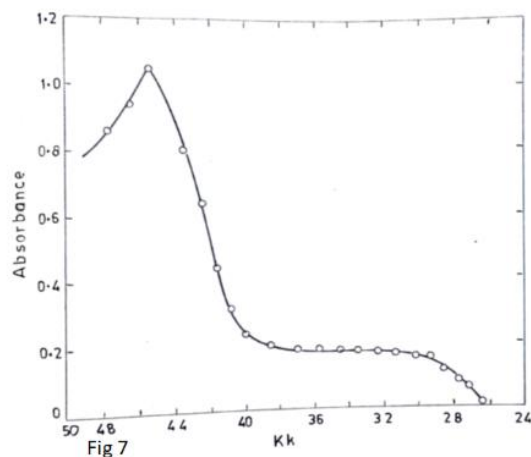| S No	Solvents	Cu(II) complex	Ni(II) complex	Fe(II) complex	Co(II) complex	Zn(II) complex	Cd(II) complex	Hg(II) complex
1	Acetone	0.591	1.36	1.39	3.00	0.41	0.51	0.59
2	Chloroform	0.618	4.56	4.97	13.31	0.69	1.40	1.60
3	Methanol	0.527	0.46	0.53	2.10	0.13	0.26	0.30
4	Ethanol	0.581	0.60	0.71	2.40	0.24	0.27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

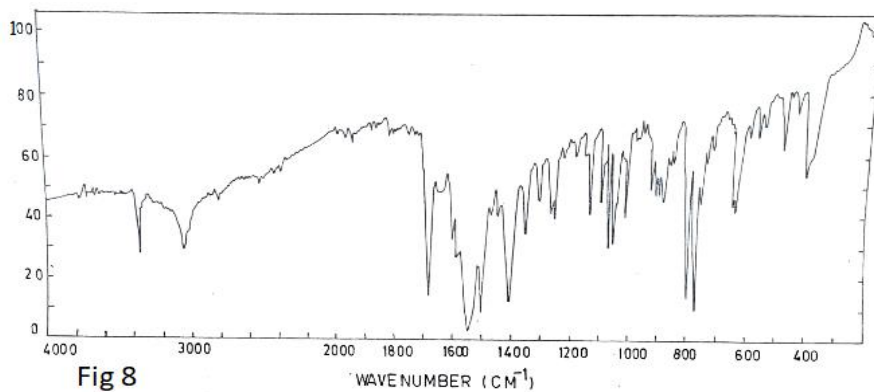**Fig. 7. Electronic spectra in methanol**

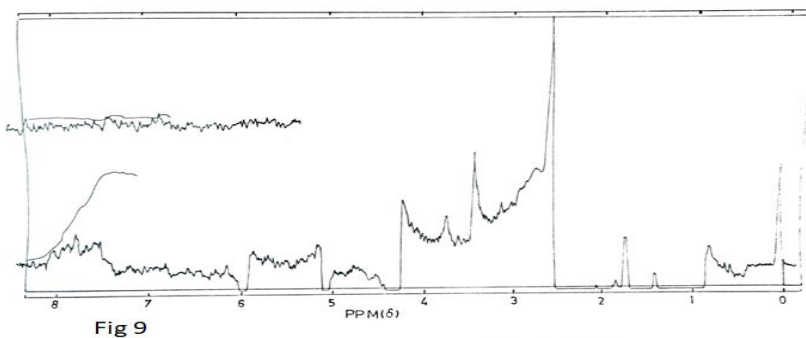**Fig. 8. Infrared spectra in KBr of HINMANAP**

Fig. 9. PMR spectra of HINMANAP in DMSO

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

| Temp °C	$\chi_g \times 10^{-6}$ cgs units	$\chi_M \times 10^{-6}$ cgs units	χ^1_M corr μ_{eff} = 2.828	$(\chi^1_M - N) \times T$	$1/\chi^1_M$
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
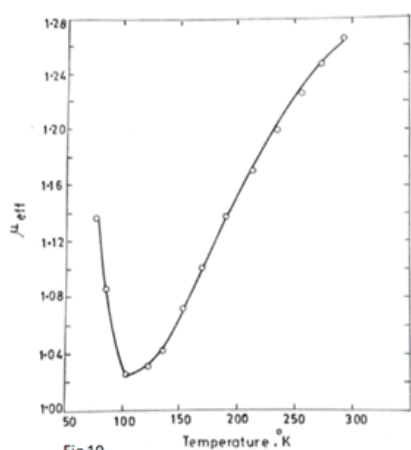
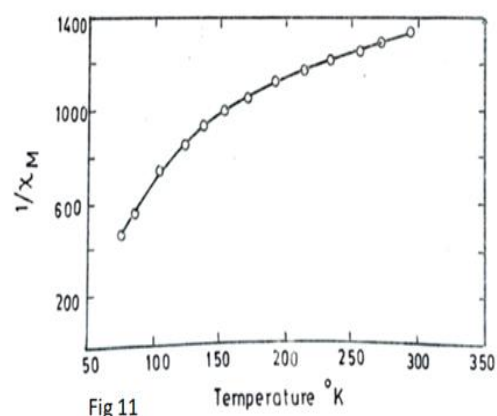**Fig. 10. Magnetic behaviour of Cu(INMANAP)Cl at low temperatures, μ_{eff} vs T**

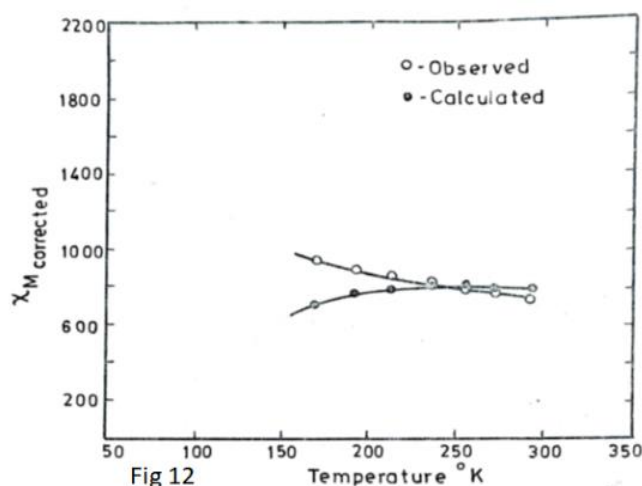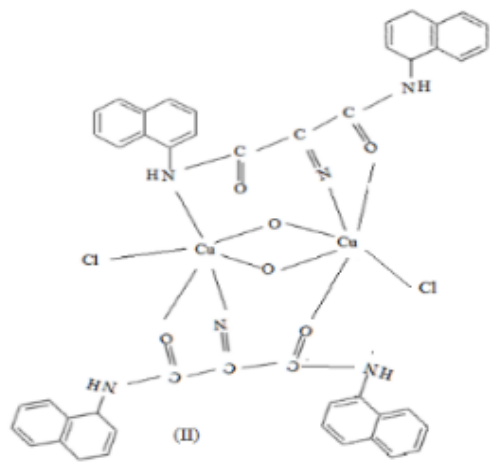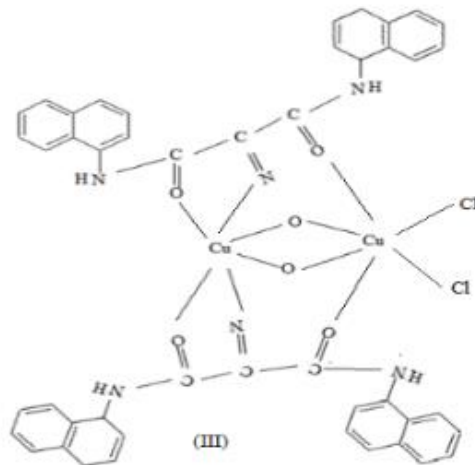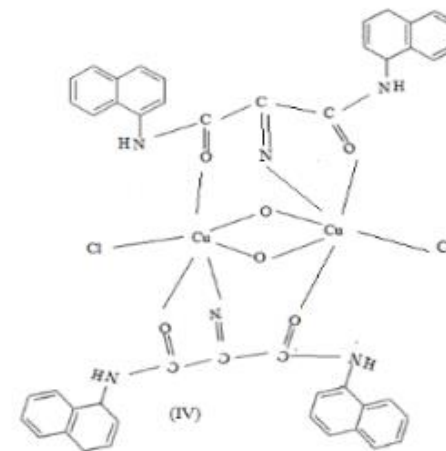**Fig. 11. Magnetic behaviour of Cu(INMANAP)Cl complex at low temp $1/\chi^1_M$ vs T**

Fig. 12. Magnetic susceptibility of Cu(INMANAP)Cl complex at various temp, χ^1_M corr vs T

Structure II - Proposed Cu(II) complex

Structure III- Proposed Cu(II) complex

Structure IV- Proposed Cu(II) complex

Structure V- Proposed Cu(II) complex
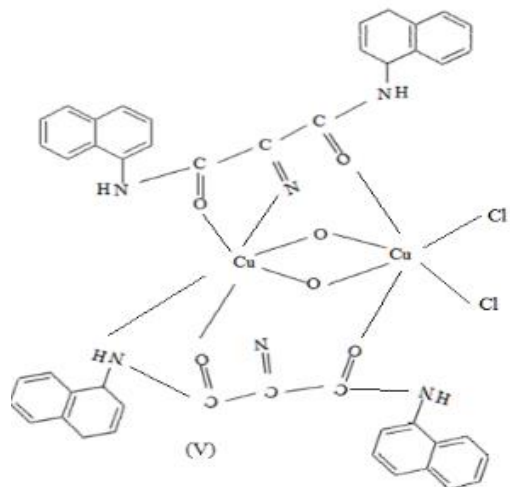
Structure VI- Proposed Cu(II) complex

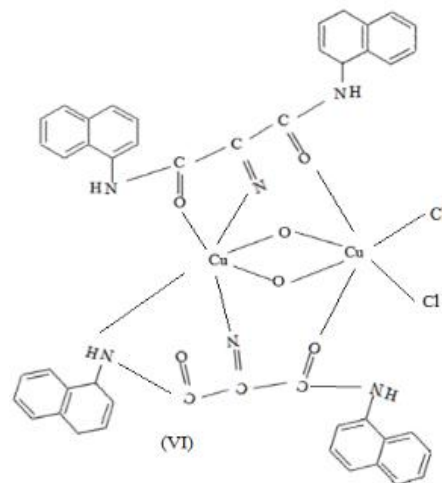**Structure VII- Proposed Cu(II) complex**

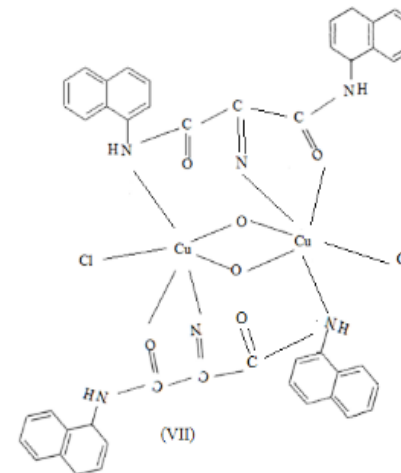**Structure VIII- Proposed Cu(II) complex**

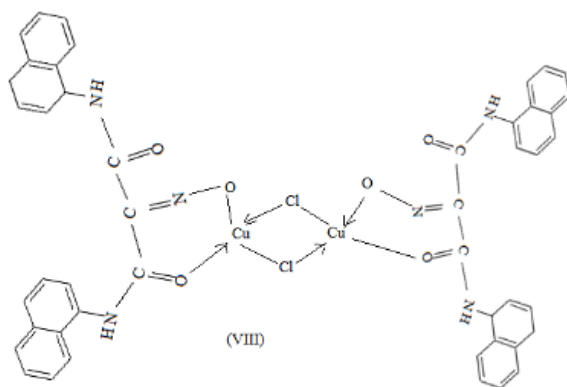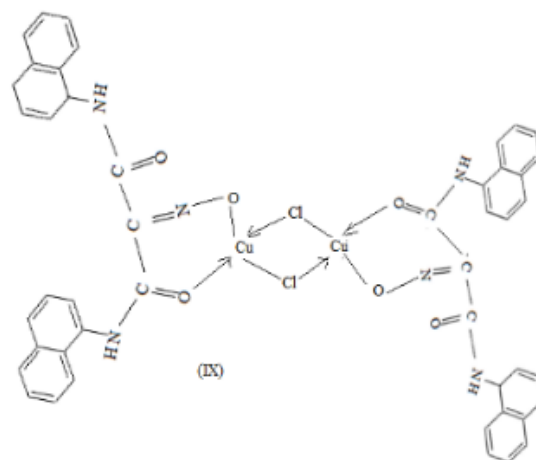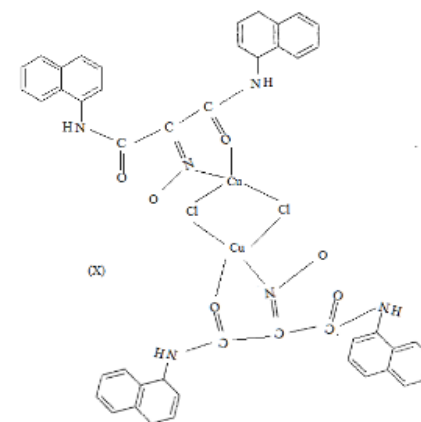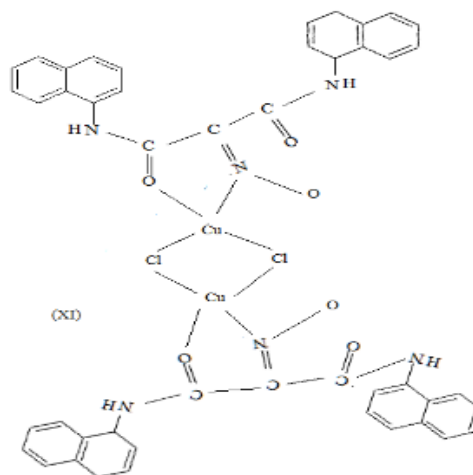**Structure IX- Proposed Cu(II) complex**

Structure X- Proposed Cu(II) complex

Structure XI- Proposed Cu(II) complex

Table 3. Calculations of χ^1_M using Bleaney Bowers equation for Cu(INMANAP)Cl complex – 2J = 280; g = 2.008 (ESR); $N\beta^2g^2/3K$ = 0.4970; $\chi^1_M = N\beta^2g^2/3K$ 1 + 1/3 3^{-25}/KT + N_α

| Temp ^{o}C	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}	χ^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
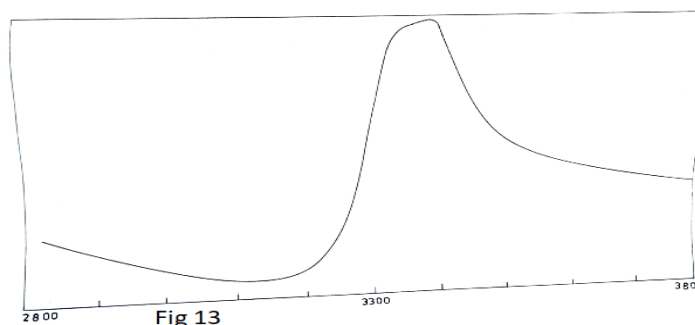
Fig. 13. ESR spectra of Cu(INMANAP)Cl complex (DMSO)
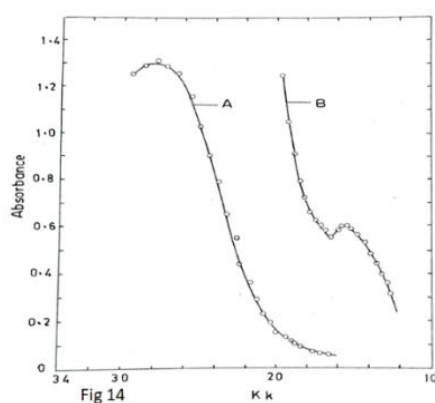
Fig. 14. Electronic spectra of Cu(INMANAP)Cl in CA = 2.5 x 10-4M, CB = 2.5 x 10-3M
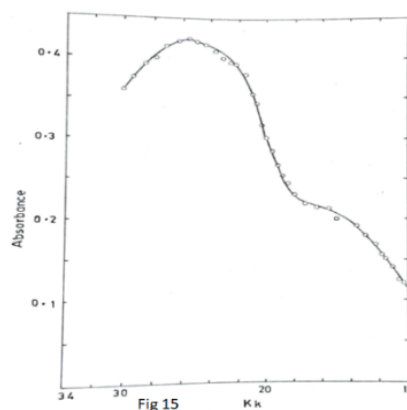
Fig. 15. Diffuse reflectance spectra of Cu(INMANAP)Cl pyridine

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 Chakravorty et al 1971; Kalia & Chakravorty 1970; Slade et al 1968). 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.

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 (Wells, 1947; Wells, 1962;Barraclough & Ng, 1964; Willett et al., 1963).The pyramidal five coordinated structure (Martin & Waterman, 1957; 1959); (Ciampolini & Nardi, 1966); Nakamoto et al, 1961) are also ruled out which 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.

3.2.3 Nickel(II) complex (Pale Yellow) – Ni(INMANAP)$_2$

The results of solution studies and chemical analysis suggest the composition of the pale yellow complex as Ni(INMANAP)$_2$. 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 (Cotton & Wilkinson, 1979).

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 stat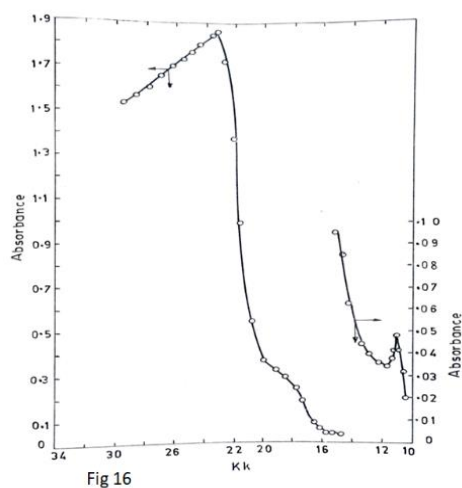e upon complex formation. A shoulder around 18,520 cm^{-1} corresponds to the first d-d transition, while the band at 11,110 cm^{-1} represents the second d-d transition. These spectral features and the observed magnetic moment suggest an Oh structure for the yellow complex (Goodenough, 1960).

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.

3.2.4 Iron(II) complex (Dark Blue) – Fe(INMANAP)$_2$

The dark blue Fe(II) complex, Fe(INMANAP)$_2$, is paramagnetic with a magnetic moment (μ) of 5.2 BM at room temperature, characteristic of a high-spin octahedral (Oh) configuration (Khatavkar & Haldar, 1974). 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 (Nakamoto et al, 1961). Electronic Spectrum (Fig. 18): In chloroform, the complex shows a strong band at 30,300 cm^{-1} corresponds to a π-π* transition and 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.
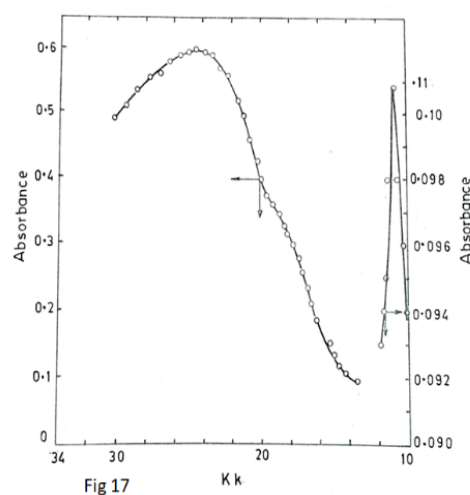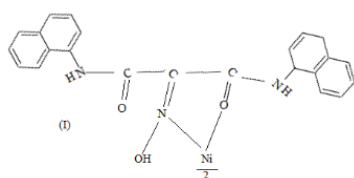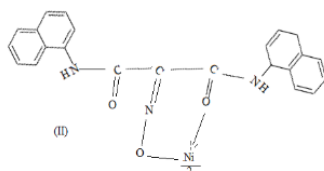

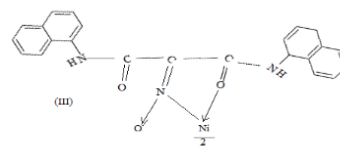**Fig. 16. Electronic spectra of Ni(R)$_2$ in Chloroform**

Fig. 17. Diffuse reflectance spectra of Ni(R)$_2$ complex

Structure XII - Proposed Ni(II) complex

Structure XIII- Proposed Ni(II) complex
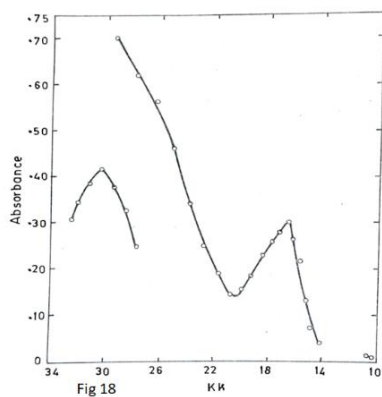

Structure XIV- Proposed Ni(II) complex

Fig. 18. Electronic spectra of Fe(R)$_2$ in chloroform
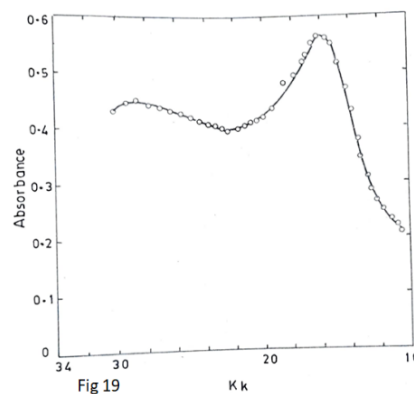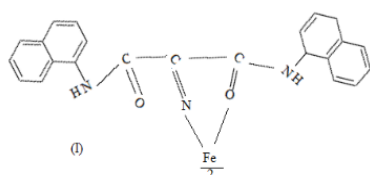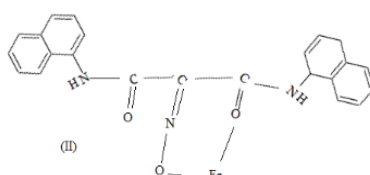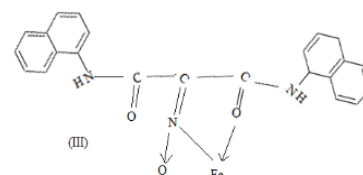

Fig. 19. Diffuse reflectance spectra of Fe(R)$_2$ complex

Structure XV- Proposed Fe(II) complex

Structure XVI- Proposed Fe(II) complex

Structure XVII- Proposed Fe(II) 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.

3.2.5 Cobalt(III) Complex: Co(INMANAP)$_3$ (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^6), which favors d^{2}sp^3 hybridization. Feeble paramagnetism in this complex may arise due to two mechanisms (Tanabe, 1958; Van Vleck, 1932 ; Griffith & Orgel, 1957;.Kernahan,1955).

1. Temperature-independent contribution from high-frequency terms in Van Vleck's formula, $\chi_M = \chi_d + \chi_p$, 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)$_3$, χ_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}, and a weak band at 10,870 cm^{-1}. These observations suggest a low-symmetry ligand field, where the splitting of the $^1A_1g \rightarrow {}^1T_1g$ band into two transitions ($^1A_1g \rightarrow {}^1Eag$ and $^1A_1g \rightarrow {}^1A_2g$) occurs due to symmetry lowering (Sengupta et al, 1980). The transitions can be assigned to $^1A_1g \rightarrow {}^1Eag$, $^1A_1g \rightarrow {}^1A_2g$, and $^1A_1g \rightarrow {}^1T_2g$, characteristic of octahedral Co(III) complexes (Lever, 1968). 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, and a band at 11,630 cm⁻¹ (d-d transitions).

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)$_3$.
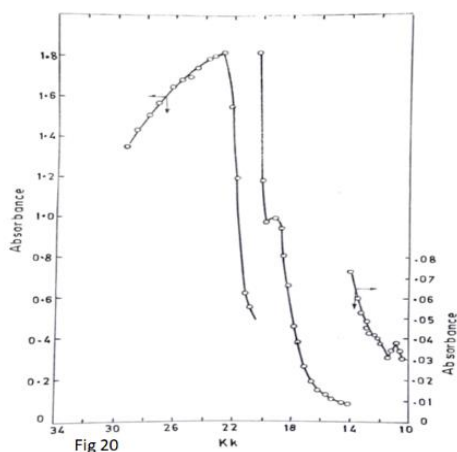

Fig. 20. Electronic spectra of Co(R)$_3$ in chloroform

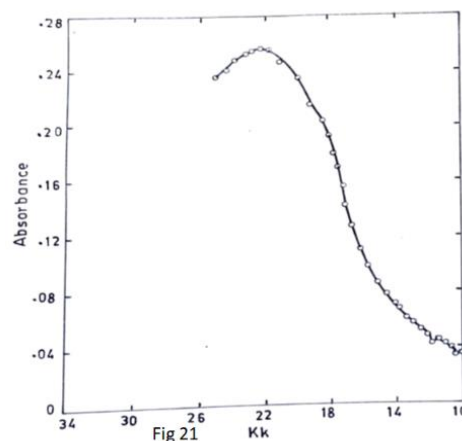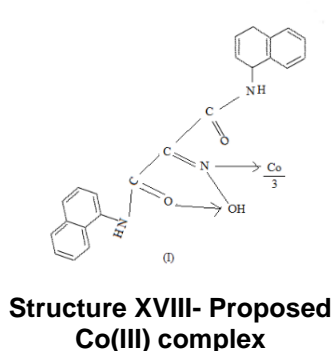**Fig. 21. Diffuse reflectance spectra of Co(R)$_3$ complex**
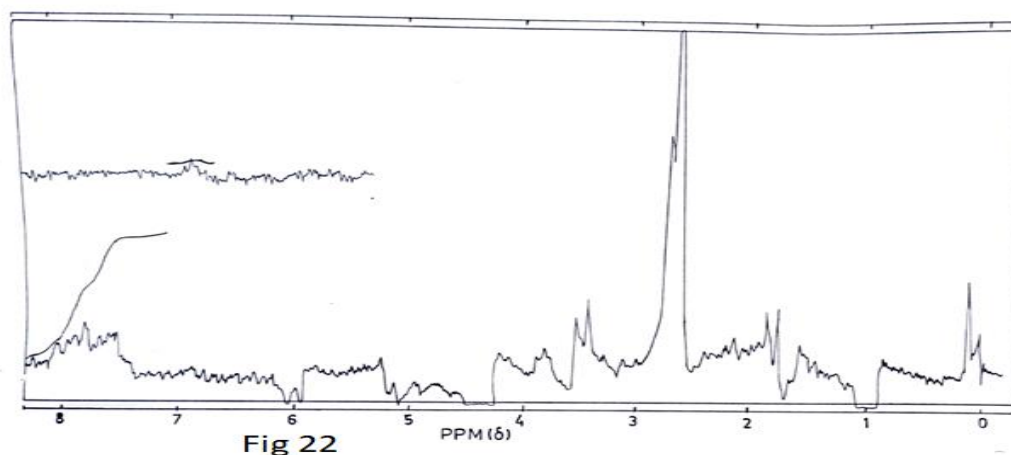
Fig. 22. PMR spectra of Co(INMANAP)$_3$ in DMSO

Structure XVIII- Proposed Co(III) complex

Structure XIX- Proposed Co(III) complex

Structure XX- Proposed Co(III) complex
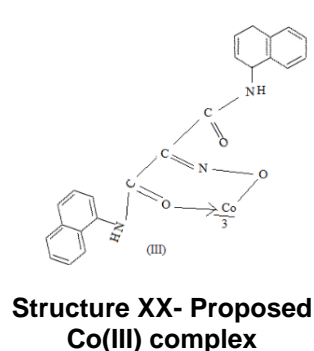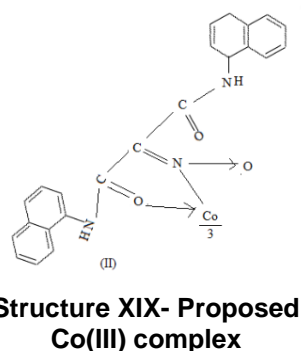
3.2.6 Zinc(II), Cadmium(II), and Mercury(II) complexes

Analytical data indicates that Zn(II), Cd(II), and Hg(II) complexes can be represented as M(INMANAP)$_2$, 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.

These complexes are diamagnetic, with molar magnetic susceptibilities deviating from Pascal's additivity law (Winefordner, 1971). 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, four structures are proposed as the most probable representations of these complexes.
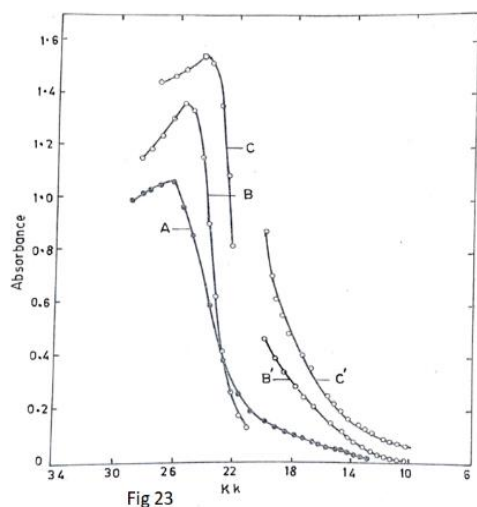
3.3 Interpretation, Structure Finalization, and Conclusion based on Infrared Spectra General Observations from Ligand (Table 4, Fig. 8)

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 (Nakamoto & McCarthy, 1968). 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 (Cotton & Wilkinson, 1979; Ueno & Martell, 1955; Talwar & Haldar, 1975.; Jain, & Chaturvedi, 1975; Paigankar & Haldar, 1969; Talwar & Haldar, 1970 ; P. L. Pathak, 1968; R. T. Desai, 1975; Umadikar & Haldar, 1974).

Fig. 23. Electronic spectra of A – Zn(II) complex B & B' – Cd(II) complex C-C' – Hg(II) complex
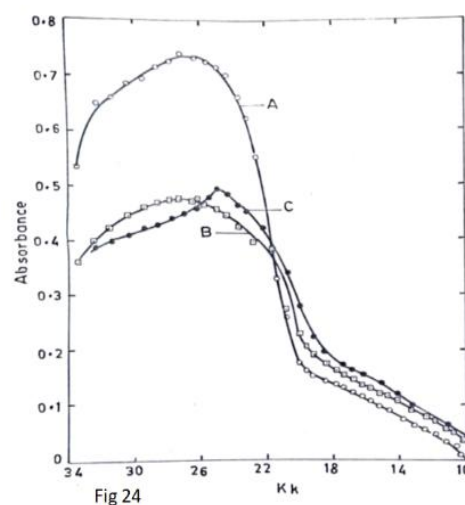

Fig. 24. Diffuse reflectance spectra of A – Zn(II) complex; B – Cd(II) complex; C – Hg(II) complex in chloroform
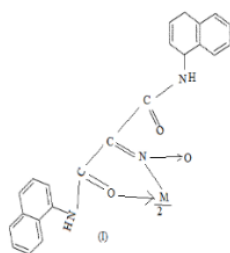
Structure XXI- Proposed M(II) complex
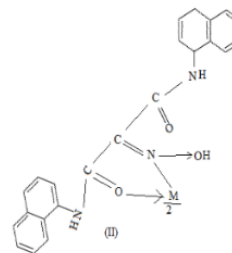
Structure XXII- Proposed M(II) complex
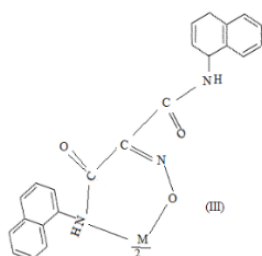
Structure XXIII- Proposed M(II) complex
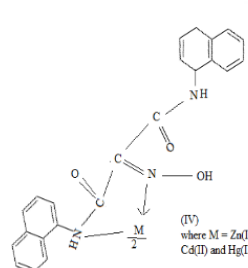
Structure XXIV- Proposed M(II) complex
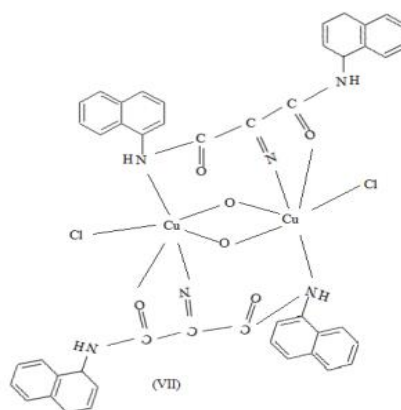
Structure XXV– Proposed trans Cu(II) complex

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 (Burger et al., 1965 ; Thakkar & Haldar, 1980).

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

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 Schonbaum et al, 1959; Watt & Klett, 1966).

Table 4. Infrared spectral bands of ligand and metal complexes in the region 4000 cm^{-1} to 400 cm^{-1} in KBr medium (Figs. 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	Winefordner, 1971;Nakamoto & McCarthy, 1968
3	1660	1680	1660	1665	1660	1600	1600	1600	C=O stretching	-O-coordinated, frequency shift	Khatavkar & Haldar, 1974; Talwar & Haldar, 1970; Burger et al, 1965; Jain & Rivest 1962,64,67
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	Talwar & Haldar, 1970; Burger et al, 1965;
6	1295	1265 (str)	1285 (str)	1285 (str)	1250 (b)	1285 (b)	1285 (b)	1285 (b)	N-Oxide linkage	Frequency shift	Khatavkar & Haldar, 1974; Thakkar & Haldar, 1980; Shaunbaum et al, 1959
7		600	590	595	595	600	605	600	M=N/M-O vibration	New frequencies	Ueno, 1955; Haldar, 1975; Watt, 1966; Jain, 1967

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

Structure XXVI - Proposed Ni(II) Cis structure

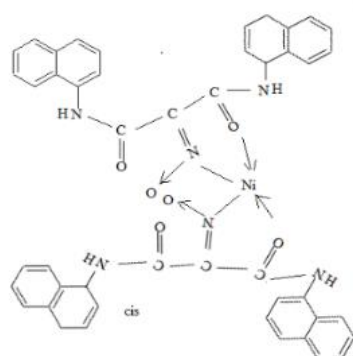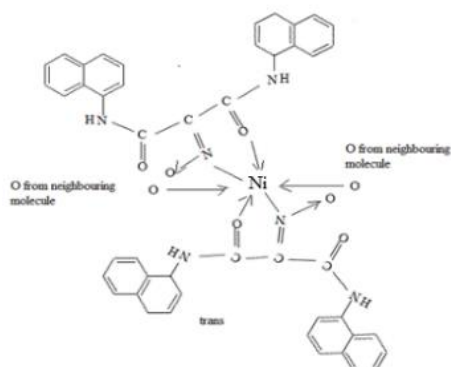**Structure XXVII- Proposed Ni(II) Trans structure**

Structure XXVIII – Proposed Fe(II) complex - cis
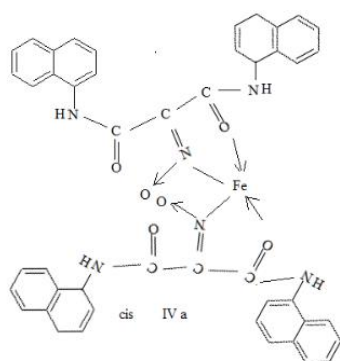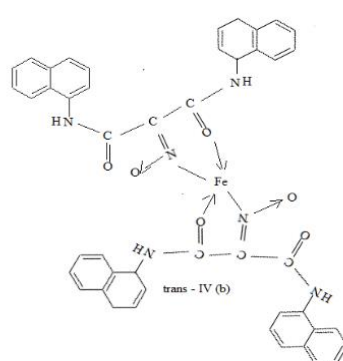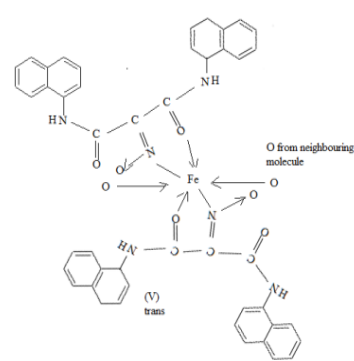

Structure XXIX – Proposed Fe(II) complex - trans

Structure XXX– Proposed Fe(II) complex - trans

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.

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) (Jain & Rivest, 1967, 1962, 1964). The Co(III) complex is a low-spin Oh, tris-chelate complex, represented by 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 them to be isostructural: 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 sp³ orbital hybridization, forming covalent bonds between metal ions and the ligand (Jain & Rivest, 1967, 1962, 1964). The observed deviation in molar magnetic susceptibility supports this stereochemistry, which is represented by the trans-isomer.
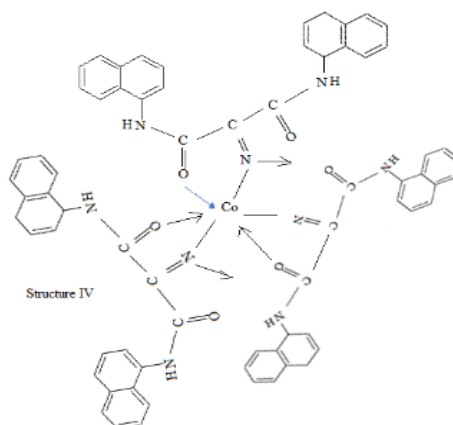
Structure XXXI- Proposed Co(III) complex
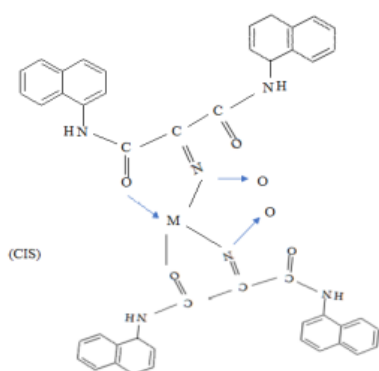
Structure XXXII – Proposed M(II) complex - cis
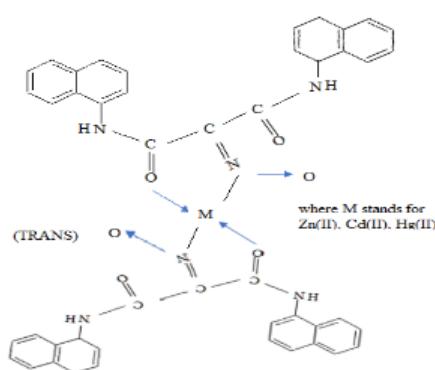
Structure XXXIII – Proposed M(II) complex - trans

4. CONCLUSION

Whitley (Whiteley, 1903) reported the preparation of mesoximes, including malon-di-(α-naphthyl) amide-oxime (isonitroso malon-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. These may be useful as complexing agents in analytical chemistry or in organic chemistry synthesis.

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 act as an oxime anion (INMANAP$^-$) after losing a proton. Solution studies using methods like Job's and Yoe-Jones mole ratio etc, are suitable for predicting the structural geometry, supported by magnetic and spectral data (infrared, electronic, reflectance, ESR, and PMR). Cu(II) exhibits antiferromagnetic behaviour with a subnormal magnetic moment (1.3 BM), suggesting a polymeric structure, supported by Bleaney-Bower's equation. 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.

DISCLAIMER (ARTIFICIAL INTELLIGENCE)

Author(s) hereby declare that NO generative AI technologies such as Large Language Models (ChatGPT, COPILOT, etc.) and text-to-image generators have been used during the writing or editing of this manuscript.

ACKNOWLEDGEMENTS

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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