CHAPTER II

EXPERIMENTAL AND PHYSICAL MEASUREMENTS

Binuclear complexes of Cu(II) of the type [Cu(TSB) $CuCl_2$] and [$Cu(TSB)_2.Cu$] $(ClO_4)_2$ where TSB = tetradentate Schiff's base ligand obtained by the condensation of Ethylenediamine or 1,2-Propylenediamine with Salicylaldehyde on one end and hydroxy ketone at the other end are reported in the literature[1-9]. Some polymeric complexes of Ni(II), Co(II) and Cu(II) are also reported in the literature[10-12].

Various types of polymeric Schiff's base complexes containing heterocyclic hydroxy aldehydes and ketones with polymethylenediamine are reported by Judd,[13] Berg and Alam[14].

Binuclear complexes of Schiff's bases derived from Benzidine with Cu(II), Ni(II) and Zn(II) have been reported from our laboratory[15].

In the present investigations binuclear complexes of symmetrical tetradentate Schiff's bases of the type [$M_2L_2.4H_2O$] have been synthesised and characterised by elemental analysis, U.V. and I.R. spectral studies, X-ray diffraction and magnetic moment measurements. They are also studied for their various applications.

2.1 Materials Used :

Hydrazine, m-Phenylenediamine, p-Phenylenediamine, Benzidine, Glycine, DL-Alanine, L-Histidine, Salicylaldehyde, o-Vaniline, 2-Hydroxy-1-naphthaldehyde, Terephthaldehyde, Cupric acetate monohydrate, Nickel acetate tetrahydrate and

Zinc chloride were of Analar Grade, purchased directly from the market and used as such. 2,4-Dihydroxybenzaldehyde (β-Resorcylaldehyde) and Thiocarbohydrazide have been prepared in the laboratory as follows :

2.1.1 Preparation of 2,4-dihydroxybenzaldehyde :

It was prepared by Vilsmier reaction as reported[16].

Resorcinol (22 gm, 0.2 mole) was dissolved in dry Dimethylformamide (16 ml) and Phosphorous oxychloride (15 ml) was added dropwise with continuous strirring and cooling the mixture externally with ice. The reaction mixture was left at room temperature for two hours. Then 50% Sodium acetate solution (150 ml) was added and heated gently to obtain clear solution. It was then cooled in ice bath when precipitates separated out, were filtered and washed with water to remove unreacted Resorcinol, (or it was extracted with ether) It was recrystallised from hot water to obtain colourless needles, m.p. 135^{o}C (reported 134^{o}C)[16].

2.1.2 Preparation of Thiocarbohydrazide :

It was prepared according to the method reported by Audrieth, Scott and kipper[17]. To the solution of 50 ml (85%) Hydrazine hydrate (1 mole) in 30 ml water, 15 ml (0.2 mole) of Carbon disulfide was added dropwise. The tempterature of the solution rose to 62^{o}C. The reaction mixture was refluxed for 30 minutes. Then kept in an ice-bath for 30 minutes. The precipitated Thiocarbohydrazide was filtered and washed with

ethanol and ether, and air dried. It was then purified from water to get fine colourless flakes, m.p. 171^{o}C (reported 171^{o}C).

2.2 Synthesis of tetradentate Schiff's bases (Ligands) :

2.2.1 Ligands derived from diamines and hydroxy aldehydes:

The Schiff's bases (Fig. II.1 (a-e) were synthesised by refluxing alcoholic solutions of diamines (except Thiocarbohydrazide) and aldehydes in (1 : 2) molar ratio, for half an hour. The mixture was cooled, filtered and recrystallised from the proper solvent : Melting Points physical and analytical data are presented in Table (II.1). In case of Thiocarbohydrazide, solution was prepared in DMF and used.

2.2.2 Ligands derived from Terephthaldehyde and amino acids (Fig. II.2)

To alcoholic solution of Terephthaldehyde (.01 mole) an aqueous solution of amino acids (Glycine, DL-Alanine or L-Histidine) (.02moles) was added with constant shaking, the mixture was refluxed for 15-20 minutes on sand bath. It was cooled, the solid seperated was filtered and washed with hot water followed by hot alcohol to remove the unreacted materials. Melting points and analytical data are included in Table (II.1).

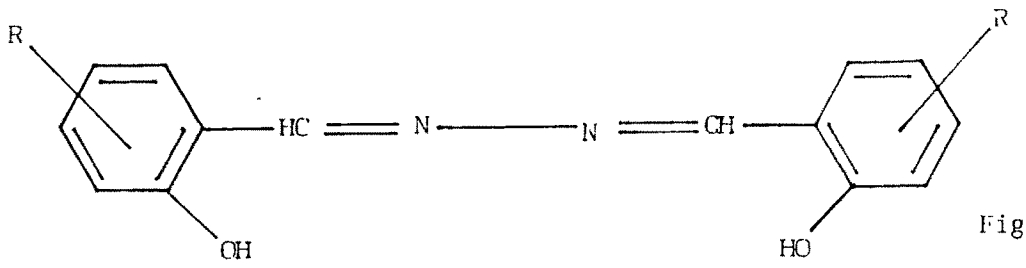

Fig. (II. 1a)

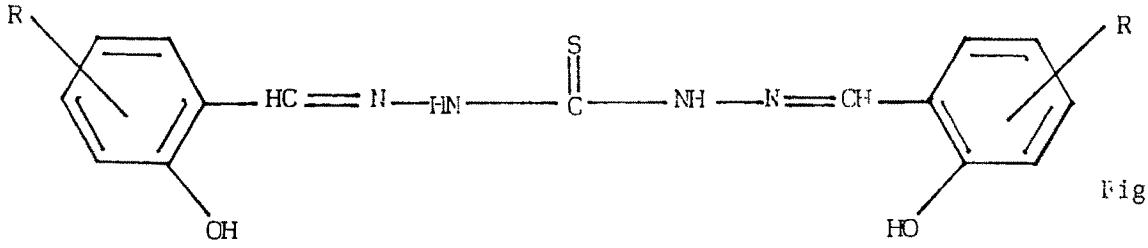

Fig. (II. 1b

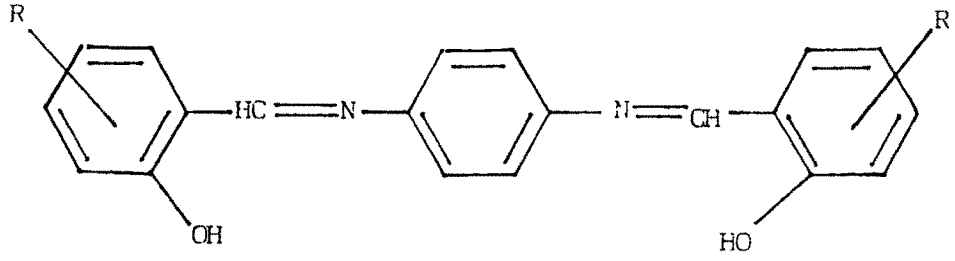

Fig. (II. 1c)

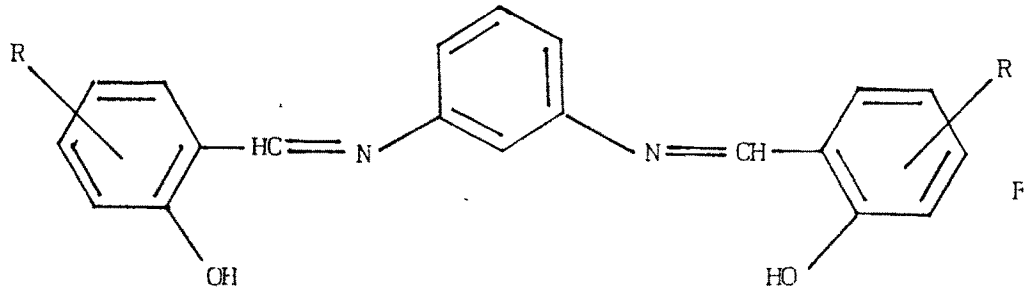

Fig. (II. 1d)

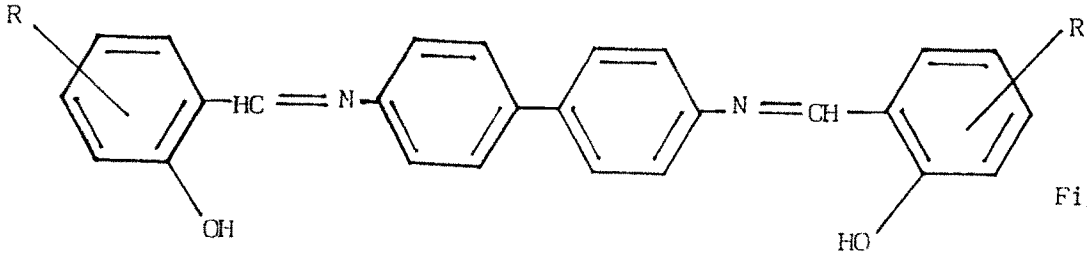

Fig. (II. 1e)

Fig. (II. 1(a-e) : R = H, -OH, -OCH , -ph

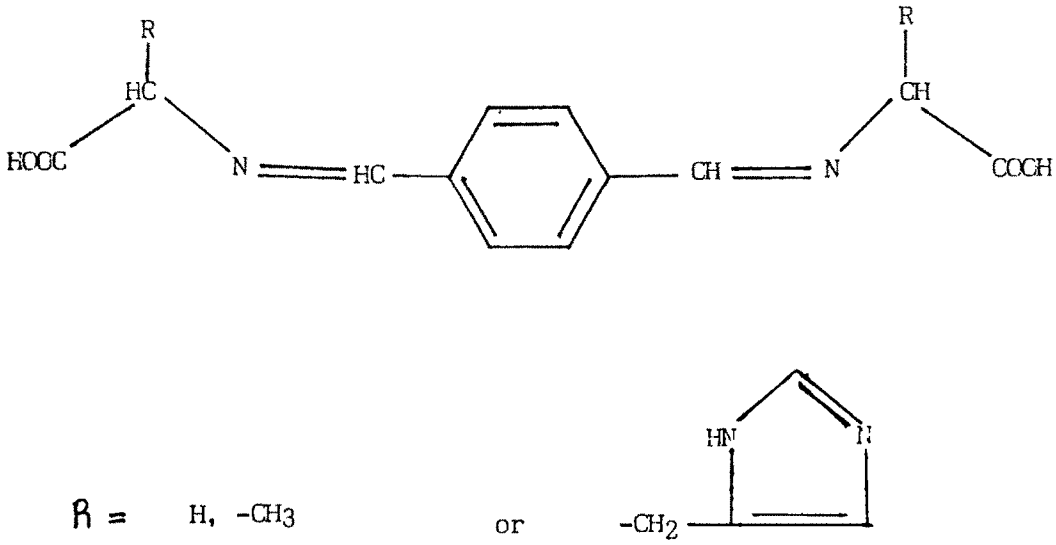

Fig (II. 2)

2.2.3 Synthesis of Binuclear Schiff's Base Complexes of $[M_2L_2.4H_2O]$ type :

General Procedure :

A solution of (0.02 mole) metal salt in hot DMF (30-40 ml) was added slowly with continuous shaking to the hot solution of the ligand (0.02 mole) in DMF (30 ml), the whole mixture was then refluxed on sand-bath for 2-3 hrs to obtain the desired complexes $[M_2L_2.4H_2O]$ (where M=Cu(II), Ni(II) or Zn(II). It was then filtered, washed with DMF and Alcohol and dried.

In case of the ligands derived from Terephthaldehyde and amino acids (Glycine, DL-Alanine or L-Histidine) which are insoluble in most of the organic solvents, the following procedure was adopted for the synthesis of their complexes :

The solution of Glycine or DL-Alanine or L-Histidine (0.02 mole) in 10 ml water was added to the solution of (0.02 mole) Terephthaldehyde in 10 ml DMF and the mixture was warmed on sand-bath for 10 minutes and then to this, a solution of metal acetate (0.01 mole) in 15 ml H_2O + DMF (1:1) mixture was added with constant stirring. The whole mixture was refluxed for 1-2 hrs. The isolated complex was filtered and washed with hot water, followed by DMF and finally with hot alcohol to remove the excess of metal ions and unreacted organic compounds.

2.3 Elemental analysis and magnetic measurements :

The isolated Schiff's bases and their complexes were analysed for carbon, hydrogen and nitrogen by microanalysis (Table II.1).

The metal estimations were done by using complexometric titrations using EDTA[18].

The magnetic susceptibility measurements were carried out using the Guoy's method[19] at room temperature.

The compound was first finely powdered, then it was filled in the calibrated tube (whose tube constant (β) was previously determined) up to the mark. The tube was then suspended with its bottom at the centre of the gap between the pole faces of the electromagnets. The tube was weighed with and without the magnetic field and difference in weight of the tube ($\triangle$ w) containing (w) gm of the sample was determined.

The difference in the weight of the empty tube (δ) was also determined at the same field strength.

The volume of the sample in the tube was determined in order to apply correction due to air displaced by the sample. The tube was calibrated using conductivity water ($x = -0.72 \times 10^{-6}$ c.g.s.u) and $Hg[Co(CNS)_4]$ ($x=16.44 \times 10^{6}$ c.g.s.u) as the standards.

The specific susceptibility was calculated using the following expression :

$$x_g = \frac{\alpha + B\,dw}{w}$$

Where,

α = $x_2 \delta_2 V = 0.029\ V \times 10^{-6}$

B = tube constant

dw = $\Delta w - \delta$ in milligrams

Δw = apparent change in weight of the tube containing (w) gm of the sample on application of field.

δ = difference in the weight of the empty tube.

w = weight of the complex taken in grams.

The molar susceptibility (x_m) was obtained by multiplying the gm susceptibility (specific) by the molecular weight. Diamagnetic correction was applied using Pascal's Constants[20] to get the corrected molar susceptibility x_m(corr.). Using values of x_m (corr.), magnetic moments were calculated from the expression.

$$\mu_{eff} = 2.828\ [x_m\ (corr.) - N_\alpha]\ T$$

Where, N_α = temperature independent paramagnetic moment.

= 60×10^{-6} c.g.s.u.

The μ_{eff} values of all binuclear complexes are given in Table (II.1).

2.4 Ultraviolet and Infrared Spectroscopy

Electronic spectral study was carried out for soluble compounds in DMF with 1 cm matched quartz cell on Hitachi U-200 spectrophotometer.

In case of insoluble complexes reflectance spectra were obtained on Shimadzo-240 spectrophotometer-Japan. Barium sulphate was used as standard for light reflectance and as the base material to dilute the complexes in order to obtain appropriate intensities in the reflected light. The preparation of the sample for the spectral measurements involves the following steps :

The compound was first ground in a small Agate mortar and mixed with previously ground Barium sulphate, and grinding of the mixture was further continued till homogenity was achieved. The spectrophotometer was checked for wave-length calibration by using mercury lamp before and after each measurements.

The spectra was taken at room temperature. Electronic and reflectance spectra recorded for some representative compounds are given in Table (II.3).

The Infrared spectra of the Schiff's bases and their complexes are recorded in KBr on Perkin-Elmer 427 Grating Spectrophotometer in the range of 400-4000cm^{-1}.

The band positions of the ligands and the Complexes are given in Table (II.2).

2.5 **X-ray Diffraction Analysis :**

X-ray diffracttion analysis were recorded on a X-ray diffractometer of Rigaka-Japan, using CuK_{α} 1.5418 A^{o} radiations. The single monochromotor was obtained at scanning speed of 0.06 (or 0.08) degree ($2\theta/S$), at 10-35^{o} (2θ), using the scale 1^{o} = 0.4 cm. The diffraction pattern was indexed by the inspection and trial method[21,24].

Analytical methods of indexing involve arithmetical manipulation of the observed $\sin^2\theta$ values in an attempt to find certain relationships among them. Since each crystal system is characterised by particular relationships identifies the crystal system and leads to a solution of the line indices. The analytical methods are mainly due to Lipson[23].

Tetragonal System :

Here $Sin^2\theta$ values must obey the relation

$$Sin^2\theta = A(h^2 + k^2) + Cl^2 \ldots\ldots\ldots (1)$$

(A & C are constants for any one pattern)

Where $A = \lambda^2/4a^2$ (Constant)

$C = \lambda^2/4c^2$ (Constant)

The value of A is obtained from the (hko) lines. When l=O, equ.(1) becomes

$$Sin^2\theta = A\ (h^2 + K^2) \ldots\ldots\ldots\ldots (1.1)$$

The permissible values of $(h^2 + k^2)$ are 1,2,4,5, 8,9, 10,13,16,17.....etc. Therefore the (hko) lines must have $Sin^2\theta$ values in the ratio of these integers, and A will be some number which is 1, 1/2, 1/4, 1/5, 1/8.....etc, times the $Sin^2\theta$ values of these lines.

C is obtained from the other lines on the pattern and the use of equ.(1) in the form

$$Sin^2\theta - A(h^2 + k^2) = Cl^2 \ldots\ldots\ldots\ldots (1.2)$$

Differences represented by the left-hand side of equ.(1.2) are set up, for various assumed values of h and k, in an attempt to find a consistent set of Cl^2 values, which must be in the ratio 1, 4, 9, 16.....etc. Once these values are found, C can be calculated. The X-ray powder diffraction data for some representative compounds are given in Tables (II.4 to II.9..) and some representative graphs are given in Figures (II.1 to II.3..).

To find out the volumes of the unit cells the following expression for tetragonal system is used :

$$V = a^2C$$

Where V = volume of the unit cell.

a & c = Unit-cell edges parallel to X and Z axes respectively (Note : in tetragonal system $a=b \neq c$)

'a' can be found from the expression :

$$A = \lambda^2/4a^2$$

$$= a^2 = \lambda^2/4A \qquad \text{or} \qquad a = \sqrt{\lambda^2/4A}$$

C also can be found from the expression

$$C = \lambda^2/4c^2$$

$$c^2 = \lambda^2/4C \qquad \text{or} \qquad c = \sqrt{\lambda^2/4C}$$

The density was calculated by using the equation

$$\rho = \frac{n \times m}{L \times V}$$

Where : ρ = density

n = number of molecules of the compound per unit cell

m = formula weight of the compound

L = Avogadro's number

V = Volume of the unit cell

The observed density have been found experimentally by preparing tablets under pressure of 8 tonn/$(inch)^2$. Then by finding out the volume & mass of the tablet, the density can be found.

List of the Schiff's base ligands synthesised and their Abbreviations

Sr. No.	Name of the ligand (Abbreviation)	Molecular Formula
1.	N,N'-Bis (2-hydroxybenzylidene) hydrazone (BHBH)	$C_{14}H_{12}N_2O_2$
2.	N,N'-Bis(2,4-dihydroxy benzylidene) hydrazone (BDBH)	$C_{14}H_{12}N_2O_4$
3.	N,N'-Bis (2-hydroxy-3-methoxybenzylidene) hydrazone (BHMBH)	$C_{16}H_{16}N_2O_4$
4.	N,N'-Bis (2-hydroxy-1-naphthylidene) hydrazone (BHNH)	$C_{22}H_{16}N_2O_2$
5.	N,N'-Bis (2-hydroxybenzylidene) thio -carbohydrazone (BHBT)	$C_{15}H_{14}N_4O_2S$
6.	N,N'-Bis (2,4-dihydroxybenzylidene) thiocarbohydrazone (BDBT)	$C_{15}H_{14}N_4O_4S$
7.	N,N'-Bis (2-hydroxy-3-methoxybenzylidene) thiocarbohydrazone (BHMBT)	$C_{17}H_{18}N_4O_4S$
8.	N,N'-Bis (2-hydroxy-1-naphthylidene) thio -carbohydrazone (BHNT)	$C_{23}H_{18}N_4O_2S$
9.	N,N'-Bis (2-hydroxybenzylidene) -p-Phenylenediamine (BHB-p-PD)	$C_{20}H_{16}N_2O_2$
10.	N,N'-Bis (2,4-dihydroxybenzylidene) -p-Phenylenediamine (BDB-p-PD)	$C_{20}H_{16}N_2O_4$
11.	N,N'-Bis (2-hydroxy-3-methoxybenzylidene) -p-Phenylenediamine (BHMB-p-PD)	$C_{22}H_{20}N_2O_4$
12.	N,N'-Bis (2-hydroxy-1-naphthylidene) -p-Phenylenediamine (BHN-p-PD)	$C_{28}H_{20}N_2O_2$

13.	N,N'-Bis (2-hydroxybenzylidene) -m-Phenylenediamine (BHB-m-PD)	$C_{20}H_{16}N_2O_2$
14.	N,N'-Bis (2,4-dihydroxybenzylidene) -m-Phenylenediamine (BDB-m-PD)	$C_{20}H_{16}N_2O_4$
15.	N,N'-Bis (2-hydroxy-3-methoxybenzylidene) -m-Phenylenediamine (BHMB-m-PD)	$C_{22}H_{20}N_2O_4$
16.	N,N'-Bis (2-hydroxy-1-naphthylidene) -m-Phenylenediamine (BHN-m-PD)	$C_{28}H_{20}N_2O_2$
17.	N,N'-Bis (2-hydroxybenzylidene) Benzidine (BHBB)	$C_{26}H_{20}N_2O_2$
18.	N,N'-Bis (2,4-hydroxybenzylidene) Benzidine (BDBB)	$C_{26}H_{20}N_2O_4$
19.	N,N'-Bis (2-hydroxy-3-methoxybenzylidene) Benzidine (BHMBB)	$C_{28}H_{24}N_2O_4$
20.	N,N'-Bis (2-hydroxy-1-naphthylidene) Benzidine (BHNB)	$C_{34}H_{24}N_2O_2$
21.	Terephthal bis(iminoglycine) (TBIG)	$C_{12}H_{12}N_2O_4$
22.	Terephthal bis(iminoalanine) (TBIA)	$C_{14}H_{16}N_2O_4$
23.	Terephthal bis(iminohistidine) (TBIH)	$C_{20}H_{20}N_2O_4$

TABLE II.1

Analytical and characterisation data of Schiff's bases (Ligands) and their Complexes.

Sr. No.	Compound	Molecular Formula	Colour	m.p (^{o}C)	Elemental Analysis found/(calculated)				μ_{eff} (B.M.)
					Metal	Carbon	Hydrogen	Nitrogen	
1.	BHBH-BHMBH	$C_{14}H_{12}N_2O_2$	Yellowish White	201^{o}C	-	70.23 (70.000)	5.34 (5.000)	11.15 (11.666)	-
2.	Cu(II)-BHBH	$Cu_2C_{28}H_{20}N_4O_4.4H_2O$	Brown	-	18.64 (18.814)	50.00 (49.777)	3.96 (4.548)	7.90 (8.296)	1.70
3.	Ni(II)-BHBH	$Ni_2C_{28}H_{20}N_4O_4.4H_2O$	Yellowish green	-	17.24 (17.643)	50.75 (50.495)	3.94 (4.207)	8.42 (8.415)	3.03
4.	Zn(II)-BHBH	$Zn_2C_{28}H_{20}N_4O_4.4H_2O$	Dark Yellow	-	18.86 (19.262)	50.00 (49.500)	4.22 (4.125)	8.25 (8.250)	-
5.	BDBH	$C_{14}H_{12}N_2O_4$	Yellow	195^{o}C	-	61.66 (61.764)	4.60 (4.411)	10.12 (10.294)	-
6.	Cu(II)-BDBH	$Cu_2C_{28}H_{20}N_4O_8.4H_2O$	Brown	300^{o}C	16.92 (17.185)	45.40 (45.466)	3.75 (3.788)	7.72 (7.577)	1.62
7.	Ni(II)-BDBH	$Ni_2C_{28}H_{20}N_4O_8.4H_2O$	Yellowish green	-	16.50 (16.095)	46.00 (46.065)	4.02 (3.838)	7.77 (7.677)	2.85
8.	Zn(II)-BDBH	$Zn_2C_{28}H_{20}N_4O_8.4H_2O$	Yellow	-	17.24 (17.602)	44.88 (45.237)	3.50 (3.769)	7.98 (7.539)	-
9.	BHMBH	$C_{16}H_{16}N_2O_4$	Lemon Yellow	182^{o}C	-	64.44 (64.000)	5.80 (5.333)	9.12 (9.333)	-
10.	Cu(II)-BHMBH	$Cu_2C_{32}H_{28}N_4O_8.4H_2O$	Brown	300^{o}C	15.50 (15.974)	48.55 (48.301)	4.50 (4.528)	7.40 (7.044)	1.66
11.	Ni(II)-BHMBH	$Ni_2C_{32}H_{28}N_4O_8.4H_2O$	Light green	-	14.46 (14.947)	48.82 (48.892)	4.21 (4.583)	7.11 (7.130)	3.01

Sr. No.	Compound	Molecular Formula	Colour	m.p (^{o}C)	Elemental Analysis found/(calculated)				μ_{eff} (B.M.)
					Metal	Carbon	Hydrogen	Nitrogen	
13.	BHNH	$C_{22}H_{16}N_2O_2$	Dark Yellow	210^{o}C	-	71.00 (70.967)	4.33 (4.301)	7.42 (7.526)	-
14.	Cu(II)-BHNH	$Cu_2C_{44}H_{28}N_4O_4.4H_2O$	Dark Brown	-	14.60 (14.514)	60.12 (60.342)	4.34 (4.114)	6.73 (6.400)	1.48
15.	Ni(II)-BHNH	$Ni_2C_{44}H_{28}N_4O_4.4H_2O$	Yellowish brown	-	13.55 (13.565)	60.88 (61.012)	4.35 (4.159)	6.15 (6.470)	3.03
16.	Zn(II)-BHNH	$Zn_2C_{44}H_{28}N_4O_4.4H_2O$	deep yellow	-	14.44 (14.878)	59.77 (60.086)	4.10 (4.096)	6.15 (6.372)	-
17.	BHBT	$C_{15}H_{14}N_4O_2S$	White	203^{o}C	-	57.00 (57.324)	4.54 (4.458)	18.12 (17.834)	-
18.	Cu(II)-BHBT	$Cu_2C_{30}H_{24}N_8O_4S_2.4H_2O$	Green	-	15.56 (15.431)	43.96 (43.742)	3.72 (3.888)	13.60 (13.608)	1.38
19.	Ni(II)-BHBT	$Ni_2C_{30}H_{24}N_8O_4S_2.4H_2O$	Yellowish brown	-	14.00 (14.433)	44.53 (44.258)	4.02 (3.934)	13.46 (13.769)	2.98
20.	Zn(II)-BHBT	$Zn_2C_{30}H_{24}N_8O_4S_2.4H_2O$	Yellowish Orange	-	15.66 (15.813)	43.55 (43.544)	4.06 (3.870)	13.58 (13.547)	-
21.	BDBT	$C_{15}H_{14}N_4O_4S$	Orange	-	-	51.47 (52.023)	4.24 (4.046)	16.16 (16.184)	-
22.	Cu(II)-BDBT	$Cu_2C_{30}H_{24}N_8O_8S_2.4H_2O$	brown	-	14.64 (14.317)	40.55 (40.586)	3.33 (3.607)	12.66 (12.626)	1.68
23.	Ni(II)-BDBT	$Ni_2C_{30}H_{24}N_8O_8S_2.4H_2O$	light green	-	13.55 (13.380)	41.24 (41.030)	3.92 (3.647)	12.22 (12.764)	2.96

Sr. No.	Compound	Molecular Formula	Colour	m.p (^{o}C)	Elemental Analysis found/(calculated)				μ_{eff} (B.M.)
					Metal	Carbon	Hydrogen	Nitrogen	
25.	BHMBT	$C_{17}H_{18}N_4O_4S$	Light Yellow	212^{o}C	-	55.08 (54.545)	4.31 (4.812)	15.13 (14.973)	-
26.	Cu(II)-BHMBT	$Cu_2C_{34}H_{32}N_8O_8S_2.4H_2O$	Dark Green	-	13.73 (13.467)	43.30 (43.266)	4.24 (4.241)	11.82 (11.876)	1.33
27.	Ni(II)-BHMBT	$Ni_2C_{34}H_{32}N_8O_8S_2.4H_2O$	Light Brown	-	12.62 (12.577)	44.00 (43.711)	4.15 (4.285)	12.30 (11.999)	3.01
28.	Zn(II)-BHMBT	$Zn_2C_{34}H_{32}N_8O_8S_2.4H_2O$	Dark Yellow	-	13.40 (13.809)	43.44 (43.095)	4.08 (4.225)	11.92 (11.830)	-
29.	BHNT	$C_{23}H_{18}N_4O_2S$	light orange	-	-	67.02 (66.666)	4.54 (4.347)	13.53 (13.526)	-
30.	Cu(II)-BHNT	$Cu_2C_{46}H_{32}N_8O_2S_2.4H_2O$	dark green	-	12.65 (12.414)	54.14 (53.958)	3.90 (3.910)	11.21 (10.948)	1.72
31.	Ni(II)-BHNT	$Ni_2C_{46}H_{32}N_8O_2S_2.4H_2O$	Yellowish green	-	11.14 (11.584)	54.16 (54.470)	4.07 (3.947)	11.55 (11.051)	2.95
32.	Zn(II)-BHNT	$Zn_2C_{46}H_{32}N_8O_2S_2.4H_2O$	deep yellow	-	12.00 (12.733)	53.61 (53.762)	3.82 (3.895)	11.30 (10.908)	-
33.	BHB-P-PD	$C_{20}H_{16}N_2O_2$	Dark Orange	198^{o}C	-	76.02 (75.949)	5.25 (5.063)	9.00 (8.860)	-
34.	Cu(II)-BHB-P-PD	$Cu_2C_{40}H_{28}N_4O_4.4H_2O$	Brown	-	14.94 (15.356)	58.41 (58.041)	4.42 (4.353)	6.87 (6.771)	1.82

Sr. No.	Compound	Molecular Formula	Colour	m.p (^{o}C)	Elemental Analysis found/(calculated)				μ_{eff} (B.M.)
					Metal	Carbon	Hydrogen	Nitrogen	
35.	Ni(II)-BHB-P-PD	$Ni_2C_{40}H_{28}N_4O_4.4H_2O$	Green	-	14.61 (14.362)	58.52 (58.722)	4.42 (4.404)	7.11 (6.850)	3.02
36.	Zn(II)-BHB-P-PD	$Zn_2C_{40}H_{28}N_4O_4.4H_2O$	greenish yellow	-	15.48 (15.737)	57.55 (57.779)	4.36 (4.333)	6.96 (6.740)	-
37.	BDB-P-PD	$C_{20}H_{16}N_2O_4$	shining orange	215^{o}C	-	69.23 (68.965)	4.61 (4.597)	8.00 (8.045)	-
38.	Cu(II)-BDB-P-PD	$Cu_2C_{40}H_{28}N_4O_8.4H_2O$	brown	-	14.55 (14.253)	54.13 (53.872)	4.00 (4.040)	6.22 (6.285)	1.76
39.	Ni(II)-BDB-P-PD	$Ni_2C_{40}H_{28}N_4O_8.4H_2O$	yellowish green	-	13.62 (13.319)	54.85 (54.458)	4.47 (4.084)	6.56 (6.353)	2.98
40.	Zn(II)-BDB-P-PD	$Zn_2C_{40}H_{28}N_4O_8.4H_2O$	yellow	-	14.50 (14.612)	53.42 (53.646)	4.32 (4.023)	6.72 (6.258)	-
41.	BHMB-P-PD	$C_{22}H_{20}N_2O_4$	Redish Orange	230^{o}C		69.88 (70.212)	5.20 (5.319)	7.05 (7.446)	-
42.	Cu(II)-BHMB-P-PD	$Cu_2C_{44}H_{36}N_4O_8.4H_2O$	Black	-	13.50 (13.410)	55.97 (55.755)	4.54 (4.646)	6.08 (5.913)	1.71
43.	Ni(II)-BHMB-P-PD	$Ni_2C_{44}H_{36}N_4O_8.4H_2O$	Redish Brown	-	12.76 (12.524)	56.56 (56.326)	4.48 (4.693)	6.00 (5.973)	3.04
44.	Zn(II)-BHMB-P-PD	$Zn_2C_{44}H_{36}N_4O_8.4H_2O$	Greenish Yellow	-	13.44 (13.751)	55.08 (55.535)	4.81 (4.627)	5.83 (5.890)	-

Sr. No.	Compound	Molecular Formula	Colour	m.p (^{o}C)	Elemental Analysis found/(calculated)				μ_{eff} (B.M.)
					Metal	Carbon	Hydrogen	Nitrogen	
45.	BHN-P-PD	$C_{28}H_{20}N_2O_2$	Redish Orange	335^{o}C	-	81.01 (80.769)	4.38 (4.807)	6.43 (6.730)	-
46.	Cu(II)-BHN-P-PD	$Cu_2C_{56}H_{36}N_4O_4 \cdot 4H_2O$	Brown	-	12.00 (12.366)	65.34 (65.433)	4.59 (4.284)	5.79 (5.452)	1.76
47.	Ni(II)-BHN-P-PD	$Ni_2C_{56}H_{36}N_4O_4 \cdot 4H_2O$	light green	-	11.50 (11.539)	66.29 (66.050)	4.33 (4.324)	5.73 (5.504)	2.96
48.	Zn(II)-BHN-P-PD	$Zn_2C_{56}H_{36}N_4O_4 \cdot 4H_2O$	deep yellow	-	12.60 (12.684)	65.47 (65.195)	4.08 (4.268)	5.26 (5.432)	-
49.	BHB-m-PD	$C_{20}H_{16}N_2O_2$	Bright Yellow	90^{o}C	-	75.77 (75.949)	5.26 (5.063)	9.02 (8.860)	-
50.	Cu(II)-BHB-m-PD	$Cu_2C_{40}H_{28}N_4O_4 \cdot 4H_2O$	Brown	--	15.50 (15.356)	57.35 (58.041)	4.35 (4.353)	6.66 (6.771)	1.58
51.	Ni(II)-BHB-m-PD	$Ni_2C_{40}H_{28}N_4O_4 \cdot 4H_2O$	Light Green	--	14.30 (14.362)	58.72 (58.722)	4.14 (4.404)	6.88 (6.850)	3.03
52.	Zn(II)-BHB-m-PD	$Zn_2C_{40}H_{28}N_4O_4 \cdot 4H_2O$	yellow	-	15.50 (15.737)	57.67 (57.779)	4.61 (4.333)	6.73 (6.740)	-
53.	BDB-m-PD	$C_{20}H_{16}N_2O_4$	shining yellow	117^{o}C	-	69.05 (68.965)	4.56 (4.597)	8.29 (8.045)	-
54.	Cu(II)-BDB-m-PD	$Cu_2C_{40}H_{28}N_4O_8 \cdot 4H_2O$	light brown	-	14.56 (14.253)	53.84 (53.872)	4.29 (4.040)	6.04 (6.285)	1.78

Sr. No.	Compound	Molecular Formula	Colour	m.p (^{O}C)	Elemental Analysis found/(calculated)				μ_{eff} (B.M.)
					Metal	Carbon	Hydrogen	Nitrogen	
55.	Ni(II)-BDB-m-PD	$Ni_2C_{40}H_{28}N_4O_8.4H_2O$	brownish yellow	-	13.82 (13.319)	54.76 (54.458)	3.77 (4.084)	6.33 (6.353)	2.98
56.	Zn(II)-BDB-m-PD	$Zn_2C_{40}H_{28}N_4O_8.4H_2O$	deep yellow	-	14.00 (14.612)	53.58 (53.646)	4.23 (4.023)	6.65 (6.258)	-
57.	BHMB-m-PD	$C_{22}H_{20}N_2O_4$	Orange	120^{O}C	-	69.99 (70.212)	5.62 (5.319)	7.72 (7.446)	-
58.	Cu(II)-BHMB-m-PD	$Cu_2C_{44}H_{36}N_4O_8.4H_2O$	Dark Brown	-	13.54 (13.410)	55.29 (55.755)	4.18 (4.646)	5.73 (5.913)	1.64
59.	Ni(II)-BHMB-m-PD	$Ni_2C_{44}H_{36}N_4O_8.4H_2O$	yellowish brown	-	12.50 (12.524)	56.33 (56.326)	4.36 (4.693)	6.00 (5.973)	3.02
60.	Zn(II)-BHMB-m-PD	$Zn_2C_{44}H_{36}N_4O_8.4H_2O$	deep yellow	-	13.53 (13.751)	55.53 (55.536)	4.28 (4.627)	6.11 (5.890)	-
61.	BHN-m-PD	$C_{28}H_{20}N_2O_2$	Orange	165^{O}C	-	81.14 (80.769)	4.81 (4.807)	6.55 (6.730)	-
62.	Cu(II)-BHN-m-PD	$Cu_2C_{56}H_{36}N_4O_4.4H_2O$	Dark Green	-	12.50 (12.366)	65.65 (65.433)	4.36 (4.284)	5.44 (5.452)	1.80
63.	Ni(II)-BHN-m-PD	$Ni_2C_{56}H_{36}N_4O_4.4H_2O$	yellowish green	-	11.50 (11.539)	66.56 (66.050)	4.32 (4.324)	5.28 (5.504)	2.97
64.	Zn(II)-BHN-m-PD	$Zn_2C_{56}H_{36}N_4O_4.4H_2O$	yellowish orange	-	12.25 (12.684)	59.89 (65.195)	4.42 (4.268)	5.58 (5.432)	-

Sr. No.	Compound	Molecular Formula	Colour	m.p (^{O}C)	Elemental Analysis found/(calculated)				μ_{eff} (B.M.)
					Metal	Carbon	Hydrogen	Nitrogen	
65.	BHBB	$C_{26}H_{20}N_2O_2$	Light Yellow	-	-	79.39 (79.591)	5.35 (5.102)	7.11 (7.142)	-
66.	Cu(II)-BHBB	$Cu_2C_{52}H_{36}N_4O_4.4H_2O$	Dark green	-	13.00 (12.972)	63.57 (63.738)	4.55 (4.494)	5.72 (5.720)	1.82
67.	Ni(II)-BHBB	$Ni_2C_{52}H_{36}N_4O_4.4H_2O$	Light Green	-	12.54 (12.110)	64.33 (64.369)	4.50 (4.538)	5.49 (5.776)	2.98
68.	Zn(II)-BHBB	$Zn_2C_{52}H_{36}N_4O_4.4H_2O$	orange		13.52 (13.303)	63.52 (63.495)	4.44 (4.477)	5.77 (5.698)	-
69.	BDBB	$C_{26}H_{20}N_2O_4$	Yellow	-	-	73.28 (73.584)	4.61 (4.716)	6.54 (6.603)	-
70.	Cu(II)-BDBB	$Cu_2C_{52}H_{36}N_4O_8.4H_2O$	brown	-	12.50 (12.176)	59.60 (59.827)	4.41 (4.218)	5.33 (5.369)	2.02
71.	Ni(II)-BDBB	$Ni_2C_{52}H_{36}N_4O_8.4H_2O$	light green	-	11.58 (11.360)	60.52 (60.382)	4.25 (4.257)	5.34 (5.419)	3.02
72.	Zn(II)-BDBB	$Zn_2C_{52}H_{36}N_4O_8.4H_2O$	yellow	-	12.50 (12.490)	59.66 (59.613)	4.61 (4.203)	5.11 (5.353)	-
73.	BHMBB	$C_{28}H_{24}N_2O_4$	Dark Orange	250^{O}C	-	74.30 (74.336)	5.30 (5.309)	6.23 (6.194)	-
74.	Cu(II)-BHMBB	$Cu_2C_{56}H_{44}N_4O_8.4H_2O$	Brown	-	11.50 (11.555)	61.12 (61.146)	4.45 (4.731)	5.19 (5.095)	1.75

75.	Ni(II)-BHMBB	$Ni_2C_{56}H_{44}N_4O_8.4H_2O$	Redish Brown	-	10.50 (10.776)	62.06 (61.685)	4.22 (4.773)	5.32 (5.140)	3.02
76.	Zn(II)-BHMBB	$Zn_2C_{56}H_{44}N_4O_8.4H_2O$	Yellow	-	11.70 (11.855)	61.29 (60.939)	4.50 (4.715)	5.00 (5.078)	-
77.	BHNB	$C_{34}H_{24}N_2O_2$	Orange	324°C	-	82.82 (82.926)	4.74 (4.878)	6.00 (5.610)	-
78.	Cu(II)-BHNB	$Cu_2C_{68}H_{44}N_4O_4.4H_2O$	Brown	-	10.50 (10.771)	68.89 (69.211)	4.45 (4.410)	4.61 (4.749)	1.28
79.	Ni(II)-BHNB	$Ni_2C_{68}H_{44}N_4O_4.4H_2O$	Light Green	-	10.50 (10.039)	69.58 (69.779)	4.52 (4.446)	4.70 (4.788)	2.98
80.	Zn(II)-BHNB	$Zn_2C_{68}H_{44}N_4O_4.4H_2O$	Yellow	-	11.40 (11.053)	69.23 (68.992)	4.40 (4.396)	4.91 (4.734)	-
81.	TBIG	$C_{12}H_{12}N_2O_4$	Orange	300°C	-	58.36 (58.064)	4.65 (4.838)	11.12 (11.290)	-
82.	Cu(II)TBIG	$Cu_2C_{24}H_{20}N_4O_8.4H_2O$	Brown	--	18.56 (18.379)	41.06 (41.678)	4.51 (4.052)	8.38 (8.104)	1.54
83.	Ni(II)-TBIG	$Ni_2C_{24}H_{20}N_4O_8.4H_2O$	Bright Yellow	--	17.20 (17.229)	41.96 (42.265)	4.35 (4.109)	8.29 (8.218)	3.06
84.	Zn(II)-TBIG	$Zn_2C_{24}H_{20}N_4O_8.4H_2O$	Dark Yellow	-	19.25 (18.818)	41.43 (41.454)	4.43 (4.030)	8.50 (8.060)	-

Sr. No.	Compound	Molecular Formula	Colour	m.p (^{o}C)	Elemental Analysis found/(calculated)				μ_{eff} (B.M.)
					Metal	Carbon	Hydrogen	Nitrogen	
85.	TBIA	$C_{14}H_{16}N_2O_4$	Light Orange	300^{o}C	-	61.02 (60.869)	5.54 (5.797)	10.37 (10.144)	-
86.	Cu(II)-TBIA	$Cu_2C_{28}H_{28}N_4O_8.4H_2O$	Yellowish Green	-	16.50 (17.001)	44.55 (44.979)	4.96 (4.819)	7.41 (7.496)	1.96
87.	Ni(II)-TBIA	$Ni_2C_{28}H_{28}N_4O_8.4H_2O$	Yellowish Brown	-	15.58 (15.920)	45.90 (45.565)	4.62 (4.882)	7.43 (7.594)	3.01
88.	Zn(II)-TBIA	$Zn_2C_{28}H_{28}N_4O_8.4H_2O$	Light Yellow	-	17.50 (17.414)	44.50 (44.755)	4.83 (4.795)	7.18 (7.459)	-
89.	TBIH	$C_{20}H_{20}N_6O_4$	-	-	-	-	-	-	-
90.	Cu(II)-TBIH	$Cu_2C_{40}H_{36}N_{12}O_8.4H_2O$	Brown	-	12.00 (12.561)	47.16 (47.477)	4.33 (4.352)	16.27 (16.617)	2.03
91.	Ni(II)-TBIH	$Ni_2C_{40}H_{36}N_{12}O_8.4H_2O$	Pink	-	11.50 (11.723)	47.76 (47.932)	4.45 (4.393)	16.42 (16.776)	3.02
92.	Zn(II)-TBIH	$Zn_2C_{40}H_{36}N_{12}O_8.4H_2O$	Yellow	-	13.00 (12.884)	47.82 (47.302)	4.52 (4.336)	16.55 (16.555)	-

TABLE II.2

Principle Infrared Spectral Bands (Cm^{-1}) and their assignments

Sr. No.	Compounds	√C=N	√M-N	√M-O	√OH	√-N-N-
A. Hydrazone series						
1.	BHBH	1615	-	-	2900(m)	950
2.	Cu(II)-BHBH	1605	430	500	3000-3500(b),825	990
3.	Ni(II)-BHBH	1600	430	510	3000-3500(b),825	995
4.	Zn(II)-BHBH	1605	430	505	3000-3500(b),825	990
5.	BDBH	1600(s)	-	-	2900 (m)	950
6.	Cu(II)-BDBH	1585	445	495	3000-3500(b),825	985
7.	Ni(II)-BDBH	1590	440	495	3000-3500(b),825	990
8.	Zn(II)-BDBH	1585	435	490	3000-3500(b),825	990
9.	BHMBH	1600(s)	-	-	2900(m)	940(s)
10.	Cu(II)-BHMBH	1580	430	510	3000-3500(b),825	990
11.	Ni(II)-BHMBH	1585	430	510	3000-3500(b),825	995
12.	Zn(II)-BHMBH	1585	435	505	3000-3500(b),825	995
13.	BHNH	1595(s)	-	-	2900(m)	950(s)
14.	Cu(II)-BHNH	1585	420	500	3000-3500(b),825	990
15.	Ni(II)-BHNH	1580	425	505	3000-3500(b),825	990
16.	Zn(II)-BHNH	1580	425	505	3000-3500(b),825	990

Sr. No.	Compounds	√C=N	√M-N	√M-O	√OH	√c=s
B.	**Thiocarbohydrazone series :**					
17.	BHBT	1600(s)			2635(m)	1090
18.	Cu(II)-BHBT	1590	420	500	3300-3500(b),840	1090
19.	Ni(II)-BHBT	1590	425	500	3300-3500(b),840	1090
20.	Zn(II)-BHBT	1590	415	500	3300-3500(b),840	1090
21.	BDBT	1600(s)			2600(m)	1100
22.	Cu(II)-BDBT	1590	415	490	3300-3500(b),835	1100
23.	Ni(II)-BDBT	1585	415	495	3300-3500(b),835	1100
24.	Zn(II)-BDBT	1585	410	500	3300-3500(b),835	1100
25.	BHMBT	1605			2630(m)	1090
26.	Cu(II)-BHMBT	1590	430	505	3300-3500(b),825	1090
27.	Ni(II)-BHMBT	1595	425	500	3300-3500(b),825	1090
28.	Zn(II)-BHMBT	1585	425	505	3300-3500(b),825	1090
29.	BHNT	1600(s)			2600(m)	1090
30.	Cu(II)-BHNT	1590	415	495	3300-3500(b),840	1090
31.	Ni(II)-BHNT	1585	420	500	3300-3500(b),840	1090
32.	Zn(II)-BHNT	1585	425	495	3300-3500(b),840	1090

Sr. No.	Compounds	√C=N	√M-N	√M-O	√OH
C.	**p-Phenylenediamine series :**				
33.	BHB-P-PD	1600(s)			2900(m)
34.	Cu(II)-BHB-P-PD	1590	440	530	3000-3500(b),820
35.	Ni(II)-BHB-P-PD	1590	430	530	3000-3500(b),820
36.	Zn(II)-BHB-P-PD	1585	430	520	3000-3500(b),820
37.	BDB-P-PD	1600(s)			2900(m)
38.	Cu(II)-BDB-P-PD	1590	420	510	3000-3500(b),820
39.	Ni(II)-BDB-P-PD	1585	415	515	3000-3500(b),820
40.	Zn(II)-BDB-P-PD	1585	420	515	3000-3500(b),820
41.	BHMB-P-PD	1605(s)			2900(m)
42.	Cu(II)-BHMB-P-PD	1590	420	520	3000-3500(b),830
43.	Ni(II)-BHMB-P-PD	1590	430	520	3000-3500(b),830
44.	Zn(II)-BHMB-P-PD	1590	425	515	3000-3500(b),830
45.	BHN-P-PD	1600(s)			2900(m)
46.	Cu(II)-BHN-P-PD	1580	420	525	3000-3500(b),825
47.	Ni(II)-BHN-P-PD	1585	420	530	3000-3500(b),825
48.	Zn(II)-BHN-P-PD	1585	430	530	3000-3500(b),825
D.	**m-Phenylenediamine series :**				
49.	BHB-m-PD	1600(s)			2870(m)
50.	Cu(II)-BHB-m-PD	1585	420	500	3300-3500(b),800
51.	Ni(II)-BHB-m-PD	1585	420	505	3300-3500(b),800
52.	Zn(II)-BHB-m-PD	1580	415	495	3300-3500(b),800
53.	BDB-m-PD	1600(s)			2900(m)
54.	Cu(II)-BDB-m-PD	1575	410	505	3300-3500(b),805

Sr. No.	Compounds	√C=N	√M-N	√M-O	√OH
55.	Ni(II)-BDB-m-PD	1585	420	510	3300-3500(b),805
56.	Zn(II)-BDB-m-PD	1580	425	500	3300-3500(b),805
57.	BHMB-m-PD	1605(s)			2890(m)
58.	Cu(II)-BHMB-m-PD	1590	400	495	3350-3500(b),810
59.	Ni(II)-BHMB-m-PD	1585	410	500	3350-3500(b),810
60.	Zn(II)-BHMB-m-PD	1590	405	495	3350-3500(b),810
61.	BHN-m-PD	1595			2900(m)
62.	Cu(II)-BHN-m-PD	1575	405	510	3300-3500(b),800
63.	Ni(II)-BHN-m-PD	1580	415	510	3300-3500(b),800
64.	Zn(II)-BHN-m-PD	1575	410	515	3300-3500(b),800
E.	**Benzidine series** :				
65.	BHBB	1610(s)			2890(m)
66.	Cu(II)-BHBB	1595	430	490	3300-3500(b),850
67.	Ni(II)-BHBB	1590	425	495	3300-3500(b),850
68.	Zn(II)-BHBB	1595	430	500	3300-3500(b),850
69.	BDBB	1605(s)			2900(m)
70.	Cu(II)-BDBB	1590	420	500	3300-3500(b),840
71.	Ni(II)-BDBB	1595	425	500	3300-3500(b),840
72.	Zn(II)-BDBB	1595	425	495	3300-3500(b),840
73.	BHMBB	1610(s)			2850(m)
74.	Cu(II)-BHMBB	1600	410	505	3300-3500(b),850
75.	Ni(II)-BHMBB	1595	415	515	3300-3500(b),850
76.	Zn(II)-BHMBB	1595	420	515	3300-3500(b),850
77.	BHNB	1610(s)			2850(m)

Sr. No.	Compounds	ν C=N	ν M-N	ν M-O	ν OH	ν COO^-
78.	Cu(II)-BHNB	1595	400	510	3300-3500(b),850	-
79.	Ni(II)-BHNB	1590	410	515	3300-3500(b),850	-
80.	Zn(II)-BHNB	1595	410	515	3300-3500(b),850	-
F.	**Terephthaldehyde series :**					
81.	TBIG	1600(s)			3200(m)	1450,2500
82.	Cu(II)TBIG	1590	400	520	3000-3500(b),825	1470,1310,1500
83.	Ni(II)-TBIG	1590	400	515	3000-3500(b),825	1470,1310,1500
84.	Zn(II)-TBIG	1585	405	515	3000-3500(b),825	1470,1310,1500
85.	TBIA	1600(s)			3200(m)	1445,2500
86.	Cu(II)-TBIA	1575	410	515	3000-3500(b),825	1470,1310,1500
87.	Ni(II)-TBIA	1570	405	525	3000-3500(b),825	1470,1310,1500
88.	Zn(II)-TBIA	1580	400	520	3000-3500(b),825	1470,1310,1500
89.	TBIH	1600(s)			3200(m)	1450,2500
90.	Cu(II)-TBIH	1580	405	510	3000-3500(b),825	1470,1310,1500
91.	Ni(II)-TBIH	1585	410	515	3000-3500(b),825	1470,1310,1500
92.	Zn(II)-TBIH	1585	405	510	3000-3500(b),825	1470,1310,1500

s = sharp, m = medium, b = broad

Table II.3 : Elecctronic and Reflectance Spectra of some selected complexes.

Sr. No.	Compound	ν_{max} (Cm^{-1})	Assignment
1.	BHMBH - Cu(II)	16200	$^3T_{2g} \leftarrow {}^3Eg$
		26000	Charge transfer.
2.	BHMBH-Ni(II)	9300	$^3A_{2g}(F) \longrightarrow {}^3T_{2g}(F)$
		14000	$^3A_{2g}(F) \longrightarrow {}^3T_{1g}(F)$
		23300	$^3A_{2g}(F) \longrightarrow {}^3T_{1g}(P)$
3.	BHMBH - Zn(II)	31000	Charge transfer
4.	BHBT-Ni(II)	10900	$^3A_{2g}(F) \longrightarrow {}^3T_{2g}(F)$
		16100	$^3A_{2g}(F) \longrightarrow {}^3T_{1g}(F)$
		27770	$^3A_{2g}(F) \longrightarrow {}^3T_{1g}(P)$
5.	BHMBT-Ni(II)	10950	$^3A_{2g}(F) \longrightarrow {}^3T_{2g}(F)$
		17200	$^3A_{2g}(F) \longrightarrow {}^3T_{1g}(F)$
		28900	$^3A_{2g}(F) \longrightarrow {}^3T_{1g}(P)$
6.	BHBT-Cu(II)	15625	$^3E_g \longrightarrow {}^3T_{2g}$
7.	BHMBT-Cu(II)	15870	$^3E_g \longrightarrow {}^3T_{2g}$
8.	BHMBT-Zn(II)	33330	Charge-Transfer
9.	BHN-p-PD-Ni(II)	9600	$^3A_{2g}(F) \longrightarrow {}^3T_{2g}(F)$
		16000	$^3A_{2g}(F) \longrightarrow {}^3T_{1g}(F)$
		25500	$^3A_{2g}(F) \longrightarrow {}^3T_{1g}(P)$
10.	BHN-p-PD-Cu(II)	17200	$^3T_{2g} \leftarrow {}^3E_g$
		19100	
11.	BDB-m-PD-Ni(II)	11200	$^3A_{2g}(F) \longrightarrow {}^3T_{2g}(F)$
		15600	$^3A_{2g}(F) \longrightarrow {}^3T_{1g}(F)$
		24300	$^3A_{2g}(F) \longrightarrow {}^3T_{1g}(P)$
12.	BHN-m-PD-Ni(II)	11300	$^3A_{2g}(F) \longrightarrow {}^3T_{2g}(F)$
		15300	$^3A_{2g}(F) \longrightarrow {}^3T_{1g}(F)$
		23800	$^3A_{2g}(F) \longrightarrow {}^3T_{1g}(P)$
13.	BDB-m-PD-Cu(II)	13888	d-d transition
		26666	Charge transfer
		32250	Charge transfer

Sr. No.	Compound	λ max (Cm^{-1})	Assignment
14.	BHN-m-PD-Cu(II)	13900	d-d transition
		32200	Charge transfer
15.	BHMBB-Ni(II)	9220	$^3A_{2g}(F) \longrightarrow {}^3T_{2g}(F)$
		14530	$^3A_{2g}(F) \longrightarrow {}^3T_{1g}(F)$
		25340	$^3A_{2g}(F) \longrightarrow {}^3T_{1g}(P)$
16.	BHMBB-Cu(II)	17200	$^2B_{1g} \longrightarrow {}^2A_{1g}$
17.	TBIG-Ni(II)	10200	$^3A_{2g}(F) \longrightarrow {}^3T_{2g}(F)$
		15150	$^3A_{2g}(F) \longrightarrow {}^3T_{1g}(F)$
		27800	$^3A_{2g}(F) \longrightarrow {}^3T_{1g}(P)$
18.	TBIG-Cu(II)	19150	$^2B_{1g} \longrightarrow {}^2A_{1g}$

TABLE II. 4

X-ray diffraction data for BHBH

Ser No :	2θ	$Sin^2\theta$ (obsd)	$Sin^2\theta$ (calcd)	(hkl)	d	I/Io
1-	11.30	0.0096	0.0098	(210)	7.824	60
2-	13.780	0.0143	0.0146	(202)	6.421	1
3-	15.250	0.0176	0.0176	(300)	5.805	83
4-	16.040	0.0194	0.0196	(310)	5.521	15
5-	17.740	0.0237	0.0231	(203)	4.996	10
6-	19.290	0.0280	0.0271	(321)	4.598	1
7-	20.780	0.0325	0.0322	(322)	4.271	4
8-	21.410	0.0345	0.0349	(313)	4.147	64
9-	21.800	0.0357	0.0352	(330)	4.074	2
10-	22.740	0.0388	0.0392	(420)	3.907	26
11-	25.180	0.0475	0.0466	(403)	3.534	10
12-	25.970	0.0504	0.0509	(510)	3.428	7
13-	26.770	0.0535	0.0526	(511)	3.328	100
14-	27.580	0.0568	0.0568	(520)	3.232	3
15-	28.170	0.0592	0.0585	(521)	3.165	1
16-	29.150	0.0633	0.0636	(522)	3.061	7
17-	30.440	0.0689	0.0683	(531)	2.934	22
18-	30.820	0.0706	0.0705	(600)	2.899	1
19-	31.530	0.0738	0.0734	(532)	2.835	4
20-	31.740	0.0747	0.0742	(611)	2.817	7
21-	32.410	0.0782	0.0784	(620)	2.754	3
22-	33.450	0.0828	0.0820	(541)	2.677	2
23-	34.000	0.0854	0.0852	(622)	2.635	3

A = 0.00196, C = 0.0017

TABLE II. 5

X-ray diffraction data for BHBH-Ni(II)

Ser No :	2θ	$Sin^2\theta$ (obsd)	$Sin^2\theta$ (calcd)	(hkl)	d	I/Io
1-	11.44	0.0099	0.0097	(210)	7.729	19
2-	11.650	0.0103	0.0097	(210)	7.590	28
3-	11.810	0.0105	0.0097	(210)	7.487	49
4-	12.580	0.0120	0.0125	(112)	7.031	40
5-	18.910	0.0269	0.0274	(321)	4.689	36
6-	19.390	0.0283	0.0281	(312)	4.574	93
7-	19.490	0.0286	0.0281	(312)	4.551	100
8-	28.820	0.0619	0.0624	(440)	3.095	19

A = 0.00195, C = 0.00215

TABLE II. 6

X-ray diffraction data for BHBT

Ser No :	2θ	$\sin^2\theta$ (obsd)	$\sin^2\theta$ (calcd)	(hkl)	d	I/Io
1-	5.100	0.0019	0.0019	(100)	17.314	100
2-	10.200	0.0079	0.0079	(102)	8.665	54
3-	15.320	0.0177	0.0171	(300)	5.779	87
4-	16.460	0.0204	0.0205	(311)	5.381	1
5-	19.380	0.0283	0.0287	(222)	4.576	1
6-	19.740	0.0293	0.0304	(400)	4.494	5
7-	20.260	0.0309	0.0307	(322)	4.380	11
8-	20.490	0.0316	0.0319	(401)	4.331	3
9-	22.320	0.0374	0.0375	(005)	3.980	3
10-	23.660	0.0420	0.0430	(314)	3.757	8
11-	24.840	0.0462	0.0458	(413)	3.582	3
12-	25.680	0.0493	0.0494	(510)	3.466	27
13-	26.180	0.0512	0.0509	(511)	3.401	1
14-	28.360	0.0600	0.0608	(440)	3.144	5
15-	28.550	0.0607	0.0608	(440)	3.124	6
16-	28.870	0.0621	0.0629	(513)	3.090	8
17-	29.420	0.0644	0.0646	(530)	3.034	2
18-	29.820	0.0662	0.0661	(531)	2.994	1
19-	30.000	0.0669	0.0668	(442)	2.976	2
20-	34.660	0.0887	0.0895	(623)	2.586	1
21-	35.100	0.0909	0.0910	(426)	2.555	1
22-	35.190	0.0913	0.0926	(525)	2.548	1
23-	36.280	0.0969	0.0965	(711)	2.474	2
24-	41.970	0.1282	0.01290	(626)	2.151	1

A = 0.0019, C = 0.0015

TABLE II. 7

X-ray diffraction data for BHBT-Cu(II)

Ser No :	2θ	$Sin^2\theta$ (obsd)	$Sin^2\theta$ (calcd)	(hkl)	d	I/Io
1-	5.820	0.0025	0.002	(110)	15.173	100
2-	14.520	0.0159	0.01560	(214)	6.093	33
3-	14.920	0.0168	0.0160	(220)	5.993	27
4-	15.190	0.0174	0.0180	(300)	5.828	28
5-	17.620	0.0234	0.0236	(304)	5.029	30
6-	17.930	0.0242	0.0248	(402)	4.943	25
7-	26.540	0.0526	0.0526	(324)	3.356	30
8-	26.790	0.0536	0.0531	(333)	3.326	28
9-	27.060	0.0547	0.0540	(504)	3.293	33

A = 0.0022, C = 0.0015

TABLE II.8

X-ray diffraction data for BHMB-P-PD

Ser No :	2θ	$Sin^2\theta$ (obsd)	$Sin^2\theta$ (calcd)	(hkl)	d	I/Io
1-	11.640	0.0102	0.0100	(210)	7.596	8
2-	11.840	0.01063	0.0100	(210)	7.469	24
3-	11.930	0.01079	0.0100	(210)	7.412	28
4-	13.620	0.0140	0.0140	(202)	6.496	52
5-	13.730	0.0142	0.0140	(202)	6.444	91
6-	13.900	0.0146	0.0140	(202)	6.366	100
7-	14.180	0.0150	0.0155	(103)	6.276	4
8-	18.300	0.0252	0.0260	(320)	4.844	4
9-	18.380	0.0255	0.0260	(320)	4.821	4
10-	19.140	0.0276	0.0275	(321)	4.633	19
11-	19.280	0.0280	0.0280	(114)	4.600	26
12-	21.480	0.0350	0.0355	(411)	4.117	14
13-	21.790	0.0357	0.0355	(411)	4.075	16
14-	22.640	0.0385	0.0380	(402)	3.924	6
15-	22.780	0.0390	0.0395	(323)	3.901	10
16-	22.920	0.0394	0.0395	(323)	3.877	6
17-	23.910	0.0429	0.0420	(332)	3.719	4
18-	25.910	0.0502	0.0500	(500)	3.436	5
19-	26.570	0.0528	0.0520	(510)	3.352	13
20-	26.820	0.0537	0.0535	(511)	3.321	15
21-	27.730	0.0574	0.0575	(315)	3.214	6
22-	27.890	0.0580	0.0580	(520)	3.196	8
23-	27.990	0.0584	0.0580	(520)	3.185	7

A = 0.002, C = 0.0015

TABLE II. 9

X-ray diffraction data for BHMB-p-PD-Cu(II)

Ser No :	2θ	$Sin^2\theta$ (obsd)	$Sin^2\theta$ (calcd)	(hkl)	d	I/Io
1-	15.300	0.01772	0.0176	(220)	5.786	85
2-	17.620	0.02345	0.0234	(311)	5.029	100
3-	18.950	0.02709	0.0276	(312)	4.679	81
4-	23.510	0.04150	0.0412	(323)	3.781	70

A = 0.0022, C = 0.0014

TABLE II. 10

X-ray diffraction data for BHMB-p-PD-Zn(II)

Ser No :	2θ	$Sin^2\theta$ (obsd)	$Sin^2\theta$ (calcd)	(hkl)	d	I/Io
1-	15.040	0.0171	0.0176	(220)	5.886	93
2-	15.360	0.0178	0.0176	(220)	5.764	100
3-	17.340	0.0227	0.0220	(222)	5.110	28
4-	21.370	0.0344	0.0340	(313)	4.155	24
5-	22.770	0.0389	0.0387	(411)	3.902	64
6-	23.980	0.0432	0.0434	(314)	3.708	29
7-	25.690	0.0494	0.0493	(422)	3.465	31
8-	26.230	0.0515	0.0516	(333)	3.395	62
9-	26.860	0.0539	0.0533	(305)	3.317	46
10-	27.420	0.0562	0.0560	(423)	3.250	36
11-	30.410	0.0688	0.0687	(405)	2.937	69
12-	31.060	0.0717	0.0717	(441)	2.877	64

A = 0.0022, C = 0.00134

TABLE II. 11

X-ray diffraction data for BHN-p-PD

Ser No :	2Θ	$Sin^2\theta$ (obsd)	$Sin^2\theta$ (calcd)	(hkl)	d	I/Io
1-	10.830	0.0089	0.0092	(200)	8.163	56
2-	11.010	0.0092	0.0092	(200)	8.030	100
3-	11.250	0.0096	0.0092	(200)	7.859	36
4-	12.210	0.0113	0.0113	(201)	7.243	7
5-	12.410	0.0116	0.0115	(210)	7.127	13
6-	15.620	0.0184	0.0184	(220)	5.669	14
7-	15.710	0.0186	0.0189	(003)	5.636	16
8-	15.930	0.0192	0.0199	(212)	5.559	10
9-	19.900	0.0298	0.0291	(302)	4.458	10
10-	20.030	0.0302	0.0304	(213)	4.429	18
11-	20.140	0.0305	0.0304	(213)	4.405	19
12-	22.190	0.0370	0.0373	(223)	4.003	8
13-	22.270	0.0372	0.0373	(223)	3.989	7
14-	22.960	0.0396	0.0391	(410)	3.870	8
15-	24.840	0.0462	0.0460	(420)	3.582	11
16-	25.000	0.0468	0.0460	(420)	3.582	20
17-	25.110	0.0472	0.0475	(412)	3.544	15
18-	25.200	0.0473	0.04755	(412)	3.531	9
19-	25.990	0.0505	0.0498	(332)	3.426	17
20-	26.170	0.0512	0.0498	(332)	3.402	29
21-	28.410	0.0602	0.0603	(333)	3.139	19
22-	28.740	0.0615	0.0619	(511)	3.104	8

A = 0.0023, C = 0.0021

TABLE II. 12

X-ray diffraction data for BHN-p-PD-Cu(II)

Ser No :	2θ	$Sin^2\theta$ (obsd)	$Sin^2\theta$ (calcd)	(hkl)	d	I/Io
1-	11.610	0.0102	0.0102	(210)	7.616	37
2-	11.710	0.0104	0.0102	(210)	7.551	58
3-	12.060	0.01103	0.0110	(112)	7.333	89
4-	12.230	0.0113	0.0110	(112)	7.231	100
5-	12.330	0.0115	0.0110	(112)	7.173	87
6-	12.660	0.0121	0.0119	(211)	6.987	69
7-	21.290	0.0341	0.0340	(410)	4.170	33
8-	21.640	0.0352	0.0357	(411)	4.103	61
9-	23.640	0.0419	0.0417	(420)	3.761	30
10-	23.770	0.0424	0.0430	(332)	3.740	37
11-	23.860	0.0427	0.0430	(332)	3.726	35
12-	27.250	0.0558	0.0551	(423)	3.258	23
13-	27.580	0.0568	0.0570	(502)	3.232	23
14-	29.290	0.0639	0.0640	(440)	3.047	17
15-	29.460	0.0646	0.0640	(440)	3.030	18

A = 0.002, C = 0.00175

TABLE II. 13

X-ray diffraction data for BHBB

Ser No :	2θ	$Sin^2\theta$ (obsd)	$Sin^2\theta$ (calcd)	(hkl)	d	I/Io
1-	12.020	0.01100	0.0110	(210)	7.357	100
2-	16.050	0.0195	0.0195	(212)	5.518	36
3-	19.090	0.0275	0.0279	(203)	4.645	35
4-	19.520	0.0287	0.0286	(320)	4.544	57
5-	19.700	0.0293	0.03015	(213)	4.503	62
6-	20.060	0.0303	0.0305	(312)	4.423	30
7-	23.880	0.0430	0.0437	(402)	3.723	5
8-	24.170	0.0438	0.044	(420)	3.679	17
9-	24.700	0.0457	0.0459	(412)	3.602	65
10-	25.410	0.0484	0.0481	(332)	3.502	10
11-	28.720	0.0615	0.0625	(324)	3.106	21
12-	29.370	0.0643	0.0641	(215)	3.039	10

A = 0.0022, C = 0.002125

TABLE II. 14

X-ray diffraction data for BHBB-Ni(II)

Ser No :	2θ	$Sin^2\theta$ (obsd)	$Sin^2\theta$ (calcd)	(hkl)	d	I/Io
1-	10.530	0.0084	0.0084	(200)	8.395	82
2-	11.570	0.0102	0.0102	(202)	7.645	20
3-	12.400	0.0116	0.0114	(112)	7.132	40
4-	15.310	0.0177	0.0177	(212)	5.783	32
5-	16.630	0.0209	0.0207	(301)	5.327	96
6-	17.390	0.0228	0.0228	(311)	5.095	100
7-	17.900	0.02420	0.0246	(203)	4.951	33
8-	18.340	0.0254	0.0251	(302)	4.834	22
9-	19.610	0.0290	0.0291	(321)	4.523	77
10-	24.810	0.04614	0.0450	(332)	3.586	50
11-	26.420	0.0522	0.0525	(500)	3.371	37
12-	28.360	0.0600	0.0609	(520)	3.144	32

A = 0.0021, C = 0.0018

TABLE II. 15

X-ray diffraction data for BHMBB

Ser No :	2θ	$\sin^2\theta$ (obsd)	$\sin^2\theta$ (calcd)	(hkl)	d	I/Io
1-	12.110	0.0111	0.0110	(210)	7.303	4
2-	13.970	0.0147	0.0146	(003)	6.334	9
3-	14.360	0.0156	0.0153	(202)	6.163	100
4-	14.650	0.0162	0.0168	(103)	6.042	13
5-	16.330	0.0201	0.0192	(221)	5.424	24
6-	17.390	0.2280	0.022	(310)	5.095	10
7-	19.580	0.0289	0.0286	(320)	4.530	14
8-	19.840	0.0296	0.0302	(321)	4.471	2
9-	20.580	0.0319	0.0322	(223)	4.312	10
10-	20.870	0.0328	0.322	(223)	4.253	11
11-	22.190	0.0370	0.374	(410)	4.003	17
12-	23.110	0.0401	0.0407	(005)	3.846	6
13-	24.240	0.0440	0.044	(420)	3.669	23
14-	25.820	0.0499	0.0498	(403)	3.448	21
15-	26.130	0.0511	0.0517	(215)	3.408	3
16-	27.320	0.0557	0.0550	(500)	3.262	4
17-	28.560	0.0608	0.0605	(305)	3.123	5
18-	28.780	0.0617	0.0615	(502)	3.100	5
19-	29.000	0.0626	0.0627	(315)	3.077	3
20-	31.350	0.0729	0.0720	(441)	2.851	2
21-	32.980	0.0805	0.0808	(601)	2.714	4
22-	38.350	0.1078	0.1078	(007)	2.345	4

A = 0.0022, C = 0.00163

TABLE II. 16

X-ray diffraction data for BHMBB-Cu(II)

Ser : No	2θ	$\sin^2\theta$ (obsd)	$\sin^2\theta$ (calcd)	(hkl)	d	I/Io
1-	10.820	0.0089	0.0089	(210)	8.170	30
2-	14.110	0.0150	0.0150	(212)	6.272	16
3-	16.660	0.0209	0.0203	(222)	5.317	100
4-	17.050	0.0219	0.0221	(302)	5.196	19
5-	19.370	0.0283	0.0284	(400)	4.579	53
6-	23.110	0.0401	0.0404	(304)	3.846	18
7-	28.020	0.0586	0.0582	(433) (503)	3.182	16

A = 0.00178, C = 0.001525

TABLE II. 17

X-ray diffraction data for BHNB

Ser No :	2θ	$Sin^2\theta$ (obsd)	$Sin^2\theta$ (calcd)	(hkl)	d	I/Io
1-	13.100	0.0130	0.0132	(220)	6.753	22
2-	13.250	0.0133	0.0132	(220)	6.677	29
3-	13.600	0.0140	0.0140	(204)	6.506	100
4-	13.950	0.0147	0.0148	(300)	6.343	83
5-	15.800	0.0188	0.0183	(311)	5.604	92
6-	15.880	0.0190	0.0199	(113)	5.576	98
7-	16.160	0.0197	0.0199	(113)	5.480	45
8-	16.260	0.0199	0.0199	(113)	5.447	35
9-	18.390	0.0255	0.0248	(213)	4.821	18
10-	18.720	0.0264	0.0264	(400)	4.736	50
11-	18.820	0.0267	0.0264	(400)	4.711	60
12-	19.310	0.0281	0.0280	(410)	4.593	29
13-	19.410	0.0284	0.0280	(410)	4.569	28
14-	19.510	0.0287	0.0280	(410)	4.546	24
15-	24.410	0.0446	0.0447	(511)	3.644	27
16-	25.650	0.0492	0.0496	(520)	3.470	48
17-	25.730	0.0495	0.0496	(520)	3.460	63
18-	25.830	0.0499	0.0496	(520)	3.446	71
19-	25.990	0.0504	0.0503	(512)	3.428	74
20-	26.070	0.0508	0.0503	(512)	3.415	65
21-	26.630	0.0530	0.0528	(440)	3.345	35
22-	26.910	0.0541	0.0546	(441)	3.311	35

A = 0.00165, C = 0.00185

TABLE II. 18

X-ray diffraction data for BHNB

Ser No :	2θ	$Sin^2\theta$ (obsd)	$Sin^2\theta$ (calcd)	(hkl)	d	I/Io
1-	15.650	0.0185	0.0185	(310)	5.658	69
2-	15.830	0.0189	0.0189	(310)	5.594	72
3-	16.000	0.0194	0.0194	(313)	5.535	62
4-	20.700	0.0322	0.0324	(413)	4.288	100
5-	20.9600	0.0330	0.0333	(330)	4.219	76
6-	21.040	0.0333	0.0333	(330)		

A = 0.001853, C = 0.001775

TABLE II. 19

X-ray diffraction data for TBIG

Ser No :	2θ	$\sin^2\theta$ (obsd)	$\sin^2\theta$ (calcd)	(hkl)	d	I/Io
1-	17.440	0.0229	0.0230	(310)	5.081	28
2-	17.780	0.0238	0.0230	(310)	4.985	50
3-	18.720	0.0264	0.0264	(222)	4.736	97
4-	19.960	0.0300	0.0295	(213)	4.445	46
5-	20.290	0.0310	0.0310	(312)	4.373	41
6-	22.720	0.0387	0.0387	(303)	3.911	26
7-	23.530	0.0415	0.0414	(330)	3.778	88
8-	24.100	0.0435	0.0434	(331)	3.690	48
9-	27.710	0.0573	0.0575	(500) (430)	3.217	25
10-	28.390	0.0601	0.0598	(510)	3.141	74
11-	29.190	0.0634	0.0640	(423)	3.057	100
12-	30.020	0.0670	0.0678	(512)	2.974	93
13-	30.880	0.0708	0.0711	(414)	2.893	22
14-	34.370	0.0872	0.0871	(611)	2.607	13
15-	35.290	0.0918	0.0918	(514)	2.541	56
16-	35.990	0.0954	0.0950	(316)	2.493	43
17-	36.460	0.0978	0.0962	(533)	2.462	71
18-	38.450	0.1084	0.01075	(505)	2.339	11

A = 0.0023, C = 0.002

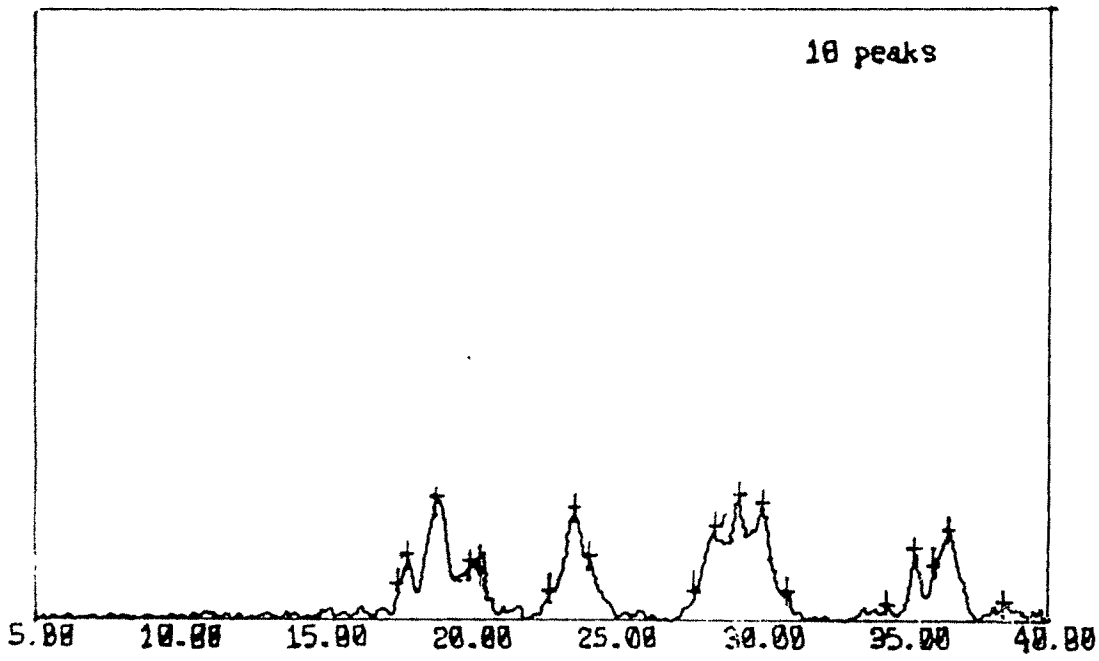

Fig.(II.1) : X-ray diffractogram of TBIG (schiff's base ligand)

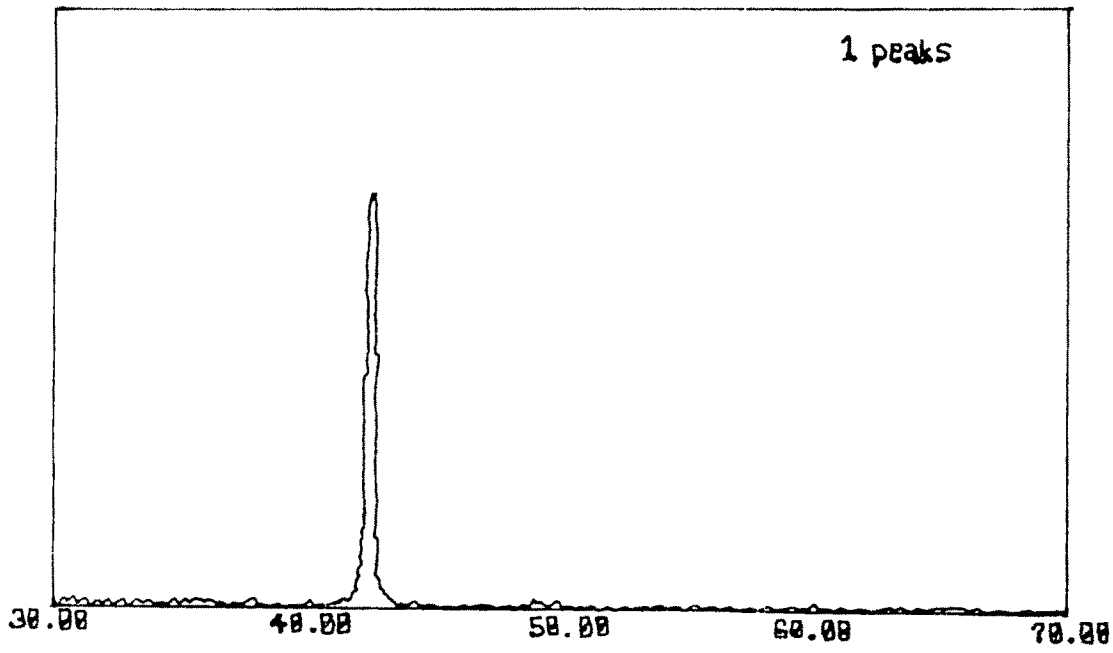

Fig.(II.2) : X-ray diffractogram of TBIG-Cu(II)

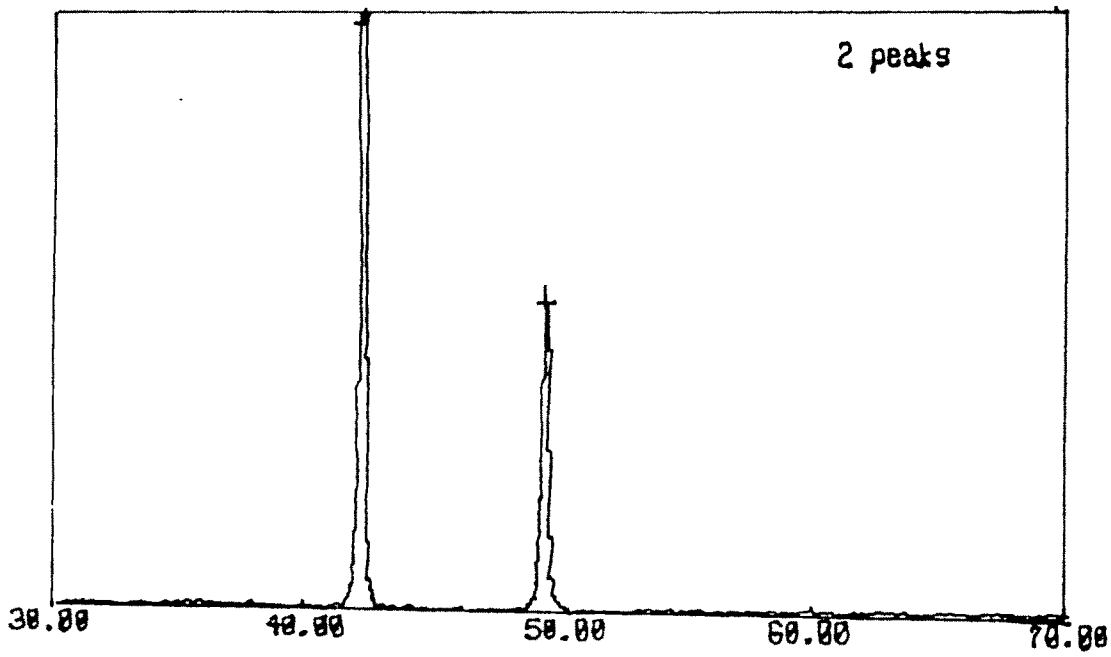

Fig.(II.3) : X-ray diffractogram of TBIG-Ni(II)

References :

1) Harris C. M. & Sinn E.; J. Inorg. Nuclear Chem.; **30** (1968) 2723

2. Sinn E. & Harris C.M.; Coord. Chem. Rev; **4** (1969) 2607

3. Coles R. B., Harris C.M. & Sinn E; Inorg. Chem.; **8** (1969) 2607

4. Baker (Jr.) W.A. & Helm F.T.; J. Am. Chem. Soc.; **97** (1975) 2295

5) Davis J. A. & Sinn E. ; J. Chem. Soc., Dalton Trans.; (1976) 165.

6) Bhattacharya P.K.; J.Ind. Chem. Soc. ; **LIX** (1982) 505

7) Patel V.K. & Bhattacharya P.K.; Ind. J. Chem; **21A** (1982) 674.

8) Poddar S.N. & Kundu B.C.; Ind.. J. Chem.; **23A** (1984) 488

9) Thaker B.T.; J. Ind. Chem. Soc.; **LXIV** (1987) 78.

10) Marvell C.S. & Tarkoy N.; J. Am. Chem. Soc.; **79** (1957) 6000.

11) Maurya P.L., Agarwala B.V. & Dey A.K.; Polym Bull. **3** (1980) 253., Proc. XXIII Int. Conf. Coord. Chem., Colorando; (1984) 354.

12) Dey A..K.; J. Ind. Chem. Soc.; **LXIII** (1986) 357

13) Judd M.C.; Ph.D Thesis, Universitty of Illions; (1958).

14) Berg E.W. & Alam A.; Anal. Chem. Acta.; **28** (1963) 126.

15) Patel V.K.; Ph.D. Thesis, M.S. University of Baroda; (1993).

16) Bisagni M. Ng. Ph. Buu-Hoi & Bayer R.; J.Chem. Soc.; (1955) 3693.

17) Audrieth L.F., Scott E..S. & Kipper P.S.; J. Org. Chem.; **19** (1954) 733.

18) Vogel's "Textbook of Quantitative Chemical Analysis"; 5th edition (English Language Book Society/Longman), (1989) 321-329.

19) Figgis B.N. & Nyholm R.S.; J.Chem. Soc.; (1959) 331.

20) Selwood P.W. "Magnetochemistry", 2nd edition, (Interscience, New York), (1956) 78,92,93.

21) Cullity B.D.; "Elements of x-ray Diffraction" 2nd edition, (Addison, Wesley Publishing Comp.INC), (1977) 324-349.

22) Henry N.F.M., Lipson H. & Wooster W..A. "Interpretation of x-ray Diffraction Photographs", (McMillan, London), (1951) 123, 179.

23) Lipson H. & Steeple H. ; "Interpretation of x-ray powder Diffraction Patterns," (McCmillan London) (1970)

24) Azaroff L.V. & Burger M.J.; "The Powder Method in x-ray Crystallography"; (McGraw-Hill, New York) (1958).