CHAPTER IV

"RESULTS AND DISCUSSION"

The Schiff's bases and their metal complexes synthesised can be subgrouped into the following :

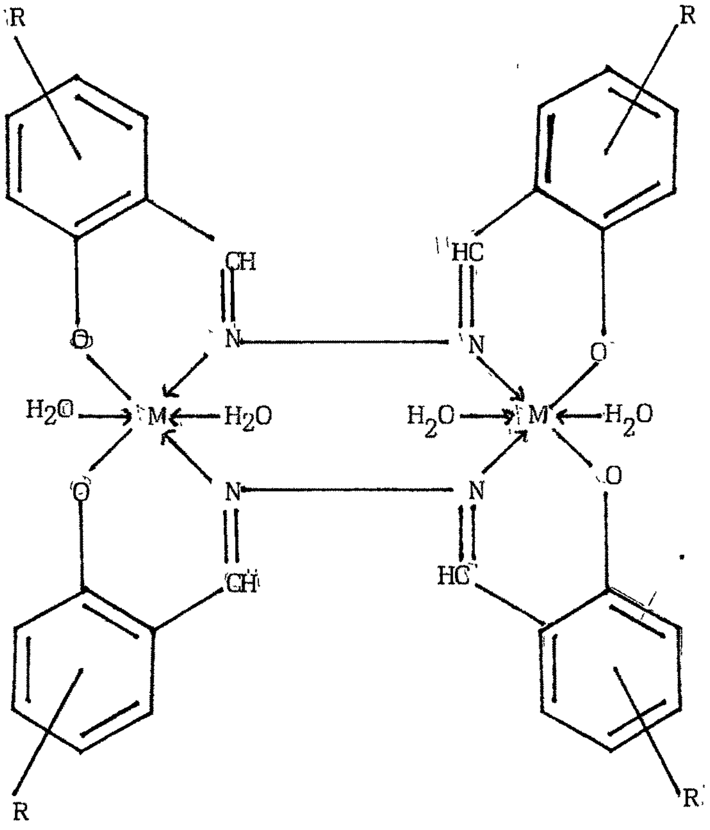
i. The Hydrazone group
ii. The Thiocarbohydrazone group
iii. The p-Phenylene diamine group
iv. The m-Phenylene diamine group
v. The Benzidine group
vi. The Terephthaldehyde group.

4.1 THE HYDRAZONE GROUP :

In this group four hydrazone compounds of Salicylaldehyde (BHBH), 2,4-dihydroxybenzaldehyde (BDBH), o-Vaniline (BHMBH) and 2-hydroxy-1-naphaldehyde (BHNH) were synthesised, twelve metal complexes were prepared from them using Cu^{2+}, Ni^{2+} and Zn^{2+} metal ions.

On the basis of elemental analysis, (table (II.1) Chapter II) the molecular formula of metal complexes works out to be $[M_2L_2.4H_2O]$, a binuclear structure, where $M=Cu^{2+}$,Ni^{2+} and Zn^{2+} metal ions and L=Schiff's base ligand. The structures can be represented in general as shown in Figure (IV.I). The complexes are insensitive to atmospheric moisture and are insoluble in common organic solvents but are soluble in DMF.

The position of principle I.R. Spectral bands are given in table (II.2). It can be observed from the table that the



R = H, -OH, OCH_3 or ph

M = Cu(II), Ni(II) or Zn(II)

Fig. (IV.1)

coordination of the ligands to the metal centres occurs via azomethine nitrogen[1] of Schiff's bases, since √C=N mode of the free ligand appearing in the region 1595-1615cm^{-1} is shifted to lower frequency by 10-20 cm^{-1} in the metal complexes. The appearance of one √c=N band in the spectra of the complexes indicate that both the azomethine nitrogens are involved in coordination[2]. A sharp band at 950 cm^{-1} due to√N-N in the spectra of the free ligands undergoes shift to higher frequency ∼ 990-995 cm^{-1}, supporting coordination via both nitrogen atoms.[3] A weak band 2900 cm^{-1} instead of a strong one at 3200 cm^{-1} (expected for phenolic free OH) was observed for ligands. This shift may be due to intramolecular hydrogen bonding between hydroxyl hydrogen and nitrogen of azomethine gorup[4]. This band is absent in complexes indicates that OH group proton is used in M-O bond formation[5].

The presence of new bands in the spectra of the metal complexes in the regions 420-435cm^{-1} and 490-505cm^{-1} are assigned to M-N and M-O respectively[5]. A broad band observed in the region 3200-3500cm^{-1} corresponds to the presence of coordinated water molecule[6] which is further confirmed by a band at 825cm^{-1}.

The electronic spectral data (table (II.3)) of representative Cu(II) complexes exhibited two bands at ∼16200 & ∽2600cm^{-1}. The broad band (unsymmetrical) at ∼16200cm^{-1} may be due to $3T_{2g} \longleftarrow 3_{Eg}$ transitions in octahedral geometry. And the band at ~2600 cm^{-1} may be due to ligand-metal charge transfer[7]. This was supported by magnetic measurements for Cu(II) complexes (1.3-1.7 B.M.) which suggests an octahedral geometry for Cu(II) complexes[8,9].

The approximate demarkation given by Figgis[10] is that μ_{eff} values above 1.90 B.M. a square planar or octahedral geometry. However normally the range for the copper complexes is 1.5-2.6 B.M.[11-12].

The abnormal values in the present complexes may be attributed as due to the appreciable magnetic interaction between the two copper ions presented in the reported binuclear complexes. Occurance of magnetic interaction in such cases may also be viewed through either the overlap of Cu-Cu orbitals or through the ligand participation.[13] However similar type of binuclear Cu(II) complexes have been reported earlier by other workers[14-16].

Electronic spectra for Ni(II) complexes shows an octahedral geometry, with electronic transitions at ~9300 cm^{-1}, ~14000 and ~23300 which may be assigned to

$3A_{2g}$ (F) ⟶ $3T_{2g}$ (F) (ν_1)
$3A_{2g}$ (F) ⟶ $3T_{1g}$ (F) (ν_2) and
$3A_{2g}$ (F) ⟶ $3T_{1g}$ (P) (ν_3) respectively.

The ratio $\nu_2/\nu_1 = 1.5$ which falls in the range required for octahedral configuration.

The electronic spectra along with magnetic susceptibility data (2.85-3.85) suggests an octahedral configuration around Ni(II) ion[8,9].

The electronic spectra of Zn(II) complexes exhibit a sharp band at high intensity at 31000cm^{-1} and it may be due to ligand-metal charge transfer[7].

The x-ray diffraction patterns for some representative ligands and complexes reported show a tetragonal geometry of the unit cell. The 2θ values for prominent peaks have been listed in tables (II.4 - II.5) in chapter II. All the main peaks have been indexed and their Sin$^2\theta$ values compared with the calculated ones. A comparison of the values reveals that there is a good agreement between the calculated and observed values of Sin$^2\theta$. The unit cell parameters have been calculated by trial and error method[17-19]. The observed values fit well in tetragonal system for ligands and their complexes with different number of molecules per unit cell. Also the calculated values of the density was in good agreement with the observed ones.

The n values, density (observed & calculated), volume of the unit cell, and a & c, of representative compounds are given in table (IV.1).

Luminescence study :

All the specimens chosen for the study show good fluorescence behaviour. It is observed that the fluorescence intensity shown by the metal complexes is higher than that shown by the free hydrazon compounds. The L $\longrightarrow$ M charge transfer is responsible for this. Some excitation energy may be getting transferred to the resonance level of the metallic ion. This further combines with the radiative atomic orbitals resulting into the narrow fluorescence bands. Possibly the narrow band is due to the $\pi^* \longrightarrow n$ transition[20]. The influence of the metallic ion on the fluorescence is the characteristic of a metal chelate compound[21]. This is of major importance from the analytical point of view e.g., the intensity is substantially low for the Zn^{2+} complexes, inspite of their diamagnetic character.

The ligands and metal complexes show quenching of the fluorescence intensity, when the specimens are subjected to the mechanical deformation. This may be due to the increased steric interaction. The azomethine group may get deformed out of plane or may be the induced intersystem crossing is responsible for this behaviour[22].

The overall measured intensities for free ligands and the metal compared are found to be much less than expected this may be due to lack of π character in the hydrazone moiety[23].

Pigmentation Study :

The studied compounds in this series show good light & rubbing fastness (Table (III.1)). The metal complexes with

Cu(II), Ni(II) and Zn(II) have shown higher light and rubbing fastness than the free Schiff's base ligands. This is because the metal chelates are capable of establishing linkage with protein or cellulose molecules and stable metal dye fiber complex is formed[24]. Also it was shown that no difference in fastness with the change in substitutents in the schiff's base ligands (H, -OH, $-OCH_3$, Ph). So the fastness is not related to the change in substituents, but related to their degree of aggregation within the fiber than the chemical structure.

Antibacterial study :

The bacterial activity of the ligands and complexes was evaluated against E. Coli bacteria. The inhibitory zone results are given in Table (III.2). From the table it is observed that ligands and their complexes possess antibacterial activity. It also shows that the ligands with methoxy group have better activity than others. It is clear from the bacterial screening data table (III.2), that most of the metal complexes are more toxic in comparison to their parent ligand itself. The toxicity of the metal complexes increases as the radius of metal ion decreases i.e. Ni > Cu > Zn. The increase in the activity of metal complexes may be due to the effect of metal ions on the normal cell process. A possible mode of toxicity may be speculated in the light of chelation theory[25].

Chelation reduces considerably the polarity of the metal ion mainly because of partial sharing of its π-electrons and delocalization over the whole chelate ring[25]. Such chelation increases the lipophilic character of the metal chelate which probably leads to break-down of permeability barrier of cells resulting in interference with normal cell process[27-29].

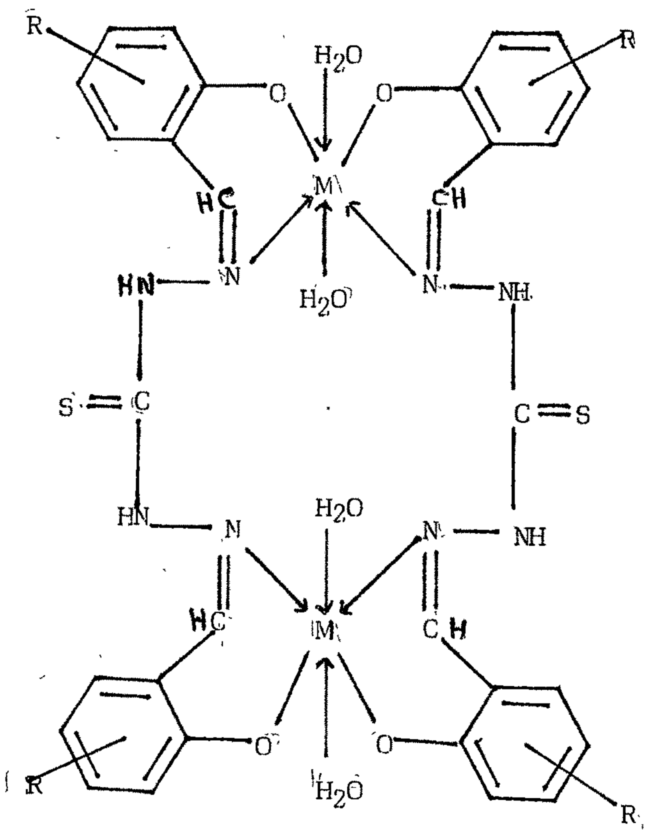
4.2 THIOCARBOHYDRAZONE GROUP :

Four organic Schiff's bases are synthesised in this group (BHBT, BDBT, BHMBT and BHNT) and their twelve complexes of Cu^{2+}, Ni^{2+} & Zn^{2+} metal ions have been isolated. The isolated metal complexes are stable at room temperature. They are isoluble in common organic solvents but soluble in DMF.

The elemental analysis shown in table (II.1) chapter II, suggests a binuclear structure of the molecular formula $[M_2L_2.4H_2O]$ The binuclear structure can be represented as in figure (IV.2)

The I.R. Spectra of the free ligands exhibit a band at 1600 cm^{-1} corresponding to $\sqrt{}$C=N frequency. This band is sifted to lower frequency and appears in the region 1585-1590 cm^{-1} in case of the metal chelates, which indicates involvement of nitrogen of azomethine group in coordination[30-31].

All the ligands and metal complexes exhibit a broad I.R. band of medium intensity around. 3300cm^{-1} which is due



R = H, -OH, OCH$_3$ or ph

M = Cu(II), Ni(II) or Zn(II)

Fig. (IV. 2)

to νNH frequency[32]. This band remains unaltered on complexation indicating non-involvement of the NH group in coordination. The band due to hydrogen bonded[33] OH appearing at 2630-2675cm^{-1} in the ligand disappears in the complexes. The high intensity band due to phenolic C-O around 1280cm^{-1} appears at 1300-1330cm^{-1} in the complexes supporting the involvement of OH groups in the complex formation[34]. The band at 1090-1100cm^{-1} in the ligands spectra which is due to >C=S band[35] does not show any change in the I.R. Spectra of complexes indicating that >C=S does not contribute into complex formation.

The presence of coordinated water molecules in all these complexes is indicated by the appearance of a broad band at 3400-3550cm^{-1} followed by a sharp peak at 840-850cm^{-1} assignable to OH streching and rocking modes respectively[6].

The conclusive evidence of bonding of the ligand to the metal ions is provided by the presence of bands at 410-430cm^{-1} (νM-N) and 485-500cm^{-1} (νM-O)[36-37].

The electronic spectra of Ni(II) complexes showed bands at 10900-10950, 16100-17200 & 27770-28900cm^{-1} due to :

$3A_{2g}$ (F) $\longrightarrow$ $3T_{2g}$ (F) (ν_1),
$3A_{2g}$ (F) $\longrightarrow$ $3T_{1g}$ (F) (ν_2)
and $3A_{2g}$ (F) $\longrightarrow$ $3T_{1g}$ (P) (ν_3) respectively.

which are consistant with the octahedral Ni(II) stereochemistry. The ratio ν_2/ν_1 for Ni (II) complexes is within the range 1.5-1.6 as required for octahedral complexes. This is further[38-39] supported by μ_{eff} values of 3.28-3.40 B.M.

A broad band at 15625-15870cm^{-1} due to

$$^3E_g \longrightarrow {}^3T_{2g} \text{ transition}$$

in the electronic spectra of Cu(II) complexes suggests distorted octahedral configuration[37] and supported by u_{eff} values of 1.12-1.68 B.M. This abnormality of magnetic moment values than what is expected is due to binuclear nature of the complexes which is may be because of either the overlap of Cu-Cu orbitals or through the ligand participation[13]. This also compared with similar type of binuclear Cu(II) complexes reported earlier[14-16,40].

The x-ray diffraction data for some compounds is shown in tables (II.8 & II.9) in chapter II. The unit cell calculations[17-19] have been done for the tetragonal symmetry of the ligands and complexes, and found to fit well in the tetragonal system. As the calculated values of $\text{Sin}^2\theta$ for tetragonal system are in good agreement. The unit cell lattice constants a & c, cell volume, n number of molecules / unit cell. observed and calculated density are given in table (IV.1).

Luminescence study :

Fluorescence study of the ligand and metal complexes was carried out on Perkin-Elmer, Luminescence spectrometer

LS-50. The organic ligands and complexes show good fluorescence property. The study was carried out using 200nm as excitation wavelength. The fluorescence spectra of ligands show number of emission peaks due to different groups present under different environmental conditions. The emission peaks observed at ~490 nm and ~ 530 nm are due to the presence of two >C=N groups under different geometrical environment. This observed peaks do not show any shift in case of fluorescence spectra of metal complexes but there is increase in the intensities. The number of peaks are reduced in metal complexes this may be due to the coordination of metal ions by different groups present in the ligand and might be brought under a symmetrical geometrical environments.

The increased in peak intensities in complexes may be due to LMCT as reported earlier[21]. The nature of the metal ion also has some influence on peak intensity as observed. Copper complexes show higher intensity by 0.1 ABU than nickel complexes.

Pigmentation study :

Similar to the hydrazone group compounds, this series also show good light & rubbing fastness (Table (III.1)). The metal chelates have shown higher light and rubbing fastness than the free Schiff's base ligands. This is because the metal chelates are capable of establishing linkage with protein or cellulose molecules and a stable metal dye fiber complex is formed[24].

Also like hydrazone group the fastness is not related to the change in substituents, but related to their degree of aggregation within the fiber than the chemical structure.

Antibacterial Study :

All the ligands and complexes of this group were screened for their antibacterial activity against E.Coli bacteria. From the table (III.2) it is observed that the presence of $>C=S$ group in the ligands shows better activity compared to those of hydrazone group. The metal chelates showed better activity. Also with the presence of $-OCH_3$ group shows enhanced activity, this may be due to $-OCH_3$ group which decreases the electron density on the overal ligand framework, and facilitating interaction with the amino acids of the micro-organism[41]. Better activities of the complexes as compared to free ligands could also be understood in terms of the chelation theory[25], which explains that a decrease in polarizability of the metal could enhance the lipophilicity of the complexes.

4.3 THE p-PHENYLENEDIAMINE GROUP :

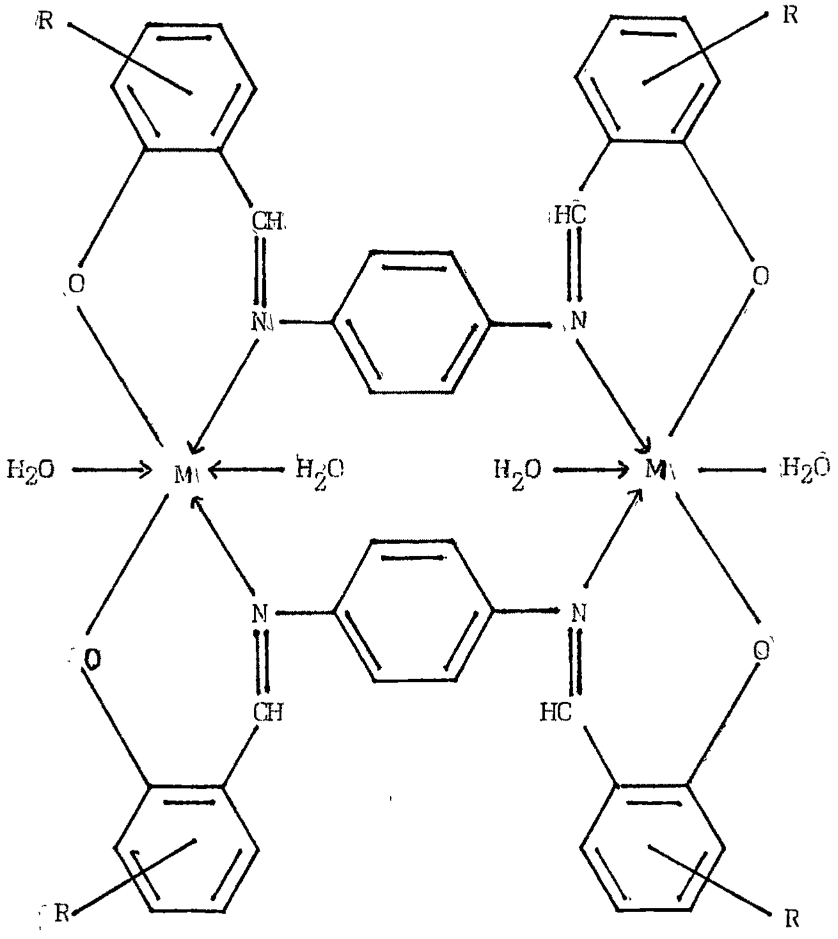
In this group the Four Schiff's base ligands prepared are : BHB-p-PD, BDB-p-PD, BHMB-p-PD and PHN-p-PD and twelve metal complexes of Cu^{2+}, Ni^{2+} & Zn^{2+} are synthesised.

The analytical data of the Schiff's base ligands and their coordination compounds are displayed in table (II.1), chapter II. Elemental analysis suggest the 1:1 (M:L) stoichiometry for these complexes, and shows [$M_2L_2.4H_2O$] binuclear structure as shown in Fig.(IV.3). The metal complexes are insoluble in organic solvents.

The I.R. Spectra of the ligands show a strong band in the region 1600-1605cm^{-1}, assigned to √C=N[42]. This band is shifted to lower energy by 10-15cm^{-1} indicating nitrogen coordination in the complexes[47]. This shift of the band towards the low frequency region may suggest wider delocalization of the electronic charge in the newly formed six membered chelate ring[43] and strong bonding between >C=N- group and metal ions on coordination. In the I.R. Spectra of the ligands, the medium band at 2900cm^{-1} (OH) disappears in metal chelates showing the deprotonation of the phenolic OH which indicates its coordination to the metal ions[15]. The broad band observed in the region 3000-3500cm^{-1} indicates the presence of water molecule, which is further confirmed by a band at the region 820-830cm^{-1} due to OH rocking modes[6].

The new bands observed in the regions 420-440cm^{-1} and 510-530cm^{-1} which are assigned to √M-N and √M-O frequencies respectively[36].

The diffuse reflectance spectra (Table (II.3), chapter II), for some representative compounds shows a distorted octahedral geometry for Ni(II) complexes with the appearance



R = H, -OH, OCH_3 or ph

M = Cu(II), Ni(II) or Zn(II)

Fig. (IV. 3)

of three bands in 9600, 16000 & 25500cm^{-1} which have been assigned to :

$3A_{2g}$ (F) $\longrightarrow$ $^{3}T_{2g}$ (ν_1),
$3A_{2g}$ (F) $\longrightarrow$ $3T_{1g}$ (F), (ν_2) and
$3A_{2g}$ (F) $\longrightarrow$ $3T_{1g}$ (P), (ν_3) respectively

and labelled as ν_1, ν_2 & ν_3 respectively. The ν_2/ν_1 for these complexes is 1.66 as required for octahedral complexes.

With their magnetic moment measurements (2.90-3.02 B.M) support distorted octahedral geometry to Ni(II) complexes[44].

In case of Cu^{2+} complexes one broad band appears at 17200-19100cm^{-1} region assigned to $3T_{2g} \longleftarrow 3E_g$ transition suggested an octahedral geometry. Which is further supported by magnetic moment measurement (1.7-1.8 B.M.)[45].

The x-ray diffraction patterns for some representative ligands and complexes are shown in Tables (II. 10 - II. 13). A comparison of the values reveals that there is good agreement between the calculated and observed values of $\sin^2\theta$ and they fit well in tetragonal system.

The unit cell lattice constants a & c, cell volume, number of molecules per unit cell "n" and density (observed & calculated) are given in table (IV.1).

The observed density is in agreement with the calculated one.

Luminescence study :

The fluorescence measurements of the above specimens with an excitation frequency of 250 nm show prominently the emission around 500 nm. Though the emission for all of them is same, variation in the intensity of the emission is observed depending on the specimen.

It is observed that the ligands with methoxy group show higher fluorescence. This can be attributed to the higher π character, and the peripheral effect of OCH_3 and OH substituents present. The process is exoergonic energy transfer between directly connected units with the sensitisation of lower energy. The emission is originating from the lowest excited triplet state[46].

The emission intensity of the compounds of this group is less than that of Benzidince due to the reduction of aromatic character, and lesser π-bonding.

The quenching of intensity in case of, 2-Hydroxy-1-naphthaldehyde is due to the steric hinderance due to naphthalene moiety.

On chelation no shift of the emission band is observed. In case of Cu(II) complexes the lowering of intensity is because of the M $\longrightarrow$ L charge transfer. The lowest excited state being located on M-L unit alongwith the emission band observed around 500 nm. The additional bands observed at 360 & 400 nm, are due to d-d transition[40-47]. The excited state being with lower energy than the lowest π, π^* excited states. The quenching of intensity in Cu(II) complexes can be expected which is in accordance with Weissman observation[48].

In case of Ni(II) complexes the intensity is observed to be higher than the Schiff's base ligands. This is due to the L → M charge transfer. The additional factor responsible is the stable nature of Ni(II) atom. The "d" orbitals which are capable of considerable interaction with ligand (π bonding) will introduce molecular character into the "d" orbitals, thereby the $\pi^* \rightarrow d$ transition will result into the enhancement in intensity[14,21].

The specimens mechanically deformed into pellets on compression show little shifting (10-30 nm) in the position of the emission band. The higher concentration due to compression is responsible for the increase in the intensity observed in these specimens. Moreover the discrete units are brought much closer to one another and made the charge transfer easier.

The thermally treated specimens do not show any shift of the emission band, though the fluorescence intensity observed is lower than the mechanically treated specimens. The thermal vibrations of the molecules may move the molecules slightly out of plane and thereby producing rarefaction. The increased separation between two units results into lesser charge transfer.

The higher intensity in these specimens compared to the untreated ligands and metal chelates must be due to the decrease in the steric interaction as the separation between two units increases on heat treatments.

Zn(II) complexes show low intensity compared to Cu(II) as well as Ni(II) complexes.

In case of Cu(II) complexes there is a shift of the fluorescence spectrum to lower wavelength side (Blue shift) relative to absorption spectrum; while Ni(II) complexes show Stoke shift[49], i.e. the shift of the fluorescence spectrum to longer wavelength side (Red shift).

Introduction of donor groups like-OH, $-OCH_3$, have increased the luminescence intensities. Binuclear or polynuclear nature does not have much effect on intensity.

Pigmentation study :

The studied compounds have shown excellent light fastness and good rubbing fastness. The metal complexes showed better fastness compared to those of free Schiff's bases. This is because metal ions are capable of forming linkages with the fibres[24]. Also the binuclear nature of the complexes shows it more stable because of presence of two metal ions in the structure which will have higher tendency with the fabrics.

Antibacterial study :

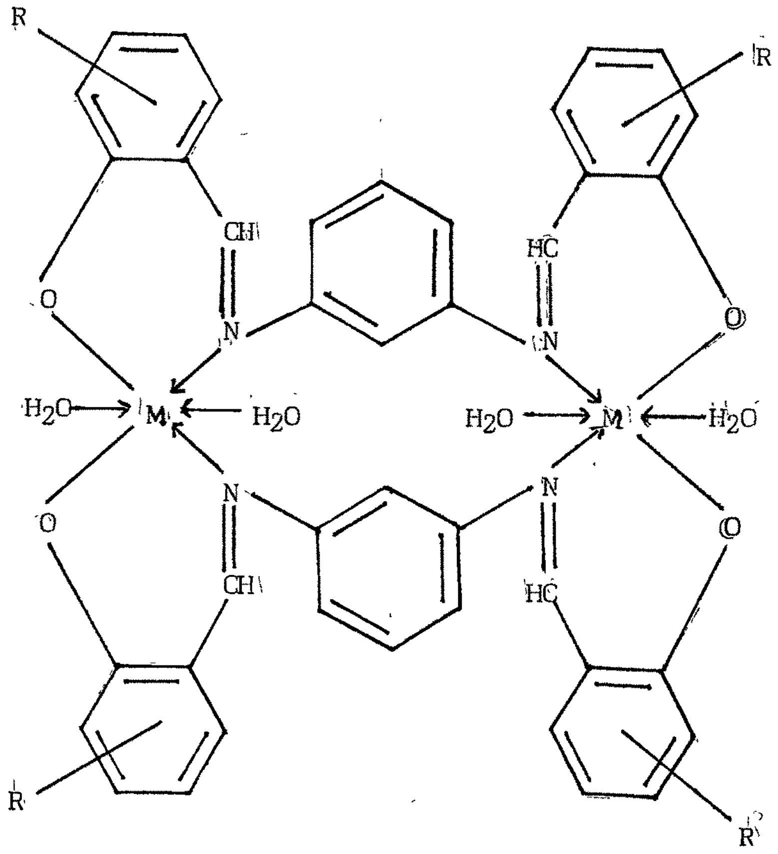
As the complexes are insoluble in most of the solvents it is not possible to carry out this study.

4.4 THE m-PHENYLENEDIAMINE GROUP :

In this group the four Schiff's bases prepared are : BHB-m-PD, BDB-m-PD, BHMB-m-PD and BHN-m-PD and their twelve metal complexes of Cu^{2+}, Ni^{2+} and Zn^{2+} have been synthesised.

The elemental analysis of metal complexes (Table (II.1), chapter II) corresponds to the expected formula $[M_2L_2.4H_2O]$. The isolated binuclear complexes can be represented by general structure as shown in figure. (IV.4) All the metal complexes in this group are insoluble in common organic solvents but soluble in hot DMF.

The I.R. spectra of the ligands show a strong band at the region 1595-1605cm^{-1} which is assigned to νC=N group[50]. The νC=N band of the ligand shifts to a lower frequency region and appears at 1575-1590cm^{-1} region which indicates coordination of the nitrogen atoms with the metal ions[50]. The band at 2800cm^{-1} in the free ligands due to ν-OH, which appears at lower frequency than expected is due to the involvement of the OH group in strong hydrogen bonding. This band disappears in metal chelates, indicating its coordination to the metal ion[15]. The broad band observed in the region 3300-3500cm^{-1} indicates the presence of coordinated water molecule[6], which is further confirmed by



R = H, -OH, OCH_3 or ph

M = Cu(II), Ni(II) or Zn(II)

Fig. (IV. 4)

the presence of a band at 800^{cm-1} due to rocking mode of water molecules[6]. The new bands observed in I.R. spectra of metal chelate at $\sim$400-420cm^{-1} region and $\sim$495-515cm^{-1} region are[51] due to νM-N and νM-O frequencies respectively.

The μ_{eff} values for Ni(II) complexes are in the range (2.88-2.97 B.M.) suggesting an octahedral configuration with $3A_{2g}$ ground term[53]. The absorption spectra of Ni(II) complexes (electronic spectra) exhibit three bands at $\sim$24300 $\sim$23800cm^{-1} , $\sim$15600-15300cm^{-1} and 11300-11200cm^{-1} which are attributed to

$3A_{2g}$ (F) $\longrightarrow$ $3T_{1g}$ (P) (ν_3)
$3A_{2g}$ (F) $\longrightarrow$ $3T_{1g}$ (F) and (ν_2)
$3A_{2g}$ (F) $\longrightarrow$ $3T_{2g}$ (F) (ν_1)

transitions respectively[35,53] which support the octahedral geometry of Nickel complexes. Also the ν_2/ν_1, ratio is 1.4 in the range required for octahedral geometry.

The μ_{eff} values for Cu(II) complexes are in the range (1..5-1.8 B.M) indicate distorted octahedral geometry of the complexes[54]. In electronic spectra a broad d-d band is observed around 13888 cm^{-1}. This approximates to the distorted octahedral configuration for Cu(II)[55,56]. The two bands occuring at 26666cm^{-1} and 32250cm^{-1} are assigned to the charge-transfer of the type L $\longrightarrow$ M. Another shoulder at 36363 cm^{-1} may be due to the $\pi \longrightarrow \pi^*$ transition[57].

Luminescence Study :

Similarly in this group the fluorescence measurements have been carried out at 250 nm excitation wavelength and showed emission at 500 nm. A variation in the intensity on the emission is observed depending on the specimens.

In case of ligands with methoxy group show higher fluorescence, this is due to higher π character and the peripheral effect of $-OCH_3$ and -OH substituents[46]. A quenching of intensity in case of 2-hydroxy-1-napthaldehyde is observed, which is due to the steric interaction responsible for the naphthalene moiety.

The fluorescence intensity observed in m-Phenylene diamine group is still smaller than that of p-Phenylene diamine, this is due to the reduced distance between two azomethine groups which leads to the greater hindrance.

On chelation the lowering of the emission is observed. In the Cu(II) complexes the lowering of intensity is because of the M $\longrightarrow$ L charge transfer. The lowest excited state being located on M - L unit[47]. The excited state being with lower π, π^* excited states, the quenching of intensity in Cu(II) complexes can be expected. This is in accordance with Weissman observation[48].

In case of Ni(II) complexes the intensity is observed to be higher than the Schiff's base ligands. This is due to the L $\longrightarrow$ M charge transfer and the stable nature of Ni(II) atom. The "d" orbitals which are capable of considerable interaction with ligand (π bonding) will introduce molecular character into the "d" orbitals, thereby the $\pi^* \longrightarrow d$ transition will result into the enhancement in intensity[21].

The mechanically deformed specimens show shifting of emission band position and increase in intensity. This is because discrete units are brought closer to one another made charge transfer easier. And the thermally treated specimens do not show any shift and show lowering of fluorescence intensity. This because of the thermal vibrations of the molecules may move the molecules slightly out of plane and thereby producing rarefaction.

Pigmentation study :

The studied compounds in this series show excellent light fastness and good rubbing fastness. The metal complexes showed better fastness compared to those of the ligands and this is due to fibres are capable of forming linkages with metal ions of the metal complexes[24]. Also it shows better fastness on silk fabrics compared to that of cotton, as NH_2 or $CONH_2$ groups of protein are better coordinating than cellulose of cotton fibres. Also due to the presence of $>C=N$ it may be forming a stronger and more stable constraint with silk fabrics which results in higher rubbing fastness of the complexes. Also the binuclear nature of the complexes shows it more stable because of presence of two metal ions in the structure which will have higher binding tendency with the fabrics.

Antibacterial study

The ligands and their metal chelates of this group were screened for their antibacterial activity against E.Coli bacteria by using DMF as solvent and agar broth medium for the growth of bacteria. It is observed from table (III.3) that the compounds of this group are more active against bacteria than those of hydrazone and thiocarbohydrozone groups.

Also similarly the presence of OCH_3 group in the ligand enhances the activity against E. Coli bacteria. This may be OCH_3 group could decrease the electron density of the overall ligand frame work thus facilitating its interaction with the amino acids of the micro-organism[41]. The complexes have shown better activity compared to those of the ligands. Chelation reduces considerably the polarity of the metal ion, because of partial sharing of its positive charge with the donor groups and possibly π-electrons delocalization over the whole chelate ring[25,26]. Such chelation increases the lipophilic character of the metal chelate which probably leads to break the permeability barrier of cells of the micro-organism[27-29].

The Ni(II) complexes showed better activity than those of Cu(II) & Zn(II) and this is in agreement with the reported results[27].

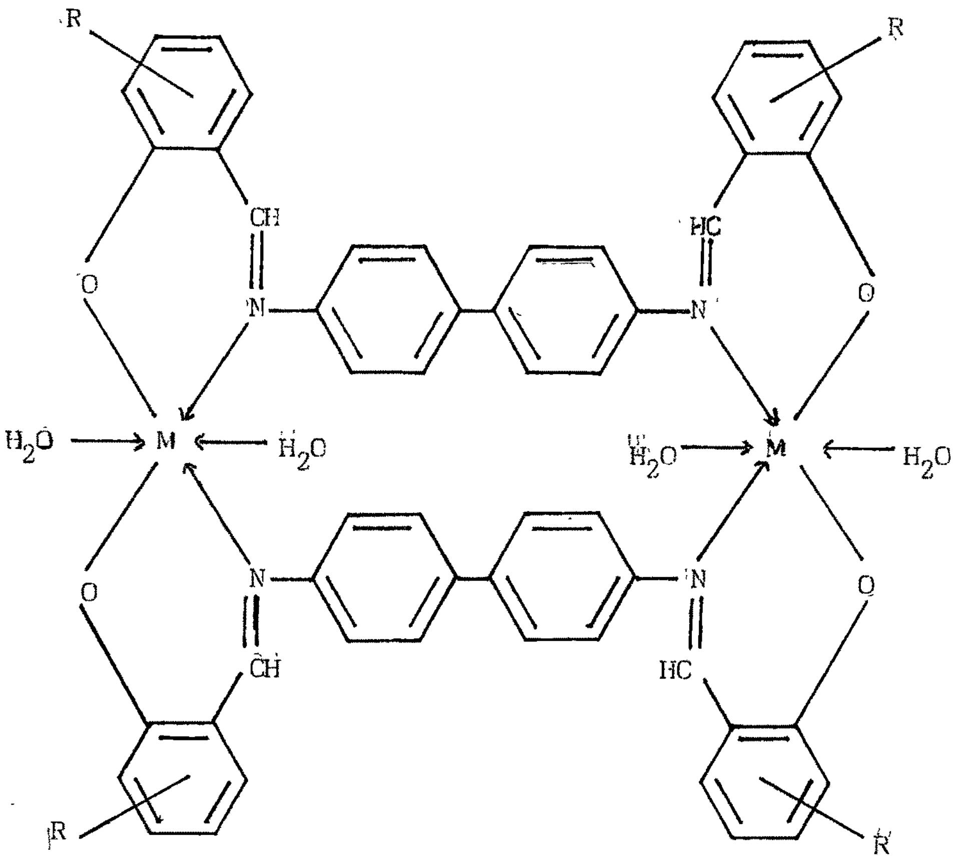
4.5 THE BENZIDINE GROUP :

The Schiff's base ligands synthesised in this group are : BHBB, BDBB, BHMBB & BHNB and twelve complexes of Cu^{2+}, Ni^{2+} and Zn^{2+} ions have been synthesised from them.

The elemental analysis of metal complexes (table (II.1), chapter II) shows a binuclear structure of the type $[M_2L_2.4H_2O]$ which can be represented as shown in figure (IV.5).

All the metal complexes of this group are found to be insoluble in common organic solvents and dissolve with difficulty on strong heating in DMF solvent.

The I.R. Spectrum of the ligands are characterised by a strong band at the region 1605-1610cm^{-1} which is attributed to C=N of azomethine group[1,27,42]. A down shift in the position of this band by 10-20cm^{-1} in the complexes suggests that nitrogen atom of azomethine group is involved in complexation[43,58]. The band at 3150 cm^{-1} in the spectrum of the ligand assigned to phenolic (OH) group have been disappeared in the sepctrum of the complexes indicates deprotonation of the -OH group and involvement in coordination[30]. A broad absorption band in the range 3300-3500cm^{-1} in the spectra of the complexes is due to -OH of coordinated water[59]. The medium to strong bands at 400-425cm^{-1} region and 490-515cm^{-1} region in the spectrum of complexes are assigned to νM-N & νM-O modes respectively[60].



R = H, -OH, OCH_3 or ph

M = Cu(II), Ni(II) or Zn(II)

Fig. (IV. 5)

The diffuse reflectance spectra (Table (II.3)) for some representative compounds shows three bands for Ni(II) complexes at 9220cm^{-1}, 14530cm^{-1} and 25340cm^{-1} assigned to

$3A_{2g} \longrightarrow 3T_{2g}$ (F) (ν_1)
$3A_{2g} \longrightarrow 3T_{1g}$ (F) (ν_2)
$3A_{2g} \longrightarrow 3T_{1g}$ (P) (ν_3)

indicating the high spin octahedral configuration. The ν_2/ν_1 for these complexes is 1.57 as required for octahedral geometry. The reflectance spectra of Cu(II) complexes showed a broad absorption at 17200^{cm-1} corresponding to

$$2B_{1g} \longrightarrow 2A_{1g}$$

transition characteristic of distorted octahedral geometry[61].

The magnetic moment data (table (II.1)) of the Cu(II) complexes (1.28-1.80 B.M) indicate distorted octahedral nature of the complexes[54]. However normally the range for the copper complexes is 1.5-2.6 B.M.[11], the abnormal values in the present complexes may be attributed due to the appreaciable magnetic interaction between the two copper ions presented in the reported binuclear complexes. Occurance of magnetic interaction in such cases may also be viewed through either the overlap of Cu-Cu orbitals or through either the ligand participation[13]. However, similar type of binuclear Cu(II) complexes have been reported earlier by other workers[14-16, 61-62].

The x-ray diffraction for some representative ligands and their chelates have been carried out. The diffraction patterns have been indexed by trial and error method[17-19] keeping in mind the characteristics of the various symmetry systems, till a good fit was obtained between the observed and the calculated $\mathrm{Sin}^2\theta$ values. All were found to fit well in tetragonal system. The calculated parameters (a & c, n, density (observed & calculated) and volume) for some representative compounds in this group is given in table (IV.1).

The fluorescence measurements have been carriedout at 250nm excitation wavelength and showed emission at ~ 500nm. Similarly the ligands of this group with methoxy group show higher flouroscence as shown by p-phenylenediamine and this is due to higher TT character of the peripheral effect of -OCH_3 and -OH substituents[46]. Similarly, quenching of intensity had been observed in case of 2-hydroxy-1-naphthaldehyde which is due to steric interaction of naphtalene moiety.

On chelation the shift of the emission band is observed. In Cu(II) complexes a lowering of intensity is observed as that of p-phenylenediamine and in case of Ni(II) complexes the intensity is observed to be higher similar to that of p-phenylenediamine.

The mechanically deformed specimens show shifting of emission band and increase in intensity. This is because discrete units are brought closer to each other and made charge transfer easier. The thermally treated specimens do not show any shift and show lowering of fluorescence intensity. This is because of the thermal vibrations of the molecules may move slightly out of plane and thereby producing rarefaction.

Pigmentation study

The studied compounds in this group show excellent light & rubbing fastness (table (III.1) chapter III). The metal chelates with Cu(II), Ni(II) and Zn(II) have shown better light and rubbing fastness than the free Schiff's base ligands. This is because the metal chelates are capable of establishing linkage with protein or cellulose molecules and stable metal dye fiber complex is formed[24].

Antibacterial study

Due to the difficulty in solubility of the compounds of this group, antibacterial test was not possible.

4.6 The Terephthaldehyde group :

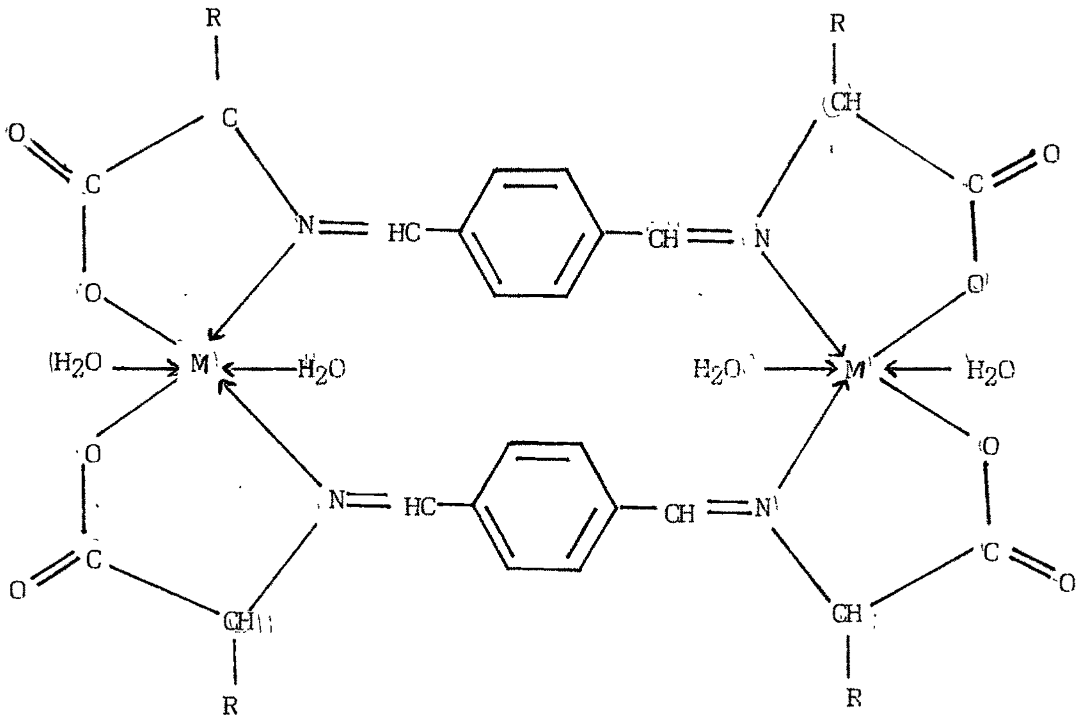
Three organic Schiff's bases are synthesised from Terephthaldehyde & Glycine, DL-Alanine and L-Histidine TBIG, TBIA & TBIH . Their nine complexes of Cu^{2+}, Ni^{2+} and Zn^{2+} have been isolated.

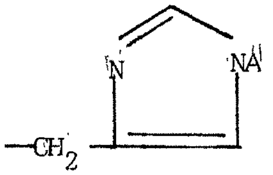
The isolated metal complexes are stable at room temperature. The analytical data (Table (II.1)) shows that the composition of the complexes is found to be [$M_2L_2.4H_2O$] a binuclear structure which can be represented as in figure (IV.6). All the complexes are insoluble in most of the solvents.

The I.R. Spectra of the free ligand exhibited a band at 1600cm-1 corresponding to νC=N frequency which is shifted to lower frequency by 10-15 cm^{-1} in case of complexes indicating the involvement of nitrogen of azomethine group in coordination[42,63]. The bands observed at $1450cm^{-1}$ corresponds to free carboxylate ion wich shows shifting in complexes to higher frequency region by 20-30cm-1 indicating coordination through carboxylic oxygen. Further the disappearance of the band observed at 2500 cm-1 which is due to νO-H of the carboxylic group in the free ligand confirms the involvement of carboxylic group on coordination[64-65]. Bands at 1310cm-1 and 1500 cm-1 corresponds to the ν_{sy} Coo-, ν_{asy} Coo- modes respectively. The difference (180) is greater than (144) indicating monodentate nature of carboxylic group of amino acids[66]. A broad band observed in the region 3000-3500 cm^{-1} corresponds to the presence of coordinated water molecule[6], which is further confirmed by a band at 825 cm^{-1}.

The bands observed in the far I.R. region 400-410 cm-1 & 500-525 cm^{-1} assigned to νM-N and νM-O respectively[60].

The diffuse reflectance spectra (Table (II.3) chapter (II)) for Ni(II) complexes shows three bands at 10200 cm^{-1}, $15150cm^{-1}$ 27800 which are assigned to



R = H , $-CH_3$ or or 

M = Cu(II), Ni(II) or Zn(II).

Fig. (IV. 6)

$3A_{2g}$ (F) $\longrightarrow$ $3T_{2g}$ (F) (ν_1)
$3A_{2g}$ (F) $\longrightarrow$ $3T_{1g}$ (F) (ν_2)
$3A_{2g}$ (F) $\longrightarrow$ $3T_{1g}$ (P) (ν_3)

Which suggests an octatedral geometry[67]. The ν_2/ν_1 ratio 1.50 falls in the range required for octahedral geometry. This has been supported by magnetic moment measurements (2.91-3.08 B.M.) for Ni(II) complexes, which also falls in normal ranges expected for magnetically dilute octahedral complexes[68].

In the case of diffuse reflectance spectra of Cu(II) complexes one broad band appears at ~19150-20200 cm-1 region assigned to $2B_{1g} \longrightarrow 2A_{1g}$ suggests an octahedral geometry. The Cu(II) compelxes exhibit magnetic moment in the range 1.85-1.96 B.M. which falls in the normal range (1.75-2.2 B.M.) expected for magnetically dilute Cu(II) complexes. Though the complexes are binuclear in character there is no involvement of antiferromagnetic exchange due to large frame work and long distance between two metal atoms[69].

The x-ray patterns have been indexed by trial and error method[17-19] keeping in mind the characteristics of the various symmetry systems, till a good fit was obtained between the observed and the calculated $\sin^2\theta$ values. The unit cell parameters were calculated for the ligand (TBIG) from the indexed data table (II.19). And the observed $\sin^2\theta$ values corresponds to tetragonal system to give a unit cell with a=18.675 A^{o}, c=23.539A^{o} and cell volume v=8209.5722 A^{o3}.

The observed value of the density 2.213 gm/cm^3 this gave n=9 i.e. nine molecules of the ligand present per unit cell. The calculated value of the density was equal to 2.131 gm/cm^3.

In case of Cu-TBIG we got only one peak at 2θ = 42.2 corresponds to d=2.140A^o as shown in figure (II.2). Similarly in case of Ni-TBIG we have two peaks, the maximum intensity was at 2θ=42.310 corresponds to d=2.134 as shown in figure (II.3). Also in case of Cu-TBIH we have got a broad peak which shows the amorphous nature of the complexes indicating polymeric nature.

Luminescence study

Luminescence study was carried out on Perkin-Elmer Luminescence spectrometer LS-50 using 200 nm as excitation wavelength. The emission peaks observed are almost same as those observed for earlier compounds having same peak positions around ~490 nm and ~530 nm but the intensities are found to be higher for complexes than ligands.

The intensities of DL-Alanine compounds are found to be lower than Glycine compounds this may be due to antieffects of the structure which might be quenching the MLCT process.

In case of Histidine compounds the intensities are very high this may be due to L ⟶ M charge transfer which is further promoted by heterocyclic π-character of Histidine molecules which may not be present in case of glycine or DL-Alanine compounds.

Pigmentation study :

The studied compounds in this series show excellent light fastness and good rubbing fastness compared to those of the ligands. This is due to metal complexes capability of forming linkages with fibres. The presence of $>C=N$ group may be forming stronger and more stable constraint with fabrics resulting in higher rubbing fastness of the complexes. The binuclear nature of the complexes is also responsible for higher fastness because the presence of two metal ions in the structure will have higher binding tendency with the fabrics.

Antibacterial study :

As the Schiff's base ligands and their metal chelates are insoluble in any solvent, it was not possible to carry out antibacterial test.

Sr. No.	Compound	a(A^{o})	c(A^{o})	V(A^{o})	n	density (gm/cm^{3}) observed/Calculated
1-	BHBH	17.3925	18.6752	5649.248	12	0.882/(0.8464)
2-	BHBH-Ni(II)	17.4370	16.6062	5049.135	6	1.312/(1.3317)
3-	BHBT	17.6650	19.8813	6204.011	11	0.960/(0.9243)
4-	BHBT-Cu(II)	16.4164	20.5791	5546.0301	5	1.223/(1.2318)
5-	BHMB-p-PD	17.2177	19.8813	5357.020	8	0.980/(0.9322)
6-	BHMB-p-PD-Cu(II)	16.4164	20.5791	5546.0716	4	1.340/(1.1339)
7-	BHMB-p-PD-Zn(II)	16.4164	21.0347	5668.8778	4	1.122/(1.1129)
8-	BHN-p-PD	16.0556	16.8027	4331.4636	7	1.135/(1.1162)
9-	BHN-p-PD-Cu(II)	17.2177	18.4065	5456.6069	4	1.256/(1.2499)
10-	BHBB	16.4164	16.70364	4501.6323	7	1.134/(1.01204)
11-	BHBB-Ni(II)	16.8027	18.1490	5124.0616	4	1.340/(1.2688)
12-	BHMBB	16.4164	19.0720	5139.8694	7	1.1008/(1.0220)
13-	BHMBB-Cu(II)	18.2507	19.7176	6567.7579	4	1.116/(1.1112)
14-	BHNB	18.9560	17.9021	6432.8283	8	1.162/(1.01587)
15-	BHNB-Cu(II)	17.8876	18.6341	5962.3349	4	1.302/(1.3132)
16-	TBIG	18.6750	23.5390	8209.5722	9	1.970/(2.131)

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