Fluorescence, Antibacterial and Pigmentation Studies of Some Binuclear Schiff Base Complexes

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Four Schiff bases derived from thiocarbohydrazide and salicylaldehyde, *o*-vanilline, 2,4-dihydroxybenzaldehyde or 2-hydroxy-1-naphthaldehyde have been synthesised and their twelve metal complexes of Cu(II), Ni(II) and Zn(II) have been isolated. The complexes are characterised by elemental analysis, electronic and IR spectral studies, magnetic measurements and X-ray diffraction studies. The complexes have been studied for their fluroscence, antibacterial and pigmentation properties. Complexes show lower fluorescence intensity compared to ligands. The ligands and their metal complexes show good antibacterial activities. The complexes are also found to be good pigments as they possess higher light and rubbing fastness. These properties have been explained on the basis of structural elucidation, charge transfer and intercomponent energy transfer.

INTRODUCTION

A number of Schiff base complexes are reported to be of great utility in pharmacological and biological aspects[1,2]. They are also reported to possess good luminescence and pigmentation properties[3-5]. In continuation of our studies[6,7] on binuclear Schiff base complexes and their fluoresence behaviour, we now report here synthesis and fluorescence, antibacterial and pigmentation studies of Cu(II), Ni(II) and Zn(II) metal chelates of Schiff's bases derived from thiocarbohydrazide with salicylaldehyde (BHBT), *o*-vanilline (BHMBT), 2,4-dihydroxybenzaldehyde (BDBT) or 2-hydroxy-1-naphthaldehyde (BHNT).

EXPERIMENTAL

All the chemicals used are of AnalaR grade. Thiocarbohydrazide was synthesised as reported method[8]. The ligands and complexes were prepared as reported in the literature[9].

The magnetic moment measurements were made using Gouy's balance at room temperature. IR spectra were recorded on Perkin-Elmer 577 grating spectrophotometer using KBr pellets. Electronic spectra were recorded on Hitachi U-2000 spectrophotometer. The X-ray diffraction was carried out using X-ray

diffractometer of Rigaka, Japan. The luminescence study was carried out on Perkin-Elmer luminescence spectrometer LS–50.

Pigmentation study was carried out on cotton, silk and polyester in an emulsion paste. The light fastness was carried out using colour Fade-o-meter type FDA-R. No. 8119 using carbon arc lamp. Rubbing fastness was carried out on Sasmira Crockmeter by using international test[10]. Antibacterial study was done by using cup-plate method[11] in DMF solvent against *Escherichia coli* (gram negative) as test organism using nutrient agar as medium.

RESULTS AND DISCUSSION

Four organic Schiff bases synthesised in this investigation (BHBT, BDBT, BHMBT and BHNT) and their twelve complexes of Cu(II), Ni(II), and Zn(II) metal ions have been isolated. The isolated metal complexes are stable at room temperature and insensitive to atmospheric moisture. They are insoluble in common organic solvents but soluble in DMF.

On the basis of elemental analysis (Table 1) the molecular formula of metal complexes may be [$M_2L_2 \cdot 4H_2O$], a binuclear structure, where M = Cu(II), Ni(II) and Zn(II) metal ions and L = Schiff base ligand. The structure can be represented in general as shown in Figure 1.
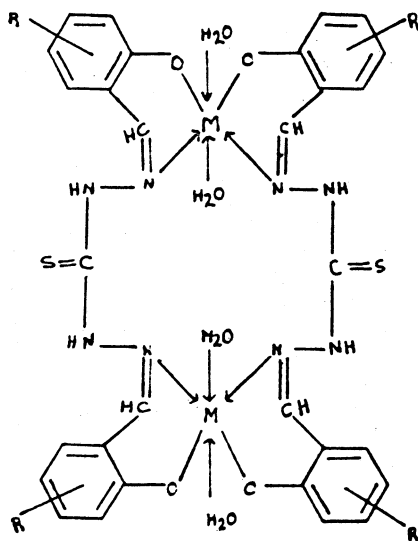

Fig. 1
R = H, –OH, OCH$_3$ or Ph
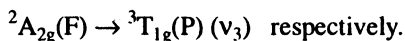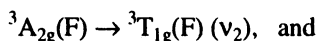M = Cu(II), Ni(II) or Zn(II)
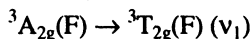
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TABLE-1

ANALYTICAL AND CHARACTERISATION DATA OF SCHIFF BASES
AND THEIR METAL(II) COMPLEXES

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S. No.	Compound (Molecular formula)	Colour	m.p. (°C)	Analysis % Found/(Calcd.)
				M	C	H	N	μ_{eff} (B.M.)
1.	BHBT ($C_{15}H_{14}N_4O_2S$)	White	203°C	—	57.00 (57.32)	4.54 (4.45)	18.12 (17.83)	—
2.	Cu(II)-BHBT ($Cu_2C_{30}H_{24}N_8O_4S_2 \cdot 4H_2O$)	Green	—	15.56 (15.43)	43.96 (43.74)	3.72 (3.88)	13.60 (13.60)	1.38
3.	Ni(II)-BHBT ($Ni_2C_{30}H_{24}N_8O_4S_2 \cdot 4H_2O$)	Yellowish brown	—	14.00 (14.43)	44.53 (44.25)	4.02 (3.93)	13.46 (13.76)	2.98
4.	Zn(II)-BHBT ($Zn_2C_{30}H_{24}N_8O_4S_2 \cdot 4H_2O$)	Yellowish orange	—	15.66 (15.81)	43.55 (43.54)	4.06 (3.87)	13.58 (13.54)	—
5.	BDBT ($C_{15}H_{14}N_4O_4S$)	Orange	—	—	51.47 (52.02)	4.24 (4.04)	16.16 (16.18)	—
6.	Cu(II)-BDBT ($Cu_2C_{30}H_{24}N_8O_8S_2 \cdot 4H_2O$)	Brown	—	14.64 (14.31)	40.55 (40.58)	3.33 (3.60)	12.66 (12.62)	1.68
7.	Ni(II)-BDBT ($Ni_2C_{30}H_{24}N_8O_8S_2 \cdot 4H_2O$)	Light green	—	13.55 (13.38)	41.24 (41.03)	3.92 (3.64)	12.22 (12.76)	2.96
8.	Zn(II)-BDBT ($Zn_2C_{30}H_{24}N_8O_8S_2 \cdot 4H_2O$)	Yellow	—	14.64 (14.67)	40.72 (40.41)	3.60 (3.59)	12.81 (12.57)	—
9.	BHMBT ($C_{17}H_{18}N_4O_4S$)	Light yellow	212°C	—	55.08 (54.54)	4.31 (4.81)	15.13 (14.97)	—
10.	Cu(II)-BHMBT ($Cu_2C_{34}H_{32}N_8O_8S_2 \cdot 4H_2O$)	Dark green	—	13.73 (13.46)	43.30 (43.26)	4.24 (4.24)	11.82 (11.87)	1.33
11.	Ni(II)-BHMBT ($Ni_2C_{34}H_{32}N_8O_8S_2 \cdot 4H_2O$)	Light brown	—	12.62 (12,57)	44.00 (43.71)	4.15 (4.28)	12.30 (11.99)	3.01
12.	Zn(II)-BHMBT ($Zn_2C_{34}H_{32}N_8O_8S_2 \cdot 4H_2O$)	Dark yellow	—	13.40 (13.80)	43.44 (43.09)	4.08 (4.22)	11.92 (11.83)	—
13.	BHNT ($C_{23}H_{18}N_4O_2S$)	Light orange	—	—	67.02 (66.66)	4.54 (4.34)	13.53 (13.52)	—
14.	Cu(II)-BHNT ($Cu_2C_{46}H_{32}N_8O_2S_2 \cdot 4H_2O$)	Dark green	—	12.65 (12.41)	54.14 (53.95)	3.90 (3.91)	11.21 (10.94)	1.72
15.	Ni(II)-BHNT ($Ni_2C_{46}H_{32}N_8O_2S_2 \cdot 4H_2O$)	Yellowish green	—	11.14 (11.58)	54.16 (54.47)	4.07 (3.94)	11.55 (11.05)	2.95
16.	Zn(II)-BHNT ($Zn_2C_{46}H_{32}N_8O_2S_2 \cdot 4H_2O$)	Deep Yellow	—	12.00 (12.73)	53.61 (53.76)	3.82 (3.89)	11.30 (10.90)	—

The IR spectra of the free ligands exhibit band at 1600 cm^{-1} corresponding to $\nu(C{=}N)$ frequency. This band is shifted to lower frequency and appears in the region 1590–1585 cm^{-1} in case of the metal complexes, which indicates the

involvement of nitrogen of azomethine group in coordination[12]. All the ligands and metal complexes exhibit a broad band of medium intensity around 3300 cm^{-1} which is due to NH frequency[13]. This band remains unaltered on complexation indicating non-involvement of the —NH group in coordination. The band due to hydrogen bonded[14] OH appearing at 2675–2630 cm^{-1} in the ligands disappears in the complexes. The high intensity band due to phenolic ν(C—O) around 1280 cm^{-1} appears at 1330–1300 cm^{-1} in the complexes supporting the involvement of —OH groups in the complex formation[15]. The band at 1100–1090 cm^{-1} in the ligands spectra which is due to ν(C=S) band[16] does not show any change in the IR spectra of complexes indicating that >C=S does not contribute in complex formation. The presence of coordinated water molecules in all these complexes is indicated by the appearence of a broad band at 3550–3400 cm^{-1} followed by a band at 850–840 cm^{-1} assignable to ν(–OH) streching and rocking modes respectively[17]. The conclusive evidence of bonding of the ligand to the metal ions is provided by the presence of non-ligand bands at 430–410 cm^{-1} ν(M—N) and 500–485 cm^{-1} ν(M—O)[18].

The electronic spectra of Ni(II) complexes in DMF showed bands at 10,950–10,900, 17,200–16,100 and 28,900–27,770 cm^{-1} due to

$$^3A_{2g}(F) \rightarrow {}^3T_{2g}(F) \; (\nu_1)$$

$$^3A_{2g}(F) \rightarrow {}^3T_{1g}(F) \; (\nu_2), \quad \text{and}$$

$$^2A_{2g}(F) \rightarrow {}^3T_{1g}(P) \; (\nu_3) \quad \text{respectively.}$$

which are consistent 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[19, 20] supported by μ_{eff} values of 3.28–3.40 B.M.

A broad band at 15,870–15625 cm^{-1} due to $^3T_{2g} \leftarrow {}^3E_g$ transition in the electronic spectra of Cu(II) complexes suggests distorted octahedral configuration[18] and supported by μ_{eff} values of 1.21–1.68 B.M. This abnormality of magetic moment values than what is expected[21, 22] (normally the range for the copper complexes in 1.5–2.6 B.M.) is due to binuclear nature of the complexes which may be because of either the overlap of Cu-Cu orbitals or through the ligand participation[23]. This is also compared with similar type of binuclear Cu(II) complexes reported earlier[24, 25] and found to be in agreement with reported work. Zn(II) complexes are diamagnetic in nature.

The X-ray diffraction pattern for representative compounds is shown in Tables 2 and 3. The unit cell parameters have been calculated by trial and error method[26]. 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 good agreement between the calculated and observed values of $\sin^2 \theta$. The observed values fit well in tetragonal system for ligands and their complexes. Also the calculated values of the density are in good agreement with the observations. The number of units per cell (n values) are found to be 11 and 5 for ligands and their complexes respectively.

TABLE-2
X-RAY DIFFRACTION DATA FOR BHBT

S. No.	2θ	$\sin^2\theta$ (obsd.)	$\sin^2\theta$ (calcd.)	(hkl)	d	I/I_0
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	0.0129	(626)	2.151	1

A = 0.0019, C = 0.015 a = 17.6650 Å, c = 19.8813 Å,
Density (observed/calculated) = 0.960/0.9243 gm/cm^3

TABLE-3
X-RAY DIFFRACTION DATA FOR BHBT-Cu(II)

S. No.	2θ	$\sin^2\theta$ (obsd.)	$\sin^2\theta$ (calcd.)	(hkl)	d	I/I_0
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, a = 16.416 Å, c = 20.5791 Å
Density (observed/calculated) = 1.223/1.2318 gm/cm^3

Luminescence Study

The luminescence study of the organic ligands and metal complexes shows good fluorescence property. The study was carried out using 200 nm 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 *ca* 490 nm and 530 nm are due to the presence of two >C=N groups under different geometrical environments. These observed peaks do not show any shift in case of fluorescence spectra of metal complexes (Fig. 2 and 3) but there is decrease in the intensities. The number of peaks are
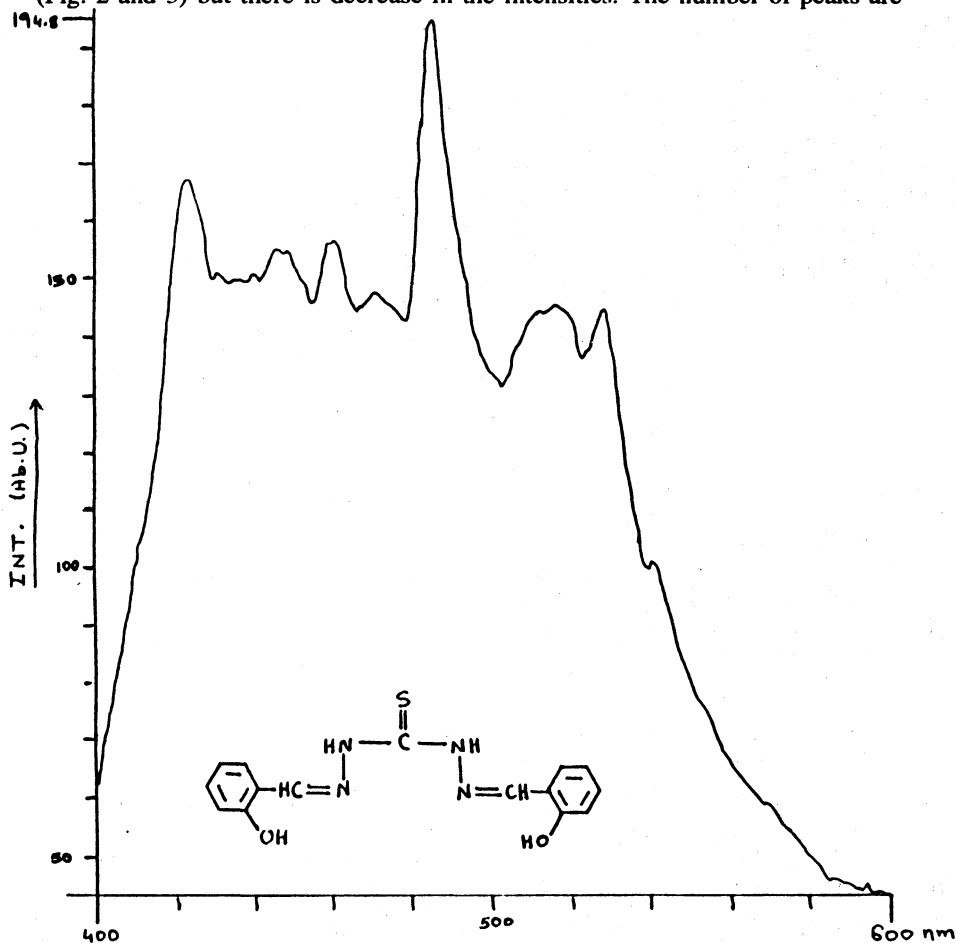

Fig. 2   Fluorescence Spectra of BHBT

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 environment.

The decrease in peak intensities in complexes may be due to CT as reported earlier[27]. The nature of the metal ion also has some influence on peak intensity
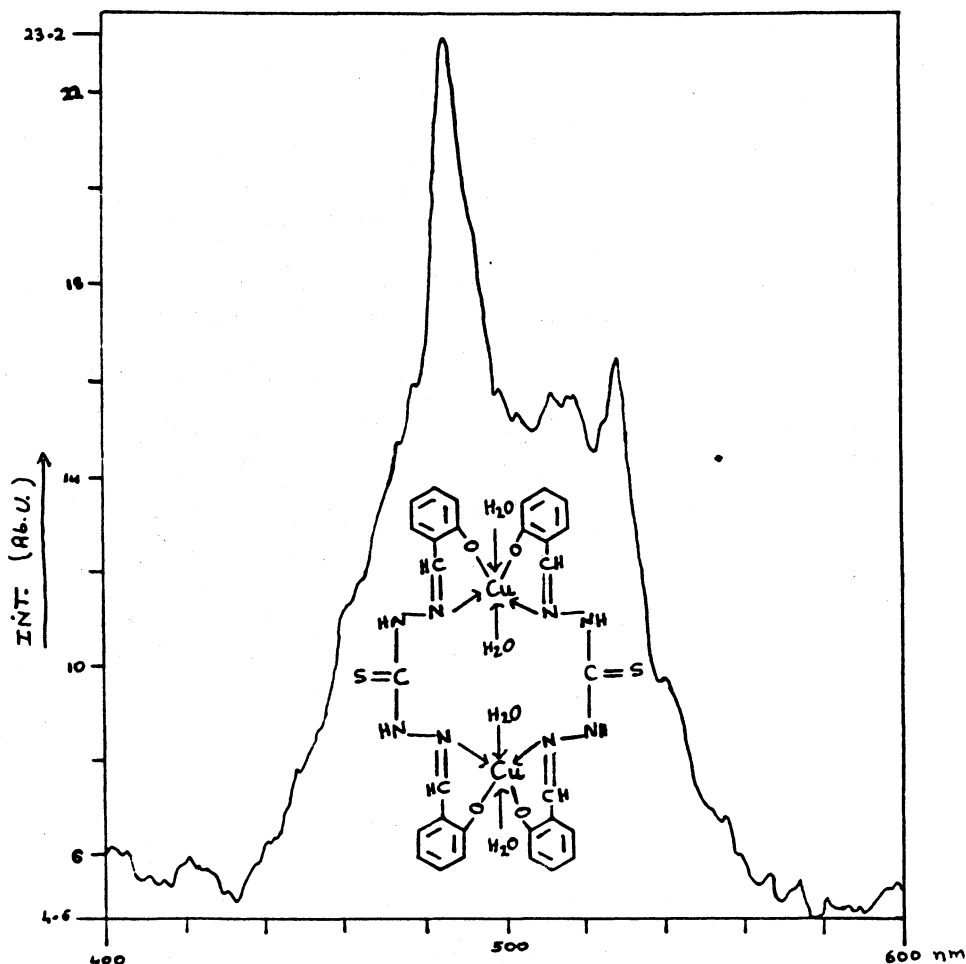
Fig. 3   Fluorescence Spectra of Cu-BHBT

as observed. Copper complexes show higher intensity by 0.1 ABU than nickel complexes. Substitution of —OCH$_3$ groups on the benzene ring shows some quenching of fluorescence intensity and this behaviour may be due to inter-component energy transfer as reported in the literature[6].

Pigmentation Study

The reported compounds show good light and rubbing fastness. The metal chelates have shown higher fastness than the free Schiff base ligands. This is because the metal chelates are capable of establishing linkages with protein or cellulose molecules of the fibres and a stable metal dye fibre complex is formed[28]. Also metal chelates show better fastness on silk fabrics compared to that of polyester and cotton, as —NH$_2$ or —CONH$_2$ groups of protein are better coordinating than ester and cellulose molecules. The binuclear nature of the complexes shows them more stable because of presence of two metal ions in the

structure which will have higher binding tendency with the fabrics. It is observed that the fastness is not related to the change in substituents, but related to their degree of aggregation within the fibre than the chemical structure. The order of the fastness measurements is:

$$\text{Silk} > \text{Polyester} > \text{Cotton}$$

Antibacterial Study

All the ligands and complexes were screened for their antibacterial activity against *E. coli* bacteria. It is observed that the ligands with —OCH_3 group show enhanced activity; this may be due to —OCH_3 group which decreases the electron density on the overall ligand framework, and facilitating interaction with the amino acids of the micro-organism[29]. It is also clear from the bacterial screening data that the metal complexes are more toxic in comparison to their parent ligands. 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. This can be explained on the basis of chelation theory[30]. As chelation reduces the polarity of the metal ion mainly because of partial sharing of its electrons and delocalisation over the whole chelate ring[30]. This decrease in polarizability of metal could enhance the lipophilicity of the complexes, which leads to break-down of permeability barrier of cell resulting in interference with normal cell process.[31, 32]

ACKNOWLEDGEMENTS

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