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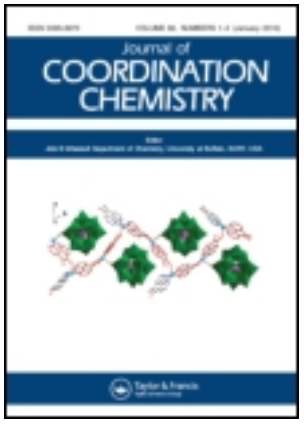

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Template synthesis and spectroscopic characterization of 16-membered [N_4] Schiff-base macrocyclic complexes of Co(II), Ni(II), Cu(II), and Zn(II): in vitro DNA-binding studies

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Template synthesis and spectroscopic characterization of 16-membered [N_4] Schiff-base macrocyclic complexes of Co(II), Ni(II), Cu(II), and Zn(II): *in vitro* DNA-binding studies

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Template condensation between o-phthalaldehyde and 3,4-diaminotoluene resulted in mononuclear 16-membered tetraimine macrocyclic complexes, [$MLCl_2$] [M = Co(II), Ni(II), Cu(II), and Zn(II)]. The proposed stoichiometry and the nature of the complexes have been deduced from elemental analyses, mass spectra, and molar conductance data. The macrocyclic framework has been inferred from ν(C=N) and ν(M–N) bands in the IR spectra and the resonances observed in ^{1}H and ^{13}C-NMR spectra. Octahedral geometry has been assigned for all these complexes on the basis of position of the bands in electronic spectra and magnetic moment data; distorted octahedral geometry has been assigned for the Cu(II) complex on the basis of EPR data. The low-conductivity data of all the complexes suggest their non-ionic nature. Interaction of these complexes with calf-thymus DNA (CT DNA) has been examined with fluorescence quenching experiments, which show that the complexes are avid binders of CT DNA.

Keywords: Macrocycles; Schiff bases; Spectral studies; Template synthesis

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1. Introduction

Coordination chemistry of macrocyclic ligands has found interest from their use as models for protein-metal binding sites for metalloproteins in biological systems, as synthetic ionophores, as models to study magnetic exchange phenomena, as therapeutic reagents in chelate therapy for the treatment of metal intoxication, as cyclic antibiotics that owe their antibiotic actions to specific metal complexation, to study the host–guest interactions, and in phase transfer catalysis [1, 2]. Macrocyclic Schiff bases are important in macrocyclic chemistry because they can selectively chelate certain metal ions depending on the number, type, and position of their donors, the ionic radii of the metal centers, and the coordinating property of counterions [3]. Complexes with azamacrocyclic ligands have been a focus, and *in situ* one pot template condensation lies at the heart of macrocyclic chemistry [4–7]. Transition metal macrocyclic complexes

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have biological activities, namely antiviral, anticarcinogenic [8], antifertile [9], antibacterial, antifungal [10], antioxidant [11], and many industrial applications [12]. Interest on synthesis of macrocyclic complexes with N_4 and N_2O_2 donors is rapidly growing for their unique structural properties and biological activities [13]. Synthetic tetraazamacrocycles [N_4] are considered to be good models for oxygen carriers due to the presence of four nitrogen donor sites in a ringed structure appropriate for metal ligand binding [14]. Studies have shown that macrocyclic complexes can interact with DNA and exhibit effective nuclease activities [15]. Binding studies of transition metal complexes have become very important in the development of DNA probes and chemotherapeutics [16]. In continuation of our ongoing interest on tetraazamacrocyclic complexes [17–19], in this article we report the synthesis, characterization, and DNA-binding of 16-membered tetraazamacrocyclic Schiff-base complexes of the type [$MLCl_2$] [M = Co(II), Ni(II), Cu(II), and Zn(II)] obtained by the template condensation between o-phthalaldehyde and 3, 4-diaminotoluene.

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2. Experimental

2.1. *Materials and methods*

The chemicals 3,4-diaminotoluene, o-phthalaldehyde, and ethidium bromide (EB, E. Merck) were used as received. Metal salts $MCl_2 \cdot 6H_2O$, M = Co(II) and Ni(II), $CuCl_2 \cdot 2H_2O$, and $ZnCl_2$ (all E. Merck) were commercially available pure samples. Methanol (AR) was used as solvent. Highly polymerized calf-thymus DNA (CT DNA) sodium salt (7% Na content) was purchased from Sigma. Other chemicals were of reagent grade and used without purification. CT DNA was dissolved in 0.5% w/w (12.5 mmol L^{-1} DNA/phosphate) in 0.1 mol L^{-1} sodium phosphate buffer (pH 7.40) at 310 K for 24 h with occasional stirring to ensure formation of homogeneous solution. The purity of the DNA solution was checked from the absorbance ratio $A260/A280$. Since the absorption ratio lies in the range $1.8 < A260/A280 < 1.9$, no further deproteinization of DNA was needed.

2.2. *Physical measurements*

Elemental analyses were obtained from the Micro-analytical Laboratory of Central Drug Research Institute (CDRI), Lucknow, India. The FT-IR spectra (4000–200 cm^{-1}) of the complexes were recorded as KBr/CsI discs on a Perkin-Elmer Spectrum RX-I spectrophotometer. ^1H and ^{13}C-NMR spectra were recorded in DMSO-d_6 using a Bruker Avance II 400 NMR spectrometer with Me_4Si as internal standard from SAIF, Punjab University, Chandigarh. Electrospray mass spectra were recorded on a micromass quattro II triple quadrupole mass spectrometer. Metals and chloride were estimated volumetrically and gravimetrically, respectively. Electronic spectra of the complexes in DMSO were recorded on a Cary 5E UV-VIS-NIR spectrophotometer at room temperature. EPR spectrum was recorded at liquid nitrogen temperature on an E-112 ESR spectrometer using TCNE as the g-marker. Magnetic susceptibility measurements were carried out using a Faraday balance at 25°C. Electrical conductivities (10^{-3} mol L^{-1} solutions in DMSO) were obtained on a Systronic type 302

conductivity bridge equilibrated at $25.00 \pm 0.1^{\circ}C$. Fluorescence measurements for the complexes were performed on a Shimadzu Spectrofluorimeter model RF-540 equipped with data recorder DR-3. A 1.00 cm quartz cell was used for measurements. For determination of binding parameters, ($30\,\mu mol\,L^{-1}$) solutions were taken in a quartz cell and increasing amounts of CT DNA was titrated. Fluorescence spectra were recorded at 310 K from 300 to 850 nm upon excitation at 308 nm for [$CoLCl_2$], 280–540 nm upon excitation at 290 nm for [$NiLCl_2$], 280–450 nm upon excitation at 280 nm for [$CuLCl_2$], and 320–820 nm upon excitation at 315 nm for [$ZnLCl_2$].

2.3. *Synthesis of the complexes*

2.3.1. Dichloro[3,4,7,8,11,12,15,16-tetrabenzo-1,6,9,14-tetraazacyclohexadecane-1,5,9,13-tetraene]metal(II), [$MLCl_2$]; [M = Co(II), Ni(II), Cu(II), and Zn(II)]. To a magnetically stirred methanolic solution (~20 mL) of metal salt (0.01 mol), methanolic solutions (~25 mL) of both 3,4-diaminotoluene (0.02 mol, 2.44 g) and o-phthalaldehyde (0.02 mol, 2.68 g) were added simultaneously with constant stirring. The reaction mixture was stirred for 12 h and then allowed to stand at room temperature, resulting in isolation of microcrystalline solid product in a few days. The product was washed with methanol and dried in vacuum.

2.4. *Fluorescence studies of EB bound to DNA in the presence of metal complexes*

Experiment was carried out at pH 7.0 in buffer containing $50\,mmol\,L^{-1}$ NaCl and $5\,mmol\,L^{-1}$ Tris-HCl. DNA and EB were dissolved in buffer at 3 and $1\,\mu g\,mL^{-1}$, respectively. The concentrations of the tested complex were $50\,\mu mol\,L^{-1}$. EB displays very weak fluorescence in aqueous solution. However, in the presence of DNA, it exhibits intense fluorescence because of the intercalation to base pairs in DNA. Complexes were added to EB bound with CT DNA and the intensity of fluorescence of EB was measured. Fluorescence spectra were recorded using excitation wavelength of 478 nm and the emission range set between 485 and 685 nm. Before examining the fluorescent properties of EB, we checked that the tested compounds did not quench the EB fluorescence.

2.5. *Binding data analysis of the complexes*

To elaborate the fluorescence quenching mechanism the Stern–Volmer equation was used for data analysis [20]

$$F_0/F = 1 + K_{SV}[Q],$$

where F_0 and F are the steady-state fluorescence intensities in the absence and presence of quencher (DNA), respectively, K_{SV} the Stern–Volmer quenching constant, and [Q] is the concentration of the quencher (DNA). The plot of F_0/F *versus* [Q] exhibited a good linear relationship (figure 1). The linearity of the Stern–Volmer plots for DNA bound complexes indicated that the interaction was purely static. The K_{SV} value of [$CoCl_2$], [$NiCl_2$], [$CuCl_2$], and [$ZnCl_2$] were calculated to be 7×10^2, 7.3×10^3, 1.07×10^4, and

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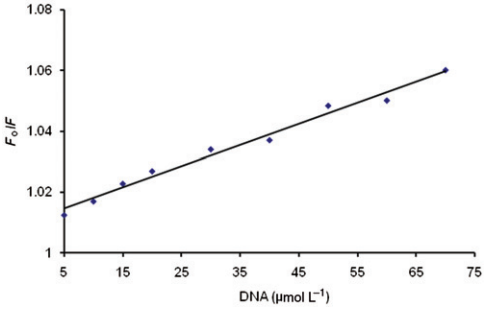

Figure 1. The Stern–Volmer plot for the binding of Co(II) complex with CT DNA.

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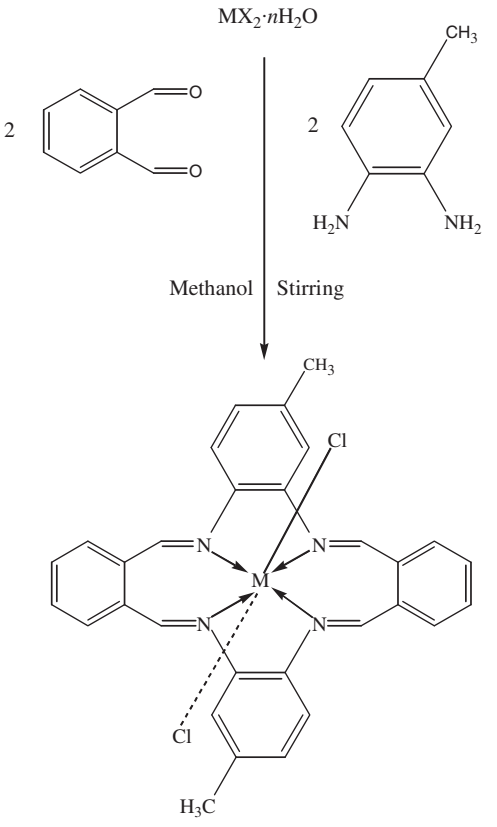
1.5×10^2 $(\text{mol L}^{-1})^{-1}$, respectively. The K_{SV} value for the complexes suggests that these macrocyclic complexes exhibit different affinities toward DNA, with the highest binding affinity for Cu(II) complex and lowest for Zn(II) complex.

3. Results and discussion

A series of 16-membered Schiff-base tetraazamacrocyclic complexes have been synthesized by [2 + 2] metal template condensation of 3,4-diaminotoluene and o-phthalaldehyde in methanol (scheme 1). The purity of the complexes was checked by running TLC on silica gel coated plates using benzene (85%) and methanol (15%) as eluent. All the complexes were microcrystalline, stable at room temperature, and soluble in most polar solvents. The formation of the Schiff-base macrocyclic complexes was confirmed by elemental analysis, molecular ion peak in the mass spectra (table 1), and characteristic bands in the FT-IR and resonance signals in the ^{1}H and ^{13}C-NMR spectra. The overall geometry of the complexes was inferred from the observed values of magnetic moments and the position of the bands in the electronic spectra. The molar conductance measurements of all the complexes recorded in DMSO exhibited their non-electrolytic nature. However, all efforts failed to grow single crystal suitable for X-ray crystallography. The DNA-binding studies suggest that these macrocyclic complexes have good binding affinity toward DNA.

3.1. *IR spectra*

Preliminary identification regarding formation of the macrocyclic complexes was obtained from IR spectral findings (table 2). The absence of bands characteristic of the amino group, υ(–NH_2) of free 3,4-diaminotoluene and carbonyl group υ(C=O) of o-phthalaldehyde suggest that complete condensation takes place. A strong intensity band at 1624–1684 cm^{-1}, characteristic of azomethine group υ(C=N), provides strong evidence for the formation of the macrocyclic framework (figure S1, Supplementary material) [21, 22], which is further confirmed by the appearance of a medium intensity band at 480–500 cm^{-1} assignable to υ(M–N) [23]. Bands at 1445–1448, 1015–1196, and 725–772 cm^{-1} were assigned to aromatic ring vibrations. A weak absorption at



M = [Co(II), Ni(II) $n = 6$, Cu(II) $n = 2$, Zn(II)]

Scheme 1. Synthesis and proposed structure of tetraazamacrocyclic complexes.

2920–2923 cm^{-1} may be assigned [19] to $–CH_3$ stretch. Bands at 250–290 cm^{-1} may be assigned to υ(M–Cl) [24].

3.2. *^{1}H and ^{13}C NMR spectra*

Strong evidence for the formation of the Schiff-base macrocyclic complexes comes from ^{1}H-NMR spectrum of the Zn(II) complex which shows a sharp signal at 8.46 ppm corresponding to azomethine protons (s, –CH=N; 4H) [25], indicating condensation between primary amine and carbonyl group of 3,4-diaminotoluene and o-phthalaldehyde, respectively (figure S2, Supplementary material). The multiplets at 7.0–7.9 ppm (m, Ar–H) may reasonably be assigned to aromatic protons of macrocyclic Zn(II) complex. A sharp signal at 2.4 ppm may be assigned to methyl protons [26].

The macrocyclic framework is further confirmed by ^{13}C-NMR spectrum of Zn(II) complex which exhibits appropriate number of resonances (figure S3, Supplementary material). A sharp signal at 157 ppm may be assigned to azomethine carbon [27], while

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Table 1. Elemental analyses, m/z value, color, yield, molar conductance, and melting point of the complexes.

Complex	m/z found (Calcd)	Color	Yield (%)	Found (Calcd) (%)					Λ_m ($\Omega^{-1}\,cm^2\,mol^{-1}$)
				M	Cl	C	H	N	
$C_{30}H_{24}N_4CoCl_2[CoLCl_2]$	571.23 (570.36)	Black	52	10.75 (10.32)	12.12 (12.43)	63.58 (63.17)	4.95 (4.23)	9.93 (9.82)	14
$C_{30}H_{24}N_4NiCl_2[NiLCl_2]$	571.78 (570.12)	Dark brown	65	10.59 (10.29)	12.83 (12.43)	63.75 (63.20)	4.68 (4.24)	9.61 (9.82)	30
$C_{30}H_{24}N_4CuCl_2[CuLCl_2]$	575.95 (574.05)	Black	61	11.51 (11.05)	12.69 (12.33)	62.89 (62.67)	4.76 (4.20)	9.89 (9.74)	33
$C_{30}H_{24}N_4ZnCl_2[ZnLCl_2]$	577.81 (576.10)	Grey	57	11.12 (11.33)	12.06 (12.29)	62.08 (62.41)	4.50 (4.19)	9.33 (9.71)	21

Table 2. IR spectral data (cm^{-1}) of complexes.

Compound	ν(C=N)	ν(C–H)	ν(M–N)	ν(M–Cl)	Phenyl ring vibrations
$[CoLCl_2]$	1684	2920	485	250	1448, 1083, 772
$[NiLCl_2]$	1626	2920	492	261	1445, 1056, 725
$[CuLCl_2]$	1682	2923	500	290	1446, 1077, 769
$[ZnLCl_2]$	1624	2920	480	274	1448, 1015, 729

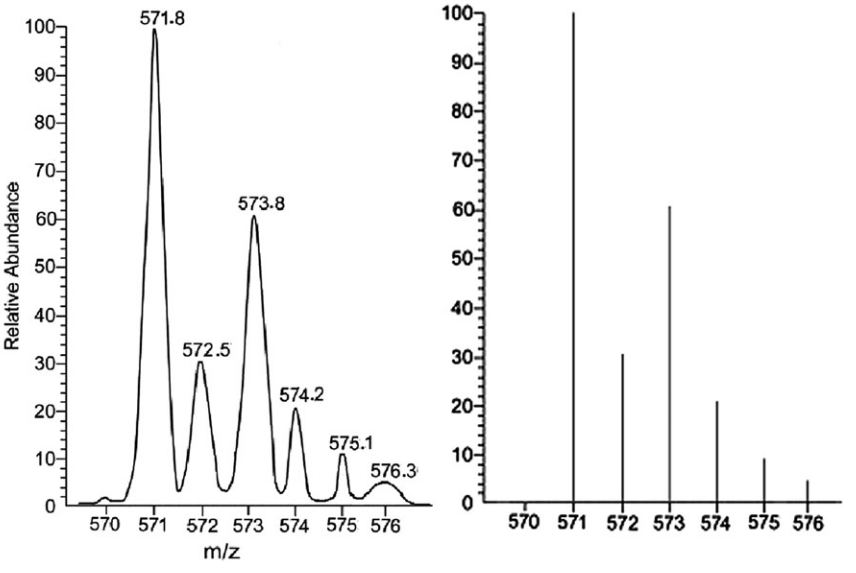

Figure 2. Observed and calculated isotopic mass distribution of molecular ion $[C_{30}H_{24}N_4CoCl_2 + H^+]^+$ at $m/z = 571$ in the ESI mass spectrum of Co(II) complex.

the signals for aromatic carbons appeared at 118–143 ppm [28]. The signal corresponding to methyl carbon appears at 21 ppm [29].

3.3. *Mass and EPR spectral studies*

Mass spectra of all macrocyclic complexes exhibited molecular ion peak $[M + H]^+$, m/z at 571, 571, 575, and 577 a.m.u corresponding to their molecular formulae $[Co(C_{30}H_{24}N_4)Cl_2]$, $[Ni(C_{30}H_{24}N_4)Cl_2]$, $[Cu(C_{30}H_{24}N_4)Cl_2]$, and $[Zn(C_{30}H_{24}N_4)Cl_2]$, respectively (table 1). The mass spectrum of macrocyclic Co(II) complex shows a molecular ion peak at m/z 571, which corresponds to $[C_{30}H_{24}N_4CoCl_2 + H^+]^+$ as the calculated m/z being 570. The theoretical and experimental isotope distributions of the molecular ion peak is shown in figure 2, revealing good agreement between observed and calculated data. The series of peaks at m/z 476, 432, 339, 285, 267, 221, and 135 a.m.u correspond to various fragments (figure S4, Supplementary material).

The EPR spectrum of polycrystalline solid Cu(II) complex was recorded at liquid nitrogen temperature. The spectrum shows single broad signal (figure S5, Supplementary material), giving $g_{\parallel} = 2.16$ and $g_{\perp} = 2.05$. The trend $g_{\parallel} > g_{\perp} > 2.0023$

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Table 3. Magnetic moment values, electronic spectral bands with their assignments.

Complex	μ_{eff} (B.M.)	Band position (cm^{-1})	Assignment
$[CoLCl_2]$	4.7	8333	$^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$
		15,384	$^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$
		20,833	$^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$
$[NiLCl_2]$	3.1	9756	$^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$
		16,129	$^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$
		27,027	$^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$
$[CuLCl_2]$	1.9	19,100	$^2B_{1g} \rightarrow {}^2E_g$
		16,300	$^2B_{1g} \rightarrow {}^2B_{2g}$

(g_e), observed for the complex, indicates that the unpaired electron is localized in $d_{x^2-y^2}$ orbital of Cu(II). These observations are characteristic of axially distorted octahedral geometry [30].

According to Hathway if $G > 4$, the exchange interaction between metal centers in polycrystalline solid has been calculated. According to Hathaway if $G > 4$ the exchange interaction is negligible and if $G < 4$ considerable exchange interaction occurs in the solid complex [31]. In Cu(II) complex, the G value is less than 4 (table 3), which indicates considerable exchange interaction between Cu(II) centers.

3.4. *Electronic spectra*

The electronic spectrum of the cobalt(II) complex exhibits three bands at 8333, 15,384, and 20,833 cm^{-1} attributed to $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$, $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$, and $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ transitions, respectively consistent with octahedral geometry around Co(II). The observed magnetic moment of 4.7 B.M. further complements the electronic spectral findings [32].

The proposed octahedral geometry around Ni(II) was confirmed by absorption bands appearing at 9756, 16,129, and 27,027 cm^{-1}, which may be attributed to $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$, $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$, and $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ transitions, respectively [33]. The observed magnetic moment value of 3.1 B.M. further corroborated the electronic spectral findings.

The electronic spectrum of Cu(II) complex showed a broad band at 19,100 cm^{-1} with a shoulder band at 16,300 cm^{-1}, assigned to $^2B_{1g} \rightarrow {}^2E_g$ and $^2B_{1g} \rightarrow {}^2B_{2g}$ transitions, respectively [32], corresponding to distorted octahedral geometry which was further confirmed by its magnetic moment value of 1.9 B.M.

3.5. *Fluorescence measurements*

3.5.1. DNA-binding of the complexes. Fluorescence quenching is a useful method to study the reactivity of chemical and biological systems since it allows non-intrusive measurements of substances in low concentration under physiological conditions [34, 35], revealing information about binding mechanisms and providing clues to the nature of binding. Fluorescence intensity of a compound can be quenched as a result of molecular interactions, such as excited state reactions, molecular rearrangements,

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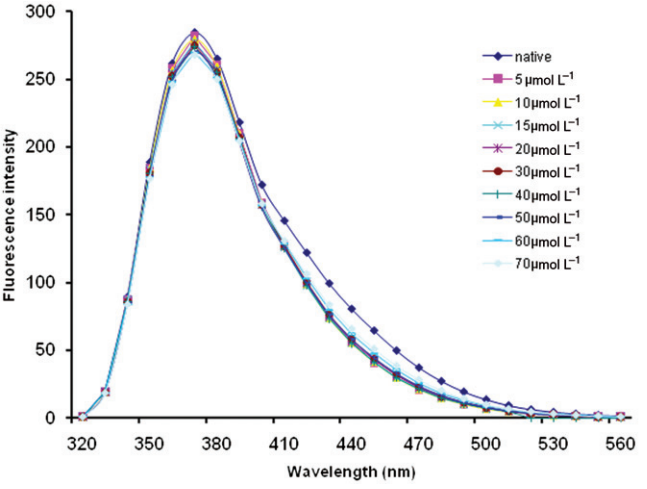

Figure 3. Fluorescence emission spectrum of Co(II) complex in the presence of increasing amount of CT DNA.

energy transfer, ground state complex formation, and collisional quenching. Fluorescence provides insight to changes taking place in the microenvironment of DNA on binding to complexes. The binding of these complexes with CT DNA was studied by monitoring changes in the intrinsic fluorescence of these compounds at varying DNA concentrations.

Quenching of fluorescence clearly indicates that binding of DNA to macrocyclic complexes changed the microenvironment of the fluorophore residue. The spectra illustrate that excess of DNA led to more effective quenching of fluorescence (figure 3 and figures S6–S8, Supplementary material). There are three major modes of DNA interaction relevant to the metal complexes depending on the presence of charged atoms, hydrophobicity, and structure of these complexes. As external binders complexes with positive charges interact with the DNA backbone due to electrostatic interaction with negatively charged phosphates. Groove binders interact with the DNA groove and hydrophobic interactions are usually important components of this binding process. Such a mode of interaction is also governed by geometric and steric factors, such as non-planar structures and the presence of methyl groups that prevent intercalation. The third mode involves insertion of a planar fused aromatic ring system between DNA base pairs leading to intercalation [36–38]. Few studies on tetra-azamacrocyclic complexes have proposed intercalation as a possible mode of DNA interaction [39, 40]. In order to examine the possible mode of interaction of the present complexes with DNA, we performed EB displacement assay. EB, a polycyclic aromatic dye, is the most widely used fluorescence probe for DNA structure, binding to DNA by intercalation within the stacked bases [41]. Enhanced fluorescence of the EB–DNA complex can be quenched at least partially by the addition of a competing molecule and this could be used to assess the relative affinity of the molecule for DNA intercalation [42]. The emission spectra of EB bound to DNA in the absence and presence of complexes is given in figure 4. The addition of these molecules to DNA complexed with EB does not cause reduction in emission intensity, indicating that none of these complexes compete with EB in binding to DNA. External interaction with DNA

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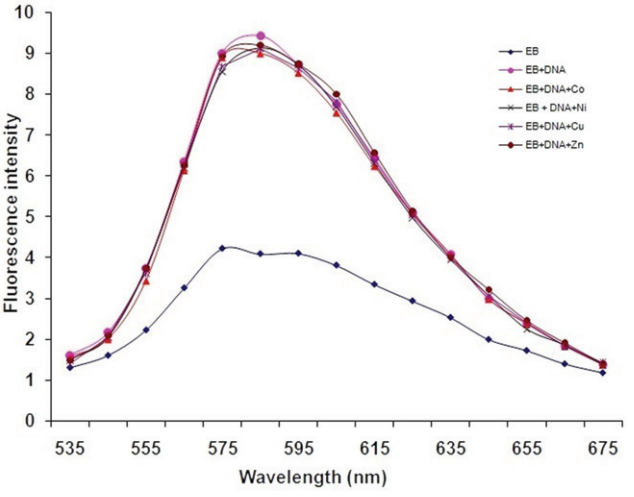

Figure 4. Fluorescence emission spectra of EB bound to DNA in the absence and presence of the Co(II), Ni(II), Cu(II), and Zn(II) complexes.

backbone was also ruled out as these complexes are non-cationic, lacking in an electrophilic center. These aromatic complexes with methyl groups possibly interact with DNA within the grooves *via* stabilization through hydrophobic cohesion. This is presumably explained due to octahedral geometry and steric hindrance encountered by methyl groups, thus preventing DNA-base intercalation of these complexes.

4. Conclusion

A series of 16-membered Schiff-base tetraazamacrocyclic complexes of Co(II), Ni(II), Cu(II), and Zn(II) have been synthesized and characterized by various spectroscopic techniques. The synthesized Schiff bases are tetradentate through coordination of azomethine. Octahedral geometry has been assigned to all the complexes. The stoichiometry and the nature of the complexes have been deduced from elemental analyses and conductance data. Formation of macrocyclic framework has been inferred from appearance of imine υ(C=N) and υ(M–N) in IR spectra and resonance signals observed in ^{1}H and ^{13}C-NMR spectra. The geometry of the complexes has been assigned on the basis of positions of bands in electronic spectra and magnetic moment data. Interaction of these complexes with CT DNA has been examined with fluorescence studies, which show that the complexes bind CT DNA in the order Cu(II) > Ni(II) > Co(II) > Zn(II).

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