

Syntheses, Characterization and Spectroscopic Studies on Schiff base Complexes of Diaminomaleonitrile

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Abstract: Three new Schiff base complexes viz, [Co(II)(bchbam)(H₂O)] (1), [Ni(II)(bchbam)] (2) and [Cu(II)(bchbam)](H₂O) (3), where bchbam = 2,3-bis(5-chloro-2-hydroxybenzylideneamino)maleonitrile, have been synthesized and characterized. The X-ray powder diffraction result shows the free ligand and complexes (1), (3) have monoclinic crystal system whereas the complex (2) was found to be triclinic in nature. Spectroscopic and analytical results suggest the tentative molecular structure of the complexes to be square planar and square pyramidal geometry where the ligand behaves as tetradentate N, O-donor ligand. A DNA binding study suggests the free ligand and its complexes were avid binders to Calf Thymus DNA (CT-DNA).

Keywords: Diaminomaleonitrile, Schiff base, powder XRD, DNA binding, spectroscopic studies.

1. Introduction

Diaminomaleonitrile (DMN) is a tetramer of HCN, has the ability to act as diamine [1], the presence of nitrile (C≡N) group in the structure of the DMN significantly affects the coordination behaviour of the DMN itself and has potentially modulate the electronic properties of the resulting coordination complexes and their chemical reactivity [2]. Schiff bases were widely studied in coordination chemistry due to their good chelating properties, stability and their ability to form complexes with a large variety of metal ions [3]. Synthesis of Schiff bases and its complexes derived from diaminomaleonitrile have gained recent interests as they have different applications in various areas [4]. They were found applicable as dye materials in colour chromatography, fluorescent light emitting devices [5], in pharmacological studies [6] and in the chemical libraries for DNA binding compounds [7], etc. Spectroscopic and DNA binding studies were presented in this paper.

2. Experimental Section

All the chemicals were of analytical reagent grade and used as received without further purifications. CT-DNA and tris-HCl were of biological grade. 5 mM – HCl/ 50 mM NaCl (pH = 7.1) buffer was used to study DNA interaction at room temperature. Elemental analyses were carried out in Perkin Elmer 2400 Series II CHN analyzer. Infrared spectra were recorded in Shimadzu FTIR-8400 spectrometer in solid using KBr discs. Electronic spectra were recorded in Perkin-Elmer Lamda 35 UV/VIS Spectrometer. The magnetic susceptibility measurements were carried out with a Sheerwood Magnetic Susceptibility Balance (MSB) at room temperature and diamagnetic corrections were made using Pascal's constants. Thermal analyses were carried out on a Perkin Elmer STA 6000 Thermal Analyzer at 10°C min⁻¹

within the temperature range of 25-900°C under nitrogen atmosphere. The powder XRD patterns were recorded in PAN-analytical diffractometer with CuK α radiation of wavelength 1.54060 Å operating at a voltage of 40 kV and a current of 20 mA. The scanning rate was maintained at 1.6° mm⁻¹ over 2 θ range of 5-50° employing the reflection mode for scanning. The crystal lattice parameters were determined using a set of programs, called P-Index, which was based on least squares approach. Molar conductivity measurements were carried out on a CYBER SCAN CON 510 conductometer at room temperature (25±0.1°C). Fluorescence spectra were recorded in a Perkin Elmer Fluorescence spectrometer. Cyclic voltammetry data were recorded on a CH602C electrochemical analyzer. The reaction scheme for the synthesis of the free ligand and its complexes was summarized in Figure 1.

2.1 Synthesis of the Schiff base ligand, bchbam (2,3-bis(5-chloro-2-hydroxybenzylideneamino)maleonitrile)

Diaminomaleonitrile (107 mg, 1 mmol) was dissolved in 10 ml of hot ethanol and to it 5-chlorosalicylaldehyde (313 mg, 2 mmol) in 10 ml ethanol was added and heated for about 12 hours in presence of 2-3 drops of conc. H₂SO₄ till the colour of the solution changed to golden yellow. On cooling, yellow coloured crystalline solid obtained was filtered, washed with ethanol and made air dried.

Yield: \approx 300 mg (80 % approx.). Anal. Calc. for C₁₈H₁₀N₄O₂Cl₂ (Mr. 385 g mol⁻¹): C, 56.12; H, 2.62; N, 14.55. Found: C, 56.67; H, 2.81; N, 14.78. M. Pt. decomposes > 210°C. FT-IR bands (ν in cm⁻¹): 3406, 3303, 3201, 2248, 2210, 1633, 1602, 1556, 1479, 1390, 1278, 1163, 1093, 964, 923, 871, 821, 767, 659, 543, 503, and 393. ¹H-NMR (DMSO, D₆ ppm): s, HC=N, 8.51; m, Ar-H, 6.94-8.21; s, -OH, 10.71.

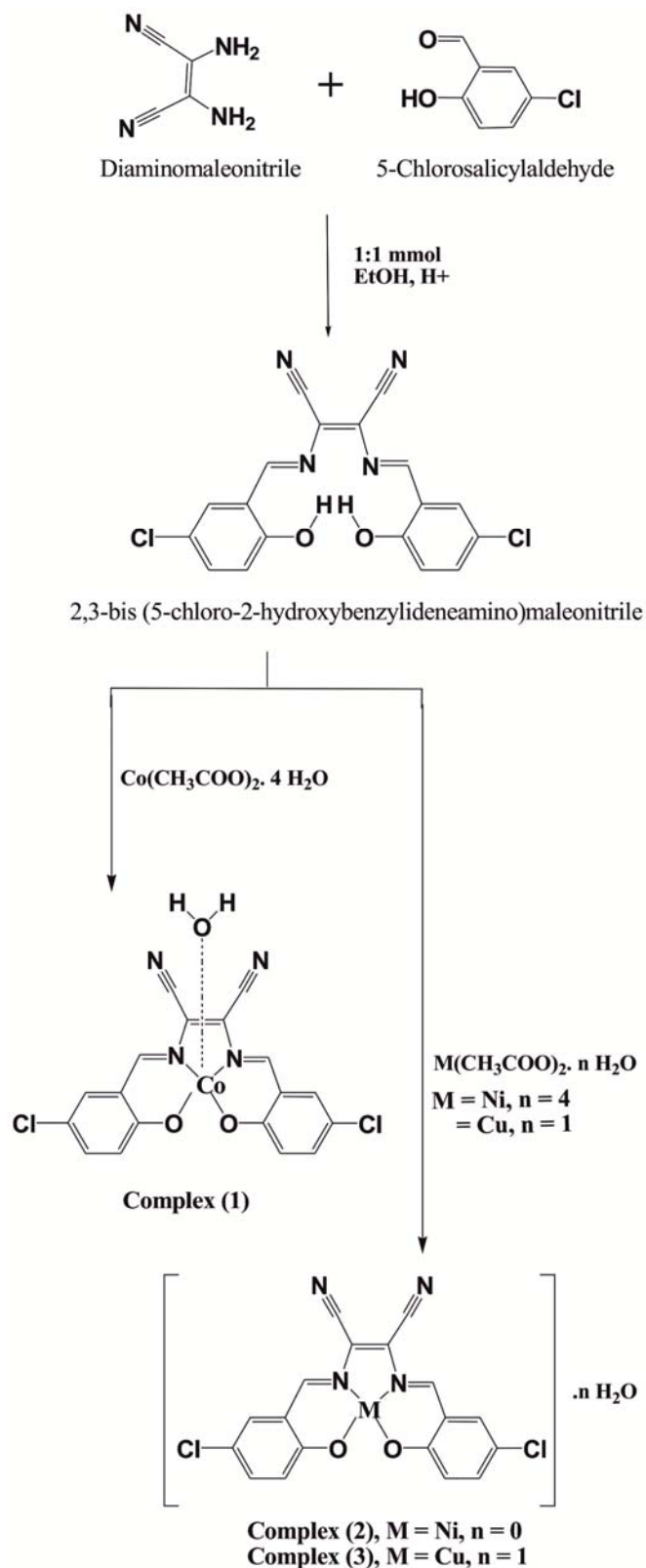


Figure 1. Reaction scheme for the synthesis of the Schiff base ligand and its complexes

2.2 Synthesis of the complexes

The prepared ligand (385 mg, 1 mmol) was solubilized in 10 ml of hot ethanol and to it 10 ml ethanolic solution of $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ (242 mg, 1 mmol) was added in 1:1 proportion. The content was then heated to reflux for several hours till complex precipitate was obtained. The final

product of the reaction was washed with mother liquor and air dried.

The complexes (2) and (3) were prepared by following the similar procedure as above. For the preparation of complex (2), $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ (240 mg, 1 mmol) and complex (3), $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ (197 mg, 1 mmol) were added in 1:1 proportion.

2.2.1 [Co(bchbam)(H₂O)] complex (1)

Rose red. Yield: 368 mg ($\approx 65\%$). Anal. Calc. for $\text{C}_{18}\text{H}_{10}\text{N}_4\text{O}_3\text{Cl}_2\text{Co}$ (Mr. 459.9 g mol^{-1}): C, 47.07; H, 2.18; N, 12.20. Found: C, 47.17; H, 2.54; N, 12.29. IR bands (ν in cm^{-1}): 3406, 3303, 2248, 2210, 1631, 1602, 1556, 1479, 1431, 1390, 1361, 1203, 1163, 1093, 964, 923, 871, 821, 767, 648, 541, 495, 459. Magnetic moment, $\mu_{\text{eff}} = 2.29$ B.M.

2.2.2 [Ni(bchbam)] complex (2)

Brown. Yield: 357 mg ($\approx 80\%$). Anal. Calc. for $\text{C}_{18}\text{H}_8\text{N}_4\text{O}_2\text{Cl}_2\text{Ni}$ (Mr. 441.7 g mol^{-1}): C, 49.01; H, 1.82; N, 12.71. Found: C, 49.10; H, 1.89; N, 12.98. IR bands (ν in cm^{-1}): 3319, 3191, 3080, 2221, 1604, 1581, 1548, 1514, 1460, 1377, 1230, 1184, 1134, 1085, 929, 862, 813, 711, 676, 649, 582, 516, 435. Magnetic moment, $\mu_{\text{eff}} = \text{diamagnetic}$.

2.2.3 [Cu(bchbam)](H₂O) complex (3)

Purple. Yield: 415 mg ($\approx 85\%$). Anal. Calc. for $\text{C}_{18}\text{H}_{10}\text{N}_4\text{O}_3\text{Cl}_2\text{Cu}$ (Mr. 464.54 g mol^{-1}): C, 44.57; H, 2.47; N, 11.56. Found: C, 44.69; H, 2.52; N, 11.77. IR bands (ν in cm^{-1}): 3620, 3384, 2223, 1612, 1589, 1510, 1452, 1417, 1328, 1361, 1236, 1174, 1095, 1033, 962, 825, 763, 667, 570, 536, and 459. Magnetic moment, $\mu_{\text{eff}} = 1.87$ B.M.

3. Results and Discussion

3.1 FT-IR spectra

In the IR spectrum of the free ligand, the phenolic $\nu(\text{O-H})$ band was observed *ca.* 3406, 3303 cm^{-1} , which is much lower than that expected for $\nu(\text{O-H})$ bands (3700-3584 cm^{-1}). The lowering of the absorption band is due to the intramolecular hydrogen bonding established by resonance. The IR spectrum of the ligand exhibit an absorption band at 1633 cm^{-1} which is assigned to the azomethine $\nu(\text{C=N})$ band, an indication of Schiff base formation [8]. In all the complexes, the $\nu(\text{C=N})$ band shifted towards the lower frequency range of 1631-1581 cm^{-1} suggesting coordination of the azomethine nitrogen atom to the respective metal(II) ions. The appearance of medium bands in the range of 3629-3426 and 1602-1589 cm^{-1} was assigned to $\nu(\text{O-H})$ and $\delta(\text{H-O-H})$ respectively, for complex (1). Absorption bands at 871 and 541 cm^{-1} were assigned to $\rho_r(\text{H}_2\text{O})$ and $\rho_w(\text{H}_2\text{O})$ for coordinated water molecules in the complex (1). IR bands in the range of 462-470 and 360-574 cm^{-1} was assigned to $\nu(\text{M-N})$ and $\nu(\text{M-O})$ vibration modes respectively. The absorption bands at 2210, 2185, 2221 and 2223 cm^{-1} was assigned to $\nu(\text{C}\equiv\text{N})$ for the prepared Schiff base ligand, complexes (1), (2) and (3) [9], respectively.

3.2 Electronic spectra

The electronic spectra of the free ligand and its complexes were recorded in DMSO (Figure 2).

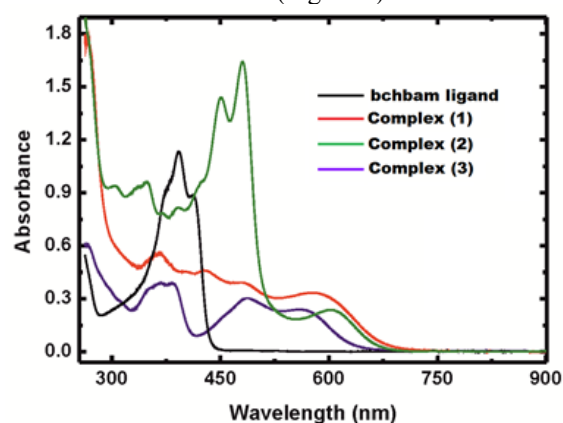


Figure 2. Electronic spectra of the free ligand and its complexes in DMSO solvent

The free ligand exhibited three absorption bands at 380, 392 and 412 nm. The bands at 380 and 392 nm were attributed to $n \rightarrow \pi^*$ transitions of conjugation between the lone pair of electrons of p-orbitals of N- and C=N group and a conjugated π -bond of phenyl and maleonitrile moiety whereas the band at 412 nm was attributed to $\pi \rightarrow \pi^*$ transitions within the ligand molecule. The electronic absorption bands *ca.* 478 and 577 nm were assigned to ${}^2A_1 \rightarrow {}^2E$ and ${}^2A_1 \rightarrow {}^2B_1$ transitions for complex (1), indicating a square pyramidal geometry around Co(II) ion. The complex (2) shows absorption bands at 451, 480 and 603 nm which were assigned to ${}^1A_{1g} \rightarrow {}^1B_{1g}$, ${}^1A_{1g} \rightarrow {}^1A_{2g}$ and ${}^1A_{1g} \rightarrow {}^1E_g$ transitions respectively, suggesting a four coordinated nickel(II) complex. The electronic spectrum of the complex (3) showed broad absorption bands at 368, 383, 406 and 559 nm, the first absorption band might be charge transfer transition, the other two transitions were assigned to ${}^2B_{1g} \rightarrow {}^2E_g$ and ${}^2B_{1g} \rightarrow {}^2B_{2g}$ transitions respectively, suggesting a square planar geometry around copper(II) ion [10], [11]. The ligand to metal charge transfer transition (LMCT) bands of the complexes were observed in the range 304 – 428 nm respectively.

3.3 Magnetic moment and conductivity measurements

The room temperature magnetic moment (μ_{eff}) values of the complexes (1), (2) and (3) were found to be 2.29, diamagnetic and 1.87 B. M. respectively. The value (2.29 B. M.) of complex (1) suggests the presence of one unpaired electron with low spin square pyramidal configuration. The complex (2) shows diamagnetism. The μ_{eff} value (1.87 B. M.) of the complex (3) is in good agreement with the spin only value (1.73 B. M.) suggesting the complex to be paramagnetic [12]. The molar conductivity of the complexes (1), (2), (3) were recorded in DMSO and was found to be 2.7, 9.0 and 2.6 $\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ respectively which suggested that the prepared complexes behave as non-electrolytes in DMSO.

3.4 Thermal analysis

The complex (1) shows weight loss curve in the temperature ranging from 80-230, suggesting presence of one coordinated water molecule. The TG curve of the complex (3) shows a weight loss curve in the temperature range of 70 – 135 °C which is attributed to the removal of one lattice water molecule with an endothermic DTA peak at *ca.* 111 °C. The decomposition steps within the temperature range of 230 – 700, 218 – 590 and 135 – 600 °C have been assigned to the removal of one molecule of Schiff base ligand for the complexes (1), (2) and (3) with the corresponding exothermic peaks at 624, 411 and 402 °C respectively.

Thermodynamic parameters of decomposition steps of the complexes, namely, activation energy were evaluated graphically by employing the Coats-Redfern method and Horowitz Metzger for TG curves and Borchardt-Daniels method for DTA curves [13]-[15], Table 1. Entropy of activation (ΔS), enthalpy of activation (ΔH) and the free energy change (ΔG) were calculated.

Table 1. Kinetic parameters using the Coats-Redfern (CR); Horowitz-Metzger (HM) for TG and Borchardt-Daniels (BD) for DTA curve of the complexes

Complexes/ Stage	Ea* (kJmol ⁻¹)	ΔH (kJ mol ⁻¹)	ΔS (JK ⁻¹ mol ⁻¹)	ΔG (kJ mol ⁻¹)
Complex (1)	-37	48	298	-
Co(bchbam) → CoO				-8.23 x10 ⁻³
Complex (2)	-65	54	28	-
Ni(bchbam) → NiO				-2.38 x10 ⁻⁴
Complex (3)	-	191	81	-
Cu(bchbam) → CuO	266			-2.37 x10 ⁻⁶

(bchbam)=[2,3-bis(5-chloro-2-hydroxybenzylideneamino)maleonitrile] ligand

From the TG curves the activation energies of decomposition were found to be in the range -37- (-) 266 k J mol⁻¹ by Coats-Redfern and 48-191 k J mol⁻¹ by Horowitz-Metzger method. Borchardt-Daniels method gives activation energy value in the range 28-298 k J mol⁻¹ for DTA curves of the complexes. The values suggest that the complexes were thermally stable. The negative value of ΔH and ΔS clearly indicates the exothermic behaviour of the degradation of the complexes. The reaction for which ΔG and ΔS is negative is considered as favourable or as spontaneous reaction i.e., the complexes were kinetically stable. The entropy of activation was found to have negative values in all the complexes which indicate that the decomposition reactions proceed with a lower rate

than normal ones. If we consider the order of stability with respect to the activation energy, the following trend could be observed for the complexes: Co(II) > Ni(II) > Cu(II). But no systematic trend is apparent for the prepared complexes.

3.5 X-ray powder crystallographic studies

The powder XRD diffraction pattern of the free ligand and complexes shows the crystalline nature, **Figure 4**. The crystallite sizes of the complexes were calculated by following Debye-Scherrer equation [16], [17].

$$D = 0.9 \lambda / \beta \cos \Theta \quad \text{--- (1)}$$

where, D = Crystallite Size; λ = wavelength of X-ray diffraction; β = Full Width at Half Maximum (FWHM) of observed peaks; Θ = Angle of diffraction.

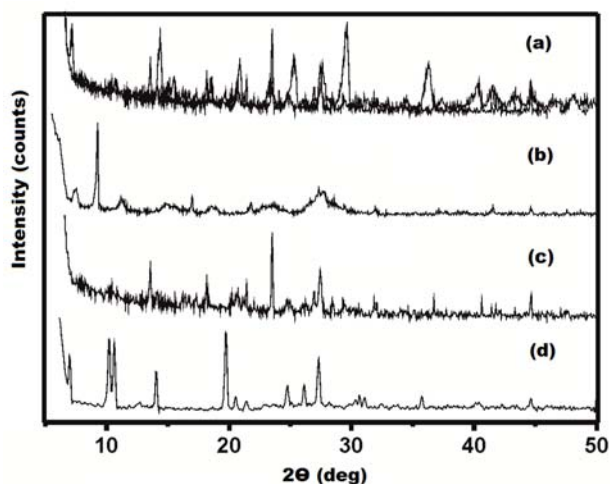


Figure 4. X-ray powder diffraction patterns of (a) bchbam ligand (b) nickel(II) complex, (c) cobalt(II) complex and (d) copper(II) complex.

The crystallite size (D) of the free ligand and complexes (1), (3) is found to be 20.56, 64.37, 35.6 nm respectively and have monoclinic crystal system whereas complex (2) has triclinic system having crystallite size 49.43 nm. Crystallographic details of the free ligand and complex (1) is described in Table 2.

3.6 DNA binding studies

A DNA binding study with the newly prepared ligand and its metal(II) complexes was carried out by monitoring electronic absorption titrations, a thermal behaviour study, cyclic voltametry and viscosity measurement methods. Electronic absorption titrations were carried out on a Perkin Elmer UV-vis Lambda 35 spectrophotometer. By maintaining a constant concentration of the free ligand and complexes (approximately 1×10^{-5} M) and varying the concentration of the CT-DNA (0.6 to 5.2×10^{-6} M) solution added, the absorbance for each addition of the DNA concentration was then recorded. The intrinsic binding constant was determined from the absorption spectral data by using the equation [18],

$$[\text{DNA}] / (\epsilon_a - \epsilon_f) = [\text{DNA}] / (\epsilon_b - \epsilon_f) + 1 / K_b (\epsilon_b - \epsilon_f) \quad (2)$$

where, ϵ_a , ϵ_f and ϵ_b corresponds to extinction coefficients of the apparent, free and bound metal complexes, respectively. [DNA] is the molar concentration of DNA and was measured by electronic absorption spectroscopy using the molar absorption coefficient ($6600 \text{ M}^{-1} \text{ cm}^{-1}$) at 258 nm. The solution of CT-DNA was prepared by using a 5 mM, tris-HCl buffer (pH = 7.1). The ratio of UV-absorbance at 260 nm and 280 nm, A_{260}/A_{280} , was found to be *ca.* 1.9, indicating that the DNA was satisfactorily free of protein [19].

Table 2. Crystallographic data of the ligand (bchbam) and complex (1)

	Ligand (bchbam)	Complex (1)
Empirical formula	$\text{C}_{18}\text{H}_{10}\text{N}_4\text{O}_2\text{Cl}_2$	$\text{C}_{18}\text{H}_{10}\text{N}_4\text{O}_3\text{Cl}_2\text{Co}$
Formula Weight (g/mol)	385	459.9
Temperature (K)	298	298
Wavelength (Å)	1.54060	1.54060
Crystal system	Monoclinic	Monoclinic
Unit		
Cell dimensions (Å)	$a = 26.5202$	$a = 16.6671$
	$b = 6.1531$	$b = 4.8835$
	$c = 8.5126$	$c = 6.2807$
	$\alpha = \gamma = 90^\circ$	$\alpha = \gamma = 90^\circ$
	$\beta = 144.813^\circ$	$\beta = 128.750^\circ$
Volume (Å ³)	800.46	399.68
2 Θ Range	5°-50°	5°-50°
Limiting Indices	$0 \leq h \leq 5$ $0 \leq k \leq 2$ $-2 \leq l \leq 0$	$1 \leq h \leq 4$ $0 \leq k \leq 1$ $-2 \leq l \leq 1$
Merit of Fitness	M(10) = 13.9 F(10) = 11.1	M(10) = 29.6 F(10) = 31.7
Crystallite size, D (nm)	20.56	64.37

A plot of $[\text{DNA}] / (\epsilon_b - \epsilon_f)$ vs. $[\text{DNA}]$ was plotted with K_b calculated by a ratio of the slope to the y-intercept. The

absorption spectrum of the free ligand, complexes (1) and (2) in presence of increasing concentration of the CT-DNA ($0.6, 1.3, 1.9, 2.6, 3.2, 3.9, 4.5, 5.2 \times 10^{-6}$ M) showed a considerable amount of hyperchromism with a slight red shift whereas in the absorption spectra of complex (3) hypochromic effect was observed with a slight blue shift, Figure 5. The intrinsic binding constant (K_b) of the free ligand and complexes (1), (2) and (3) was found to be $9.18, 7.95, 7.11$ and $6.06 \times 10^5 \text{ M}^{-1}$ respectively.

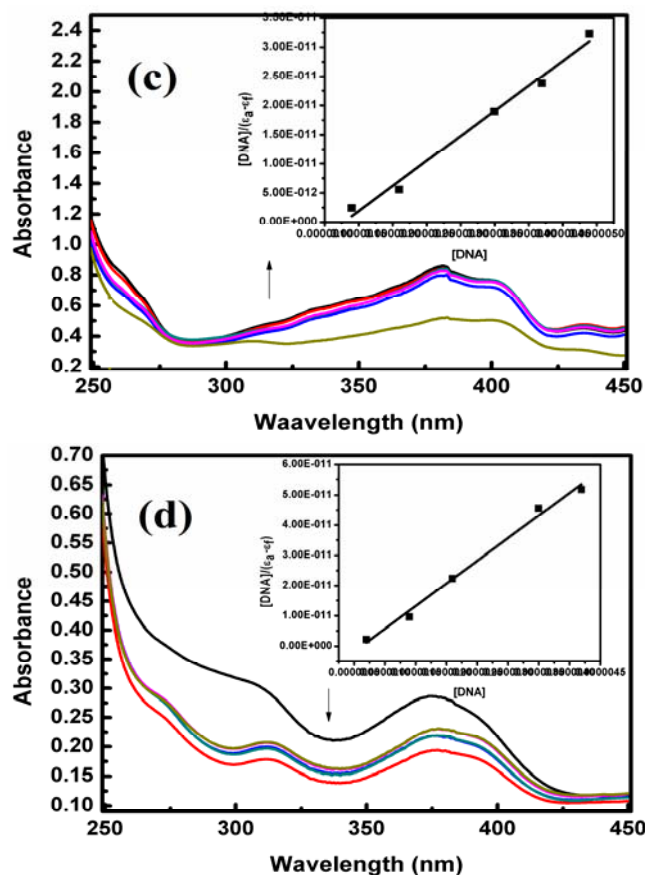
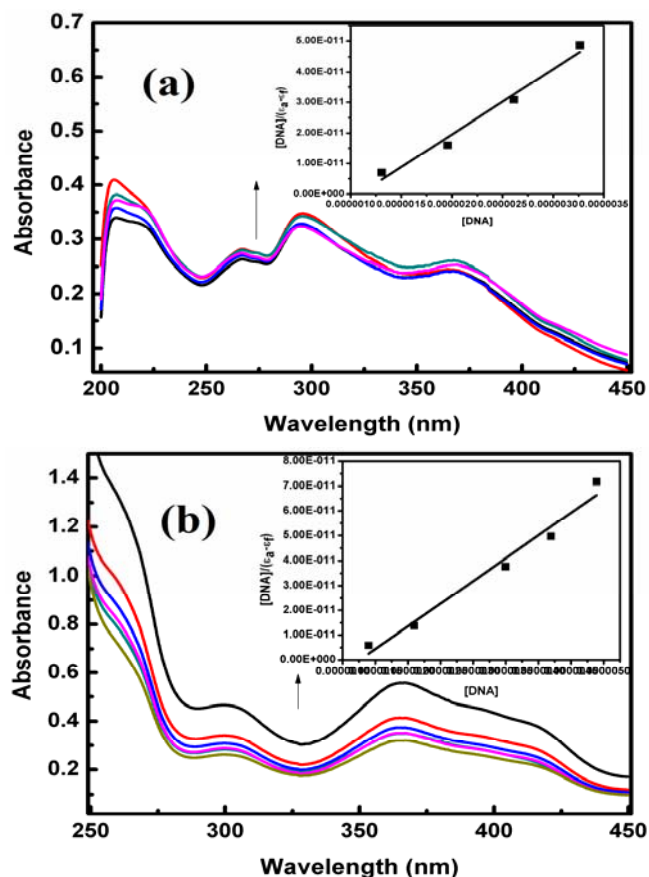


Figure 5. Absorption spectra of the (a) free ligand, (b) complex (1), (c) complex (2) and (d) complex (3) in absence and presence of different concentrations of CT-DNA. The arrow indicates the effect of DNA on absorption curve of the respective compounds. Inset plot of $[DNA]/(\epsilon_a - \epsilon_f)$ vs $[DNA]$ and a linear fit of the titration curve.

A thermal behaviour study of DNA was performed by measuring the absorption intensity of CT-DNA at 258 nm at a temperature range of 25-100°C, both in the absence and presence of the free ligand and complexes. The thermal denaturation behaviour in the presence of the ligand and complexes provides insight into conformational changes when the temperature is raised. The strength of interaction between the ligand and complexes and the DNA can also be monitored. As the temperature of the solution increases, the double stranded DNA tends to dissociate into a single strand thereby displaying a hyperchromic effect on the absorption spectra of DNA, which was observed. The DNA melting temperature, T_m , where half of the total base pairs becomes non-bonded, was determined experimentally and found to be 76°C which increases to 82-83°C for the free ligand and complex (1), 78-80°C for complexes (2) and (3) with increasing ratio of DNA to compound concentrations (0, 0.1, 0.2 and 0.4), respectively. The increased in T_m values indicated that the interaction mode of DNA with the ligand and complex (1) might be an intercalative mode whereas complexes (2) and (3) might have non-intercalative mode of DNA binding [20], [21].

The cyclic voltammogram (CV) of the complexes in absence and presence of the CT-DNA concentrations were recorded in the range -1.0 to 1.0 V. The CV data of the complexes shows a quasi-reversible electron transfer process. In presence of variable concentrations of the CT-DNA (20-100

μl), the cyclic voltammogram of the complexes showed a minor but significant anodic and cathodic shift with a decrease in the current peaks respectively. The decreased in the peak currents of the complex in presence of CT-DNA might be the result of slow diffusion of the complex to the DNA molecules, forming an equilibrium mixture of the free and DNA-bound complex to the electrode surface [22]. As a complement to the absorption spectral titrations, emission spectroscopy and a DNA melting temperature experiments, the CV data suggests that the respective complexes bind the DNA helix.

In order to clarify further the DNA interaction mode, viscosity measurements have been carried out (on an Ostwald's viscometer at $25 \pm 0.1^\circ\text{C}$) with CT-DNA ($20 \mu\text{M}$) by using variable concentrations of the free ligand and its complexes ($1.66\text{-}8.33 \mu\text{M}$). Flow time was measured with a digital stop watch and each sample was measured at least three times and an average flow time was calculated and the data were presented as $(\eta/\eta_0)^{1/3}$ vs. $[\text{Q}]/[\text{DNA}]$, where, η = viscosity of the DNA in presence of the ligand and complexes; η_0 = viscosity of DNA alone; $[\text{Q}]$ = concentrations of the free ligand and its complexes. Hydrodynamic measurements such as viscosity measurements which are sensitive to length increase are regarded as the least ambiguous and the most critical tests of binding in solution in the absence of crystallographic structural data [23].

In classical intercalation, the DNA helix lengthens as base pairs are separated to accommodate the bound adducts leading to increased DNA viscosity whereas a partial non-classical intercalation causes a bend in the DNA helix reducing its effective length and its viscosity. The effect of free ligand and its complexes were shown in Figure 7.

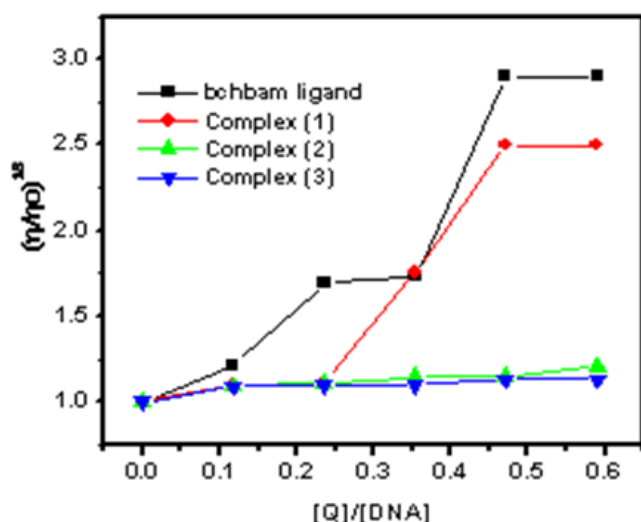


Figure 7. Effect of increasing amount of the ligand (filled square) and respective compounds on the relative viscosity of CT-DNA in a Tris- HCl buffer. $[\text{DNA}] = 20 \mu\text{M}$, $[\text{ligand}]$ and $[\text{Complexes}] = 1.66\text{-}8.33 \mu\text{M}$.

It has been observed that on addition of free ligand and complex (1), the relative viscosity increases steadily, which suggested that the newly prepared ligand and its complex (1) are bound to CT-DNA by an intercalative mode of binding whereas in case of addition of complexes (2) and (3), no

significant change in viscosity were observed and hence a non-intercalative mode of binding is suggested [24]-[26]. The said results were consistent with our spectroscopic and cyclic voltammetry measurements.

4. Conclusion

A simple synthetic method is described for the synthesis of the new Schiff base ligand, [2,3-bis(5-chloro-2-hydroxybenzylideneamino)maleonitrile] of diaminomaleonitrile and its metal(II) complexes. A DNA binding study suggests that the free ligand and its complexes were avid binders of CT-DNA.

5. Acknowledgements

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