Spectrochimica Acta Part A 71 (2009) 1851–1856

Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: www.elsevier.com/locate/saa

Synthesis and spectroscopic studies on complexes of N,N'-bis-(2-pyridinecarboxaldimine)-1,8-diaminonaphthalene (L); DNA binding studies on Cu(II) complex

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ARTICLE INFO

Article history:
Received 26 March 2008
Received in revised form 2 July 2008
Accepted 3 July 2008

Keywords:
Schiff base
Condensation
Spectroscopic studies
Octahedral geometry
Calf thymus DNA

ABSTRACT

The Schiff base ligand, N,N'-bis-(2-pyridinecarboxaldimine)-1,8-diaminonaphthalene (L), obtained by the condensation of 2-pyridinecarboxaldehyde and 1,8-diaminonaphthalene, has been used to synthesize the mononuclear complexes of the type $[MLCl_2]$ [M = Co(II), Ni(II), Cu(II) and Zn(II)]. The newly synthesized ligand (L) and its complexes have been characterized on the basis of results of elemental analysis, molar conductance, magnetic susceptibility measurements, Job's method and spectroscopic studies viz., FT-IR, Mass, ^1H and ^{13}C NMR. The UV–vis and magnetic moment data revealed an octahedral geometry around Co(II), Ni(II) and Cu(II) ions and conductivity data show a non-electrolytic nature of the complexes. Absorption and fluorescence spectroscopic studies support that Cu(II) complex exhibits significant binding to calf thymus DNA.

1. Introduction

Hugo Schiff described the condensation reaction between an aldehyde and an amine leading to the formation of a Schiff base in 1864 [1]. The chelating structures, moderate electron donation and easy tunable electronic and steric effects proved Schiff bases as versatile ligands capable of stabilizing different metals in various oxidation states with unusual structural features and controlling the performance of metals in variety of useful catalytic transformations [2–9]. Characteristically Schiff base provides geometrical cavity control for host-guest interaction and modulation of its lipophilicity offers remarkable selectivity, sensitivity and stability for a specific metal ion [10]. Among the inorganic mimics of enzymes, metal complexes containing porphyrin, salen and phthalocynine ligands have been investigated as possible alternative catalysts in many oxidation and hydroxylation reactions [11–13]. Salen ligands give complexes which in addition to alkene epoxidation also hold promise in enantioselective cyclopropanation of styrenes, asymmetric aziridination and enantioselective ring opening [14]. It has been suggested that the azomethine linkage is responsible for the biological activities of Schiff bases such as, antitumor, antibacterial, antifungal and herbicidal activities [15–20]. The use of Co(III) Schiff base complexes as antiviral agent has also been reported in view of labile axial ligands which exhibit higher activities, possibly due to axial binding of Co(III) ion to biological targets (proteins and nucleic acids) [21,22]. It has been observed that most of the metals make 1:1 metal complexes with Schiff bases [10]. Chemists over a period of years reported the binding of cationic metal complexes with DNA [23–26]. The factors that determine the affinity and selectivity in binding of small molecules to DNA would be valuable in the rational design of new diagnostic and therapeutic agents [27–30], thus the metal complexes binding to DNA through a variety of modes may be exploited in probe development. These metal complexes are known to bind to DNA through a series of interactions, such as π stacking interaction associated with interaction of aromatic heterocyclic groups between the base pairs, hydrogen bonding and Van der Waals interactions in the case of binding to the groove of DNA helix [31]. Recently coordination chemistry of Schiff bases derived from 2-pyridinecarboxaldehyde has received much attention [32–35]. As a part of our ongoing interest in the coordination chemistry of Schiff base ligands derived from 2-pyridinecarboxaldehyde, we have reported a Schiff base ligand L (1,2-diaminophenyl-N,N′-bis-(2-pyridinecarboxaldimine) derived from condensation reaction of 1,2-diaminobenzene with 2-pyridinecarboxaldehyde and its metal complexes [36]. The fluorescence and UV–vis absorption studies performed on its Cu(II) complex revealed a significant binding ability to DNA. Herein we report the synthesis and spectroscopic studies of Schiff base ligand (L) and its complexes of the type

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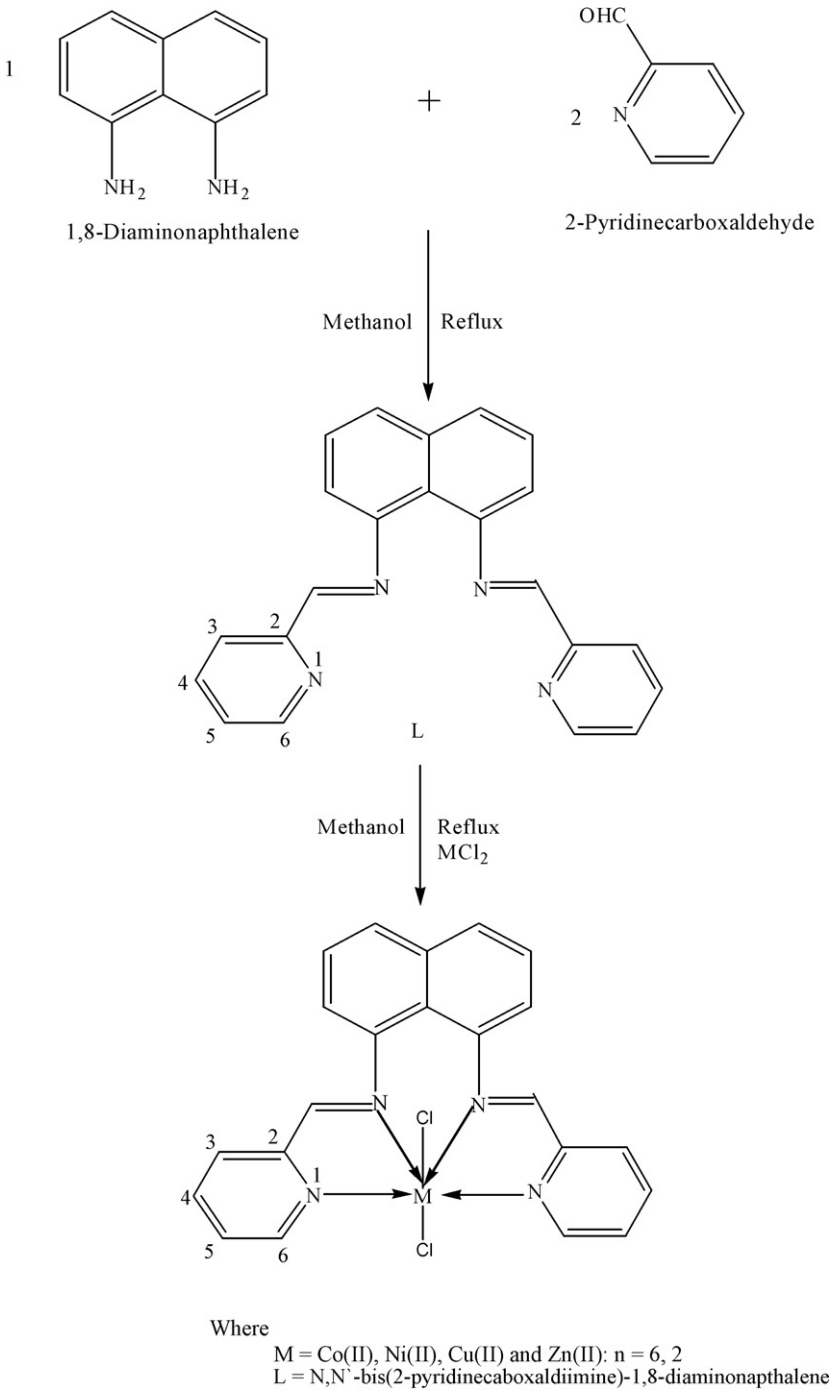
doi:10.1016/j.saa.2008.07.002



Scheme 1. Synthesis and proposed structures of ligand and its complex.

$[MLCl_2]$ [M = Co(II), Ni(II), Cu(II) and Zn(II)] derived from condensation of 2-pyridinecarboxal-dehyde and 1,8-diaminonaphthalene and binding study of its Cu(II) complex with calf thymus DNA.

2. Physical measurements

The Elemental analyses data recorded on Perkin–Elmer 2400 CHN Elemental Analyser, FT-IR spectra (4000–200 cm^{-1}) recorded as KBr/CsI disc on a Perkin–Elmer 621 spectrophotometer and ^1H and ^{13}C NMR spectra recorded in DMSO-d_6 using Bruker Avance II 400 NMR spectrometer were obtained from SAIF, Punjab University University, Chandigarh (India). Mass spectra recorded on micro mass V G-7070 H spectrometer for ESI were from CSMCRI, Bhavnagar, Gujarat (India). Metals and chlorides were estimated volumetrically and gravimetrically [37,38]. The electronic spectra of the complexes in DMSO were recorded on Pye-Unicam 8800 spectrophotometer. The electrical conductivities of 10^{-3} M solution in DMSO were obtained on a Systronic type 302 conductivity bridge equilibrated at 25 °C ± 0.01 °C. The magnetic susceptibility measurements were carried out using Faraday balance at room temperature. Fluorescence measurements were made using Shimadzu spectrofluorimeter Model RF-5301PC equipped with a 150W Xenon lamp and a slit width of 5 nm. For the determination of binding parameters, 30 μM of complex solution was taken in a

quartz cell and increasing amounts of ct DNA solution was titrated. The fluorescence spectra were recorded in the range of 700–840 nm upon excitation at 290 (λ_{ex} was 772 nm) at temperatures 310 K. The absorption spectra were recorded on Shimadzu double beam spectrophotometer (Model UV 1700) using a cuvette of 1 cm path length. The absorbance values of ct DNA in the absence and presence of Cu(II) complex were made in the range of 220–300 nm. DNA concentration was fixed at 0.1 mM, while the compound was added in increasing concentration.

3. Experimental

3.1. Materials

The metal salts, $MCl_2{\cdot}6H_2O$ [M = Co(II) and Ni(II)], $CuCl_2{\cdot}2H_2O$ and $ZnCl_2$ (All Aldrich) were pure samples. The chemicals 1,8-diaminonaphthalene and 2-pyridinecarboxaldehyde (Both E. Merck) were used as received. Methanol used as a solvent was of A.R. grade. Highly polymerized calf-thymus DNA sodium salt (7% Na content) was purchased from Sigma Chemical Co. Other chemicals were of reagent grade and used without further purification. The stock solution of (12.5 mM DNA/phosphate) calf thymus DNA was prepared by dissolving 0.5% w/w in 0.1 M sodium phosphate buffer (pH 7.40) at 310 K for 24 h with occasional stirring to ensure homogeneity of solution. The absorption ratio A_{260}/A_{280} in the range 1.8–1.9 indicated that DNA was sufficiently free from protein. The stock solution of [$CuLCl_2$] with 5 mg/ml concentration was also prepared.

4. Synthesis of N,N'-bis-(2-pyridinecarboxaldimine)-1,8-diaminonaphthalene: (L)

Methanolic solution of 2-pyridinecarboxaldehyde (2 mmol 0.192 ml) was added dropwise to a stirring methanolic solution of 1,8-diaminonaphthalene (1 mmol 0.158 g). The reaction mixture was refluxed for about 3–4 h resulting in a clear brown colored solution. The resultant solution was then kept for evaporation at room temperature leading to the isolation of brown colored microcrystalline product in few weeks time. The product was filtered, washed several times with methanol and vacuo dried. F.W. 336.39; Yield: 59%; M.P. 110–112 °C; Color: brown; Anal. Cal. for L: C, 78.55; H, 4.79; N, 16.65%. Found: C, 78.52; H, 4.75; N, 16.62%. ^{1}H NMR (DMSO-d_6) (δ ppm): 9.23 (s, 2H, –CH = N), 7.40–8.25 (m Ar–H) and 7.25–8.21 (Pyridine). ^{13}C NMR (DMSO-d) (δ ppm): 192.90 (–CH = N), 120.5–137.1 (Aromatic), 127.8–159.8 (pyridine); ESI mass (m/z): 336.34 $[L]^+$; IR (KBr cm^{-1}): 1635 (C = N).

5. Synthesis of complex [$MLCl_2$] [M = Co(II), Ni(II), Cu(II) and Zn(II)]

A solution of the ligand L (1 mmol 0.336 g) dissolved in methanol was magnetically stirred in a round bottom flask followed by dropwise addition of methanolic solution of metal salt (1 mmol). The reaction mixture was refluxed for 2–3 h leading to the formation of colored solid product. The product thus formed was filtered off, washed with methanol and dried in vacuo.

[$CoLCl_2$]: F.W. 466.23; Yield 63%; M.P. >300; Color: Dark Brown; Molar Conductance: 15.6; Magnetic Moment: 4.51 B.M; Anal. Cal: Co, 12.64; C, 56.67; H, 3.45; N, 12.01%. Found: Co, 12.61; C, 56.63; H, 3.41; N, 11.98%. ESI mass (m/z): 466.21 $[CoLCl_2]^+$; IR (KBr, cm^{-1}): 1615 (–CH = N), 525 (M–N), 225 (M–N_{Py}), 295 (M–Cl).

[$NiLCl_2$]: F.W. 465.99; Yield 64%; M.P. >300; Color: Brownish Red; Molar Conductance: 17.2; Magnetic Moment: 3.09; Anal. Cal: Ni, 12.59; C, 56.70; H, 3.46; N, 12.02%. Found: Ni, 12.57; C, 56.68; H, 3.43; N, 12.00%. ESI mass (m/z): 465.96 $[NiLCl_2]^+$; IR (KBr cm^{-1}): 1620 (–CH = N), 520 (M–N), 235 (M–N_{Py}), 270 (M–Cl).

[$CuLCl_2$]: F.W. 470.84; Yield 68%, M.P. >300; Color: Dark Brown; Molar Conductance: 18.0; Magnetic Moment: 1.78 B.M; Anal. Cal; Cu, 13.49; C, 56.12; H, 3.42; N, 11.89%. Found: Cu, 13.48; C, 56.08; H, 3.40; N, 11.87%. ESI mass (m/z): 470.80 $[CuLCl_2]^+$; IR (KBr cm^{-1}): 1625 (–CH = N), 527 (M–N), 245 (M–N_{Py}), 285 (M–Cl).

[$ZnLCl_2$]: F.W. 472.68; Yield 61%; M.Pt. >300; Color: Brown; Molar Conductance: 14.4; Anal. Cal.: Zn, 13.83; C, 55.90; H, 3.41; N, 11.85%. Found: Zn, 13.80; C, 55.87; H, 3.38; N, 11.82%. ESI mass (m/z) 472.64 $[ZnLCl_2]^+$; IR (KBr cm^{-1}): 1617 (–CH = N), 530 (M–N), 255 (M–N_{Py}), 290 (M-Cl). ^{1}H NMR (DMSO-d_6) (δ ppm): 9.43 (s, 2H (–CH = N), 7.40–8.65 (m Ar–H) and 7.41–8.50 (Zn–Py). ^{13}C NMR (DMSO-d) (δ ppm): 193.90 (CH = N), 121.5–138.5 (Aromatic), 128.9–161.8 (pyridine).

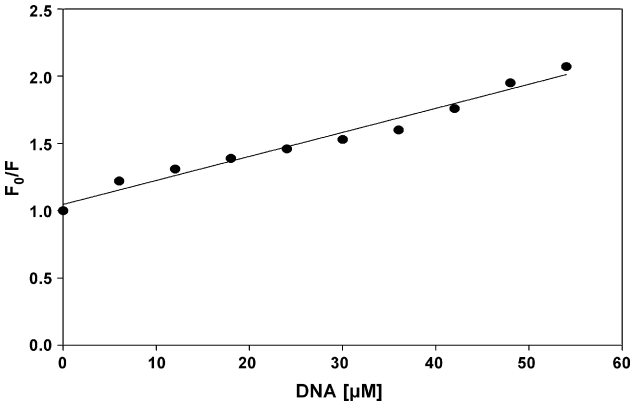


Fig. 1. Stern–Volmer plot for the binding of Cu(II) complex with DNA.

6. Binding data analysis of [$CuLCl_2$] complex

Stern–Volmer equation-1 was used for data analysis to elaborate the fluorescence quenching mechanism [39]:

$$\frac{F_0}{F} = 1 + K_{SV}[Q] \quad (1)$$

where F_0 and F are the steady-state fluorescence intensities in the absence and presence of quencher, respectively. K_{SV} is the Stern–Volmer quenching constant and [Q] is the concentration of quencher (DNA). The K_{SV} for the Cu(II) complex was found to be of the order of 10^4. The linearity of the F_0/F versus [Q] (Stern–Volmer) plots for DNA–Cu(II) complex (Fig. 1) depicts that the quenching may be static or dynamic, since the characteristic Stern–Volmer plot of combined quenching (both static and dynamic) is an upward curvature. The equilibrium between free and bound molecules is given by the equation (2) [40]:

$$\log\left[\frac{(F_0 - F)}{F}\right] = \log K + n \log[Q] \quad (2)$$

where K and n are the binding constant and the number of binding sites, respectively. Thus, a plot of $\log (F_0 - F)/F$ versus $\log [Q]$ can be used to determine K as well as n.

7. Results and discussion

Schiff base ligand, L was synthesized by condensation of 1,8-diaminonaphthalene and 2-pyridinecarboxaldehyde in 1:2 molar ratio in methanolic medium (Scheme 1). The purity of the complexes was checked by running TLC on silica gel coated plate. The complexes of the type [$MLCl_2$] [M = Co(II), Ni(II), Cu(II) and Zn(II)]

Table 1
Magnetic susceptibility and electronic spectral values

Compounds	μ_{eff} (B.M.)	Band position (cm^{-1})	Assignments
$[CoLCl_2]$	4.51	20,500	$^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$
		16,000	$^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$
$[NiLCl_2]$	3.09	24,200	$^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$
		17,000	$^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$
		10,500	$^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$
$[CuLCl_2]$	1.78	16,129	$^2B_{1g} \rightarrow {}^2B_{2g}$

were synthesized by the reaction of the ligand L and the metal salt in 1:1 molar ratio in methanolic medium. All the Schiff base complexes were stable at room temperature, and were soluble in DMSO and MeOH. The low molar conductivity values of all the complexes suggest their non-ionic nature [41]. The analytical data agree well with the proposed composition of the ligand and its complexes. The compositions of the complexes were further corroborated by using Job's method, where a maximum corresponding to 0.5 on the mole ratio of the ligand scale suggests that the complexes have 1:1 composition. The positions of molecular ion peak (m/z) of the ligand and its complexes in the ESI mass spectra further corroborated the proposed molecular formulae. The formation of Schiff base ligand, L and its complexes and the bonding modes were inferred from the characteristic band positions in FT-IR spectra and resonance signals in ^1H and ^{13}C NMR spectra corresponding to coordinated Schiff base moiety. The geometry around Co(II), Ni(II) and Cu(II) ions in the complexes was deduced from the positions of absorption bands observed in UV–vis spectra and magnetic moment values. The binding parameters were found to be $K = 0.34 \pm 0.46 \times 10^4\ M^{-1}$; $n = 0.68$. These parameters suggested that the complex $[CuLCl_2]$ has good binding affinity toward the DNA molecule.

8. IR Spectra

The IR spectrum of the ligand showed the absence of bands at 1730 and 3415 cm^{-1} due to $\nu_{(CO)}$ and $\nu_{(NH2)}$ stretching vibrations, respectively. The appearance of a new strong intensity band at 1635 cm^{-1} assigned to azomethine group, $\nu_{(CH=N)}$ suggest the condensation of amino moiety with the carbonyl group [42]. The IR spectra of all the complexes exhibited a negative shift of ~20 cm^{-1} in $\nu_{(CH=N)}$ stretching vibration indicating the coordination of nitrogen of imine moiety of Schiff base to the metal ion. This is further confirmed by the appearance of a medium intensity band in the region 520–530 cm^{-1} in all the complexes, characteristic of ν_{M-N} stretching mode [42,43]. The characteristic bands corresponding to pyridine ring vibrations in 2-pyridinecarboxaldehyde appeared in the region 625–645 cm^{-1} (in plane ring deformation) and 425–430 cm^{-1} (out of plane ring deformation) were found to be slightly positively shifted in the complexes as compared to the free ligand, L suggesting the coordination of pyridine nitrogen to the metal ion [44,45]. However, ring vibrations in the higher frequency regions were not affected appreciably. This is further corroborated by appearance of a strong intensity band in the IR spectra of all the complexes in the region 225–255 cm^{-1} assigned to $\nu_{(M-Py)}$ vibration [45]. A medium intensity band appearing in the region 270–295 cm^{-1} may reasonably be assigned to $\nu_{(M-Cl)}$ vibration [46].

9. Electronic spectra and magnetic susceptibility data

The electronic spectra and magnetic moment data of the complexes are summarized in Table 1. The electronic spectrum of Co(II) complex exhibited two bands at 20,500 and 16,000 cm^{-1} assignable to $^4T_{Ig}(F) \rightarrow {}^4T_{Ig}(P)$ and $^4T_{Ig}(F) \rightarrow {}^4A_{2g}(F)$ transitions, respectively, corresponding to an octahedral geometry around Co(II) ion [47]. The observed magnetic moment of 4.51 B.M. for Co(II) further complements the electronic spectral findings [48]. The electronic spectrum of Ni(II) complex exhibited three bands at 24,200, 1700 and 10,500 cm^{-1} attributed to $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$, $^3A_{2g}(F) \rightarrow {}^3T1g(F)$ and $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ transitions, respectively, characteristic of an octahedral environment for Ni(II) complex which is further supported by its magnetic moment value of 3.09 B.M. (47, 48). A broad band at 16,129 cm^{-1} due to $^2B_{Ig} \rightarrow {}^2B_{2g}$ transition in Cu(II) complex and effective magnetic moment of 1.78 B. M. are suggestive of an octahedral geometry around Cu(II) ion [47,48].

10. ^1H and ^{13}C NMR spectra

The ^1H NMR spectra of ligand, L and its Zn(II) complex $[ZnLCl_2]$ recorded in DMSO-d_6 at room temperature were compared. The down field shift in chemical shift values for pyridine ring protons in complex (8.50 ppm (d H_3), 8.27 ppm (t H_4), 7.41 ppm (t H_5) and 7.61 ppm (d H_6)) as compared to free ligand, L (7.29 ppm (d H_3), 8.12 ppm (t H_4), 7.25 ppm (t H_5) and 8.21 ppm (d H_6)) justify the coordination of pyridine nitrogen in the complexes [49]. Similarly the down field shift in chemical shift values in azomethine group proton in complex 9.43 ppm (–CH = N) as compared to free ligand 9.23 ppm and naphthalene protons in complex 7.40–8.65 ppm (m Ar–H) against the free ligand 7.40–8.25 ppm indicate the involvement of azomethine nitrogen in coordination with Zn(II) ion [49,50].

The ^{13}C NMR spectrum of Zn(II) complex revealed the presence of expected number of signals corresponding to different types of carbon atoms. A strong NMR signal appearing at 192.90 ppm may reasonably be assigned to azomethine carbon. The chemical shifts of naphthalene and pyridine carbons appear at 120.5, 137.1, 126.5, 125.4, 123.8, 123.1, 159.8, 152.1, 141.4, 134.1 and 127.8 ppm [50]. These values were found to be downfield shifted by about 1.0–2.0 ppm as compared with free ligand L.

11. Mass spectrometry

The observed molecular ion peak(s) at m/z 336.34 corresponding to ligand, L and at m/z 466.21, 465.96, 470.80 and 472.64 for Co(II), Ni(II), Cu(II) and Zn(II) complexes, respectively, are consistent with the proposed molecular formulae of the ligand and the complexes.

12. Job's plot

Job's method of continuous variation was used for determining the composition of the complexes [51]. These solutions were prepared in a manner that the total concentration of the metal and ligand remains constant, while ligand: metal ratio varies from flask to flask, that is:

$$C_M + C_L = K$$

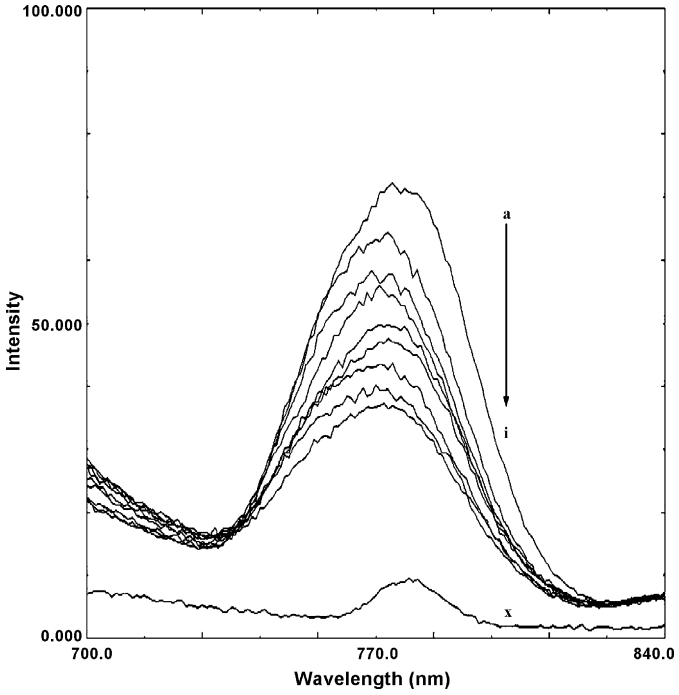


Fig. 2. Fluorescence emission spectra of Cu(II) complex in the absence and presence of increasing amount of DNA from (a) to (i); pH 7.4 and (*X*) represents the DNA alone.

where C_M and C_L are analytical concentrations of the metal and the ligand, respectively, and *K* is the constant. The absorbance is plotted as a function of mole fraction (*X*) of the ligand or metal in the flasks. The resulting curve is known as Job's plot.

where, $X = X_L$ or X_M; $X_L = C_L/C_M + C_L$; X_L = Mole fraction of ligand; X_M = Mole fraction of metal.

The Job diagrams for Co(II) and Cu(II) complexes at 525 and 600 nm, respectively, showed straight lines intersecting at $X = 0.5$, suggesting 1:1 composition of the complexes. The same profiles were observed when the diagrams were constructed at different wave lengths.

13. Fluorescence measurement

13.1. Binding of Cu(II) complex with DNA

The fluorescence spectroscopy provides insight of the changes taken place in the microenvironment of DNA molecule on ligand binding. The interaction of the metal complex to DNA was studied by monitoring the changes in the intrinsic fluorescence of these compounds at varying DNA concentration. The representative fluorescence emission spectrum of the synthesized compound upon excitation at 290 nm is shown in Fig. 2. The addition of DNA caused a gradual decrease in the fluorescence emission intensity of the synthesized molecule with a conspicuous change in the emission spectra. A higher excess of DNA led to more effective quenching of the fluorophore molecule fluorescence which clearly indicated that the binding of the DNA to Cu(II) complex changed the microenvironment of fluorophore residue. The marked shift in the emission peak illustrates the drastic change in the vicinity of the fluorophore. The reduction in the intrinsic fluorescence of synthesized molecule upon interaction with DNA could be due to masking or burial of compound fluorophore upon interaction between the stacked bases with in the helix and/or surface binding at the reactive nucleophilic sites on the heterocyclic nitrogenous bases of DNA molecule.

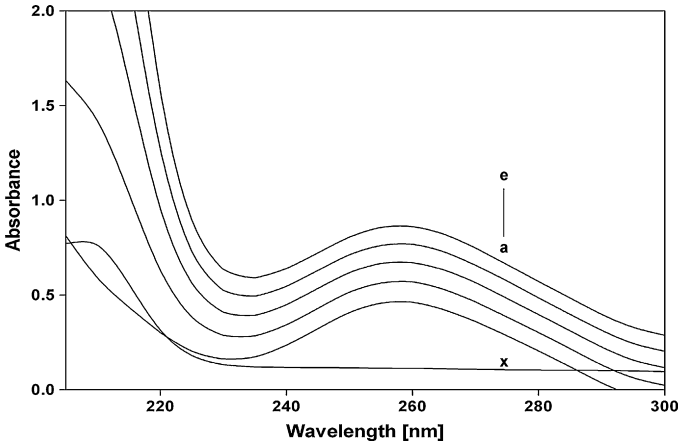


Fig. 3. Absorbance spectra of DNA and DNA–Cu(II) complex system. DNA concentration was 0.10 mM (a), Cu(II) complex concentration for Cu(II)–DNA complex system was at 5 μM (b), 10 μM (c), 15 μM (d) and 20 μM (e). A concentration of 5 μM Cu(II) complex (*X*) was used for Cu(II) complex only.

13.2. Absorption spectroscopy

UV–vis absorption studies were performed to further ascertain the DNA-Cu(II) complex interaction. The UV absorbance showed an increase with the increase in the Cu(II) complex concentration Fig. 3. Since Cu(II) complex does not give any interfering peak in this region Fig. 3, hence the rise in the DNA absorbance is suggestive of the interaction between DNA and Cu(II) complex. DNA exhibited hyperchromism on addition of Cu(II) complex. As hypochromism and hyperchromism are both the spectral features of DNA concerning its double helix structure, hypochromism means the DNA binding mode of a complex via electrostatic effect or intercalation where as hyperchromism means the breakage of the secondary structure of DNA on binding of the complex. So we primarily speculate that complex interacting with secondary structure of the calf thymus DNA resulting in its perturbation [52,53].

Acknowledgements

Chairman, Department of Chemistry, Aligarh Muslim University, Aligarh, India is acknowledged for providing necessary research facilities. Mr. Mohammad Azam is grateful to U.G.C. for financial support. Dr. Shama Parveen, Young Scientist, under SERC fast track scheme acknowledges the financial assistance from Department of Science and Technology (DST), New Delhi, Vide Project No. SR/FTP/CS-11-2007. Mr. Avtar Singh, SAIF, Punjab University, Chandigarh is acknowledged for providing NMR facilities. Mr. Mahindra Kumar Shukla, CSMCRI, Bhavnagar is acknowledged for providing mass spectral data.

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