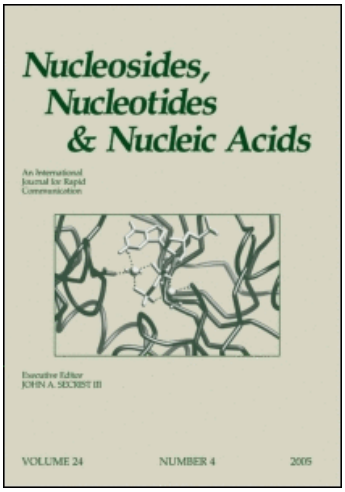

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Synthesis and DNA Binding Studies of Mg(II) Complex of Schiff Base Derived from Vanillin and L-Tryptophan

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SYNTHESIS AND DNA BINDING STUDIES OF Mg(II) COMPLEX OF SCHIFF BASE DERIVED FROM VANILLIN AND L-TRYPTOPHAN

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□ *The Mg(II) complex of Schiff base (K[HL]) derived from vanillin and L-tryptophan could bind with herring sperm DNA. The binding behaviors between them in physiological pH environment (pH 7.40) have been studied by spectroscopy, cyclic voltammetry and viscosity methods. Binding ratios of $n_{Mg(II)}$: $n_{K[HL]}$ = 1:1 and $n_{Mg(II)L}$: n_{DNA} = 5:1 were confirmed. The obtained thermodynamic parameters suggest that the interaction between Mg(II)L and DNA is driven mainly by entropy. Combined with fluorimeteric studies, cyclic voltammetry, CD spectroscopy and viscosity methods, the results indicate the interaction modes between Mg(II)L and DNA are mainly with intercalation and involving some electrostatic interaction.*

Keywords Vanillin; L-tryptophan; Mg(II) complex of Schiff base; herring sperm DNA; interaction

INTRODUCTION

It is well known that divalent metal ions are critical to the proper functioning of various biomolecules, such as replication processes and protein biosynthesis. These ions are essential in the stabilization of noncanonical forms of nucleic acids.[1,2] Therefore, the interaction between divalent metal ions (such as Ca^{2+} and Mg^{2+}) and nucleic acids have got a number of investigations. Effect of Mg^{2+} on solubility, viscosity, and melting temperature of DNA molecule are attributed to the existence of a strong binding between Mg^{2+} and DNA phosphates.[3] At the same time, Schiff base metal complexes are an area of increasing interest and have numerous applications. They are

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considered to new kinds of potential anticancer reagent, anti-bactericide reagent and antivirus reagent.[4–7] The metal ions may enhance the activities of Schiff base ligands.[8] Generally, the complexes are known to bind to DNA by a series of noncovalent interactions such as intercalation, electrostatic interaction and groove binding.[9, 10]

In this article, a Schiff base derived from vanillin and L-tryptophan and its Mg(II) complex have been synthesized. The interaction of this complex with DNA has been investigated systematically by spectroscopy, cyclic voltammetry and viscosity methods.

EXPERIMENTAL

Materials and Methods

Herring sperm DNA was purchased from Sigma Biological Co. (USA) and used as received. Purity of DNA was checked by monitoring the ratio of absorbance at 260 to that at 280 nm. The ratio of A_{260}/A_{280} was 1.89, indicating that DNA was free from protein.[11] The DNA was dissolved in doubly distilled deionized water with 50 mM NaCl and dialyzed for 48 hours against a buffer solution at 4°C. The concentration of DNA stock solution was determined by UV absorbance at 260 nm using a molar absorption coefficient $\varepsilon = 6600\ \text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$. A tris-HCl buffer (Its concentration is 0.05 $\text{mol}\cdot\text{L}^{-1}$ and pH is 7.40, examined by acidometer.) was used to control the pH of the reaction system. All of the samples were dissolved in the Tris-HCl buffer. $MgSO_4\cdot 7H_2O$ was purchased from Chongqing Beibei Chemical Plant, China. L-Tryptophan was purchased from Chengdu-China Kelong Chemical Plant (A.R., China). Vanillin was purchased from Xian-China Chemical Plant (A.R., China) Acridine orange (AO) was purchased from Shanghai-China Medicine Chemical Plant (A.R., China). Other reagents were at least analytical grade and were used without further purification.

Carbon, hydrogen, and nitrogen were obtained using a Vario EL CUBE (Germany). The infrared (IR) spectra (400–4000 cm^{-1}) were recorded as KBr pellets on Spectrum One FTIR system (USA). The absorption spectra were measured on an UV-210 spectrophotometer (Japan). The fluorescence spectra were performed with a FL-4500 spectrofluorophotometer (Japan). Circular dichroism (CD) measurements were recorded on a Jasco-815 spectropolarimeter (Japan). Electrochemical experiments were carried out using a computer controlled model CHI-760C electrochemical workstation (China) with a conventional three-electrode system. The pH was recorded on a pHS-2C digital pH-meter (China) with a combined glass-calomel electrode.

Synthesis of K[HL] and Mg(II) Complex

The Schiff base (K[HL]) derived from vanillin and L-tryptophan was prepared using a method similar to the literature.[12] To a solution of vanillin

(0.180 g, 1.2 mmol) in MeOH (10 cm^3), L-tryptophan (0.204 g, 1 mmol) in MeOH (15 cm^3) containing KOH (0.056 g, 1 mmol) was added. The above solution was then magnetically stirred for 5 hours at 50∼60°C on a water bath. The volume of brownish red solution was reduced in vacuo using rotary evaporator, and then washed with absolute ethanol. After standing for several days yielded black product. Et_2O was added to wash the black product and it was dried in vacuo.

Mg(II)SO_4 (0.5 mmol) was dissolved in MeOH (10 cm^3) and the solution was added dropwise into a (15 cm^3) methanolic solution of K[HL] ligand (0.5 mmol). The above mixture was magnetically stirred for 2 hours at 50∼60°C on a water bath. The volume of above solution was reduced in vacuo using rotary evaporator, and remained about 10 mL. After standing for several days yielded brown product. The brown product obtained was washed with EtOH and dried in vacuo.

Absorption Spectral Measurements

A solution (3 mL) containing an appropriate concentration of K[HL] in 1.0 cm quartz cells was titrated by successive additions of a certain concentration of Mg(II)SO_4 stock solution; and A solution (3 mL) containing an appropriate concentration of Mg(II)L in 1.0 cm quartz cells was titrated by successive additions of a certain concentration of DNA stock solution. Appropriate blanks corresponding to the buffer were used as the reference. The absorption spectra were measured 5 minutes after each addition.

Fluorescence Spectral Measurements

A solution (3 mL) containing an appropriate concentration of AO-DNA in 1.0 cm quartz cells was titrated by stock solution of Mg(II)L. The widths of both the excitation slit and the emission slit were set at 5.0 nm; and the excite wavelength was set at 411.7 nm. The fluorescence spectra were measured 5 minutes after each addition.

Circular Dichroism (CD) Measurements

Circular dichroism (CD) measurements were performed at room temperature on a Jasco-815 spectrophotometer, using 1 cm path-length quartz cells. The CD spectroscopy of DNA and Mg(II)L-DNA were recorded in the range of 200 to 450 nm with a scan rate of 50 $nm \cdot min^{-1}$.

Electrochemical Experiments

Electrochemical experiments were carried out with a conventional three-electrode system. The glassy carbon (GC) electrode was used as the working electrode, a platinum wire as the counter electrode, and an Ag/AgCl electrode as the reference electrode. The GC electrode surface was polished

firstly with Al_2O_3 polishing powder, and then cleaned ultrasonically for 5 minutes in doubly distilled water.

In tris-HCl buffer solution (pH 7.40), an appropriate amount of Mg(II)L solution and DNA were added in sequence and mixed homogeneously. The voltammograms were scanned in a potential range of −1.0 to about 0.0 V (vs. Ag/AgCl), with a scan rate of 0.05 $V \cdot S^{-1}$.

Viscosity Measurements

The viscosity experiments were realized using a viscometer, which was immersed in a thermostat water-bath at room temperature. Different amounts of Mg(II)L were then added into the viscometer to give a value of $c_{Mg(II)L}$ while keeping the DNA concentration constant. The flow times of the samples were repeatedly measured with an accuracy of ±0.2 s by using a digital stopwatch. Each point value was the average of at least three times. The buffer flow time (t_0) was observed, and relative viscosities for DNA in the presence and absence of Mg(II)L were calculated from the relation $\eta = (t–t_0)/t_0$, where t is the observed flow time. The data were presented as $(\eta/\eta_0)^{1/3}$ versus $c_{Mg(II)L}/c_{DNA}$, where η and η_0 are the viscosity of DNA in the presence and absence of Mg(II)L, respectively.

RESULTS AND DISCUSSION

Interaction Between Mg(II) and K[HL]

The absorption spectrum of K[HL] exhibits three absorption bands at 213, 280, and 343 nm regions, respectively. The band at 343 nm region is assigned to π-π^* transition of C=N chromophore.[13] With the addition of $Mg(II)SO_4$, this band was decreased (Figure 1), suggesting the coordination of imino nitrogen with the central metal ion. In order to determine the stoichiometry for Mg(II) with K[HL], the mole ratio method introduced by Yoe and Jones[14] was done. The values of absorbance versus $c_{Mg(II)}/c_{K[HL]}$ molar ratio plotted at 343 nm allow us to find a stoichiometry of $n_{Mg(II)}:n_{K[HL]}$ = 1:1 for the complex (Figure 1).

The IR spectra data of K[HL] and its Mg(II)L complex are listed in Table 1. In the ligand, the band at 1627 cm^{-1} can be assigned to the azomethine stretching vibration ν(C=N). In complex, this band is shifted to 1631 cm^{-1} because of the coordination of the nitrogen to the metal ion.[15] The

TABLE 1 Infrared spectral data of Schiff base ligand and its Mg(II) complex (cm^{-1})

Compound	ν(O−H)	ν(C=N)	ν_{asym}(COO−)	ν_{sym}(COO−)	ν(M−N)	ν(M−O)
$K[HL] \cdot 2H_2O$	3398	1627	1593	1390	–	–
$Mg(II)L(H_2O) \cdot 2H_2O$	3407	1631	1609	1404	622	455

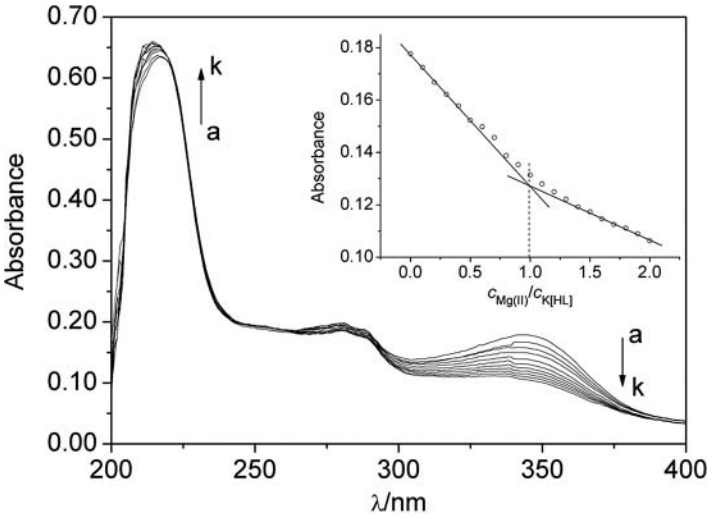
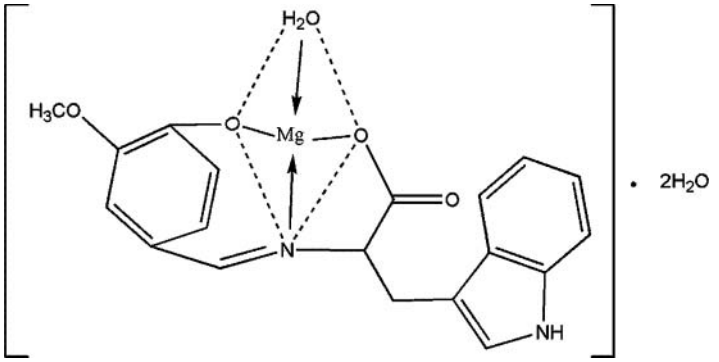


FIGURE 1 Absorption spectra of K[HL] in different concentration of Mg(II)SO_4 (pH 7.40); from curve a–k, $c_{K[HL]} = 2.00 \times 10^{-5}$ mol·L^{-1}, $c_{Mg(II)} = 0.00$, 0.04, 0.08, 0.12, 0.16, 0.20, 0.24, 0.28, 0.32, 0.36, and 0.40×10^{-4} mol·L^{-1}, respectively. Insert: Mole ratio plots of Mg(II)-K[HL] in a tris-HCl buffer (pH 7.40); $c_{K[HL]} = 2.00 \times 10^{-5}$ mol·L^{-1}, $\lambda = 343$ nm.

asymmetric carboxyl stretching ν_{asym}(COO−) and the symmetric carboxyl stretching ν_{sym}(COO−) are shifted to higher frequency at 1609 $cm^{-1}$and 1404 cm^{-1}, respectively, indicating the linkage between the metal ion and carboxylato oxygen atom.[15,16] In the low frequency region, band at 622 cm^{-1} is assigned to ν(M–N) (imino nitrogen) and the band at 455 cm^{-1} is attributed to ν(M–O) (phenolic oxygen, carboxylato oxygen atoms).[17–19] And the broad band at 3398 cm^{-1}, which can be attributed to the stretching vibration of the −OH group. Namely, the spectrum indicates that the Schiff base ligand is coordinated to the central metal atom Mg(II) as tridentate ligand (Scheme 1). The bonding sites are the phenolic oxygen, imino nitrogen



SCHEME 1 The proposed molecular structure of Mg(II)L complex.

and carboxylato oxygen atoms, respectively. Most time, metal centre has d^8 electron configuration, the complex is square planar. Metal centre has d^0, d^{10} (sometime d^9) electron configuration, the complex is tetrahedral. Because Mg^{2+} has d^0 electron configuration, Mg(II)L complex is tetrahedral. Anal. Cal. for Mg(II)$C_{19}H_{16}N_2O_4(H_2O)\cdot 2H_2O$: C, 55.07; H, 5.31; N, 6.76%. Found: C, 53.49.; H, 5.06; N, 6.45%.

Binding of Mg(II)L Complex with DNA

The DNA interaction of metal complexes has been characterized classically through absorption titrations.[20] Simply, if metal complexes interact with DNA, changes in absorbance (hypochromism) and in the position of the band (red shift) should occur. It indicates that metal complexes have intercalated into DNA base pairs, and is involved in a strong interaction in the molecular stack between the aromatic chromophore and the base pairs:[21,22] the empty π^*-orbital of the metal complexes couple with the π^*-orbital of the DNA base pairs, which causes an energy decrease, and a decrease of the π-π^* transition energy.

In this work, a solution (3 mL) containing an appropriate concentration of Mg(II)L in 1.0 cm quartz cells was titrated by successive additions of a certain concentration of DNA solution. Then, the absorption spectra were obtained (Figure 2). With the addition of DNA, the intensity of 200–300 nm regions was increased gradually, but 300–400 nm regions decreased. The hypochromicity indicated the presence of intercalation between Mg(II)L complex and DNA.

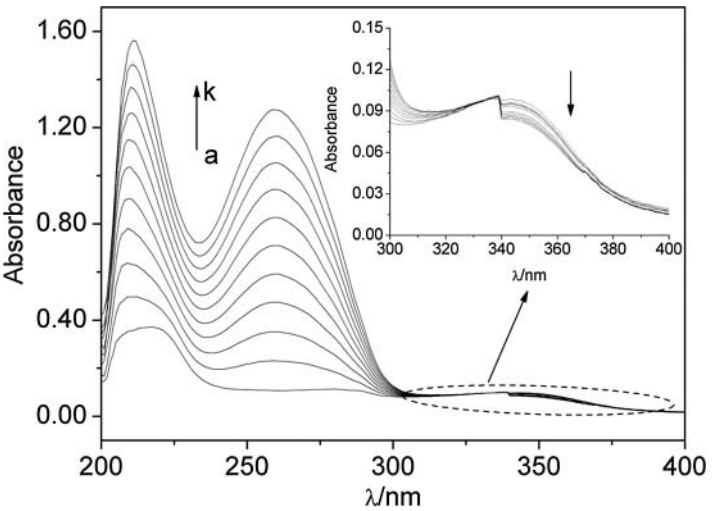


FIGURE 2 Absorption spectra of Mg(II)L in different concentration of DNA (pH 7.40); from curve a–k, $c_{Mg(II)L} = 1.00 \times 10^{-5}$ mol·L^{-1}, $c_{DNA} = 0.00$, 0.04, 0.08, 0.12, 0.16, 0.20, 0.24, 0.28, 0.32, 0.36, and 0.40×10^{-5} mol·L^{-1}, respectively.

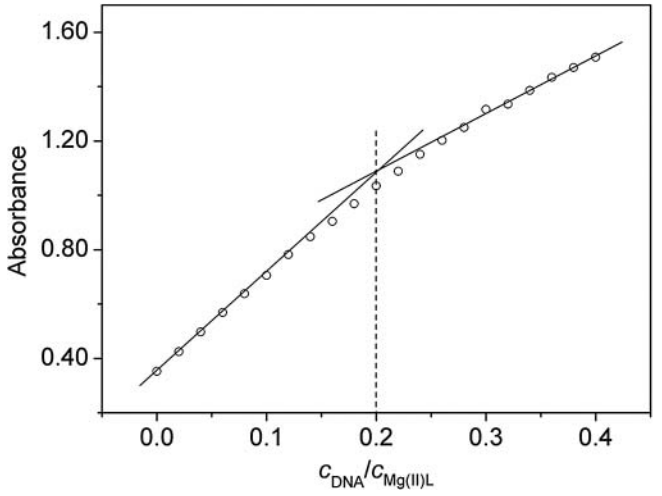


FIGURE 3 Mole ratio plots of Mg(II)L-DNA in a tris-HCl buffer (pH 7.40); $c_{Mg(II)L} = 1.00 \times 10^{-5}$ mol·L^{-1}, $\lambda = 209$ nm.

Additionally, based on the absorbance values obtained in the spectroscopic titration, the mole ratio method experiment[14] was also done at 209 nm. The molar ratio of $n_{Mg(II)L}$:$n_{DNA} = 5$:1 is obtained (Figure 3). According to Lambert-Beer law: $A = \varepsilon bc$, where A is the absorbance of the Mg(II)L-DNA; ε is the apparent molar absorption coefficient of Mg(II)L-DNA; c is the concentration of Mg(II)L-DNA. The apparent molar absorption coefficient of Mg(II)L-DNA was counted: $\varepsilon = 5.43 \times 10^5$ L·mol^{-1}·cm^{-1}.

Thermodynamic Parameters

In order to further characterize the interaction forces between Mg(II)L and DNA, the thermodynamic parameters dependent on temperatures were analyzed at 13 and 37°C, respectively. According to the following relationship:[23–25]

$$1/(A_0 - A) = 1/A_0 + 1/(K \times A_0 \times c_{DNA}), \quad (1)$$

where A_0 and A are the absorbencies of Mg(II)L in the absence and in the presence of DNA, respectively. K is the binding constant between Mg(II)L and DNA, c_{DNA} refers to the concentration of DNA. The plots of $1/(A_0 - A)$ versus $1/c_{DNA}$ were linear (at 13 and 37°C, respectively.) and the binding constants were calculated from the ratio of the intercept on the vertical (Figure 4): $K^{\theta}_{B13°C} = 4.32 \times 10^4$ L·mol^{-1}, $K^{\theta}_{B37°C} = 2.92 \times 10^5$ L·mol^{-1}. This suggests that increasing temperature benefits Mg(II)L binding with DNA.

The thermodynamic parameters of binding reaction are the main evidence for confirming the binding force.[26] If the enthalpy change (ΔH)

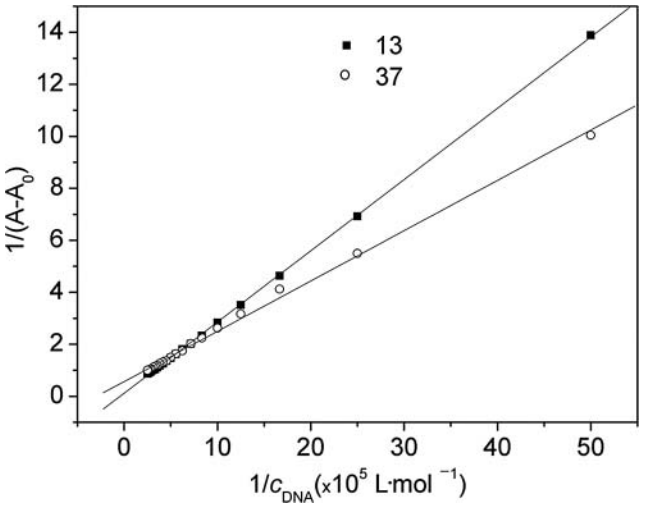


FIGURE 4 Double reciprocal plots of Mg(II)L-DNA in a tris-HCl buffer(pH 7.40) at 13 and 37°C, respectively; $c_{\mathrm{Mg(II)L}} = 1.00 \times 10^{-5}$ mol·L^{-1}.

does not vary significantly over the temperature range studied, then standard molar reaction enthalpy ($\Delta_r H_m^\ominus$) value can be determined from the van't Hoff equation:

$$\ln K_2^\ominus / K_1^\ominus = -\Delta_r H_m^\ominus (1/T_2 - 1/T_1)/R, \tag{2}$$

where $K_1^\ominus$ and $K_2^\ominus$ are the standard binding constant of Mg(II)L and DNA at 13 and 37°C, respectively. T_1 is 286.15 K, T_2 is 310.15 K. Then $\Delta_r H_m^\ominus$ is 5.87×10^4 J·mol^{-1}. This result shows that the binding of Mg(II)L to DNA is endothermic.

The standard molar reaction Gibbs free energy ($\Delta_r G_m^\ominus$) and the standard molar reaction entropy ($\Delta_r S_m^\ominus$) are estimated from the following relationship:

$$\Delta_r G_m^\ominus = \Delta_r H_m^\ominus - T\Delta_r S_m^\ominus \tag{3}$$

$$\Delta_r G_m^\ominus = -RT\mathrm{In}K^\Theta, \tag{4}$$

where T is 286.15 K; $K^\ominus$ is the standard binding constant of Mg(II)L and DNA at 13°C. Then $\Delta_r G_m^\ominus$ is -2.54×10^4 J·mol^{-1} and $\Delta_r S_m^\ominus$ is 294.08 J·mol^{-1}·K^{-1}. The negative value of $\Delta_r G_m^\ominus$ as observed supports that the binding process is spontaneous, while the positive $\Delta_r H_m^\ominus$ and $\Delta_r S_m^\ominus$ values associated with the interaction of Mg(II)L with DNA indicate that the binding is mainly entropy driven and the enthalpy is unfavorable for it.

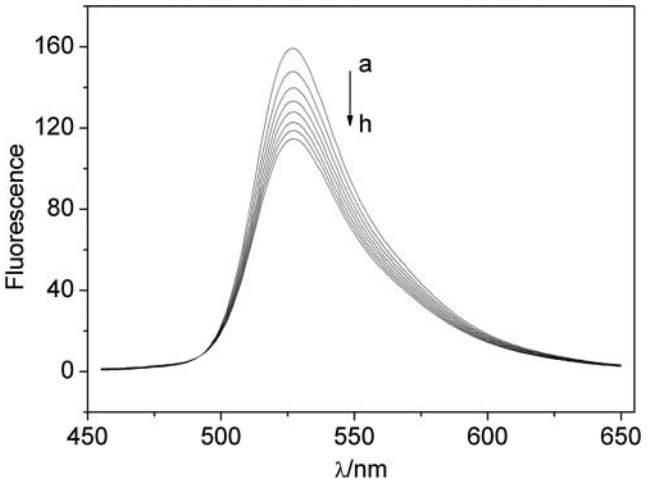


FIGURE 5 Emission spectra of DNA-AO in different concentration of Mg(II)L (pH 7.40; $\lambda_{ex} = 411.7$ nm); from curve a–h, $c_{DNA\text{-}AO} = 2.00 \times 10^{-6}$ mol·L^{-1}, $c_{Mg(II)L} = 0.00$, 0.02, 0.04, 0.06, 0.08, 0.10, 0.12 and 0.14×10^{-4} mol·L^{-1}, respectively.

Competitive Binding Between AO and Mg(II)L Complex for DNA

The fluorescence method can give some information of the binding between metal complexes and DNA. In order to test if Mg(II)L complex could bind to DNA by intercalation, acridine orange (AO) was employed. Because of its planar aromatic chromophore, it can insert between two adjacent base pairs in a DNA helix.[27] Competitive binding of metal complexes to DNA and AO will result in displacement of bound AO and a decrease in the fluorescence intensity.[28]

The emission spectra of AO bound to DNA in the absence and the presence of Mg(II)L are given in Figure 5. The fluorescence intensity of DNA-AO decrease with the concentration of Mg(II)L increased. This phenomenon suggests that AO was substituted by Mg(II)L in DNA-AO system which led to a decrease in the emission intensity of DNA-AO system. It is indicated the presence of intercalation between Mg(II)L complex and DNA,[29] which is consistent with the above results.

Circular Dichroism Spectroscopy

CD spectroscopy is useful in diagnosing DNA interaction of metal complexes, as the positive band due to base stacking and the negative one due to right-handed helicity are quite sensitive to the interaction mode of DNA with small molecules.[30,31] The changes in CD signals of DNA observed on interaction with drugs may often be assigned to the corresponding changes in DNA structure.[32] Simple groove binding and electrostatic interaction show less or no perturbation on the base-stacking and helicity bands, while

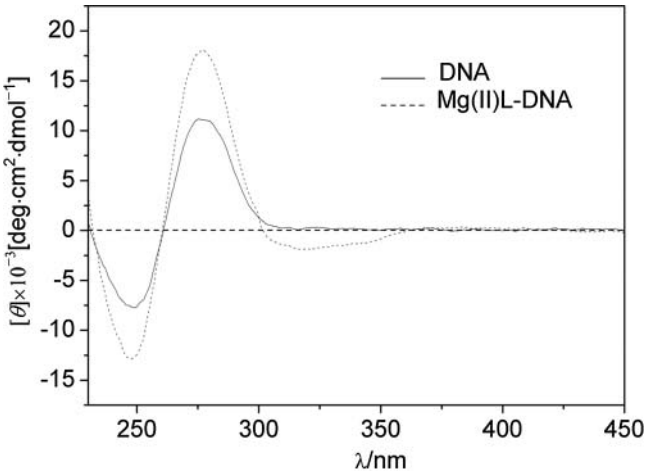


FIGURE 6 Circular dichroism spectra of DNA in the presence of Mg(II)L complex; $c_{DNA} = 1.00 \times 10^{-5}$ mol·L^{-1}, $c_{Mg(II)L} = 5.00 \times 10^{-5}$ mol·L^{-1}.

intercalation enhances the intensities of both the bands stabilizing the right-handed B conformation of CT-DNA as observed for the classical intercalator methylene blue.[33] In the presence of Mg(II)L complex, the CD spectrum of DNA undergoes changes in both the positive and negative bands (Figure 6). The opposite band at 276 nm and negative band at 247 nm indicates that the DNA remains right-handed. And the intensity of both bands is increased in relevance to that of free DNA, which is typical of intercalation involving π-stacking. Thus, the CD spectral results are consistent with the intercalative mode of DNA binding for Mg(II)L complex.

Cyclic Voltammetry

In order to further investigate the interaction between Mg(II)L and DNA, cyclic voltammetry was employed. Figure 7 shows the cyclic voltammogram of Mg(II)L in tris-HCl buffer solution within the potential range of $0.0 \leq E/V \leq -1.0$. From Figure 7, a well-defined cathodic current peak was observed at -0.648 V but no corresponding anodic peak (curve a). It suggests that the electrode reaction of Mg(II)L is an irreversible process. As shown in Figure 7, on addition of different amounts of DNA, peak current was decreased, indicating that an electrochemically nonactive complex could have been formed.[34] And peak potential shift towards negative direction, suggesting the existence of electrostatic interaction between Mg(II)L and DNA.[35,36]

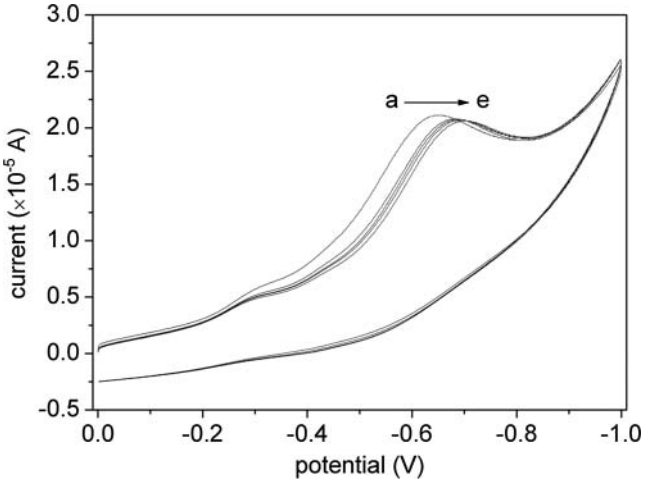


FIGURE 7 Cyclic voltammograms of Mg(II)L in the absence and presence of DNA; from curve a-e, $c_{Mg(II)L} = 2.00 \times 10^{-5}$ mol·L^{-1}, $c_{DNA} = 0.00$, 0.40, 0.80, 0.12, and 0.16×10^{-5} mol·L^{-1}.

Viscosity Method

In addition to spectroscopy and cyclic voltammetry methods, viscosity experiment was performed, which is regarded as less ambiguous and the most critical test for a DNA binding model in solution, and provides stronger arguments for intercalation mode.[37,38] A classical intercalation mode is known to cause a significant increase in the viscosity of a DNA solution, as base pairs are separated to accommodate the binding ligand. In contrast, a partial intercalation mode could bend (or kink) the DNA helix, resulting in

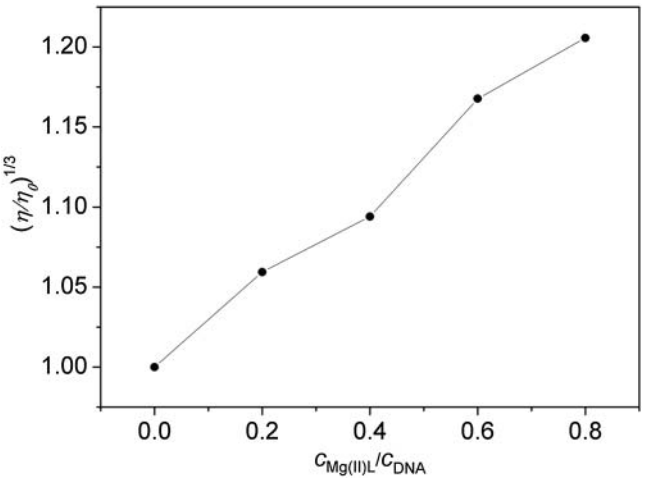


FIGURE 8 Effect of increasing amounts of Mg(II)L on the relative viscosities of DNA; $c_{DNA} = 1.00 \times 10^{-4}$ mol·L^{-1}.

the decrease of the effective length and viscosity. And the dis-intercalation binding causes no obvious increase of DNA viscosity.[38,39]

The values of $(\eta/\eta_0)^{1/3}$ (where η_0 and η are the specific viscosity contributions of DNA in the absence and in the presence of the Mg(II)L, respectively) were plotted against $c_{\mathrm{Mg(II)L}}/c_{\mathrm{DNA}}$ (Figure 8). With increasing the amounts of Mg(II)L complex, the increased relative viscosity of DNA indicates the intercalation of Mg(II)L into DNA. Such behavior further suggest that intercalation should be the interaction mode between Mg(II)L complex and DNA.

CONCLUSIONS

A Schiff base complex of Mg(II) was synthesized and its DNA-binding behavior was evaluated by spectroscopy, cyclic voltammetry and viscosity methods, where the Schiff base was derived from vanillin and L-tryptophan. The experimental results suggest that Mg(II)L could bind to DNA mainly with intercalation and involving some electrostatic interaction. In addition, the binding constants of Mg(II)L with DNA($K^{\mathrm{o}}_{\mathrm{B}13^{\circ}\mathrm{C}} = 4.32 \times 10^4\ \mathrm{L{\cdot}mol^{-1}}$ and $K^{\mathrm{o}}_{\mathrm{B}37^{\circ}\mathrm{C}} = 2.92 \times 10^5\ \mathrm{L{\cdot}mol^{-1}}$) were obtained, and the thermodynamic parameters ($\Delta_{\mathrm{r}}H^{\mathrm{o}}_{\mathrm{m}} = 5.87 \times 10^4\ \mathrm{J{\cdot}mol^{-1}}$, $\Delta_{\mathrm{r}}G^{\mathrm{o}}_{\mathrm{m}} = -2.54 \times 10^4\ \mathrm{J{\cdot}mol^{-1}}$ and $\Delta_{\mathrm{r}}S^{\mathrm{o}}_{\mathrm{m}} = 294.08\ \mathrm{J{\cdot}mol^{-1}{\cdot}K^{-1}}$) were calculated as well. This work will be helpful to enrich the binding information between amino acid Schiff base complexes and DNA.

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