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NOTE

Synthesis and Calf-thymnus DNA Interaction Studies of Ni(II)L Complex

JIAN-HONG BI*, WEN-BO TAO† and LIN WANG
Deparment of Chemistry and Chemical Engineering, Hefei Normal University, Hefei, P.R. China
E-mail: bi010101@126.com

The tetraza macrocyclic nickel(II)L complex, L = 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazamacrocyclic-4,11-diene$(ClO_4)_2$, was synthesized by hydrothermal method and characterized by IR spectra and elemental analysis. The interaction of nickel(II)L with calf thymus DNA was studied using UV-vis spectrum, fluorescence-based assays and viscometry. All experimental results indicated that the complex interacted with DNA by the main mode of interaction between nickel(II)L and DNA is a partial intercalation mode.

Key Words: Tetraza macrocycle, Nickel(II) complex, Synthesis, DNA, Intercalation.

The studies of small molecule complexes interaction with DNA is great practical significance. On one hand, this interaction can be used as a biological probe established highly sensitive analysis determination method of DNA. On the other hand, these small molecule complexes can be used as targeted molecules to research the role model, mechanism and the relationship of biological activity of they interactions with DNA[1-4].

In this paper, the tetraza macrocyclic nickel(II)L complex, L = 5,5,7,12, 12,14-hexamethyl-1,4,8,11-tetraazamacrocyclic-4,11-diene$(ClO_4)_2$, was synthesized by hydrothermal method. The interaction of nickel(II)L with calf thymus DNA was studied using viscometry, UV-vis and fluorescence spectrum.

All reagents were of AR grade and used without further purification. The nickel(II)L complex was characterized by IR spectra spectrophotometer (Nexus-870) and elemental analyzer (Elementar Vario EL-III). Calf thymus DNA was supplied by Huamei Chemical (China). The UV-vis spectra, fluorescence spectra and viscosity measurements were recorded using UV-2550, F-4500 FL spectrophotometers and ubbelodhe viscosity gauge. All experiments were carried out at 25 ºC. Water was double distilled. All solutions were deoxygenated *via* purging with argon for 1 min prior to measurement.

Synthesis: The L$(ClO_4)_2$, was synthesized according to the reported literature[5]. A mixture of 10 mL methanol solution of L (1 mmol) and 10 mL H_2O solution of $Ni(OAc)_2{\cdot}4H_2O$ (1 mmol), were carried out in a autoclave and heated to 80 ºC for

†Pharmaron Beijing Limited Co., No.18, South Xihuan Road, BDA, Beijing, 100176, P.R. China.

72 h. After cooling, the product was obtained as yellow bulk crystals. IR spectrum (KBr, cm^{-1}): 3478 (N-H); 1663 (C=N); 1088, 625($C1O_4^-$). Elemental analysis (%): calcd. (found); C, 35.72 (35.90); H, 5.99 (5.88); N, 10.41 (10.21).

Spectroscopy studies of the interaction: UV-Vis and fluorescence spectra are most suitable to interaction studies related to small molecule complexes interaction with DNA. The spectra of the nickel(II)L (1×10^{-4} mmol/L) aqueous solution and the mixture solution of nickel(II)L (1×10^{-4} mmol/L, 10 mL) and DNA(1×10^{-4} mmol/L, 10 mL) were recorded at 25 ºC after the complex had been incubated with DNA for 0.5 h at 25 ºC by UV-2550 and F-4500 FL spectrophotometers at pH 6.86.

Viscosity studies of the interaction: Viscosity measurements were performed after complexes had been incubated with DNA for 0.5 h at 25 ºC with a ubbelohde viscometer. Flow time was measured with a digital stopwatch at 25.0 ± 0.1 ºC in a constant temperature bath. C_{DNA} is 5×10^{-5} mmol/L and $C_{nickel(II)L}$ is changed. The data were reported as $(\eta/\eta_0)^{1/3}$ *versus* the $C_{Nickel(II)L}/C_{DNA}$ ratio, where η_0 refers to the viscosity of the DNA aqueous solution alone.

Spectroscopy studies of the interaction between the nickel(II)L and DNA: Typical UV-vis absorption spectra and fluorescence spectra of nickel(II)L for a aqueous solution without DNA and in the presence of DNA are shown in Figs. 1 and 2. The relative viscosity of the interaction between the nickel(II)L and DNA is

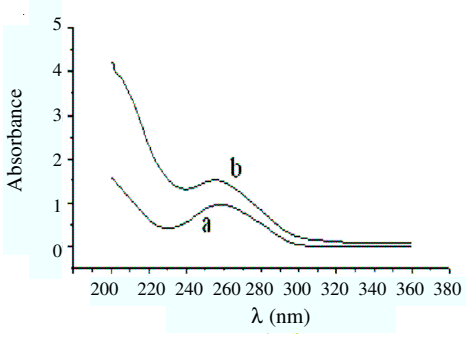

Fig. 1. UV Spectrum of nickel(II)L (a) and Ni(II)L + CT-DNA (b, $C_{Nickel(II)L}/C_{DNA}$ = 1:1)

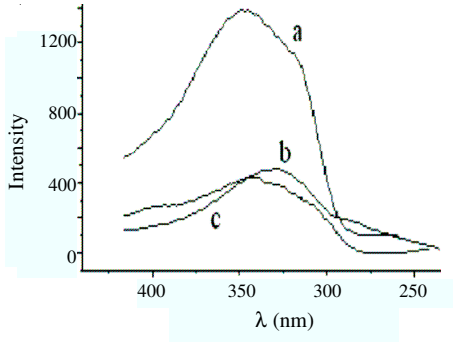

Fig. 2. Fluorescence spectra of CT-DNA (a), Ni(II)L (b) and Ni(II)L + DNA (c)

shown in Fig. 3, respectively. Fig. 1 shows that nickel(II)L complex exhibits a typical absorption band at 258 nm and increases little in the presence of DNA($C_{nickel(II)L}/C_{DNA}$ = 1:1). It may be deduced that nickel(II)L complex interacts with DNA by part intercalation[6]. Fig. 2 indicates the fluorescence spectra curves of DNA, nickel(II)L and nickel(II)L in the presence of DNA($C_{Nickel(II)L}/C_{DNA}$ = 1:1). When the complex was added into the solution, the DNA fluorescence was quenches and the quenches constant K is 4.3×10^3. It indicates that the weak intercalation interaction between the nickel(II)L and DNA had happened[7,8]. In Fig. 3, the specific viscosity of the DNA sample increases weakly with the addition of the nickel(II)L

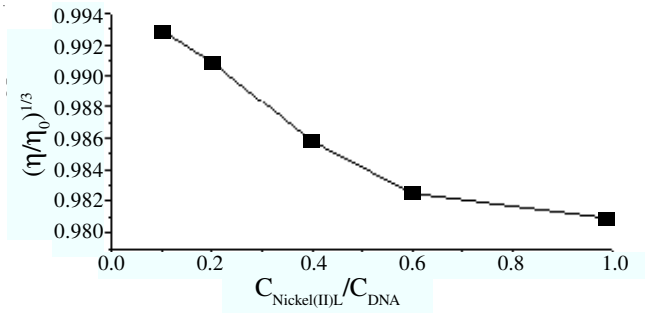

Fig. 3. Relative viscosity of the interaction of nickel(II)L and CT-DNA

complex, which is indicative of the complex insertion between base pairs[9]. This experimental results are consistent with that of UV-vis spectra and fluorescence spectra measurements. So, it is deduced that the main mode of interaction between nickel(II)L and CT-DNA is a partial intercalation mode.

Conclusion

In summary, a tetraza macrocyclic nickel(II) complex was synthesized by hydrothermal method. The interaction of the complex with CT-DNA were studied by UV-vis spectrum, fluorescence-based assays and viscometry. The experimental results indicate that the main mode of interaction between nickel(II)L and CT-DNA is a partial intercalation mode.

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REFERENCES

1. B. Norden, P. Lincoln, B. Akermann and E. Tuite, in ed.: H. Sigel, Metal Ions in Biological Systems, Marcel Decker, New York (1996).
2. A.E.F. Nassar and J.E. Rusling, *J. Am. Chem. Soc.*, **118**, 3043 (1996).
3. U.S. Singh, R.T. Scannell, H. An, B.J. Carter and S.M. Hecht, *J. Am. Chem. Soc*., **117**, 12691 (1995).
4. M.J. Abalson and W. Stubbe, *J. Biochem*., **34**, 2076 (1995).
5. J.H. Bi, Y. Chen, Z.X. Huang, M. Cui and N.L. Hu, *Asian J. Chem*., **20**, 4887 (2008).
6. J.B. Lepecq and C. Paoletti, *J. Mol. Biol*., **27**, 87 (1967).
7. J.W. Kang, H.X. Wu, X.Q. Lu, Y.S. Wang and L. Zhou, *Spectrochim. Acta*, **62A**, 2041 (2005).
8. B.C. Baguley and M. LeBert, *Biochemistry*, **23**, 937 (1984).
9. S. Kashanian and J.E.N. Dolatabadi, *Food Chem*., **116**, 743 (2009).

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