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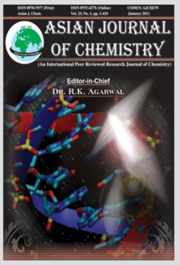

NOTE

Hydrothermal Synthesis and DNA Interaction Studies of Copper(II)L Complex

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The tetraazamacrocyclic complex of copper with the composition Cu(II)L, 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 Cu(II)L with calf thymus DNA was studied using viscometry, fluorescence and UV-VIS spectra. Results indicated that the Cu(II)L interacted with DNA is a partial intercalation mode.

Key Words: Synthesis, Tetraazamacrocycle, Copper(II) complex, DNA, Intercalation.

In recent years, the studies on transition metal complexes and DNA interaction has become an attractive research field[1,2]. Because the combination of transition metal complexes and DNA and possible DNA damage are closely related to the genetic mutations of biological system and cancer generating process[3,4].

In this paper, the tetraazamacrocyclic complex, copper(II)L, 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 Cu(II)L with calf thymus DNA was studied using viscometry, fluorescence and UV-VIS spectra.

All reagents were of AR grade and used without further purification. Calf thymus DNA was supplied by Huamei Chemical (China). The complex Cu(II)L was characterized by elemental analyzer (Elementar Vario EL-III) and IR spectra spectrophotometer (Nexus-870). The viscosity measurements, fluorescence and UV-VIS spectra, were recorded using Ubbelodhe viscosity gauge, F-4500 FL and UV-2550 UV spectrophotometers. The electrical conductivities of 1 × 10^{-3} mol/L solutions in DMF were obtained on a DDS-11A conductometer at 25 ºC. All experiments water was double distilled.

Synthesis of Cu(II)L: The L(ClO_4)$_2$ was synthesized according to the literature[5], IR spectrum (KBr, ν_{max}, cm^{-1}): 3192 (N-H); 1663 (C=N); 1080, 627 ($C1O_4^-$). m.p. 85.5-87.0 ºC.

A mixture of 1 mmol L(ClO_4)$_2$ and 1 mmol Cu(OAc)$_2$·H_2O and 20 mL H_2O, were carried out in a autoclave and heated to 80 ºC for 72 h. After cooling, the product was obtained as purple flake crystals. IR spectrum (KBr, ν_{max}, cm^{-1}): 3445 (N-H); 1672 (C=N); 1086, 626 (ClO_4^-). Elemental analysis (%) calcd. for $C_{16}H_{32}N_4O_8Cl_2Cu$: C, 35.40; H, 5.94; N,10.32. Found: C, 35.71; H, 6.08; N, 10.23. The molar conductive values for the complexes in DMF solution is 135 S cm^2 mol^{-1} and suggest them to be 1:2 electrolytic nature[6].

Viscosity studies of the interaction: Viscosity measurements were carried out after Cu(II)L had been reacted with DNA for 0.5 h at 25 ± 0.1 ºC with a Ubbelohde viscometer. In a constant temperature bath, flow times were measured with a digital stopwatch. C_{DNA} is 5 × 10^{-5} mol/L and $C_{Cu(II)L}$ is changed. The data were reported as $(\eta/\eta_0)^{1/3}$ *versus* the $C_{Cu(II)L}/C_{DNA}$ ratio, where η_0 refers to the viscosity of the DNA aqueous solution alone.

Spectroscopy studies of the interaction: The fluorescence and UV-VIS spectra of the Cu(II)L (1 × 10^{-4} mol/L) aqueous solution and the mixture solution of Cu(II)L (1 × 10^{-4} mol/L, 10 mL) and DNA (1 × 10^{-4} mol/L, 10mL) were recorded at 25 ± 0.1 ºC after the complex had been reacted with DNA for 0.5 h by F-4500 FL and UV-2550 spectrophotometers at pH = 6.86.

Spectroscopy studies of the interaction between the copper(II)L and DNA: Typical fluorescence and UV-VIS spectra of Cu(II)L for the aqueous solution without and in the presence of DNA are illustrated in Figs. 1 and 2. The relative viscosity of the reaction between the Cu(II)L and DNA is shown in Fig. 3, respectively. Fig. 1 indicates the fluorescence spectra curves of DNA(A), Cu(II)L(B) and Cu(II)L + DNA(C) ($C_{Cu(II)L}/C_{DNA}$ = 1:1). When the complex was added into the solution, the DNA fluorescence was quenches and the quenches constant K = 4.0×10^3. It shows that the weak intercalation interaction between the Cu(II)L and DNA had happened[7,8]. Fig. 2 shows that complex Cu(II)L exhibits a typical absorption band at λ = 258 (nm) and increases little in the presence of DNA ($C_{Cu(II)L}/C_{DNA}$ = 1:1). It may be indicated that the complex interacts with DNA by part intercalation[9]. In Fig. 3, the specific viscosity of the DNA sample increases weakly with the addition of the Cu(II)L complex, which is indicative of the complex insertion between base pairs[10].

So, it is deduced that the main mode of interaction between Cu(II)L and DNA is present in a partial intercalation mode.

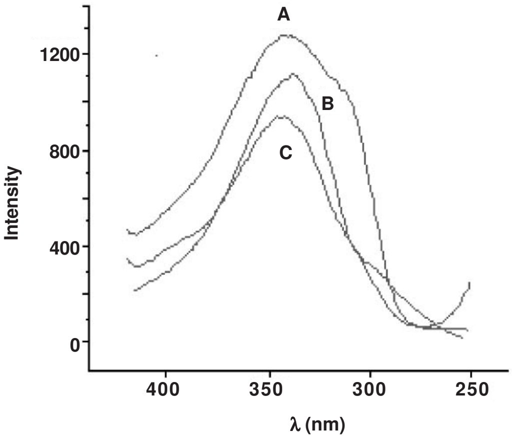

Fig. 1. Fluorescence spectra of DNA(A), Cu(II)L(B) and Cu(II)L + DNA(C)

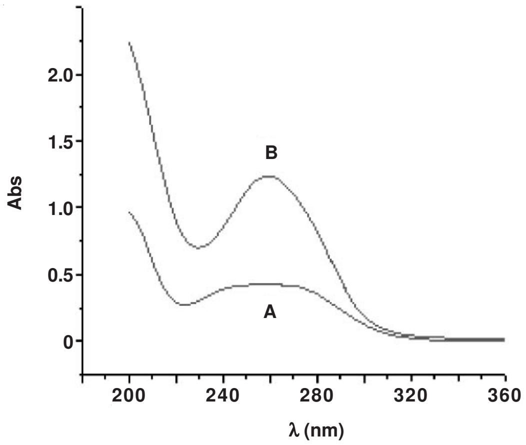

Fig. 2. UV Spectra of Cu(II)L(A) and Cu(II)L + DNA(B, $C_{Cu(II)L}/C_{DNA}$ = 1:1)

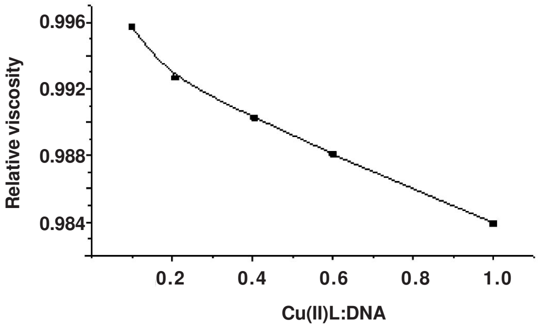

Fig. 3. Relative viscosity of the interaction of Cu(II)L and DNA

Conclusion

In summary, a tetraazamacrocyclic complex Cu(II)L was synthesized by hydrothermal method. The interaction of the complex with DNA were studied by fluorescence, UV-VIS spectra and viscometry. The experimental results indicate that the main mode of interaction between Cu(II)L and DNA is a partial intercalation mode.

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. J.H. Bi, W.B. Tao and L. Wang, *Asian J. Chem.*, **22**, 8270 (2010).
3. S.S. Matkar, L.A. Wrischnik, P.R. Jones and U. Hellmann-Blumberg, *Biochem. Biophys. Res. Commun.*, **343**, 754 (2006).
4. J.H. Bi, M. Li, F.H. Yao and Y. Chen, *Asian J. Chem.*, **22**, 7343 (2010).
5. G.A. Meison, Coordination Chemistry of Macrocyclic Compounds, Plenum, New York (1979).
6. W.J. Geary, *Coord. Chem. Rev.*, **7**, 81 (1971).
7. J.W. Kang, H.X. Wu, X.Q. Lu, Y.S. Wang and L. Zhou, *Spectrochim. Acta A*, **61**, 2041 (2005).
8. B.C. Baguley and M. Lebert, *Biochemistry*, **23**, 937 (1984).
9. S.A. Tysoe, R.J. Morgan, A.D. Baker and T.C. Strekas, *J. Phys. Chem.*, **97**, 1707 (1993).
10. J.B. Lepecq and C. Paoletti, *J. Mol. Biol.*, **27**, 87 (1967).