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Electrochemical Study on the Interaction Between the Macrocyclic Copper(II) and Nickel(II) Complexes and Calf thymus DNA

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The interaction of the two tetraazamacrocyclic transition-metal complexes, $ML(ClO_4)_2$ (M = Cu^{2+}, Ni^{2+}, L = 5,12-dimethyl-7,14-diphenyl-1,4,8,11-tetraazamacrocyclic-4,11-diene) with calf thymus-DNA (CT-DNA) were studied by cyclic voltammetry. In the presence of CT-DNA, the oxidion peaks of $[CuL]^{2+}$ and $[NiL]^{2+}$ shifted to more positive values and the peak current increased significantly. The experimental results indicate that the two complexes could interact with CT-DNA mainly by intercalation binding mode.

Key Words: Azamacrocyclic transition-metal complex, DNA, Cyclic voltammetry, Intercalation.

INTRODUCTION

Binding studies of transition metal complexes have become a very important field in the development of DNA molecule probes and chemotherapeutics[1,2]. Schiff base macrocyclic polyamine transition-metal complexes have been subjects of numerous investigations in recent years[3,4]. These complexes have unusual functions, such as, in the treatment of cancer, as antibactericide agents, as antivirus agents, as fungicide agents and for other biological properties[5-7]. Recently, electrochemical methods have been used to study the interactions of DNA with other small molecules in solution[8,9].

In this paper, the interaction of the two tetraazamacrocyclic transition-metal complexes, $ML(ClO_4)_2$ (M = Cu^{2+}, Ni^{2+}, L = 5,12-dimethyl-7,14-diphenyl-1,4,8,11-tetraazamacrocyclic-4,11-diene) with Calf thymus DNA (CT-DNA) have been investigated by electrochemistry method, which was simpler, faster and needed less CT-DNA samples.

EXPERIMENTAL

All reagents were of AR grade and used without further purification. The 5,12-dimethyl-7,14-diphenyl-1,4,8,11-tetraazamacrocyclic-4,11-diene (L) and its copper(II)

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and nickel(II) complexes $CuL(ClO_4)_2$ and $NiL(ClO_4)_2$ were synthesized according to the reported literature[10,11]. Calf thymus DNA obtained from Huamei Chemical (China). Water was double distilled. Cyclic voltammetric measurements of $CuL(ClO_4)_2$ and $NiL(ClO_4)_2$ were accomplished with CHI 660B(CHInstrument, shanghai, China) and LK2005 (Electrochemical analyzer, Tianjin Lanlike Instrument Company, China). The three-electrode system was composed of a glassy carbon electrode (GCE) as working electrode, an electrode Ag/AgCl as the reference electrode and a platinum electrodeas auxiliary electrode. All experiments were carried out at 25 ºC. All solutions were deoxygenated *via* purging with Ar for 20 min prior to measurement.

Electrochemical studies of the interaction between $CuL(ClO_4)_2$ and CT-DNA: Different quantities of 1.00×10^{-3} mol L^{-1} complex $CuL(ClO_4)_2$ were added to 5 mL DMF. The differential pulse voltammetry and cyclic voltammetry curves were recorded on a CHI660B electrochemical analyzer with the three-electrode system described above. Then different quantities of CT-DNA were added to the solution followed by recording the CV curves. The potential scanning range is from -1.5 to 0.6 V. The scanning rate is 0.2 V s^{-1}. The sample interval is 0.001 V and the quiet time is 2 s.

Electrochemical studies of the interaction between $NiL(ClO_4)_2$ and CT DNA: Different quantities of 5.00×10^{-3} mol L^{-1} complex $NiL(ClO_4)_2$ were added to 5 mL DMF. The differential pulse voltammetry and cyclic voltammetry curves were recorded on a LK2005 electrochemical analyzer with the three-electrode system described above. Then different quantities of CT-DNA were added to the solution followed by recording the CV curves. The potential scanning range is from -1.2 to 0.5 V. The scanning rate is 0.2 V s^{-1}. The sample interval is 0.001 V and the quiet time is 2 s.

RESULTS AND DISCUSSION

Determination of the electrochemical analysis conditions

Effect of solvent: DMF, acetonitrile, acetone, methanol and water were used as solvent. Among them, scanning results show that DMF is best solvent for $CuL(ClO_4)_2$ and $NiL(ClO_4)_2$ in cyclic voltammetric analysis.

Effect of pH: The relationship between the pH value and the variation of the peaks current (ΔI_{pa}) of $[CuL]^{2+}$ and $[NiL]^{2+}$ before and after adding DNA was studied. Consequently, 2.76 and 6-7 were chosen for $[CuL]^{2+}$ and $[NiL]^{2+}$, respectively as the best pH values of the reactions.

Effect of scanning rate: The relationship between I_{pa} and scanning rate was studied. I_{pa} of $[CuL]^{2+}$ and $[NiL]^{2+}$ were directly proportional to the square root of the scanning rate in the range from 0.01 to 0.20 V s^{-1}, which indicates that the electrode process of the complexes are controlled by the diffusion of $[CuL]^{2+}$ and $[NiL]^{2+}$ on the electrode surface. Therefore 0.2 V s^{-1} is suitable scanning rate for the electrode reactions of the $[CuL]^{2+}$ and $[NiL]^{2+}$.

Electrochemical studies of the interaction between the complexes and DNA: Typical cyclic-voltammetric behavior of $[CuL]^{2+}$ and $[NiL]^{2+}$ for a solution without CT-DNA and in the presence of CT-DNA are shown in Figs. 1 and 2, respectively.

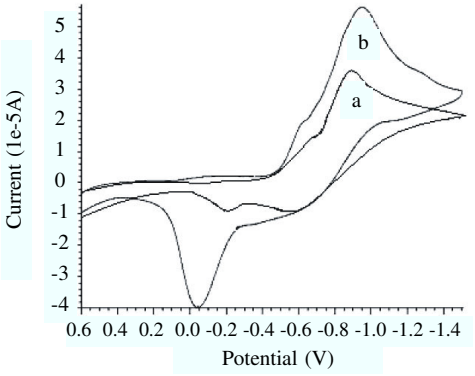

Fig. 1. Cyclic voltammograms of 1×10^{-5} mol/L $[CuL]^{2+}$, in the (a) absence and (b) presence of CT-DNA ($C_{DNA} = 5 \times 10^{-3}$ g/L)

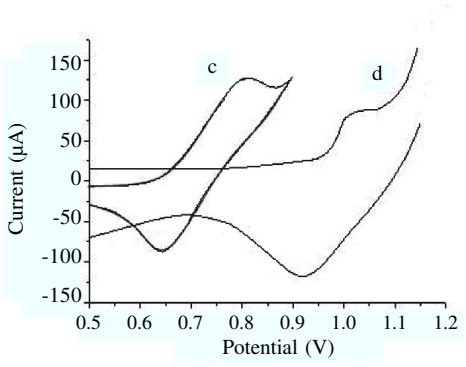

Fig. 2. Cyclic voltammograms of 5×10^{-3} mol/L $[NiL]^{2+}$, in the (c) absence and (d) presence presence of CT-DNA ($C_{DNA} = 3 \times 10^{-1}$ g/L)

The cyclic voltammetry curves of $CuL(ClO_4)_2$ are shown in Fig. 1. In the absence of CT-DNA (Fig. 1a), there are two oxidation peaks and one reduction peak. The Epc(1), Epc(2), Epa, ΔEp(1) and ΔEp(1) are -0.21, -0.58, -0.89, 0.68 and 0.31 V, respectively. In the presence of CT-DNA (Fig. 1b), the Epc, Epa and ΔEp are -0.05, -0.95 and 0.9 V, respectively. It can be seen that the currents of $[CuL]^{2+}$ were increased greatly and the oxidation and reduction peaks potential shifted to more positive and negative values *vs.* a solution without CT-DNA. This indicated that the macrocyclic cooper(II) complex could interact with DNA molecules.

The cyclic voltammetry curves of $NiL(ClO_4)_2$ are shown in Fig. 2. In the absence of CT-DNA (Fig. 2c), it could be seen that there are a pair of quasi-reversible redox peaks. The Epc, Epa and ΔEp are 0.64, 0.81 and 0.17 V. In the presence of CT-DNA (Fig. 2d), the Epc, Epa and ΔEp are 0.92, 1.01 and 0.09 V. It can be seen that the oxidation peak current of $[NiL]^{2+}$ were increased dramatically and the redox peaks potential shifted to more positive values *vs.* a solution without CT-DNA. This indicated that the macrocyclic nickel(II) complex could interact with DNA molecules.

According to Bard *et al.*[12], if the peak potential shifted to more positive value when small molecules interacted with DNA, the binding mode was the intercalation. The experimental results suggest that the two macrocyclic complexes could interact with CT-DNA mainly by intercalative binding, which provide useful information for further study on designing new antitumor drugs.

Conclusion

The experimental results indicate that the macrocyclic copper(II) and nickel(II) complexes could interact with CT-DNA mainly by intercalative binding mode, which provide useful information for further study on designing new antitumor drugs.

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REFERENCES

1. D.S. Sigman, A. Mazumder and D.M. Perrin, *Chem. Rev.*, **92**, 2295 (1993).
2. B.H. Geierstanger, M. Mrksich, P.B. Dervan and D.E. Wemmer, *Science*, **266**, 646 (1994).
3. J.H. Bi, *Acta Cryst.*, **E65**, m633 (2009).
4. J.H. Bi, W.T. Bi, Z.X. Huang and N.L. Hu, *Asian J. Chem.*, **21**, 6619 (2009).
5. V. Elangovan, N. Sekar and S. Govindasamy, *Cancer Lett.*, **87**, 107 (1994).
6. A.S. Sitlani, E.C. Long and J.K. Barton, *J. Am. Chem. Soc.*, **114**, 2303 (1992).
7. Y.M. Song, Q. Wu, P.J. Yang, N.N. Luan, L.F. Wang and Y.M. Liu, *J. Inorg. Biochem.*, **100**, 1685 (2006).
8. Y.M. Temerk, M.S. Ibrahim and M. Kotb, *Spectrochim. Acta A*, **71**, 1830 (2009).
9. H. Li, W.J. Mei, Z.H. Xu, D.W. Pang, L.N. Ji and Z.H. Lin, *J. Electroanal. Chem.*, **600**, 243 (2007).
10. J.H. Bi, Z.X. Huang and B.Z. Li, *Asian J. Chem.*, **21**, 6610 (2009).
11. J.H. Bi, J.M. Song, Z.X. Huang, Y.H. Wang, L.T. Kong and N.L. Hu, *Asian J. Chem.*, **18**, 2365 (2006).
12. A.J. Bard, M.T. Carter and M. Rodriguez, *J. Am. Chem. Soc.*, **111**, 8901 (1989).

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