



Synthesis, Crystal Structure and DNA-Binding Property of Mononuclear Mn(II) Complex

KAI CHENG^{1,*}, JING JIE YAN² and YUE QIU³

¹School of Chemistry and Pharmaceutical Engineering, Shandong Polytechnic University, Jinan 250353, P.R. China

²College of Chemical Engineering, Qingdao University of Science & Technology, Qingdao 266042, P.R. China

³Department of Chemistry, Dezhou University, Dezhou 253023, P.R. China

*Corresponding author: E-mail: kai861218@163.com

(Received: 11 April 2012;

Accepted: 31 August 2012)

AJC-12063

The mononuclear Mn(II) complex [Mn(DMTD)(1,10-phen)₂Cl] (**1**) (DMTD = 2,5-dimercapto-1,3,4-thiadiazole and 1,10-phenanthroline) was synthesized and structurally characterized by elemental analysis, IR and single-crystal X-ray diffraction. Fluorescence spectroscopy and ultraviolet (UV) spectroscopy techniques were used to study the interaction between herring sperm DNA with the complex [Mn(DMTD)(1,10-Phen)₂Cl] (**1**) in *Tris*-HCl buffer solution (pH = 7.66). The results of the experiments indicate that the complex bind to HS-DNA *via* the intercalative mode.

Key Words: Mononuclear complex, Spectroscopy, Intercalative binding.

INTRODUCTION

There are many studies on the design and synthesis of metal complexes due to their potential applications as functional materials in the area of magnetism, nonlinear optical behaviour, porosity and luminescence¹⁻³. The research of the interactions between metal complexes with DNA plays an important role in the development of DNA molecule probes and chemotherapeutics. We designed and synthesized a new complex based on thiadiazole. Furthermore, we studied the interaction between the complex and DNA by UV absorption titration, fluorescence titration. The result reveals that the intercalation is the main binding mode between the complex and DNA.

EXPERIMENTAL

UV spectra were carried out by a Shimadzu UV-2450 spectrometer. Elemental analysis was performed on a Perkin-Elmer 240C element analyzer. The fluorescence spectra of the complexes bind to DNA were recorded on a F-4500 equipped with a xenon lamp and a quartz carrier at room temperature.

Synthesis of [Mn(DMTD)(1,10-phen)₂Cl] (1**):** A mixture of MnCl₂·6H₂O (39.6 mg, 0.2 mmol), 2,5-dimercapto-1,3,4-thiadiazole (DMTD) (60 mg, 0.4 mmol), 1,10-phenanthroline (198.22 mg, 1 mmol), NaOH (16 mg, 0.4 mmol) and distilled water (10 mL) was sealed in a 25 mL teflon-lined stainless steel vessel and heated to 150 °C for 36 h. After slowly cooling to room temperature, the products were orange crystals and

were washed with distilled water to give pure sample (Yield: 30.4 % based on Mn). Elemental anal. calcd. (%) for C₂₆H₁₇N₆S₃MnCl: C, 51.96; H, 2.83; N, 13.99. Found: C, 51.88; H, 2.76; N, 13.90. Main IR frequencies (KBr, cm⁻¹): 3430, 2922, 2363, 1623, 1514, 1424, 1327, 1254, 1141, 1094, 844, 726, 638.

X-ray crystal structure determination: Diffraction intensity data of single crystals of the two compounds were collected on a Bruker SMART APEX II CCD diffractometer equipped with a graphite monochromated Mo-K_α radiation (λ = 0.71073 Å) by using an ω-scan mode. An empirical absorption correction was applied using the SADABS programs. The structure was solved by direct methods and refined by full-matrix least-squares methods on F² using the program SHELX 97⁴.

DNA-binding study: The absorption titrations of the complex in *Tris*-HCl buffer was performed by maintaining a constant concentration of the complex (10 μM) and gradually increasing the concentration of HS-DNA. When measuring the absorption spectra, equal amounts of HS-DNA were added to both the complex and reference solutions to eliminate the absorbance of HS-DNA itself.

In the fluorescence titration experiment, fixed amounts of the complex (10 μM) were titrated with adding different amounts of HS-DNA solution respectively in *Tris*-HCl buffer solution. The samples were excited at 332 nm and the fluorescence emission intensity was monitored at 420 nm.

RESULTS AND DISCUSSION

Crystal Structure of [Mn(DMTD)(1,10-Phen)₂Cl] (1):

The single-crystal X-ray diffraction study shows that the complex **1** crystallizes in the triclinic system, P-1 space group. Each Mn(II) cation is coordinated by four nitrogen atoms of two different 1,10-phen [Mn-N, ranging from 2.2866 Å to 2.3356 Å], a sulfur atom of DMTD [Mn-S = 2.5988 Å] and one Cl(I) ion [Mn-Cl = 2.4609 Å] in a distorted octahedral geometry coordination environment shown in Fig. 1. The bond angles around the Mn(II) center range from 71.50 (5)° to 162.30 (6)°. In the polyhedron of Mn atom, the N1 atom lies on the bottom and S1 atom situated at the apical station. The Mn-S1 bond length (2.5988 Å) is longer than those in the basal plane, which is similar to other manganese complexes⁵.

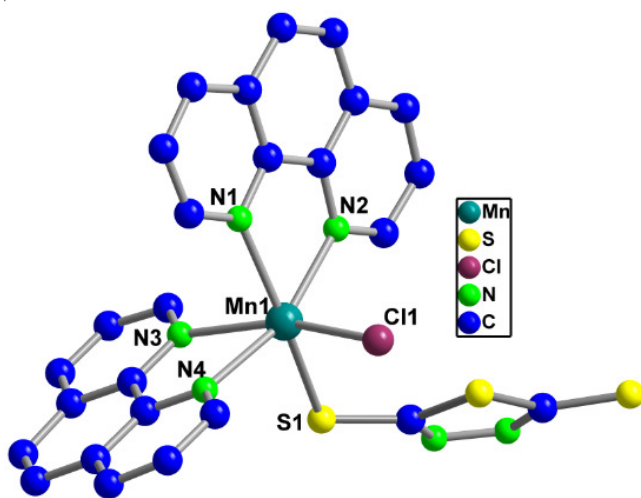


Fig. 1. Structure of [Mn(DMTD)(1,10-phen)₂Cl]

DNA-binding property: The UV spectra have been widely employed to determine the binding characteristics of metal complexes and DNA⁶. The absorption spectra of the complex **1** in the absence and presence of HS-DNA (at a constant concentration of complex) was given in Fig. 2. The electronic spectra of complex **1** shows hypochromism at *ca.* 280 nm, while the HS-DNA was titrated into solution. The observed hypochromism may be attributed to intercalative interactions between HS-DNA and [Mn(DMTD)(1,10-phen)₂Cl], as reported in the literature⁷.

To further clarify the interaction between [Mn(DMTD)(1,10-phen)₂Cl] and DNA fluorescence spectroscopic studies were carried out. The spectra of complex were performed by using a fixed complex concentration (10⁻⁵ M) while gradually increasing the volume of HS-DNA (10⁻² M) with the range from 0 to 40 μL, as shown in Fig. 3. The complex exhibits luminescence with maximum emission appearing at *ca.* 420 nm upon the excitation at 332 nm. The fluorescence intensity of [Mn(DMTD)(1,10-phen)₂Cl] was weak in the absence of DNA (curve 1), but it was gradually enhanced with increasing concentrations of DNA (curve 2-5) after adding DNA to the solution of the complex. The results showed that the fluorescence quenching of complex **1** could be inhibited by HS-DNA. Fig. 3 was the typical fluorescence spectra of energy transfer for [Mn(DMTD)(1,10-phen)₂Cl] at different

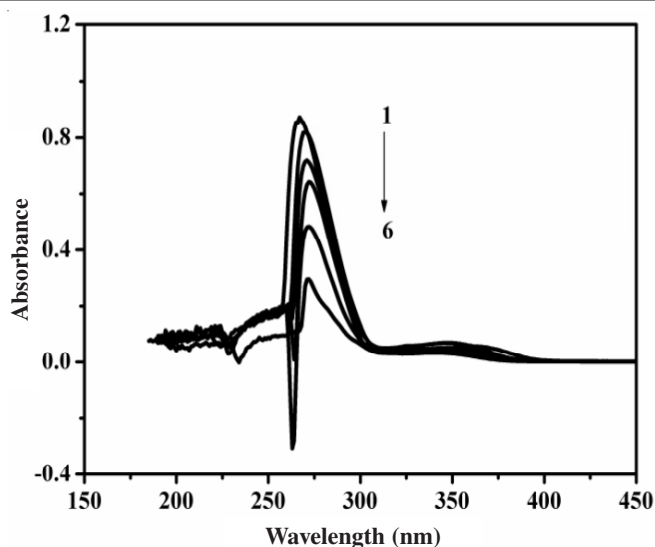


Fig. 2. UV spectra of [Mn(DMTD)(1,10-phen)₂Cl] in Tris-HCl buffer upon addition of HS-DNA

concentrations of DNA and the fluorescence intensity of complexes gradually increased with the increasing of HS-DNA indicated that complex has a strong intercalation with HS-DNA⁸.

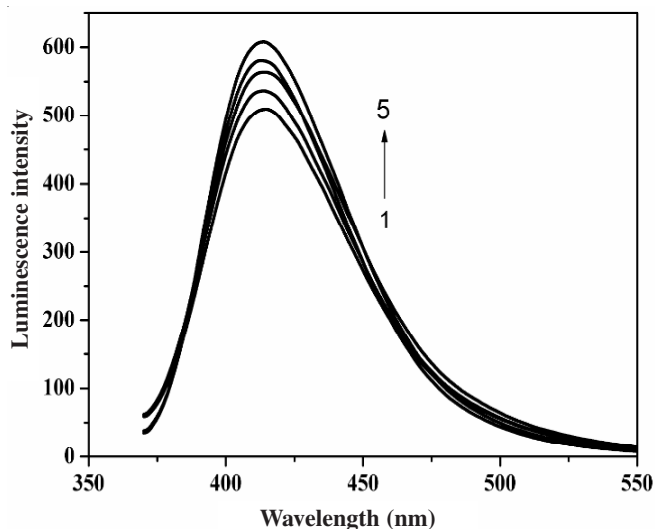


Fig. 3. Fluorescence emission spectra of [Mn(DMTD)(1,10-phen)₂Cl] in the absence and presence of HS-DNA

Conclusion

The new metal complex has been prepared under hydrothermal conditions and their binding mode with HS-DNA was studied using UV absorption titration, fluorescence titration. The data suggests that the binding mode between the [Mn(DMTD)(1,10-phen)₂Cl] with HS-DNA was intercalation, as reported earlier⁹.

ACKNOWLEDGEMENTS

The authors gratefully acknowledged the financial support from the National Natural Science Foundation of Shandong Province (No. ZR2010BL010) and Science & Technology Program of Shandong Province (No. 2010GWZ20251).

REFERENCES

1. F. Guo, L. Tian, B. Li, B.Y. Zhu and X.L. Zhang, *J. Inorg. Organomet. Polym.*, **21**, 207 (2011).
2. S.S. Kaye, A. Dailly, O.M. Yaghi and J.R. Long, *J. Am. Chem. Soc.*, **129**, 14176 (2007).
3. L. Pan, H. Liu, X. Lei, X. Huang, D. Olson, N. Turro and J. Li, *Angew. Chem. Int. Ed.*, **42**, 542 (2003).
4. G.M. Sheldrick, SHELXTL NT Version 5.1. Program for Solution and Refinement of Crystal Structures, University of Göttingen, Germany (1997).
5. Y.L. Pan, Q.Y. Jin, J.F. Chen, Y. Zhang and D.X. Jia, *Inorg. Chem.*, **48**, 5412 (2009).
6. H. Li, X.Y. Le, D.W. Pang, H. Deng, Z.H. Xu and Z.H. Lin, *J. Inorg. Biochem.*, **99**, 2240 (2005).
7. M.A. Pyle, P.J. Rehmann, R. Meshoyrer, J.N. Kumar, J.N. Turro and K.J. Barton, *J. Am. Chem. Soc.*, **111**, 3053 (1989).
8. B.D. Wang, Z.Y. Yang and T.R. Li, *Bioorg. Med. Chem.*, **14**, 6012 (2006).
9. S.S. Zhang, S.Y. Niu, B. Qu, G.F. Jie, H. Xu and C.F. Ding, *J. Inorg. Biochem.*, **99**, 2340 (2005).