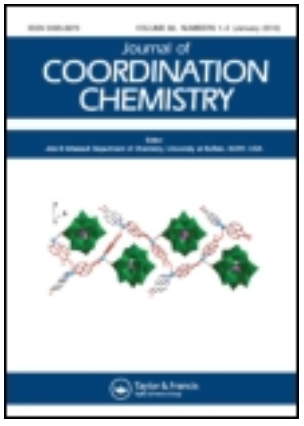

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gcoo20

Synthesis, characterization, and DNA-binding of a four-coordinate cobalt(II) complex with 1,3-bis(1-ethylbenzimidazol-2-yl)-2-oxopropane

Hui-Lu Wu [a], Fan Kou [a], Fei Jia [a], Bin Liu [a], Jing-Kun Yuan [a] & Ying Bai [a]

[a] School of Chemical and Biological Engineering, Lanzhou Jiaotong University, Lanzhou, Gansu 730070, P.R. China

Published online: 07 Sep 2011.

To cite this article: Hui-Lu Wu, Fan Kou, Fei Jia, Bin Liu, Jing-Kun Yuan & Ying Bai (2011) Synthesis, characterization, and DNA-binding of a four-coordinate cobalt(II) complex with 1,3-bis(1-ethylbenzimidazol-2-yl)-2-oxopropane, Journal of Coordination Chemistry, 64:17, 3041-3050, DOI: 10.1080/00958972.2011.611505

To link to this article: http://dx.doi.org/10.1080/00958972.2011.611505

Journal of Coordination Chemistry
Vol. 64, No. 17, 10 September 2011, 3041–3050

Synthesis, characterization, and DNA-binding of a four-coordinate cobalt(II) complex with 1,3-bis(1-ethylbenzimidazol-2-yl)-2-oxopropane

HUI-LU WU*, FAN KOU, FEI JIA, BIN LIU, JING-KUN YUAN and YING BAI

School of Chemical and Biological Engineering, Lanzhou Jiaotong University, Lanzhou, Gansu 730070, P.R. China

(*Received 27 May 2011; in final form 25 July 2011*)

A new four-coordinate cobalt(II) complex with 1,3-bis(1-ethylbenzimidazol-2-yl)-2-oxopropane (Etobb), $Co(Etobb)Cl_2$, has been synthesized and characterized by elemental analysis, electrical conductivities, infrared, and UV-Vis spectral measurements. The crystal structure has been determined by single-crystal X-ray diffraction. Cobalt(II) is a distorted tetrahedral geometry, surrounded by two nitrogens from Etobb and two chlorides. DNA-binding properties of Etobb and its Co(II) complex have been investigated by electronic absorption, fluorescence, and viscosity measurements. The experimental results suggest that the ligand and its Co(II) complex bind to DNA *via* intercalation, and the binding affinity of the Co(II) complex to DNA is greater than Etobb.

Keywords: 1,3-Bis(1-ethylbenzimidazol-2-yl)-2-oxopropane; Cobalt(II) complex; Crystal structure; DNA-binding property; Intercalation mode

1. Introduction

Multidentate ligands designed to constrain the coordination arrangements of metals have found several applications [1–6]. In bioinorganic chemistry, bis-benzimidazole complexes have been used extensively to model the active sites of metalloproteins [7]. Substantial progress has been made to develop metal-based small molecules as DNA foot-printing as well as therapeutic agents capable of binding and cleaving DNA under physiological conditions [8–22]. Metal complexes binding nucleic acid are investigated as DNA structural probes, DNA foot printing and sequence-specific cleavage agents and potential anticancer drugs [23–26]. The important criteria for development of metallodrugs as chemotherapeutic agents are the ability of the metallodrug to bring about DNA cleavage. A large number of transition metal complexes, because of their redox properties, promote DNA cleavage. Transition metal complexes bring about DNA cleavage either oxidatively, hydrolytically, or photolytically. A large number of Cu(II), Co(II), Mn(II), and Fe(II) complexes promote oxidative DNA cleavage in the

*Corresponding author. Email: wuhuilu@163.com

Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online © 2011 Taylor & Francis
DOI: 10.1080/00958972.2011.611505

presence of a coreagent [27–34]. Cobalt is an essential metal ion and plays crucial roles in biological and biomedical processes. Some cobalt benzimidazole structures have been reported [35, 36].

In this work, we study the DNA-binding properties of a new cobalt complex derived from benzimidazole. The binding of ligand and complex with calf thymus DNA (CT-DNA) has been investigated by spectroscopic and viscosity measurements.

2. Experimental

2.1. *Materials and physical measurements*

C, H, and N elemental analyses are obtained on a Carlo Erba 1106 elemental analyzer. Infrared (IR) spectroscopy as KBr pellets is performed on a Nicolet FT-VERTEX 70 spectrophotometer from 4000 to 400 cm^{-1}. Electronic spectra are measured on a LabTech UV Bluestar spectrophotometer. Fluorescence spectral data are obtained on a LS-45 fluorescence spectrophotometer at room temperature. Electrolytic conductance measurements were made with a DDS-307 type conductivity bridge using 10^{-3} mol L^{-1} DMF solution at room temperature.

CT-DNA and ethidium bromide (EB) were purchased from Sigma Chemicals Co. (USA). All chemicals were of analytical grade. The experiments involving interaction of the ligand and the complex with CT-DNA were carried out in doubly distilled water buffer containing 5 mmol L^{-1} Tris and 50 mmol L^{-1} NaCl and adjusted to pH = 7.2 with hydrochloric acid. A solution of CT-DNA gave a ratio of UV absorbance at 260 and 280 nm of about 1.8–1.9, indicating that the CT-DNA was sufficiently free of protein [37]. The CT-DNA concentration per nucleotide was determined spectrophotometrically by employing an extinction coefficient of 6600 $(\text{mol L}^{-1})^{-1}\,\text{cm}^{-1}$ at 260 nm [38]. Absorption titration experiments were performed with fixed concentrations of the compounds, while gradually increasing the concentration of DNA. While measuring the absorption spectra, a proper amount of DNA was added to both the compound solution and the reference solution to eliminate the absorbance of DNA itself. From the absorption titration data, the binding constant was determined using the equation: $[\text{DNA}]/(\varepsilon_a - \varepsilon_f) = [\text{DNA}]/(\varepsilon_b - \varepsilon_f) + 1/K_b(\varepsilon_b - \varepsilon_f)$ [39], where [DNA] is the concentration of DNA in base pairs, ε_a corresponds to the extinction coefficient observed (A_{obsd}/[mol L^{-1}]), ε_f corresponds to the extinction coefficient of the free compound, ε_b is the extinction coefficient of the compound when fully bound to DNA, and K_b is the intrinsic binding constant. The ratio of slope to intercept in the plot of $[\text{DNA}]/(\varepsilon_a - \varepsilon_f)$ *versus* [DNA] gives the values of K_b. EB emits intense fluorescence in the presence of DNA, due to its strong intercalation between the adjacent DNA base pairs. The enhanced fluorescence can be quenched by addition of a second component [40, 41]. The quenching extent of fluorescence of EB bound to DNA is used to determine the extent of binding between the second component and DNA. The experiments of DNA competitive binding with EB were carried out in the buffer by keeping [DNA]/[EB] = 1.136 and varying the concentrations of the ligand and the Co(II) complex. The fluorescence spectra of EB were measured using excitation wavelength of 520 nm with the emission range being set between 550 and 750 nm. The spectra were analyzed according to the classical Stern–Volmer equation: $I_0/I = 1 + K_{sv}[Q]$ [40, 41], where I_0 and

I are the fluorescence intensities at 596 nm in the absence and presence of the quencher, respectively, K_{sv} is the linear Stern–Volmer quenching constant, and [*Q*] is the concentration of the ligand and the Co(II) complex ([CT-DNA] = 2.5×10^{-3} mol · L^{-1}, [EB] = 2.2×10^{-3} mol · L^{-1}). Viscosity experiments were conducted on an Ubbelodhe viscometer, immersed in a thermostated water bath maintained at 25 ± 0.1°C. Titrations were performed for the compounds (3–30 μmol L^{-1}), and each compound was introduced into the CT-DNA solution (50 μmol L^{-1}) present in the viscometer. Data were presented as $(\eta/\eta_0)^{1/3}$ *versus* the ratio of the concentration of the compound to CT-DNA, where η is the viscosity of CT-DNA in the presence of the compound and η_0 is the viscosity of CT-DNA alone. Viscosity values were calculated from the observed flow time of the CT-DNA containing solution corrected for the flow time of buffer alone (t_0) with the equation $\eta = (t - t_0)/t_0$ [42].

2.2. *Preparation the ligand and its complex*

2.2.1. 1,3-Bis(1-ethylbenzimidazol-2-yl)-2-oxopropane (Etobb). This compound was synthesized according to literature methods [43]. Yield: 4.3 g (64%); m.p.: 101–103°C (m.p.: 101–103°C in the literature [43]). ^{1}H-NMR (400 MHz, $CDCl_3$,) δ: 7.28 (m, 4H, Ph), 4.12 (s, 2H, CH_2), 4.91 (s, 2H, OCH_2), 1.49 (s, 3H, CH_3). Anal. Calcd for $C_{20}H_{22}N_4O$ (%): C, 71.8; H, 6.6; N, 16.8. Found (%): C, 71.4; H, 6.5; N, 16.6. Selected IR data (KBr ν/cm^{-1}): 756 $\nu_{(o\text{–Ar})}$, 1083 $\nu_{(C–O)}$, 1475 $\nu_{(C=N)}$, 1612 $\nu_{(C=C)}$. UV/Vis (DMF): λ = 279 nm. Λ_M (DMF, 297 K): 0.35 S · cm^2 · mol^{-1}.

2.2.2. Co(Etobb)Cl_2. The syntheses of the ligand and the Co(II) complex are displayed as figure 1. To a stirred solution of 1,3-bis(1-ethylbenzimidazol-2-yl)-2-oxopropane (0.1336 g, 0.40 mmol) in hot MeOH (5 mL) was added Co(II) chloride hexahydrate (0.0476 g, 0.20 mmol) in MeOH (5 mL). A deep brown crystalline product formed rapidly. The precipitate was filtered off, washed with MeOH and absolute Et_2O, and dried *in vacuo*. The dried precipitate was dissolved in DMF resulting in a brown solution. Brown crystals suitable for X-ray diffraction studies were obtained by ether diffusion into DMF after several days at room temperature. Yield: 0.080 g (70%); Anal.

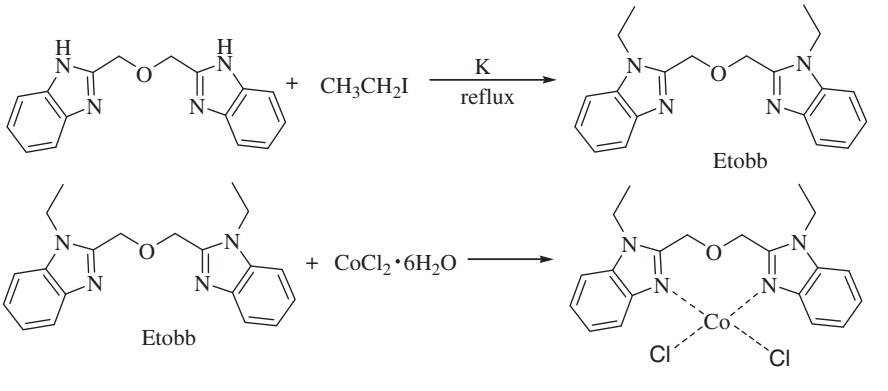

Figure 1. The synthesis of Etobb and the Co(II) complex.

Table 1. Crystal data and structure refinement for Co(Etobb)Cl_2.

Empirical formula	$C_{20}H_{22}Cl_2CoN_4O$
Formula weight	464.25
Crystal system	Monoclinic
Space group	$C2/c$
Unit cell dimensions (Å, °)	
a	9.9103(7)
b	15.2042(11)
c	13.4999(10)
α	90
β	99.4910(10)
γ	90
Volume (Å^3), Z	2006.3(3), 4
Calculated density (g cm^{-3})	1.141
$F(000)$	956
ρ_{cald} (g cm^{-3})	1.537
Crystal size (mm^3)	$0.25 \times 0.19 \times 0.15$
θ range for data collection (°)	2.03–27.51
$h/k/l$ (max, min)	−12, 12/−19, 19/−17, 17
Goodness-of-fit on F^2	1.055
Final R_1, wR_2 indices [$I > 2\sigma(I)$]	0.0248, 0.0649
R_1, wR_2 indices (all data)	0.0280, 0.0668
Largest difference peak and hole (e Å^{-3})	0.335 and −0.318

Calcd for $C_{20}H_{22}Cl_2CoN_4O$ (%): C, 49.34; H, 4.60; N, 12.79; O, 3.65. Found (%): C, 49.44; H, 4.50; N, 12.89; O, 3.55. Selected IR data (KBr ν/cm^{-1}): 773 $\nu_{(o\text{–Ar})}$, 1127 $\nu_{(C\text{–}O)}$, 1494 $\nu_{(C=N)}$, 1612 $\nu_{(C=C)}$. UV/Vis (DMF): $\lambda = 280$, 610 nm. Λ_M (DMF, 297 K): 3.15 S · cm^2 · mol^{-1}.

2.3. *X-ray crystallography*

A suitable single crystal was mounted on a glass fiber and intensity data were collected on a Bruker APEX-II CCD (Japan) diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at 296(2) K. Data reduction and cell refinement were performed using SAINT programs [44]. The absorption correction was carried out by empirical methods. The structure was solved by direct methods and refined by full-matrix least-squares against F^2 using SHELXTL software [45]. All hydrogens were found in difference electron maps and subsequently refined in a riding model approximation with C–H distances from 0.95 to 0.99 Å and $U_{iso}(H) = 1.2\ U_{eq}(C)$ or $1.5\ U_{eq}(C_{methyl})$. The crystal data and experimental parameters relevant to the structure determination are listed in table 1.

3. Results and discussion

The complex is soluble in DMF and DMSO but insoluble in water and organic solvents, such as methanol, ethanol, acetone, petroleum ether, and trichloromethane. The results of the elemental analyses show Co(Etobb)Cl_2. Molar conductance shows the complex is a non-electrolyte in DMF [46].

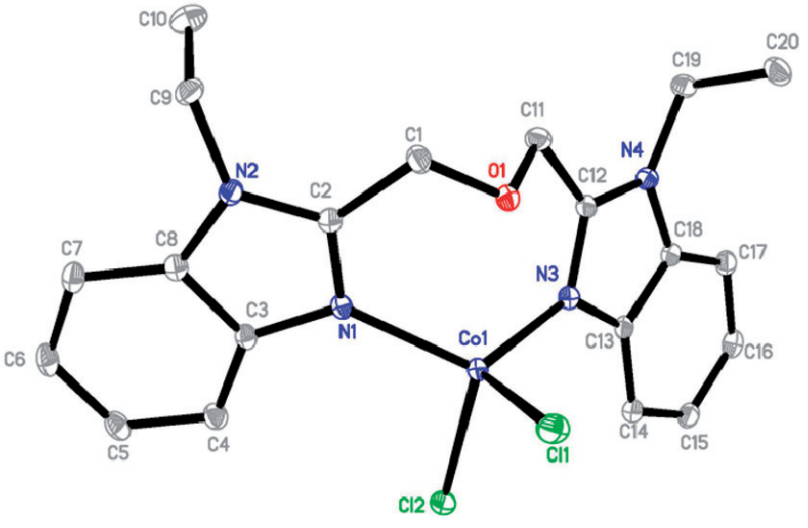

Figure 2. The molecular structure of the complex in the crystal with displacement ellipsoids at the 30% probability level; H atoms are omitted for clarity.

Table 2. Selected bond lengths (Å) and angles (°) of Co(II) complex.

Co(1)–N(3)	2.0560(12)	Co(1)–N(1)	2.0705(12)
Co(1)–Cl(1)	2.2779(4)	Co(1)–Cl(2)	2.3031(4)
N(3)–Co(1)–N(1)	118.97(5)	N(3)–Co(1)–Cl(1)	113.17(4)
N(1)–Co(1)–Cl(1)	109.24(3)	N(3)–Co(1)–Cl(2)	103.95(4)
N(1)–Co(1)–Cl(2)	104.62(3)	Cl(1)–Co(1)–Cl(2)	105.502(16)
C(1)–O(1)–C(11)	114.25(11)	C(1)–O(1)–Co(1)	109.99(8)
C(2)–N(1)–Co(1)	121.48(10)	C(3)–N(1)–Co(1)	133.30(9)

3.1. *Crystal structure of Co(Etobb)Cl_2*

The Co(II) complex crystallizes in the monoclinic space group $C2/c$ and its structure along with the atomic numbering scheme is shown in figure 2. The crystal structure consists of discrete Co(Etobb)Cl_2 in a distorted tetrahedral geometry, surrounded by two nitrogens and two chlorides. The dihedral angles between benzimidazole rings of the ligand are 45.13(3)°. The Co–N and Co–Cl bond lengths are normal [47]. Selected bond distances and angles are shown in table 2.

The benzimidazole rings from adjacent units arrange in an offset face-to-face fashion with the vertical distance of center to center 3.574 Å, suggesting significant π–π stacking interactions (figure 3). No intermolecular classical hydrogen-bonding is present in the crystal. Thus, the units are stacked together efficiently *via* the π–π stacking interactions of benzimidazole.

3.2. *IR and electronic spectra*

The IR spectrum of the complex shows that the strong $\nu_{C=N}$ in the free ligand shifts to lower wavenumber in the complex. The red shift indicates that nitrogens of the ligands are coordinated to cobalt(II). They are the preferred nitrogens for coordination, as

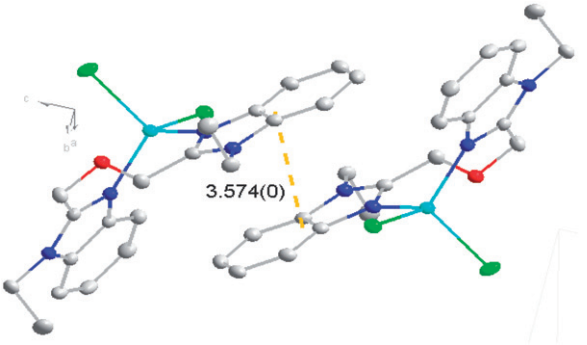

Figure 3. The structure of the Co(II) complex linked *via* π–π stacking interaction.

found in other metal complexes with benzimidazole open chain crown ether derivatives [48]. The electronic spectroscopic data of the cobalt(II) complex recorded in DMF show a red shift from that of Etobb, clear evidence of C=N coordination to cobalt. The absorption band is assigned to π–π^* (imidazole) transition. In the visible range, one peak is assigned to $[^4A_2 \rightarrow {}^4T_1(P)]$ transition [49].

3.3. *DNA-binding properties*

3.3.1. Electronic absorption titration. Electronic absorption spectroscopy is universally employed to determine the binding characteristics of metal complexes with DNA [50–52]. Absorption spectra of Etobb and the Co(II) complex in the absence and presence of CT-DNA are given in figure 4(a) and (c), respectively. Etobb has a well-resolved band at 278 nm and there is also a well-resolved band at 277 nm for the complex. With increasing DNA concentrations, hypochromism is 12.5% at 276 nm for Etobb and 13.1% at 277 nm for the Co(II) complex. The λ for the ligand increases from 276 to 277, and for the complex from 277 to 278 nm, a slight red shift of 1 nm under identical experimental conditions. The hypochromism and the slight red shift suggest that Etobb and the Co(II) complex interact with DNA [53].

The binding constant K_b for the complex has been determined from the plot of $[DNA]/(\varepsilon_A - \varepsilon_f)$ *versus* [DNA] and found to be 2.8×10^4 $(\text{mol L}^{-1})^{-1}$ ($R = 0.97738$ for 9 points). K_b for the ligand (4.05×10^3 $(\text{mol L}^{-1})^{-1}$) ($R = 0.99429$ for 8 points) is smaller than for the complex. Compared with a DNA-intercalative ruthenium complex (1.1×10^4–4.8×10^4 $(\text{mol L}^{-1})^{-1}$) and other cobalt complexes (1.6×10^4–1.47×10^5 $(\text{mol L}^{-1})^{-1}$) [54–60], the binding constants (K_b) of Etobb and the Co(II) complex suggest intercalative binding to DNA with binding affinity of the Co(II) complex stronger than that of Etobb.

3.3.2. Competitive binding with EB. For measuring the ability of a complex to affect EB fluorescence intensity in the EB–DNA adduct, the fluorescence quenching method can be used, whatever the binding mode may be. If a complex can remove EB from EB-loaded DNA, the fluorescence of the solution will be quenched due to the fact that free EB molecules are readily quenched by surrounding water molecules [61].

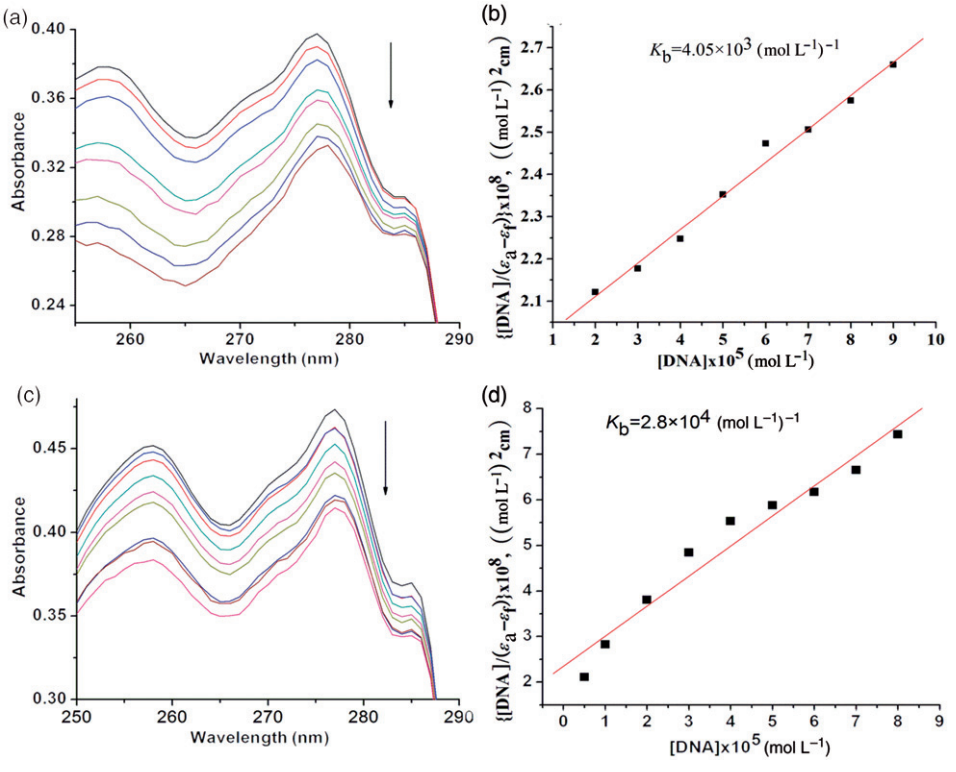

Figure 4. Electronic spectra of (a) Etobb, (c) the Co(II) complex in Tris-HCl buffer upon addition of CT-DNA. [DNA] = $0.5 \times 10^{-5} - 9 \times 10^{-5}$ mol L^{-1}. The arrows show the emission intensity changes upon increasing DNA concentration. Plots of [DNA]/($\varepsilon_a - \varepsilon_f$) *vs.* [DNA] for titration of (b) Etobb and (d) the Co(II) complex with CT-DNA.

The addition of Etobb does not provoke any significant changes of the intensity or the position of the emission band at 599 nm of the DNA–EB system, indicating that Etobb cannot replace EB from the DNA–EB complex. The fluorescence quenching of EB bound to CT-DNA by Etobb and the Co(II) complex are shown in figure 5. The quenching plots illustrate that the quenching of EB bound to DNA by the complex is in good agreement with the linear Stern–Volmer equation, proving that the complex binds to DNA. The K_{sv} value is estimated to be 1.203×10^3 (mol L^{-1})$^{-1}$ ($R = 0.99715$ for 18 points) and 3.003×10^3 (mol L^{-1})$^{-1}$ ($R = 0.99915$ for 18 points) for Etobb and the Co(II) complex, respectively. That both Etobb and the Co(II) complex showing similar DNA-binding constant indicates that Etobb is an intercalating ligand.

3.3.3. Viscosity studies. Optical photophysical probes generally provide necessary but not sufficient clues to support a binding model. Measurements of DNA viscosity that is sensitive to DNA length are regarded as the least ambiguous tests of binding in solution in the absence of crystallographic structural data [62, 63]. Intercalating agents elongate the double helix to accommodate the ligands between the bases leading to an increase in viscosity of DNA. In contrast, complexes that bind exclusively in the DNA grooves by partial and/or non-classical intercalation, under the same conditions, typically cause

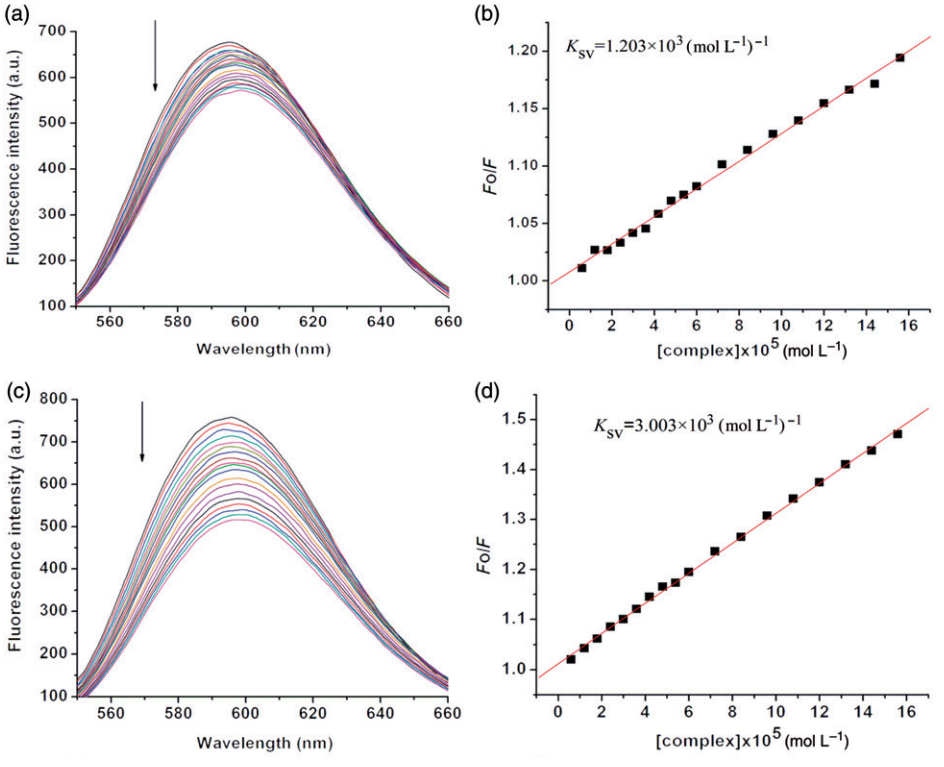

Figure 5. Emission spectra of EB bound to DNA in the presence of (a) Etobb, (c) the Co(II) complex showing the intensity changes upon increasing concentrations. A Stern–Volmer quenching plot of (b) the ligand and (d) the Co(II) complex inserting in their own fluorescence spectra with increasing concentrations of CT-DNA.

less pronounced (positive or negative) or no change in DNA solution viscosity [64]. The values of $(\eta/\eta_0)^{1/3}$ were plotted against [complex]/[DNA] (figure 6). Upon addition of the ligand and the Co(II) complex the viscosity of rod-like CT-DNA increased significantly, which suggests that Etobb and the Co(II) complex bind to DNA by intercalation [65].

4. Conclusion

We have reported here the synthesis and structural characterization of a new cobalt(II) complex. The DNA-binding properties of the ligand and the Co(II) complex were studied *via* electronic absorption titration, EB displacement, and viscosity. All results suggested that the ligand and the complex interact with DNA by intercalation. Binding affinity to DNA of the complex is greater than Etobb. Results obtained from this work are useful to understand the mechanism of interactions of small molecules with DNA and in development of biological, pharmaceutical, and physiological applications.

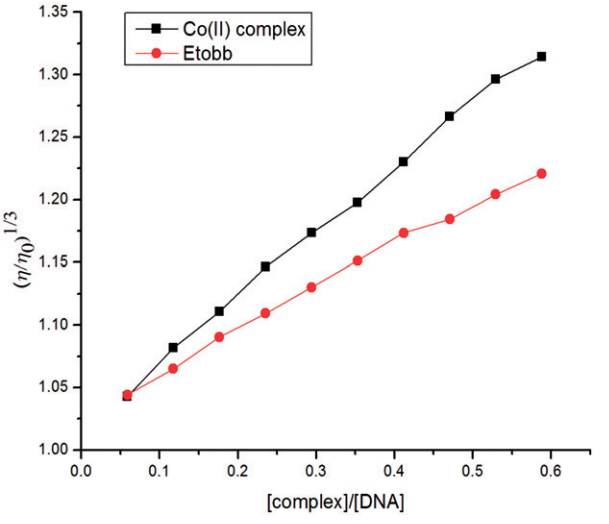

Figure 6. Effect of increasing amounts of Etobb and the Co(II) complex on the relative viscosity of CT-DNA at 25.0 ± 0.1°C.

Supplementary material

Crystallographic data (excluding structure factors) for the structure in this article has been deposited with the Cambridge Crystallographic Data Center as supplementary publication CCDC 826648. Copies of the data can be obtained, free of charge, on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK.

Acknowledgments

The authors acknowledge the financial support and grant from "Qing Lan" Talent Engineering Funds and Students' Science and Technology Innovation Funds (grant no. DXS2011-002) by Lanzhou Jiaotong University. The grant from "Long Yuan Qing Nian" of Gansu Provinces also acknowledged.

References

[1] P.J. Shapiro, E. Bunel, W.P. Schaefer, J.E. Bercaw. *Organometallics*, **9**, 867 (1990).
[2] A.L. McKnight, R.M. Waymouth. *Chem. Rev.*, **98**, 2587 (1998).
[3] G. Zi, H.W. Li, Z. Xie. *Organometallics*, **21**, 3850 (2002).
[4] G. Lanza, I.L. Fragala, T.J. Marks. *J. Am. Chem. Soc.*, **122**, 12764 (2000).
[5] C.O. Dietrich-Buchecker, J. Guilhem, J.M. Kern, C. Pascard, J.P. Sauvage. *Inorg. Chem.*, **33**, 3498 (1994).
[6] A.M. Bond, R. Colton, J.E. Kevekordes, P. Panagiotidou. *Inorg Chem.*, **26**, 1430 (1987).
[7] P.L. Holland, W.B. Tolman. *J. Am. Chem. Soc.*, **122**, 6331 (2000).
[8] D.S. Sigman, T.W. Bruice, A. Mazumder, C.L. Sutton. *Acc. Chem. Res.*, **26**, 98 (1993).
[9] D.S. Sigman, A. Mazumder, D.M. Perrin. *Chem. Rev.*, **93**, 2295 (1993).
[10] B. Meunier. *Chem. Rev.*, **92**, 1411 (1992).
[11] G. Pratviel, J. Bernadou, B. Meunier. *Adv. Inorg. Chem.*, **45**, 251 (1998).

[12] G. Pratviel, J. Bernadou, B. Meunier. *Angew. Chem., Int. Ed. Engl.*, **34**, 746 (1995).
[13] C. Metcalfe, J.A. Thomas. *Chem. Soc. Rev.*, **32**, 215 (2003).
[14] J. Reedijk. *J. Inorg. Biochem.*, **86**, 89 (2001).
[15] K.E. Erkkila, D.T. Odom, J.K. Barton. *Chem. Rev.*, **99**, 2777 (1999).
[16] B. Armitage. *Chem. Rev.*, **98**, 1171 (1998).
[17] D.R. McMillin, K.M. McNett. *Chem. Rev.*, **98**, 1201 (1998).
[18] H.T. Chifotides, K.R. Dunbar. *Acc. Chem. Res.*, **38**, 146 (2005).
[19] E.R. Jamieson, S.J. Lippard. *Chem. Rev.*, **99**, 2467 (1999).
[20] V.J. Derose, S. Burns, N.K. Kim, M. Vogt. *Compr. Coord. Chem.*, **8**, 787 (2004).
[21] S.J. Lippard, J.M. Berg. *Principles of Bioinorganic Chemistry*, University Science Books, Sausalito, CA (1994).
[22] H. Umezawa. *Prog. Biochem. Pharmacol.*, **11**, 18 (1976).
[23] S. Routier, H. Vezin, E. Lamour, J.L. Bernier, J.P. Catteau, C. Bailly. *Nucleic Acids Res.*, **27**, 4160 (1999).
[24] J.K. Speetjens, R.A. Collins, J.B. Vincent, S.A. Woski. *Chem. Res. Toxicol.*, **12**, 483 (1999).
[25] V.G. Vaidyanathan, B.U. Nair. *Eur. J. Inorg. Chem.*, 3633 (2003).
[26] X.L. Wang, H. Chao, H. Li, X.L. Hong, L.N. Ji, X.Y. Li. *J. Inorg. Biochem.*, **98**, 423 (2004).
[27] V.G. Vaidyanathan, T. Weyhermuller, B.U. Nair, J. Subramanian. *J. Inorg. Biochem.*, **99**, 2248 (2005).
[28] V. Uma, M. Kanthimathi, T. Weyhermuller, B.U. Nair. *J. Inorg. Biochem.*, **99**, 2299 (2005).
[29] V. Uma, M. Elango, B.U. Nair. *Eur. J. Inorg. Chem.*, 3484 (2007).
[30] V. Uma, A. Castineiras, B.U. Nair. *Polyhedron*, **26**, 3008 (2007).
[31] Q. Jiang, Z. Wu, Y. Zhang, A.C.G. Hotze, M.J. Hannon, Z. Guo. *Dalton Trans.*, **23**, 3054 (2008).
[32] B. Selvakumar, V. Rajendiran, P. Uma Maheswari, H.S. Evans, M. Palaniandavar. *J. Inorg. Biochem.*, **100**, 316 (2006).
[33] H.L. Wu, X.C. Huang, J.K. Yuan, F. Kou, F. Jia, B. Liu, K.T. Wang. *Eur. J. Med. Chem.*, **45**, 5324 (2010).
[34] S. Satyanarayana, J.C. Dabrowiak, J.B. Chaires. *Biochemistry*, **32**, 2573 (1993).
[35] N. Sireci, H. Kucukbay, M. Akkurt, S. Pinar Yalcin, M. Nawaz Tahir, H. Ott. *J. Coord. Chem.*, **63**, 3218 (2010).
[36] M.Y. Duan, J. Li, Y. Xi, X.F. Lu, J.Z. Liu, G. Mele, F.X. Zhang. *J. Coord. Chem.*, **63**, 90 (2010).
[37] J. Marmur. *J. Mol. Biol.*, **3**, 208 (1961).
[38] A. Wolfe, G.H. Shimer Jr, T. Meehan. *Biochemistry*, **26**, 6392 (1987).
[39] B.C. Baguley, M. Le Bret. *Biochemistry*, **23**, 937 (1984).
[40] J.R. Lakowicz, G. Weber. *Biochemistry*, **12**, 4161 (1973).
[41] M. Chauhan, K. Banerjee, F. Arjmand. *Inorg. Chem.*, **46**, 3072 (2007).
[42] D.S. Sigman, A. Mazumder, D.M. Perrin. *Chem. Rev.*, **93**, 2295 (1993).
[43] H.L. Wu, R.R. Yun, K.T. Wang, K. Li, X.C. Huang, T. Sun. *Z. Anorg. Allg. Chem.*, **636**, 629 (2010).
[44] Bruker. *APEX2 and SAINT*, Bruker AXS, Inc., Madison, WI, USA (2007).
[45] G.M. Sheldrick. *SHELXTL*, Siemens Analytical X-ray Instruments, Inc., Madison, WI, USA (1996).
[46] W.J. Geary. *Coord. Chem. Rev.*, **7**, 81 (1971).
[47] H.C. Yao, M.M. Li, G.S. Yang, Z.J. Li, Y. Zhu. *Inorg. Chim. Acta*, **360**, 3959 (2007).
[48] M. McKee, M. Zvagulis, C.A. Reed. *Inorg. Chem.*, **24**, 2914 (1985).
[49] L.K. Thompson, B.S. Ramaswamy, E.A. Seymour. *Can. J. Chem.*, **55**, 878 (1977).
[50] H. Li, X.Y. Le, D.W. Pang, H. Deng, Z.H. Xu, Z.H. Lin. *J. Inorg. Biochem.*, **99**, 2240 (2005).
[51] V.G. Vaidyanathan, B.U. Nair. *Eur. J. Inorg. Chem.*, 3633 (2003).
[52] V.G. Vaidyanathan, B.U. Nair. *Eur. J. Inorg. Chem.*, 1840 (2004).
[53] J. Liu, T.X. Zhang, L.N. Ji. *J. Inorg. Biochem.*, **91**, 269 (2002).
[54] A.M. Pyle, J.P. Rehmann, R. Meshoyrer, C.V. Kumar, N.J. Turro, J.K. Barton. *J. Am. Chem. Soc.*, **111**, 3051 (1989).
[55] X.W. Huang, X.J. Chen, J. Liang, S. Guo, J. Su. *J. Coord. Chem.*, **63**, 1570 (2010).
[56] D. Arish, M.S. Nair. *J. Coord. Chem.*, **63**, 1619 (2010).
[57] N. Raman, R. Jeyamurugan, R.U. Rani, T. Baskaran, L. Mitu. *J. Coord. Chem.*, **63**, 1629 (2010).
[58] S.A. Patil, S.N. Unki, A.D. Kulkarni, V.H. Naik, U. Kamble, P.S. Badami. *J. Coord. Chem.*, **64**, 323 (2011).
[59] L.S. Kumar, H.D. Revanasiddappa. *J. Coord. Chem.*, **64**, 699 (2011).
[60] Q.Y. Lin, Y.Y. Wang, Y.L. Feng, D.M. Yan, Y.J. Wang, F. Zhang. *J. Coord. Chem.*, **64**, 920 (2011).
[61] J.B. LePecq, C. Paoletti. *J. Mol. Biol.*, **27**, 87 (1967).
[62] S. Mahadevan, M. Palaniandavar. *Inorg. Chem.*, **37**, 693 (1998).
[63] A.B. Tossi, J.M. Kelly. *Photochem. Photobiol.*, **9**, 545 (1989).
[64] S. Satyanarayana, J.C. Dabrowiak, J.B. Chaires. *Biochemistry*, **31**, 9319 (1992).
[65] S. Satyanarayana, J.C. Dabrowiak, J.B. Chaires. *Biochemistry*, **32**, 2573 (1993).