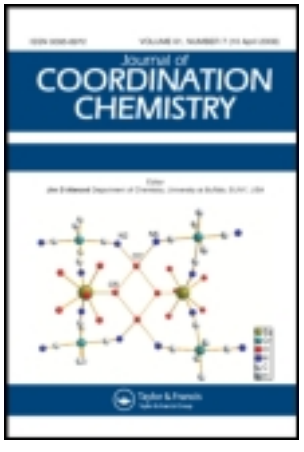

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gcoo20

A six-coordinate picrate cadmium(II) complex with a new V-shaped ligand 1,3-bis(1-ethylbenzimidazol-2-yl)-2-thiapropane: synthesis, crystal structure, and DNA-binding properties

Hui-Lu Wu [a], Kai-Tong Wang [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: 02 Aug 2011.

To cite this article: Hui-Lu Wu, Kai-Tong Wang, Fan Kou, Fei Jia, Bin Liu, Jing-Kun Yuan & Ying Bai (2011) A six-coordinate picrate cadmium(II) complex with a new V-shaped ligand 1,3-bis(1-ethylbenzimidazol-2-yl)-2-thiapropane: synthesis, crystal structure, and DNA-binding properties, Journal of Coordination Chemistry, 64:15, 2676-2687, DOI: 10.1080/00958972.2011.605442

To link to this article: http://dx.doi.org/10.1080/00958972.2011.605442

Journal of Coordination Chemistry
Vol. 64, No. 15, 10 August 2011, 2676–2687

A six-coordinate picrate cadmium(II) complex with a new V-shaped ligand 1,3-bis(1-ethylbenzimidazol-2-yl)-2-thiapropane: synthesis, crystal structure, and DNA-binding properties

HUI-LU WU*, KAI-TONG WANG, 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 5 May 2011; in final form 17 June 2011*)

A V-shaped ligand 1,3-bis(1-ethylbenzimidazol-2-yl)-2-thiapropane (L) and its picrate cadmium(II) complex have been synthesized and characterized systematically. In $[Cd(L)_2](pic)_2$, the Cd(II) is six-coordinate with N_4S_2 donors of two ligands, forming a slightly distorted octahedron. DNA binding properties were investigated by electronic absorption spectroscopy, fluorescence spectroscopy, and viscosity measurements. The compounds bind to DNA *via* intercalation and the order of binding affinity is ligand > complex.

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

1. Introduction

Interactions of small molecules with DNA have attracted a great deal of attention [1–3], because the interaction between small molecules and DNA can cause DNA damage in cancer cells, blocking the division of cancer cells and resulting in cell death [4–6]. Drug research suggests that many anticancer agents, antiviral agents, and antiseptic agents take action through binding to DNA [7–9]. Many studies indicate that transition metal complexes interact with DNA by intercalation, groove binding, or external electrostatic binding [10, 11]. A number of important applications of these complexes require that they bind to DNA in an intercalative mode which is the same as cisplatin [12]. In the broad class of heterocyclic compounds, nitrogen heterocycles play an important role [13]. Many heterocyclic compounds from benzimidazole were synthesized and their biological and pharmacological activities were investigated [14–20]. Therefore, interaction of transition metal complexes, especially containing planar aromatic heterocyclic ligands which can insert and stack into the base pairs of the DNA duplex [21–23] has attracted considerable attention [24–29].

*Corresponding author. Email: wuhuilu@163.com

Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online
DOI: 10.1080/00958972.2011.605442

A review on crystal structures of Cd(II) complexes showed that cadmium(II) has coordination numbers of 4, 5, and 6 in about 19%, 18%, and 56%, respectively [30]. In our previous work, a five-coordinate cadmium(II) complex has been reported [31]. Here we report the synthesis, crystal structure, and DNA-binding of a six-coordinate picrate Cd(II) complex with the new V-shaped ligand 1,3-bis(1-ethylbenzimidazol-2-yl)-2-thiapropane.

2. Experimental

2.1. *Materials and physical measurements*

All chemicals and solvents were of reagent grade and used without purification. Elemental analyses were determined using a Carlo Erba 1106 elemental analyzer. IR spectra were recorded on a BRUKER FT-IR VERTEX 70 spectrometer from 4000 to 400 cm^{-1} using KBr pellets. ^{1}H-NMR spectra were obtained with a Mercury plus 400 MHz NMR spectrometer with TMS as internal standard and $CDCl_3$ as solvent. Electronic spectra were taken on a LabTech UV Bluestar spectrophotometer. Fluorescence measurements were performed on a 970-CRT spectrofluorophotometer. Electrolytic conductance measurements were made with a DDS-307 type conductivity bridge using 10^{-3} mol L^{-1} solution in DMF at room temperature.

Calf thymus (CT-DNA) and ethidium bromide (EB) were obtained from Sigma Chemical Co. (USA). Tris-HCl buffer solution containing 5 mmol L^{-1} Tris-HCl/50 mmol L^{-1} NaCl (pH = 7.2) in doubly distilled water was used to prepare all stock solutions for DNA binding studies. The stock solution of DNA (2.5×10^{-3} mol L^{-1}) was prepared in Tris-HCl/NaCl buffer (pH = 7.2, stored at 4°C and used in less than 4 days). The solution of CT-DNA gave a ratio of UV absorbance at 260 and 280 nm, A_{260}/A_{280}, of 1.8–1.9, indicating that the DNA was sufficiently free of proteins [32]. The concentration of CT-DNA was determined from its absorption intensity at 260 nm with a molar extinction coefficient of 6600 $(\text{mol L}^{-1})^{-1}\,\text{cm}^{-1}$ [33, 34]. Absorption spectra of complex binding of DNA were performed by increasing amounts of DNA to complex in 5 mmol L^{-1} Tris-HCl/50 mmol L^{-1} NaCl buffer (pH = 7.2). The stock solution of ligand and complex was dissolved in DMF at 2×10^{-3} mol L^{-1}.

By fluorescence, the relative binding of complex to CT-DNA was studied with an EB-DNA complex solution in 5 mmol L^{-1} Tris-HCl/50 mmol L^{-1} NaCl buffer (pH = 7.2). Fluorescence intensities (520 nm excitation) were measured at different complex concentrations. The experiment was carried out by titrating complex into EB-DNA solution ([EB] = 8.8×10^{-6} mol L^{-1}, [CT-DNA] = 1×10^{-5} mol L^{-1}).

Viscosity experiments were carried out using an Ubbelodhe viscometer maintained at 25.0 ± 0.1°C in a thermostatic water-bath. Flow time was measured with a digital stopwatch, each sample was measured three times, and an average flow time was calculated. Titrations were performed for the complex (2–20 μmol L^{-1}) and the complex was introduced into the CT-DNA solution (50 μmol L^{-1}) present in the viscometer.

2.2. *Preparation of the ligand and its Cd(II) complex*

2.2.1. 1,3-Bis(1-ethylbenzimidazol-2-yl)-2-thiapropane (L). 1,3-Bis(benzimidazol-2-yl)-2thiapropane (5.88 g, 0.02 mol), synthesized by a literature method [35], was suspended in dry tetrahydrofuran (150 mL) and stirred under reflux with potassium (1.56 g, 0.04 mol). The solution was stirred until potassium disappeared, then iodoethane (7.70 g, 0.05 mol) was added. After 1 h, the solvents were concentrated and the resulting powder was washed with distilled water several times to remove KI. The solid substances were recrystallized with MeOH and pale-yellow powder 1,3-bis(1-ethylbenzimidazol-2yl)-2-thiapropane (L) was deposited. m.p.: 170–173°C. Anal. Calcd for $C_{20}H_{22}N_4S$ (%): C, 67.61; H, 6.19; N, 15.77. Found (%): C, 67.78; H, 6.03; N, 15.63. ^{1}H-NMR (400 MHz, $CDCl_3$), δ: 7.31 (m, 4H, Ph), 4.12 (s, 2H, CH_2), 4.28 (s, 2H, SCH_2), 1.49 (s, 3H, CH_3). IR (KBr, pellet, cm^{-1}): 1274 $\nu_{(C-N)}$, 1458 $\nu_{(C=N)}$, 1616 $\nu_{(C=C)}$.

2.2.2. $[Cd(L)_2](pic)_2$. The synthesis of the ligand and the Cd(II) complex is shown in figure 1. To a stirred solution of 1,3-bis(1-benzylbenzimidazol-2-yl)-2-thiapropane (0.175 g, 0.50 mmol) in hot MeOH (10 mL) was added Cd(II) picrate (0.143 g, 0.25 mmol) in MeOH (5 mL); yellow solution without precipitate formed rapidly. Pale yellow crystals suitable for X-ray diffraction studies were obtained by evaporation of the filtrate after 1 week at room temperature. Anal. Calcd for $C_{52}H_{48}CdN_{14}O_{14}S_2$ (%): C, 49.99; H, 2.98; N, 17.29. Found (%): C, 50.02; H, 3.01; N, 17.27. Selected IR data (KBr ν/cm^{-1}): 1267 $\nu_{(C-N)}$, 1483 $\nu_{(C=N)}$, 1631 $\nu_{(C=C)}$, 1311 $\nu_{s(Ar-NO_2)}$, 1554 $\nu_{as(Ar-NO_2)}$, 549 $\nu_{(S-Cd)}$. Λ_M (DMF, 297 K): 146.7 S cm^2 mol^{-1}.

2.3. *X-ray structure determination of $[Cd(L)_2](pic)_2$*

A suitable single crystal was mounted on a glass fiber and the intensity data were collected with a Bruker APEX II area detector with graphite-monochromated Mo-Kα

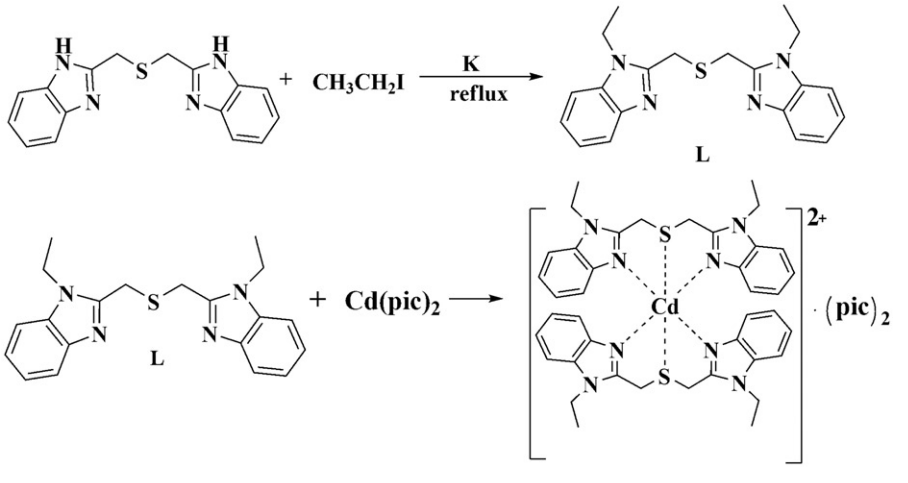

Figure 1. The synthesis of the ligand and the Cd(II) complex (pic = picrate).

Table 1. Crystal data and structure refinement for Cd(II) complex.

Formula	$[Cd(L)_2](pic)_2$
Molecular formula	$C_{52}H_{48}Cd\ N_{14}O_{14}S_2$
Molecular weight	1269.56
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimension (Å, °)	
a	10.4712(8)
b	10.7193(9)
c	12.9985(10)
α	93.9670(10)
β	96.7010(10)
γ	107.7300(10)
Volume (Å^3), Z	1371.73(19), 1
Calculated density (Mg m^{-3})	1.537
$F(000)$	650
Crystal size (mm^3)	$0.40 \times 0.38 \times 0.30$
θ min/max (°)	2.06/26.00
$h/k/l$ (max, min)	$-12, 7/-9, 13/-14, 16$
Reflections collected	7629
Independent reflection	5319 [R(int) = 0.0148]
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	5319/0/378
Goodness-of-fit on F^2	1.032
Final R_1, wR_2 indices [$I > 2\sigma(I)$]	0.0531, 0.1254
R_1, wR_2 indices (all data)	0.0583, 0.1298
Largest difference peak and hole (e Å^{-3})	0.810 and −0.715

radiation ($\lambda = 0.71073$ Å) at 296 K. Data reduction and cell refinement were performed using SAINT [36] and empirical absorption corrections were performed using SADABS [37].

The structure was solved by direct methods and refined by full-matrix least-squares against F^2 of data using SHELXTL software [38]. The non-H atoms in the structure were subjected to anisotropic refinement. Hydrogens were located geometrically and treated with the riding model. Crystal data and experimental parameters relevant to the structure determination are listed in table 1 and the final positional and thermal parameters are available as supplementary material.

3. Results and discussion

The ligand and the Cd(II) complex are stable in the atmosphere, remarkably soluble in polar aprotic solvents such as DMF, DMSO, slightly soluble in ethanol, methanol, and chloroform and insoluble in water. The molar conductivities in DMF indicate that the Cd(II) complex is a 1 : 2 electrolyte [39].

3.1. *Crystal structure of $[Cd(L)_2](pic)_2$*

The molecular structure of $[Cd(L)_2](pic)_2$ along with the atom numbering scheme is represented in figure 2 and selected bond lengths and angles are summarized in table 2.

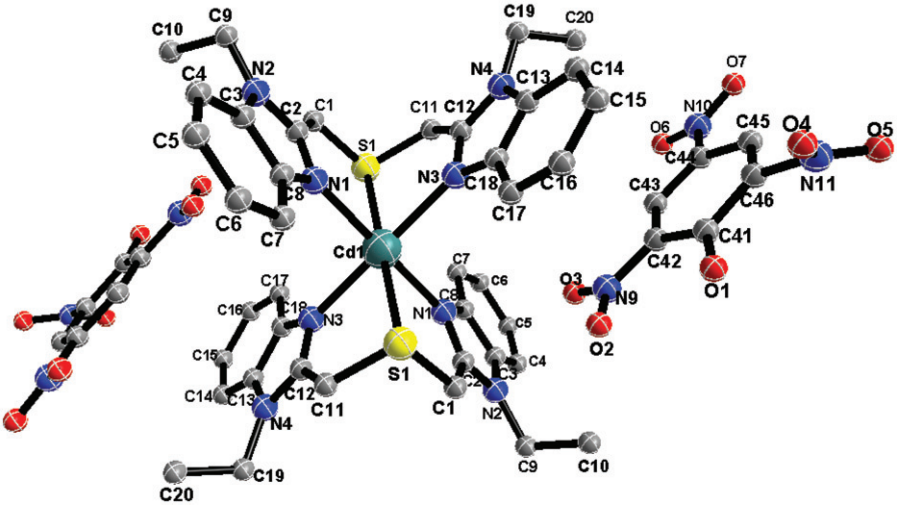

Figure 2. Molecular structure of Cd(II) complex; hydrogens have been omitted for clarity.

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

Cd(1)–N(1)	2.311(3)	Cd(1)–N(1)#1	2.311(3)
Cd(1)–N(3)	2.342(3)	Cd(1)–N(3)#1	2.342(3)
Cd(1)–S(1)	2.7097(9)	Cd(1)–S(1)#1	2.7097(9)
N(1)–Cd(1)–N(1)#1	180.0	N(1)–Cd(1)–N(3)	83.24(11)
N(1)#1–Cd(1)–N(3)	96.76(11)	N(1)–Cd(1)–N(3)#1	96.76(11)
N(1)#1–Cd(1)–N(3)#1	83.24(11)	N(3)–Cd(1)–N(3)#1	180.0
N(1)–Cd(1)–S(1)	76.67(8)	N(1)#1–Cd(1)–S(1)	103.33(8)
N(3)–Cd(1)–S(1)	76.57(8)	N(3)#1–Cd(1)–S(1)	103.43(8)
N(1)–Cd(1)–S(1)#1	103.33(8)	N(1)#1–Cd(1)–S(1)#1	76.67(8)
N(3)–Cd(1)–S(1)#1	103.43(8)	N(3)#1–Cd(1)–S(1)#1	76.57(8)
S(1)–Cd(1)–S(1)#1	180.0		

Symmetry transformations used to generate equivalent atoms: $\#1 - x, -y + 1, -z$.

The compound crystallizes in a triclinic space group $P\bar{1}$. The Cd(II) is coordinated by two tridentate 1,3-bis(1-ethylbenzimidazol-2-yl)-2-thiapropane ligands. The cadmium is six-coordinate octahedral, defined by the N_4S_2 donors from two ligands. The Cd(II) exhibits distorted octahedral geometry with N1, N1#, N3, N3# defining the equatorial plane and the two sulfurs in axial positions. The distance between Cd-S1 and Cd-S1# are 2.7097(9) Å. The bond length of the Cd-N1 and Cd-N1# [2.311(3) Å] is a bit shorter than that of the Cd-N3 and Cd-N3# [2.342(3) Å]. Angles around Cd(II) are close to ideal octahedral values of 90/180°. The complex is fairly symmetrical and symmetry transformations $\#1 - x, -y + 1, -z$ were used to generate equivalent atoms.

The crystal packing of cadmium(II) complex is shown in figure 3. Adjoining picrate anions are stabilized by weak $\pi \ldots \pi$ stacking with centroid distances 3.964(1) Å and the plane-plane distances 3.390(2) Å, $\theta = 20.496(2)$ [40]. One molecule of Cd(II) complex and two picrate anions form an interesting 2D lamellar framework.

This arrangement generates a series of interesting small tubular channels within the 2-D network running along the *a*-axis (figure 4).

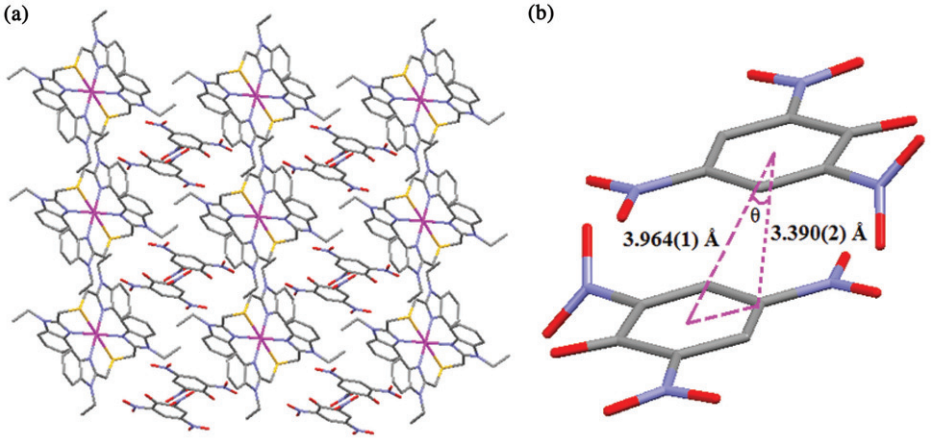

Figure 3. Packing of complex with (a) π–π stacking interactions and (b) π–π stacking by two picrate anions.

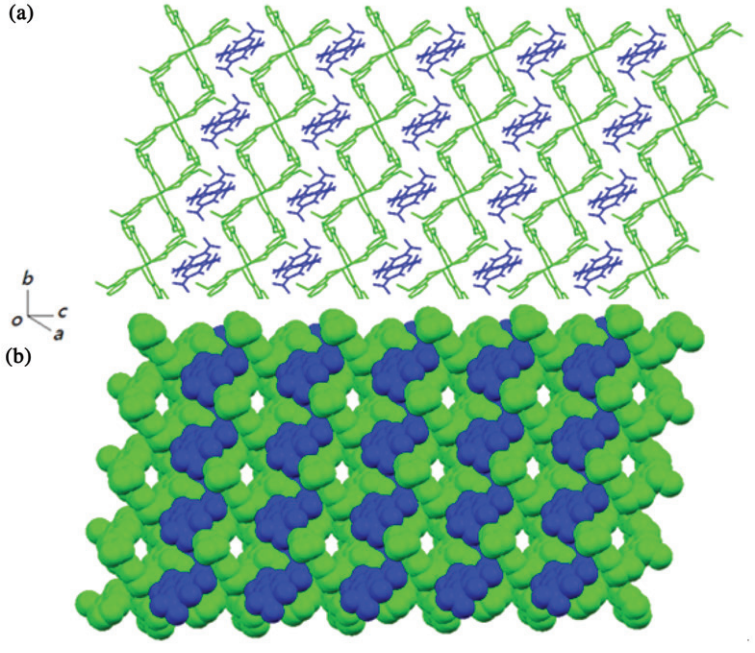

Figure 4. (a) The grid structure and (b) space-filling view of Cd(II) complex down the *a*-axis. The void space is formed by two adjacent molecules of complex.

3.2. *IR and electronic spectra*

The IR spectrum of the free ligand shows characteristic absorption bands of benzimidazole at 1274 and 1452 cm^{-1}, assigned to $\nu_{(C–N)}$ and $\nu_{(C=N)}$, respectively [41, 42]. A shift of $\nu_{(CN)}$ and $\nu_{(C=N)}$ vibrations (*ca* 1267 and 1483 cm^{-1}) of the Cd(II)

complex support the argument that coordination occurs through imine nitrogens [41, 43]. The metal complex shows one new band at 549 nm not found in the ligand, assigned to $\nu_{(S-Cd)}$ [42]. Possible bonding of the picrate may also be obtained from the IR spectra. Bands at 744, 1311, 1554, and 1631 cm^{-1} indicate that benzene rings and ionic picrates are present [44], agreeing with the result determined by X-ray diffraction.

Electronic spectra of the ligand and the metal complex were recorded in DMF at room temperature. The strong absorption band of ligand (280 nm) is only marginally red-shifted in the complex (281 nm) from (C=N–C=C) coordination to the metal. This absorption is assigned to $\pi \rightarrow \pi^*$ (imidazole) [45].

3.3. *DNA banding mode and affinity*

3.3.1. Electronic absorption spectra. Absorption titration was carried out to investigate possible binding modes and binding affinity of compounds with CT-DNA. A compound binding to DNA through intercalation is characterized by hypochromism in absorbance and red shift in wavelength from a strong stacking interaction between the aromatic chromophore and the DNA base pairs [46]. The amount of hypochromism is associated with the strength of the intercalative interaction [47–49]. In order to compare the binding strength of the ligand and complex, intrinsic binding constants K_b were obtained by monitoring the changes in absorbance at 270–280 nm for the two compounds with increasing concentration of DNA. The absorption spectral titration of the ligand and the complex binding to DNA was performed by increasing amount of DNA (5 μL) to the compounds (25 μL) and the reference solution in 2.5 mL Tris-HCl buffer to eliminate the absorption of DNA itself. Each sample solution was scanned from 200 to 500 nm. The constant (K_b) was obtained by the following equation [50]: $[DNA]/(\varepsilon_a - \varepsilon_f) = [DNA]/(\varepsilon_b - \varepsilon_f) + 1/K_b(\varepsilon_b - \varepsilon_f)$, apparent absorption coefficients ε_a, ε_f, and ε_b correspond to $A_{obsd}/[M]$, the extinction coefficient of the free compound and the extinction coefficient of the compound when fully bound to DNA, respectively. In plots of $[DNA]/(\varepsilon_a - \varepsilon_f)$ *versus* [DNA], K_b is given by the ratio of slope to the intercept [51, 52].

With increasing DNA concentration, 14.94% and 9.34% hypochromism were observed in the ligand and Cd(II) complex, and with very slight red shift in absorption titration spectra. The K_b values of the ligand and the Cd(II) complex were 1.26×10^5 $(mol\,L^{-1})^{-1}$ ($R^2 = 0.9595$ for seven points of low concentration), 2.3×10^4 $(mol\,L^{-1})^{-1}$ ($R^2 = 0.9697$ for seven points). The values can be obtained from the inset in figure 5. Compared with DNA-intercalative complexes reported before ($K_b = 2.9 \times 10^4 - 1.2 \times 10^5$ $(mol\,L^{-1})^{-1}$) [53–56], the K_b values of these two compounds are consistent with other reported values, suggesting that both ligand and complex bind to DNA *via* intercalation, involving strong π-stacking interactions between benzimidazole rings of the compounds and DNA base pairs, while the ligand has stronger binding affinity to CT-DNA than the Cd(II) complex. These two K_b values are higher than previous reports of cadmium complex (4.56×10^2 $(mol\,L^{-1})^{-1}$) [57], but lower than five-coordinate cadmium(II) complex (1.42×10^5 $(mol\,L^{-1})^{-1}$) in our previous work [31]. Different steric hindrance may cause the different binding affinity of compounds with DNA.

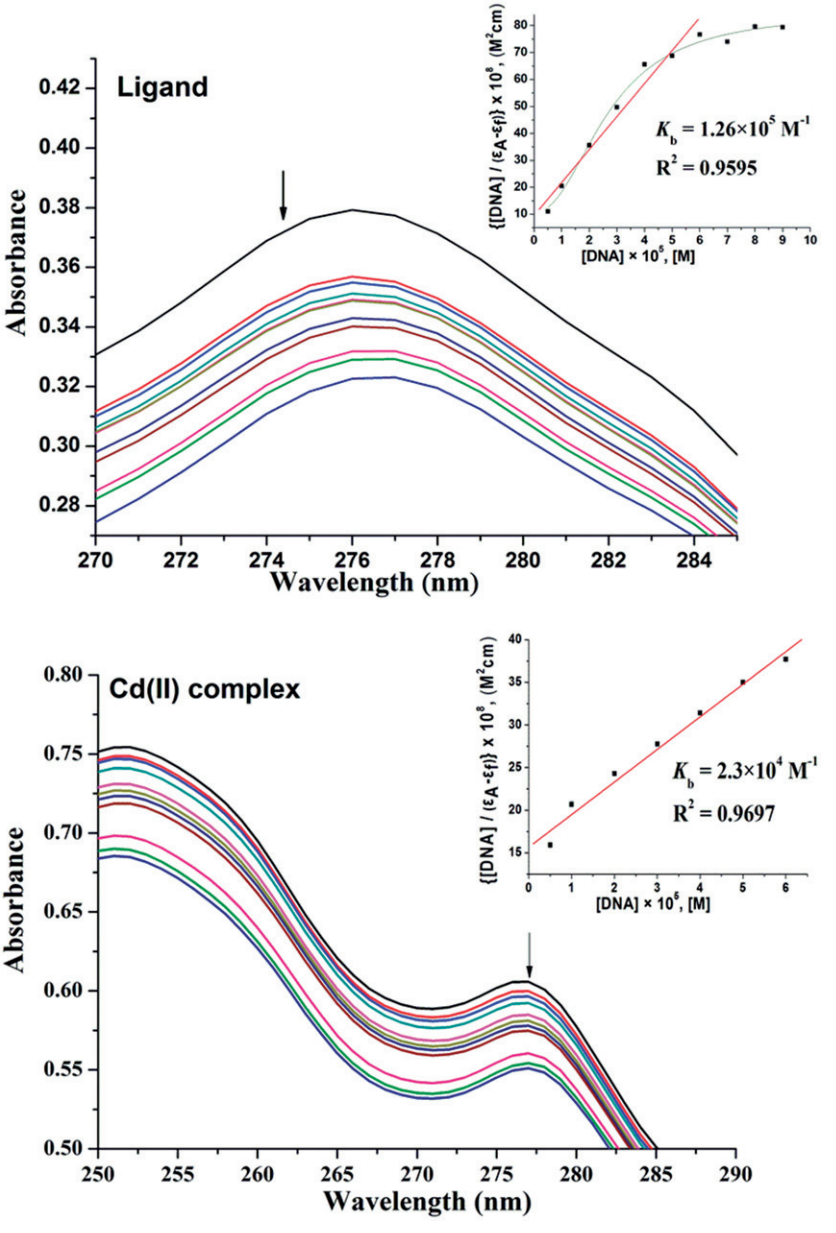

Figure 5. Absorption titration spectra of ligand and complex in the absence (top spectrum) and presence of increasing amounts of DNA (from top to bottom, 0–9 × 10^{-5} mol L^{-1}) in 5 mmol L^{-1} Tris-HCl/50 mmol L^{-1} NaCl buffer (pH = 7.2). The arrow shows the absorbance changes on increasing DNA concentration. Inset: plot of [DNA]/(ε_a–ε_f) *vs.* [DNA] for absorption titration of DNA with complex; ■, experimental data points; solid line, linear fitting of the data.

3.3.2. Fluorescence spectroscopy. No luminescence was observed for the complex at room temperature in any organic solvent or in the presence of CT-DNA. So the binding of complexes with CT-DNA cannot be directly presented in the emission spectra.

Therefore, competitive EB binding studies were undertaken to examine the binding of each complex with DNA. EB (ethidium bromide) is a conjugated planar molecule. Its fluorescence intensity is very weak in solution, but greatly increased when EB is specifically intercalated into base pairs of double-stranded DNA. In previous studies, fluorescence could be quenched by addition of the complex competing with EB to bind with DNA. This is proof that the complex intercalates to base pairs of DNA [58]. The Stern–Volmer quenching constant K_{SV} is used to evaluate the quenching efficiency for each complex, determined by the classical Stern–Volmer equation [59] $I_0/I = 1 + K_{SV}[Q]$; I_0 and I are the fluorescence intensities in the absence and presence of the quencher, respectively, and [Q] is the concentration of the complex.

The EB-DNA complex was prepared by adding 8.8 μmol L^{-1} EB and 10 μmol L^{-1} CT-DNA in 2.5 mL Tris-HCl buffer (pH = 7.2). The intercalating effect of compound with the EB-DNA complex was studied by adding solution of the complex (5 μL) step by step into the solution of the EB-DNA complex. Fluorescence intensities from 500 to 800 nm ($\lambda_{ex} = 520$ nm) were measured at different complex concentrations. The fluorescence intensity of EB-DNA system decreases upon addition of complex. The fluorescence quenching of EB-DNA by complex is shown in figure 6. The Stern–Volmer constant K_{SV} is obtained as the slope of I_0/I *versus* complex linear plot from the inset in figure 6, the K_{SV} value for the complex is 2.6×10^3 $(\text{mol L}^{-1})^{-1}$ ($R^2 = 0.9936$ for six points). To a certain extent, reduction of the emission intensity at 597 nm gives a measure of the binding propensity of the complex to CT-DNA. This quenching suggests that the complex can compete for DNA-binding sites with EB and displace EB from the EB-DNA system [60], characteristic of intercalative interaction of compound with DNA [61].

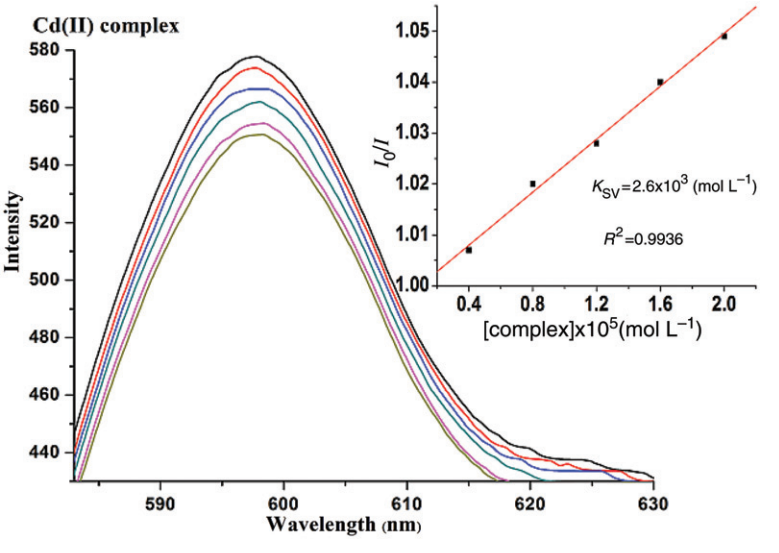

Figure 6. Fluorescence quenching curves of EB-DNA by complex ([complex] = 0–25 μmol L^{-1} from top to bottom, $\lambda_{ex} = 520$ nm). The arrow shows intensity changes on increasing complex concentration. Inset: plot of I_0/I *vs.* [complex].

3.3.3. Viscosity experiment. Further clarification of the interactions between the Cd(II) complex and DNA was carried out by viscosity measurements. Due to its sensitivity to the change of length of DNA, viscosity measurement may be the most effective means to study the binding mode of complex to DNA [62]. A significant increase in viscosity of DNA on addition of complex indicates intercalative binding to DNA. In contrast, complex that binds in the DNA grooves by partial and/or non-classical intercalation cause less pronounced (positive or negative) or no change in DNA solution viscosity. Titrations were performed for the complexes (2–20 μmol L^{-1}) and each complex was introduced into the CT-DNA solution (50 μmol L^{-1}) present in the viscometer. Viscosity values were calculated from the observed flow time of CT-DNA containing solutions corrected from the flow time of buffer alone (t_0), $\eta = (t - t_0)/t_0$ [63]. Data were presented as $(\eta/\eta_0)^{1/3}$ *versus* the ratio of the concentration of the complex to CT-DNA, where η is the viscosity of CT-DNA in the presence of the complex and η_0 is the viscosity of CT-DNA alone. Viscosity measurements were carried out on CT-DNA by varying the concentration of the compound. Figure 7 shows that ligand and complex increase the relative viscosity of DNA, indicating that the two compounds intercalate adjacent DNA base pairs, leading to an increase in separation of base pairs and, thus, an increase in overall DNA contour length. The results demonstrate that the complex binds to DNA by intercalation, which is consistent with the absorption and fluorescence spectral results.

4. Conclusion

$[Cd(L)_2](pic)_2$, with the V-shaped ligand 1,3-bis(1-ethylbenzimidazol-2-yl)-2-thiapropane, has been synthesized and characterized. The crystal structure shows a slightly

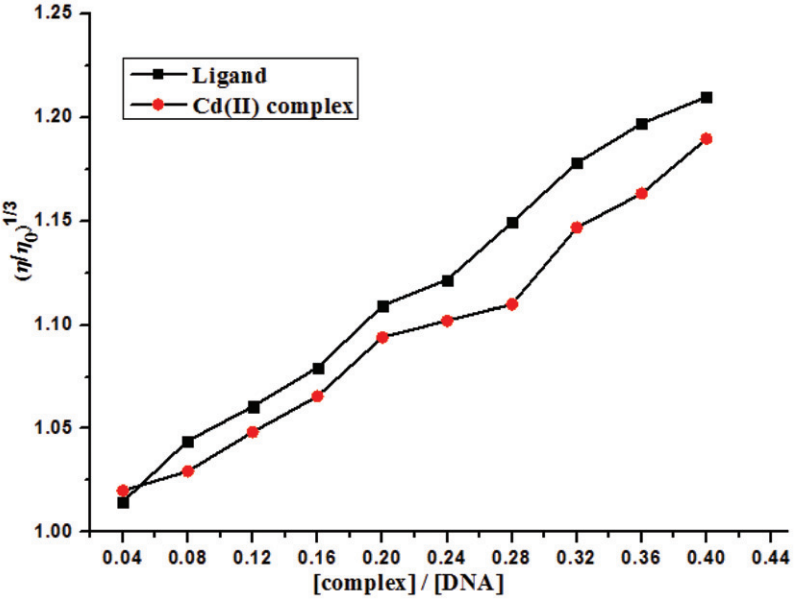

Figure 7. Effect of increasing amounts of the ligand and the complex on the relative viscosity of CT-DNA at 25 (±0.1)°C in 5 mmol L^{-1} Tris-HCl buffer (pH = 7.2, [DNA] = 50 μmol L^{-1}).

distorted octahedral geometry around Cd. The binding constant (K_b) and the linear Stern–Volmer quenching constant (K_{SV}) suggest that the ligand and complex bind to DNA *via* intercalation. The binding affinity of ligand is higher than that of the complex, probably due to steric hindrance of the V-shaped ligand is smaller than the octahedral Cd(II) complex. This information will be useful in designing probes of nucleic acid structures.

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 823994. Copies of the data can be obtained, free of charge, on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK.

Acknowledgments

We are grateful for the financial support and grant from "Qing Lan" Talent Engineering Funds and Student's Science and Technology Innovation Funds (grant no. DXS2008-041) by the Lanzhou Jiaotong University. The grant from the "Long Yuan Qing Nian" of Gansu Provinces is also acknowledged.

References

[1] Y.M. Song, Q. Wu, P.J. Yang, N.N. Luan, L.F. Wang, Y.M. Liu. *J. Inorg. Biochem.*, **100**, 1685 (2006).
[2] J. Tan, B. Wang, L. Zhu. *Bioorg. Med. Chem.*, **17**, 614 (2009).
[3] C.P. Tan, J. Liu, L.M. Chen, S. Shi, L.N. Ji. *J. Inorg. Biochem.*, **102**, 1644 (2008).
[4] V.S. Li, D. Choi, Z. Wang, L.S. Jimenez, M.S. Tang, H. Kohn. *J. Am. Chem. Soc.*, **18**, 2326 (1996).
[5] G. Zuber, J.C. Quada Jr, S.M. Hecht. *J. Am. Chem. Soc.*, **120**, 9368 (1998).
[6] S.M. Hecht. *J. Nat. Prod.*, **63**, 158 (2000).
[7] J. Liu, W.J. Mei, A.W. Xu, S. Shi, C.P. Tan, L.N. Ji. *Antiviral. Res.*, **62**, 65 (2004).
[8] B.N. Trawick, A.T. Daniher, J.K. Bashkin. *Chem. Rev.*, **98**, 939 (1998).
[9] S.C. Zhang, Y. Shao, Y. Chen. *J. Inorg. Chem.*, **22**, 1733 (2006).
[10] J.G. Liu, B.H. Ye, H. Li, Q.X. Zhen, L.N. Ji, Y.H. Fu. *J. Inorg. Biochem.*, **76**, 265 (1999).
[11] J. Jiang, X.L. Tang, W. Dou, H.H. Zhang, W.S. Liu, C.X. Wang, J.R. Zheng. *J. Inorg. Biochem.*, **104**, 583 (2010).
[12] L.M. Chen, J. Liu, J.C. Chen, S. Shi. *J. Mol. Struct.*, **881**, 156 (2008).
[13] R. Rohini, K. Shanker, P.M. Reddy, Y.P. Ho, V. Ravinder. *Eur. J. Med. Chem.*, **44**, 3330 (2009).
[14] Q. Sun, B. Gatto, C. Yu, A. Liu, L.F. Liu, E.J. La Voie. *J. Med. Chem.*, **38**, 3638 (1995).
[15] A.W. White, R. Almassy, A.H. Calvert, N.J. Curtin, R.J. Griffin, Z. Hostomsky, K. Maegley, D.R. Newell, S. Srinivasan, B.T. Golding. *J. Med. Chem.*, **43**, 4084 (2000).
[16] A.P. Combs, W. Zhu, M.L. Crawley, B. Glass, P. Polam, R.B. Sparks, D. Modi, A. Takvorian, E. McLaughlin, E.W. Yue, Z. Wasserman, M. Bower, M. Wei, M. Rupar, P.J. Ala, B.M. Reid, D. Ellis, L. Gonneville, T. Emm, N. Taylor, S. Yeleswaram, Y. Li, R. Wynn, T.C. Burn, G. Hollis, P.C.C. Liu, B. Metcalf. *J. Med. Chem.*, **49**, 3774 (2006).
[17] K. Starčević, M. Kralj, K. Ester, I. Sabol, M. Grce, K. Pavelić, G. Karminski-Zamola. *Bioorg. Med. Chem.*, **15**, 4419 (2007).
[18] T. Fonseca, B. Gigante, M.M. Marques, L.T. Gilchrist, E. de Clercq. *Bioorg. Med. Chem.*, **12**, 103 (2004).

[19] F. Victor, T. Brown, K. Campanale, B.A. Heinz, L.A. Shipley, K.S. Su, J. Tang, L.M. Vance, W.A. Spitzer. *J. Med. Chem.*, **40**, 1511 (1997).
[20] M.J. Tebbe, W.A. Spitzer, F. Victor, S.C. Miller, C.C. Lee, T.R. Sattelberg Sr, E. McKinney, J.C. Tang. *J. Med. Chem.*, **40**, 3937 (1997).
[21] A. Silvestri, G. Barone, G. Ruisi, M.T. Lo Giudice, S. Tumminello. *J. Inorg. Biochem.*, **98**, 589 (2004).
[22] W. Lewandowski, M. Kalinowska, H. Lewandowska. *J. Inorg. Biochem.*, **99**, 1407 (2005).
[23] R. Chen, C.S. Liu, H. Zhang, Y. Guo, X.H. Bu, M. Yang. *J. Inorg. Biochem.*, **101**, 412 (2007).
[24] S.J. Lippard. *Chem. Rev.*, **99**, 2467 (1999).
[25] K.E. Erkkila, D.T. Odom, J.K. Barton. *Chem. Rev.*, **99**, 2777 (1999).
[26] H.T. Chifotides, K.R. Dunbar. *Acc. Chem. Res.*, **38**, 146 (2005).
[27] B. Armitage. *Chem. Rev.*, **98**, 1171 (1998).
[28] W.K. Pogozelski, T.D. Tullius. *Chem. Rev.*, **98**, 1089 (1998).
[29] C. Metcalfe, J.A. Thomas. *Chem. Soc. Rev.*, **32**, 215 (2003).
[30] H. Sigel, R.B. Martin. *Chem. Soc. Rev.*, **23**, 83 (1994).
[31] H.L. Wu, K.T. Wang, F. Jia, B. Liu, F. Kou, J.K. Yuan, J. Kong. *J. Coord. Chem.*, **63**, 4113 (2010).
[32] J. Marmur. *J. Mol. Biol.*, **3**, 208 (1961).
[33] M.E. Reichmann, S.A. Rice, C.A. Thomas, P. Doty. *J. Am. Chem. Soc.*, **76**, 3047 (1954).
[34] C.Y. Gao, X.F. Ma, J.L. Tian, D.D. Li. *J. Coord. Chem.*, **63**, 115 (2010).
[35] J.V. Dagdigian, C.A. Reed. *Inorg. Chem.*, **18**, 2624 (1979).
[36] Bruker (2006) *APEX2, SAINT*, Bruker AXS Inc., Madison, Wisconsin, USA (2006).
[37] G.M. Sheldrick. *SADABS, Program for Empirical Absorption Correction of Area Detector Data*, University of Göttingen, Göttingen, Germany (2004).
[38] G.M. Sheldrick. *Acta Cryst. A*, **64**, 112 (2008).
[39] W.J. Geary. *Coord. Chem. Rev.*, **7**, 81 (1971).
[40] J.W. Steed, J.L. Atwood, *Supramolecular Chemistry*, John Wiley & Sons, Chichester (2000).
[41] N.M. Agh-Atabay, B. Dulger, F. Gucin. *Eur. J. Med. Chem.*, **40**, 1096 (2005).
[42] N.M. Aghatabay, M. Tulu, Y. Mahmiani, M. Somer, B. Dulger. *Struct. Chem.*, **19**, 71 (2008).
[43] C.Y. Su, B.S. Kang, C.X. Du, Q.C. Yang. *Inorg. Chem.*, **39**, 4843 (2000).
[44] H.L. Wu, K.T. Wang, R.R. Yun, X.C. Huang. *Synth. React. Inorg. Met-Org. Chem.*, **39**, 629 (2009).
[45] H.L. Wu, T. Sun, K. Li, Y. Xu, R.R. Yun, Q. Sun. *Z. Anorg. Allg. Chem.*, **635**, 146 (2009).
[46] M. Baldini, M. Belicchi-Ferrari, F. Bisceglie, P.P. Dall'Aglio, G. Pelosi, S. Pinelli, P. Tarasconi. *Inorg. Chem.*, **43**, 7170 (2004).
[47] J.K. Barton, A.T. Danishefsky, J.M. Goldberg. *J. Am. Chem. Soc.*, **106**, 2172 (1984).
[48] S.A. Tysoe, R.J. Morgan, A.D. Baker, T.C. Strekas. *J. Phys. Chem.*, **97**, 1707 (1993).
[49] J.M. Kelly, A.B. Tossi, D.J. McConnell. *Nucleic Acids Res.*, **13**, 6017 (1985).
[50] A.M. Pyle, J.P. Rehmann, R. Meshoyrer, C.V. Kumar, N.J. Turro, J.K. Barton. *J. Am. Chem. Soc.*, **111**, 3051 (1989).
[51] J. Liu, H. Zhang, C.H. Chen, H. Deng, L.N. Ji. *Dalton Trans.*, 114 (2003).
[52] J.L. Wang, L. Shuai, X.M. Xiao, Y. Zeng, Z.L. Li, T. Matsumura-Inoue. *J. Inorg. Biochem.*, **99**, 883 (2005).
[53] R. Olar, M. Badea, D. Marinescu, C.M Chifiriuc, A. Finaru. *Eur. J. Med. Chem.*, **45**, 2868 (2010).
[54] H.F. Wang, R. Shen, N. Tang. *Eur. J. Med. Chem.*, **44**, 4509 (2009).
[55] A. Tarushi, G. Psomas, V. Psycharis, D.P. Kessissoglou. *Polyhedron*, **28**, 3272 (2009).
[56] S. Mukherjee, C. Basu, S. Chowdhury, A.P. Chattopadhyay, A. Ghorai, U. Ghosh, H. Stoeckli-Evans. *Inorg. Chim. Acta*, **363**, 2752 (2010).
[57] C.Y. Gao, X.F. Ma, J.L. Tian, D.D. Li. *J. Coord. Chem.*, **63**, 115 (2010).
[58] Q. Wang, Z.Y. Yang, G.F. Qi, D.D. Qin. *Eur. J. Med. Chem.*, **44**, 2425 (2009).
[59] J.R. Lakowicz, G. Webber. *Biochemistry*, **12**, 4161 (1973).
[60] Y.B. Zeng, N. Yang, W.S. Liu, N. Tang. *J. Inorg. Biochem.*, **97**, 258 (2003).
[61] C.V. Kumar, J.K. Barton, N.J. Turro. *J. Am. Chem. Soc.*, **107**, 5518 (1985).
[62] B.C. Baguley, M. Le Bret. *Biochemistry*, **23**, 937 (1984).
[63] M.T. Carter, M. Rodriguez, A.J. Bard. *J. Am. Chem. Soc.*, **111**, 8901 (1989).