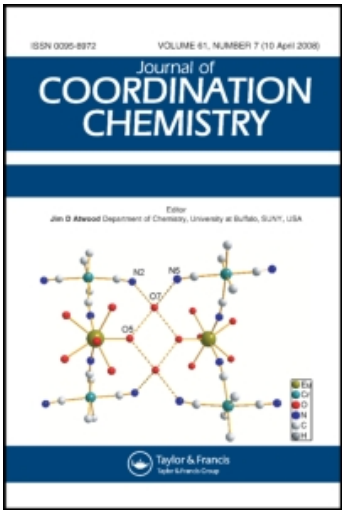

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Synthesis, characterization, and DNA band of a five-coordinate cadmium(II) complex with 1,3-*bis*(1-benzylbenzimidazol-2-yl)-2-thiapropane

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Synthesis, characterization, and DNA band of a five-coordinate cadmium(II) complex with 1,3-*bis*(1-benzylbenzimidazol-2-yl)-2-thiapropane

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A five-coordinate cadmium(II) complex with 1,3-*bis*(1-benzylbenzimidazol-2-yl)2-thiapropane (L), $[Cd(L)Br_2]\cdot DMF$, has been synthesized and characterized by elemental analysis, electrical conductivities, IR, and UV-Vis spectral measurements. The crystal structure of the complex has been determined by single-crystal X-ray diffraction. The Cd(II) is five-coordinate with two nitrogens and a sulfur from one ligand, and two bromides. The N_2SBr_2 donors are in a distorted square-pyramidal geometry ($\tau = 0.32$). Electronic absorption titration spectra, EB (ethidium bromide) competitive experiment, and viscosity measurement indicated that the complex can bind to DNA *via* intercalation.

Keywords: Synthesis; 1,3-*Bis*(1-benzylbenzimidazol-2-yl)-2-thiapropane; Crystal structure; DNA binding

1. Introduction

Coordination complexes have received attention due to their intriguing architectures and potential applications in catalysis, absorption, fluorescent materials, etc. [1–6]. The interactions of small inorganic–organic molecules with DNA have attracted a great deal of attention because of their interference with important events in cells of living organisms [7–9]. Transition metal complexes have been introduced to learn more about the mechanism of DNA binding and in particular prerequisites for specificity [10, 11]. Many applications of these complexes require that the complexes bind DNA in an intercalation mode, and thus thorough understanding of the metal complex–DNA interaction is very important. Among the factors governing DNA binding, molecular shape is the most significant [12]. In recent years, inorganic–organic metal complexes, such as benzimidazole derivatives and their transition metal complexes have been extensively investigated in interactions between complexes and DNA [13–15].

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2. Experimental

2.1. *Materials and physical measurements*

All chemicals and solvents were of reagent grade and used without purification. C, H, and N contents were determined using a Carlo Erba 1106 elemental analyzer. IR spectra were recorded in the 4000–400 cm^{-1} region with a Nicolet FI-IR AVATAR 360 spectrometer using KBr pellets. Electrolytic conductance measurements were made with a DDS-307 type conductivity bridge using 10^{-3} mol L^{-1} solution in DMF at room temperature. Electronic spectra were taken on a LabTech UV Bluestar spectrophotometer. Fluorescence measurements were recorded on a 970-CRT spectrofluorophotometer. 1H-NMR spectra were obtained with a Mercury plus 400 MHz NMR spectrometer with TMS as an internal standard and DMSO-d_6 as a solvent.

Calf thymus DNA (CT-DNA) was obtained from Sigma Chemicals Co. (USA) and used as received. All experiments involved with the interaction of the complex with DNA were carried out in double-distilled water buffer. Using the electronic absorption spectral method, the relative binding of complex to CT-DNA was studied in 5 mmol L^{-1} *Tris*-HCl/50 mmol L^{-1} NaCl buffer (pH = 7.2). A solution of CT-DNA gave a ratio of UV absorbance at 260 and 280 nm, A260/A280, of 1.8–1.9, indicating that the DNA was sufficiently free of proteins [16]. 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 not more than 4 days). The concentration of CT-DNA was determined from its absorption intensity at 260 nm with a molar extinction coefficient of 6600 (mol $L^{-1})^{-1}$ cm^{-1} [17, 18]. Absorption spectra of complex binding of DNA were studied 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 complex was dissolved in DMF at 2×10^{-3} mol L^{-1}.

By the fluorescence spectral method, 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 complex solution ([EB] = 8.8×10^{-6}, [CT-DNA] = 1×10^{-5} mol L^{-1}).

Viscosity experiments were carried out using an Ubbelohde viscometer maintained at 25.0 ± 0.1°C in a thermostatic water bath. Flow time was measured with a digital stopwatch, and 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 1,3-*bis*(1-benzylbenzimidazol-2-yl)-2-thiapropane and its complex*

2.2.1. 1,3-*Bis*(1-benzylbenzimidazol-2-yl)-2-thiapropane (L). 5.88 g (0.02 mol) 1,3-*bis*(benzimidazol-2-yl)-2-thiapropane (synthesized by the literature method [19]) with 1.56 g (0.04 mol) potassium in 150 mL distilled tetrahydrofuran was followed by adding 8.55 g (0.05 mol) benzyl bromide. The resulting solution was concentrated and recrystallized from methanol giving pale yellow block crystals of 1,3-*bis*(1-benzylbenzimidazol-2-yl)-2-thiapropane. Yield: 5.87 g (71%); m.p.: 140–142°C. Anal. Calcd for

$C_{30}H_{26}N_4S$ (%): C, 75.92; H, 5.52; N, 11.81. Found (%): C, 75.86; H, 5.43; N, 11.94. Selected IR data (KBr $\nu\,cm^{-1}$): 1157 ν(C–N), 1454 ν(C=N), 1608 ν(C=C). ^{1}H-NMR (DMSO-d_6, 400 MHz) δ: 5.5 (s, 4H, CH_2), 7.3 (m, 10H, ph), 4.2 (s, 4H, SCH_2). Λ_M (DMF, 297 K): 21.9 S cm2 mol L^{-1}.

2.2.2. [Cd(L)Br$_2$] · DMF. To a stirred solution of 1,3-*bis*(1-benzylbenzimidazol-2yl)-2-thiapropane (0.24 g, 0.50 mmol) in hot MeOH (10 mL), Cd(II) picrate (0.15 g, 0.25 mmol) and KBr (0.06 g, 0.50 mmol) in MeOH (5 mL) were added. A deep yellow 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. Yellow crystals suitable for X-ray diffraction were obtained by ether diffusion into DMF after several days at room temperature. Yield: 0.29 g (73%). Anal. Calcd for $C_{33}H_{33}Br_2CdN_5OS$ (%): C, 54.22; H, 4.55; N, 9.58; Cd, 15.38. Found (%): C, 54.16; H, 4.49; N, 9.63; Cd, 15.41. Selected IR data (KBr $\nu\,cm^{-1}$): 1163 ν(C–N), 1456 ν(C=N), 1633 ν(C=C). Λ_M (DMF, 297 K): 40.7 S cm^2 mol L^{-1}.

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

All data were obtained using a Bruker Smart CCD diffractometer with graphite monochromated Mo-Kα radiation ($\lambda = 0.071073$ Å) at 296 K. Data reduction and cell refinement were performed using SMART and SAINT programs [20]. Absorption corrections were carried out by the empirical method and the structure was solved by direct methods (Bruker SHELXTL) using all unique data [21].

The non-H atoms in the structure were subjected to anisotropic refinement. Hydrogens were located geometrically and treated with the riding model. The 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 cadmium complex is soluble in DMF and DMSO, slightly soluble in methanol, ethanol, and ether but insoluble in water. Molar conductance shows the complex is a non-electrolyte in DMF [22].

3.1. *Crystal structure of [Cd(L)Br$_2$] · DMF*

Coordination numbers of cadmium(II) complexes are six, seven, or eight [23–26]. We report a complex with Cd(II) five-coordinate in a distorted square-pyramidal geometry by N_2S donor set and two bromides. The distortion in the coordination polyhedron (τ) from a perfect trigonal bipyramidal geometry ($\tau = 1$) toward a regular tetragonal pyramid ($\tau = 0$) has been calculated according to the method of Addison *et al.* [27]. For this treatment, S1, N1A, Br1, and N1 (symmetry codes are as given in figure 1) make up the basal plane, while the apical site is occupied by Br2, and $\tau = 0.32$. The parameter τ is

Table 1. Crystal data and structure refinement for $[Cd(L)Br_2]\cdot DMF$.

Molecular formula	$C_{33}H_{33}Br_2CdN_5OS$
Molecular weight	819.92
Temperature (K)	296(2)
Crystal system	Monoclinic
Space group	$P2_1/m$
Unit cell dimensions (Å, °)	
a	9.7437(8)
b	16.7792(14)
c	10.5931(9)
α	90
β	110.0290(10)
γ	90
Volume (Å^3), Z	1627.1(2), 2
Calculated density (g cm^{-3})	1.674
$F(000)$	816
Crystal size (mm^3)	$0.36 \times 0.32 \times 0.28$
θ range for data collection (°)	2.05–26.00
Reflections collected	9062
Independent reflection	3305 [R(int) = 0.0266]
Refinement method	Full-matrix least squares on F^2
Data/restraints/parameters	3305/0/211
Goodness-of-fit on F^2	1.046
Final R indicies [$I > 2\sigma(I)$]	$R_1 = 0.0291$, $wR_2 = 0.0715$
R indices (all data)	$R_1 = 0.0393$, $wR_2 = 0.0769$
Largest differences peak and hole (e Å^{-3})	0.779 and −0.636

defined as $(\beta-\alpha)/60$ (where β = Br(1)–Cd(1)–S(1), α = N(1)–Cd(1)–N(1)#1). Selected bond distances and angles are shown in table 2.

The crystal packing of the cadmium(II) complex is shown in figure 2. The benzimidazole rings are stabilized by weak $\pi\cdots\pi$ stacking with centroid distances of 3.428(1) and 3.761(3) Å.

3.2. *IR and electronic spectra*

In the free ligand, a strong band is found at 1454 cm^{-1} along with another less strong band at 1157 cm^{-1}. By analogy with the assigned bands of imidazole, the former is attributed to $\nu_{(C=N)}$, while the latter is $\nu_{(C-N)}$ [28, 29]. Shifts to higher frequency by 2 and 6 cm^{-1} in the complex, imply direct coordination of imine nitrogen to cadmium(II); these are the preferred nitrogens for coordination, as found in other metal complexes with benzimidazoles [30]. Bands at 1608 and 1633 cm^{-1} indicate that benzene rings are present.

UV absorption spectra of the ligand and cadmium complex show bands at 279 and 281 nm, respectively. The red shift reveals that the ligand is coordinated, agreeing with X-ray diffraction [31].

3.3. *DNA binding study*

3.3.1. Electronic absorption spectra. Interaction of the complex with CT-DNA has been studied with UV spectroscopy to investigate possible binding modes to DNA and

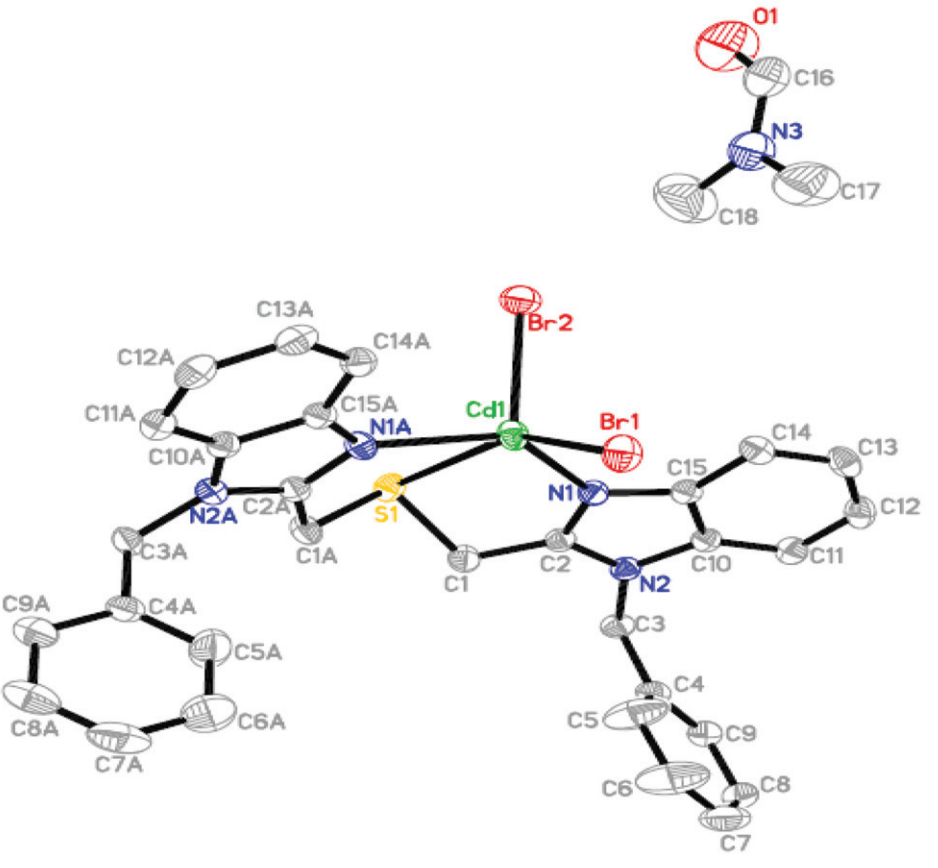

Figure 1. Structure of complex.

Table 2. Selected bond lengths (Å) and angles (°).

Br(1)–Cd(1)	2.6004(6)	Br(2)–Cd(1)	2.6038(6)
Cd(1)–N(1)	2.264(2)	Cd(1)–N(1)#1	2.264(2)
Cd(1)–S(1)	2.9784(11)		
N(1)–Cd(1)–Br(1)	103.31(6)	N(1)#1–Cd(1)–Br(1)	103.31(6)
N(1)–Cd(1)–Br(2)	102.82(6)	N(1)#1–Cd(1)–Br(2)	102.82(6)
Br(1)–Cd(1)–Br(2)	109.732(19)	N(1)–Cd(1)–N(1)#1	133.74(11)
N(1)–Cd(1)–S(1)	69.50(5)	N(1)#1–Cd(1)–S(1)	69.50(5)
Br(1)–Cd(1)–S(1)	152.80(3)	Br(2)–Cd(1)–S(1)	97.46(3)

Symmetry transformations used to generate equivalent atoms: #1: $x, -y+1/2, z$.

to calculate the binding constants to DNA (K_b). Control experiment with DMF was performed and no changes in the spectra of DNA were observed.

Absorption titration was performed with fixed concentrations of the complex and gradually increasing concentration of DNA. While measuring the absorption spectra, an equal amount of DNA was added to the complex solution and the reference solution to eliminate absorption of DNA itself. The sample solution was scanned in the range

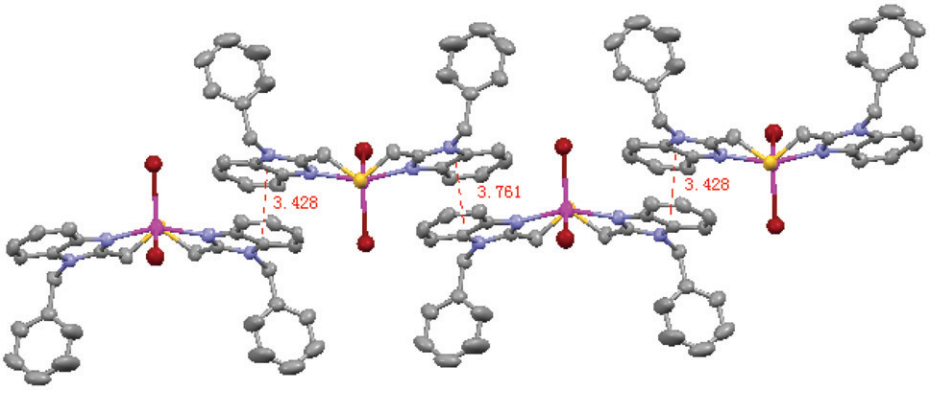

Figure 2. The structure of complex linked *via* π–π stacking interaction.

190–500 nm and the intrinsic binding constants K_b of the complex with DNA were obtained by monitoring the changes in absorbance at 270–300 nm for the complex with increasing concentration of DNA using the following equation [32]: $[DNA]/(\varepsilon_a-\varepsilon_f) = [DNA]/(\varepsilon_b-\varepsilon_f) + 1/K_b(\varepsilon_b-\varepsilon_f)$, apparent absorption coefficient ε_a, ε_f, and ε_b correspond to $A_{obsd}/[M]$, the extinction coefficient of the free complex and the extinction coefficient of the complex when fully bound to DNA, respectively. In the plots of $[DNA]/(\varepsilon_a-\varepsilon_f)$ *versus* [DNA], K_b is given by the ratio of slope to the intercept.

A complex bound to DNA through intercalation is characterized by hypochromism in absorbance and a certain shift in wavelength, due to intercalation involving a strong stacking interaction between the aromatic chromophore and the DNA base pairs [33]. The extent of hypochromism is usually consistent with the strength of the intercalative interaction [34–36]. Absorption spectra of complex in the absence and presence of DNA at different concentrations are given in figure 3(a). As DNA concentration increases, 18.81% hypochromism was observed in the complex. The constant K_b for the complex was $1.42 \times 10^5 (\text{mol L}^{-1})^{-1}$. This K_b value is lower than that of classical intercalators (EB-DNA, $1.4 \times 10^6 (\text{mol L}^{-1})^{-1}$) [37], but it is much higher than previous reports of a cadmium complex ($4.56 \times 10^2 (\text{mol L}^{-1})^{-1}$) [18]. All these suggest intercalation between the five-coordinate Cd(II) complex and CT-DNA.

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 complex cannot be directly presented in the emission spectra. To further clarify the interaction of the complex with DNA, the competitive binding experiment was carried out.

Competitive studies of the complex with EB have been investigated with fluorescence spectroscopy to examine whether the complex can displace EB from its EB-DNA complex. The EB-DNA complex was prepared by adding $8.8\,\mu\text{mol L}^{-1}$ EB and $10\,\mu\text{mol L}^{-1}$ CT-DNA in buffer (pH = 7.2). The intercalating effect of complex with the EB-DNA complex was studied by adding a certain amount of a solution of the complex step by step into the solution of the EB-DNA complex. The influence of the addition of

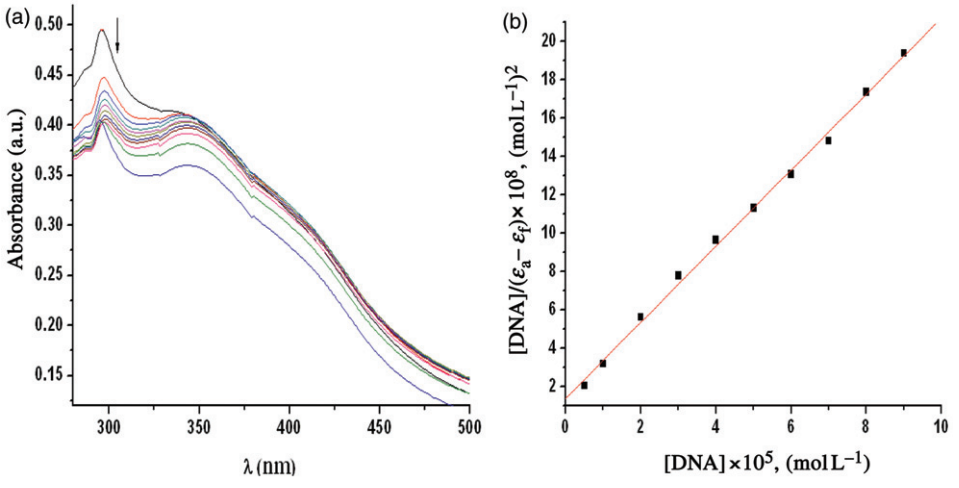

Figure 3. (a) Absorption spectra of complex (2×10^{-5} mol L^{-1}) in the absence and presence of increasing amounts of DNA ($0–9 \times 10^{-5}$ mol L^{-1}) in 5 mmol L^{-1} *Tris*-HCl/50 mmol L^{-1} NaCl buffer (pH = 7.2). The arrow shows absorbance changes on increasing DNA concentration. (b) Plot of [DNA]/(ε_a–ε_f) *vs.* [DNA] for absorption titration of DNA with complex.

the complex to the EB-DNA complex solution has been obtained by recording the variation of fluorescence emission spectra.

Fluorescence quenching of EB bound to CT-DNA by the complex is shown in figure 4(a). The addition of complex to EB-DNA solution caused obvious reduction in emission intensities, indicating that complex competitively bound to DNA with EB. The extent of reduction of the emission intensity gives a measure of the binding propensity of the complex to CT-DNA. According to the classical Stern–Volmer equation [38], $I_0/I = 1 + K_{SV}$ [Q], where I_0 and I are the fluorescence intensities in the absence and presence of the quencher, respectively, K_{SV} is a linear Stern–Volmer quenching constant, and [Q] is the concentration of the quencher. The quenching plot illustrates that the quenching of EB bound to DNA by the complex is in agreement with the linear Stern–Volmer equation, which also indicates that the complex binds to CT-DNA. The Stern–Volmer constant K_{SV} used to evaluate the quenching efficiency is obtained as the slope of I_0/I *versus* complex linear plot. The K_{SV} value for complex is 2.608×10^3 $(\text{mol L}^{-1})^{-1}$, as shown in figure 4(b). The complex may have better ability to interact with DNA through intercalation, releasing free EB from the EB-DNA complex [39].

3.3.3. Viscosity experiment. Viscosities were calculated from the observed flow time of CT-DNA containing solutions corrected from the flow time of buffer alone (t_0), $\eta = t - t_0$ [40]. Data are 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.

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, especially in the absence of crystallographic structural data [41]. A significant increase in the

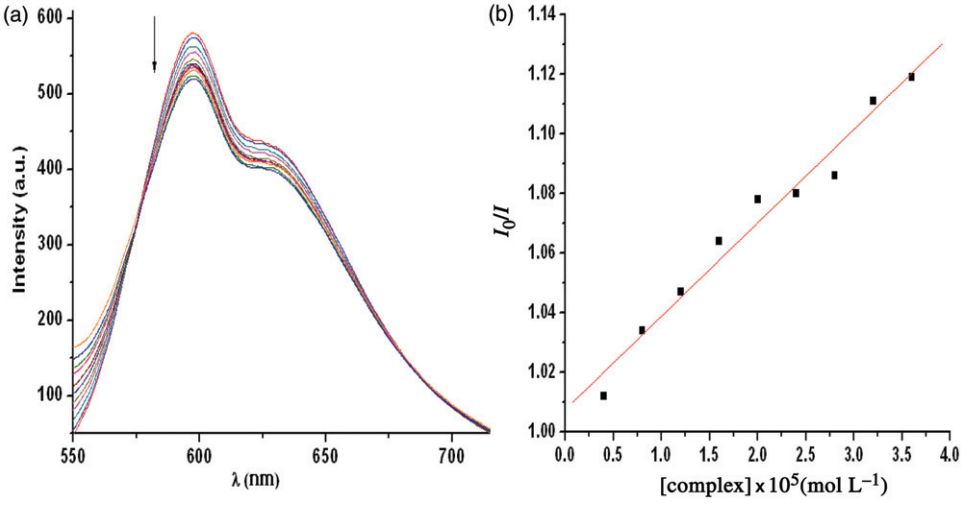

Figure 4. (a) Fluorescence quenching curves of EB-DNA by complex ([complex] = 0–40 μmol L^{-1}, λ_{ex} = 520 nm). The arrow shows the intensity changes on increasing the complex concentration. (b) Plot of I_0/I *vs.* [complex].

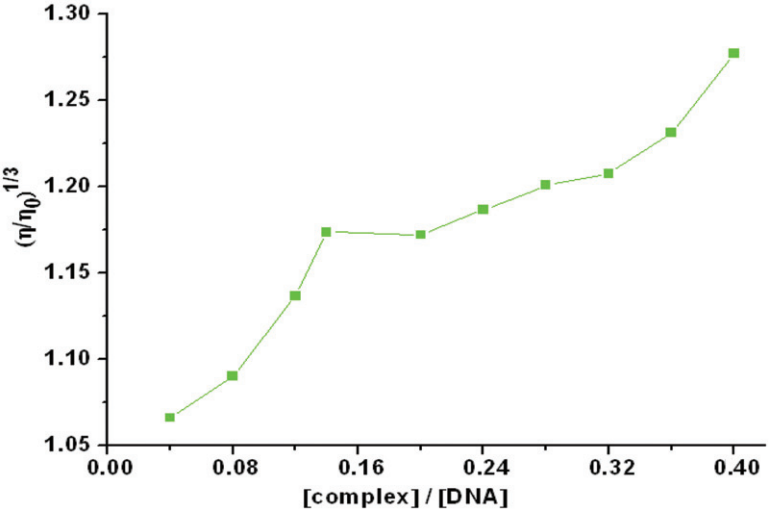

Figure 5. Effect of increasing amounts of the complex on the relative viscosity of CT-DNA at 25 (±0.1)°C in 5 mmol L^{-1} *Tris*-HCl buffer (pH = 7.2, [DNA] = 50 μmol L^{-1}).

viscosity of DNA on addition of complex indicates the intercalative mode of binding to DNA. In contrast, complexes that bind in the DNA grooves by partial and/or non-classical intercalation cause less pronounced (positive or negative) or no change in DNA solution viscosity [36]. Viscosity measurements were carried out on CT-DNA by varying the concentration of the complex. Figure 5 shows the complex that causes increase in the relative viscosity of DNA. This may be explained by insertion of the

complex in between the DNA base pairs, leading to an increase in the separation of base pairs at intercalation sites and, thus, an increase in overall DNA contour length.

4. Conclusion

We have synthesized and characterized the cadmium(II) complex with the ligand 1,3-*bis*(1-benzylbenzimidazol-2-yl)-2-thiapropane. DNA binding indicated that the complex binds to DNA *via* intercalation. Moreover, the binding affinity of the complex is strong. The results could make a contribution to design on a molecular level drugs and pharmaceuticals.

Supplementary material

Crystallographic data (excluding structure factors) for the structure in this article have been deposited with the Cambridge Crystallographic Data Center as supplementary publication CCDC 782827. Copies of the data can be obtained, free of charge, on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK.

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