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A ternary copper(II) complex for supramolecular assembly with double helices: synthesis, crystal structure, DNA-binding and DNA-cleavage properties

Lianzhi Li · Jianfang Dong · Jinghong Li · Buqin Jing · Daqi Wang

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Abstract A ternary Cu(II) complex, [Cu(naph-ser)(bipy)]·0.125CH_2Cl_2 (naph-ser = a Schiff base derived from 2-hydroxy-1-naphthaldehyde and L-serine, bipy = 2, 2′-bipyridine), has been synthesized and structurally characterized. In the crystal structure, a supramolecular assembly with left-handed double helices is formed by O–H···O hydrogen bonding interactions. The DNA-binding properties and DNA-cleavage activity of the Cu(II) complex have been investigated by spectroscopic methods and agarose gel electrophoresis. The results indicate that the Cu(II) complex can bind to CT-DNA via an intercalative mode and shows efficient cleavage activity in the absence and presence of reducer.

Introduction

Recent studies show that the combination of metal coordination and hydrogen bonding is a powerful force for supramolecular assembly [1–3]. Many intriguing helical supramolecular assemblies organized through metal coordination or hydrogen bonding have been reported [4–9]. Inclusion of chirality in the molecule is a common approach to ensure non-centrosymmetric organization in the crystals [10]. Chiral amino acids and their derivatives are a distinctive group of ligands showing flexible coordination codes and well known as excellent building blocks for hydrogen-bonded networks [11–13] and hence are expected to be good chiral building blocks for supramolecular assembly. Moreover, some metal coordination complexes with chiral Schiff bases and their nonlinear optical properties have been reported [14–17]. However, supramolecular assemblies possessing a helical superstructure formed by amino acid Schiff bases have been rarely reported. On the other hand, it has been documented that amino acid Schiff bases and their first-row transition metal complexes exhibit fungicidal, bactericidal, antiviral, and antitubercular activity [18–20]. Copper is one of the first-row transition metals and a bioessential element with relevant oxidation states, and its amino acid Schiff base complexes have received much attention [21, 22]. In our previous work, we have synthesized and structurally characterized some amino Schiff base complexes [23–25]. In this communication, we report the synthesis and structural characterization of a new ternary copper(II) complex with a chiral amino acid Schiff base ligand [naph-ser: a Schiff base derived from 2-hydroxy-1-naphthaldehyde and L-serine] and planar N, N-donor heterocyclic ligand [bipy: 2,2′-bipyridine] and its self-assembly pattern via intermolecular hydrogen bonds leading to a double left-handed helical superstructure, as well as the DNA-binding and DNA-cleavage properties of this new complex.

L. Li (✉) · J. Dong · J. Li · B. Jing · D. Wang
School of Chemistry and Chemical Engineering, Liaocheng University, 252059 Liaocheng, People's Republic of China
e-mail: lilianzhi1963@yahoo.com.cn

J. Dong
Department of Material Science, Shandong Polytechnic Technician College, 252027 Liaocheng, Shandong, People's Republic of China

Experimental

2-Hydroxy-1-naphthaldehyde was purchased from Fluka, L-serine was from Beijing Jingke Company, and CT-DNA from Sino-American Biotechnology Co. (China). Ethidium bromide (EB) was obtained from Sigma (USA). All other chemicals were AR grade and used without further

purification. Tris–HCl buffer solution was prepared by using deionized, sonicated triple distilled water. A solution of CT-DNA in 10 mM Tris–HCl/10 mM buffer (pH 7.1) gave an absorbance ratio, A260/A280, between 1.8 and 1.9, indicating that the DNA was sufficiently free of protein [26]. The DNA concentration per nucleotide was determined by absorption spectroscopy using the molar absorption coefficient (6,600 M^{-1} cm^{-1}) at 260 nm [27].

Synthesis

L-serine (0.11 g, 1 mmol) and potassium hydroxide (0.06 g, 1 mmol) were dissolved in hot methanol (10 mL) and added successively to a methanol solution (5 mL) of 2-hydroxy-1-naphthaldehyde (0.17 g, 1 mmol). The mixture was then stirred at 323 K for 2 h. Subsequently, an aqueous solution (2 mL) of cupric acetate hydrate (0.20 g, 1 mmol) was added dropwise and stirred for 2 h continuously. A methanol solution (5 mL) of 2,2′-bipyridine (0.16 g, 1 mmol) was added dropwise and stirred for another 4 h. The resultant precipitate was dissolved in dichloromethane and held at room temperature for several days, whereupon blue block crystals suitable for X-ray diffraction were obtained. Yield: 72%. Anal. Calcd for $C_{193}H_{154}Cl_2Cu_8N_{24}O_{32}$:C, 59.43, H, 3.98, N, 8.62%. Found: C, 59.55, H, 4.07, N 8.53%. IR (KBr pellets, ν/cm^{-1}): 3,397(s), 2,922(m), 1,635(vs), 1,538(w), 1,444(m), 1,417(m), 1,386(m), 1,367(m), 825(w), 770(w), 748(w), 572(w), 485(w), and 446(w).

Physical measurements

Elemental analyses for C, H, and N were performed on a Perkin-Elmer 2400 II analyzer. IR spectra were obtained as KBr pellets on a Nicolet 5700 FT-IR in the range of 4,000–400 cm^{-1}. UV–Vis absorption spectra were recorded on a Hewlett–Packard HP-8453A Diode Array spectrophotometer. Fluorescence spectra were recorded on a LS55 spectrofluorometer. Circular dichroism (CD) spectra were measured with a Jasco J-810 spectropolarimeter.

X-ray crystallography

Crystals were mounted on capillaries and data were collected on a Bruker Smart-1000 CCD area-detector with graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at 298(2) K. A semi-empirical absorption correction was applied to the data. The structure was solved by direct methods using SHELXLS-97 and refined against F^2 by full-matrix least squares using SHELXL-97. Hydrogen atoms were placed in calculated positions. A summary of pertinent crystal data, experimental details and refinement results are shown in Table 1.

Table 1 Crystallographic and structure refinement data for the complex

Empirical formula	$C_{193}H_{154}Cl_2Cu_8N_{24}O_{32}$
Formula weight	3,900.62
Temperature (K)	298(2)
Wavelength (Å)	0.71073
Crystal system, space group	Tetragonal, I4
a (Å)	20.895(8)
b (Å)	20.895(8)
c (Å)	10.268(6)
$\alpha = \beta = \gamma$ (°)	90
Volume ($Å^3$)	4,483(4)
Z, Calculated density (Mg/m^3)	1, 1.445
Absorption coefficient (mm^{-1})	1.040
$F(000)$	2,002
Crystal size (mm^3)	0.24 × 0.18 × 0.16
θ Range for data collection (°)	2.95–24.99
Completeness to theta = 25.01 (%)	98.9
Limiting indices	−24, 24; −24, 17; −10, 12
Reflections collected/unique	11,576/3,755
R(int)	0.0569
Data/restraints/parameters	3,755/15/302
Goodness-of-fit on F^2	1.033
Absolute structure parameter	–0.018(17)
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0375$, $wR_2 = 0.0682$
R indices (all data)	$R_1 = 0.0653$, $wR_2 = 0.0741$
Largest difference peak and hole ($e/Å^3$)	0.389 and −0.186

DNA-binding experiments

All the DNA-binding experiments were carried out in 10 mM Tris–HCl/10 mM NaCl, pH 7.1 buffer solutions. The UV–Vis absorption spectra were recorded by varying CT-DNA concentration in 10 mM Tris–HCl/10 mM NaCl (pH 7.1) buffer while keeping the copper(II) complex concentration as constant. Due correction was made for the absorbance of DNA itself. The complex-DNA solutions were incubated for 1 h before the absorption spectra were recorded. For fluorescence quenching experiments, the copper(II) complex was added to CT-DNA solutions treated with ethidium bromide (EB) for 30 min in 10 mM Tris–HCl/10 mM NaCl (pH 7.1) buffer. All the samples were excited at 258 nm, and emission spectra were recorded at 540–680 nm. Each spectrum was recorded at the scan speed of 200 nm/min with slit width 7 nm. CD spectra of DNA were carried out on a J-810 spectropolarimeter at room temperature with a quartz cell of 1-cm path length by increasing complex/CT-DNA ratio ($r = 0.0$, 0.4, 0.8, 1.2) in 10 mM Tris–HCl/10 mM NaCl (pH 7.1) buffer. Each sample solution was scanned in the range of 220–320 nm.

Each CD spectrum was gained after averaging 3 accumulations from which the buffer background had been subtracted, with a scan speed of 100 nm/min and 1 s response time. The concentration of CT-DNA was 1.0×10^{-4} M. For the gel electrophoresis analysis, supercoiled pBR322 DNA (0.2 μg) was treated with the copper(II) complex in the absence and presence of MPA in 50 mM Tris–HCl/10 mM NaCl buffer (pH 7.1), and the solution was then incubated for 2 h at 37 °C, after that 4 μL of a quench buffer solution containing 0.25% bromophenol blue and 40% sucrose was added. In the ensuing step, samples were immediately loaded on 0.8% agarose gel for electrophoresis in TAE buffer (40 mM Tris base, 40 mM acetic acid, 1 mM EDTA) containing 0.5 μg/mL ethidium bromide at 90 V for 1.5 h. Finally the gel was photographed under UV light.

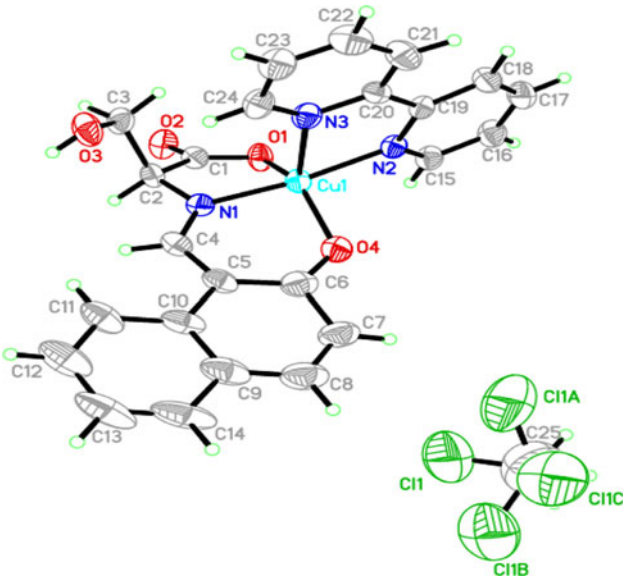

Fig. 1 Molecular structure of **1** with 30% thermal ellipsoids. The hydrogen and chlorine atoms in dichloromethane molecular are disordered

Results and discussion

IR spectra

In the IR spectra of the copper complex, the very broad absorption at 3,397 cm^{-1} is due to the free hydroxyl stretching vibration [26, 27]. Two moderate absorptions at 1,538 and 1,386 cm^{-1} for the copper(II) complex are attributed to asymmetric and symmetric stretching vibration of CO_2^- group, respectively [28], and the other very sharp absorption at 1,635 cm^{-1} suggests the imine group (C=N) exists in the copper(II) complex. In addition, the weak vibrational bands at 485 and 446 cm^{-1} can be reasonably assigned to Cu–N and Cu–O bonds [28].

Crystal structure

The complex crystallizes in the non-centrosymmetric chiral space group I4, and the main molecule of the copper(II) complex has a mononuclear [Cu(naph-ser)(bipy)] structure with a Schiff base ligand (naph-ser = a Schiff base derived from 2-hydroxy-1-naphthaldehyde and L-serine, bipy = 2,2′-bipyridine) and heterocyclic ligand (bipy). The molecular structure of the copper(II) complex with the atomic labeling scheme is shown in Fig. 1, and selected bond lengths and angles are listed in Table 2. As shown in Fig. 1, the central copper(II) atom is five-coordinate in a N_2O_3 environment with Cu–N and Cu–O bond lengths varying from 1.918(3) Å to 2.237(4) Å, in good agreement with the results published for related complexes [29]. The coordination geometry was estimated from the τ values varying from 0 for an idealized square pyramid to 1 for an idealized trigonal bipyramid [30]. On the basis of the τ value of 0.511 for this complex, the coordination geometry represents much more distorted trigonal bipyramidal than distorted square-pyramidal geometry (the axial-Cu-axial: N1-Cu1-N2 = 172.87(14)°). The copper(II) atom is out by 0.0136(19) Å from the equatorial plane that is formed by two oxygen atoms from the Schiff base ligand (Cu1-O1, 2.000(3) Å, Cu1-O4, 1.963(3) Å) and one nitrogen atom from the 2,2′-bipyridine molecule (Cu1-N3, 2.237(4) Å). The sum (359.99°) of the equatorial angles (O4-Cu1-N3 = 97.56(14)°, N3-Cu1-O1 = 120.22(13)°, O1-Cu1-O4 = 142.21(13)°) is very close to 360°, indicating that the atoms O4, N3, O1, and Cu1 are almost in the same plane. The bipy ligand is almost vertical to the equatorial plane with the dihedral angle 88.75(12)°.

It is interesting that a supramolecular self-assembly can be observed for the structural feature of the complex. The self-assembly of the complex molecule via intermolecular O–H···O interaction leads to an infinite, one-dimensional, left-handed helical superstructure in the crystal lattice, which is formed between the hydroxyl oxygen atom and uncoordinated carboxylic oxygen atom of L-serine (O3···O2($0.5 + x$, $0.5 - y$, $z - 0.5$) = 2.661(4) Å, O2···O3($0.5 - x$, y − 0.5, $0.5 + z$) = 2.661(4) Å) along the *c*-axis with a helical pitch of 20.536 Å (Fig. 2a) and a chiral channel of about 4.319 × 4.319 Å in dimension (Fig. 2b). Furthermore, two identical, left-handed, single-helical chains entangle together to produce one left-handed, double-helical chain (Fig. 2c). The two identical, single-helical chains are not isolated and there are significant short-contact interactions (C–H···O hydrogen bonds: C15···O2($0.5 - y$, $x + 0.5$, $z + 0.5$) = 3.382(5) Å, C4···O1($0.5 - y$, $0.5 + x$, $z - 0.5$) = 3.456(5) Å, C16···O3(x, y, $z + 1$) = 3.132(6) Å.) between the interweaving helices.

Table 2 Selected bond lengths (Å) and angles (°) for Cu(naphser)(bipy)]·0.125CH_2Cl_2

Cu1-N1	1.918(3)	Cu1-O4	1.963(3)
Cu1-N2	1.990(3)	Cu1-O1	2.000(3)
Cu1-N3	2.237(4)		
N1-Cu1-O4	91.94(14)	N1-Cu1-N2	172.87(14)
O4-Cu1-N2	94.49(14)	N1-Cu1-O1	82.19(13)
O4-Cu1-O1	142.21(13)	N2-Cu1-O1	94.55(13)
N1-Cu1-N3	98.36(14)	O4-Cu1-N3	97.56(14)
N2-Cu1-N3	77.74(15)	O1-Cu1-N3	120.22(13)

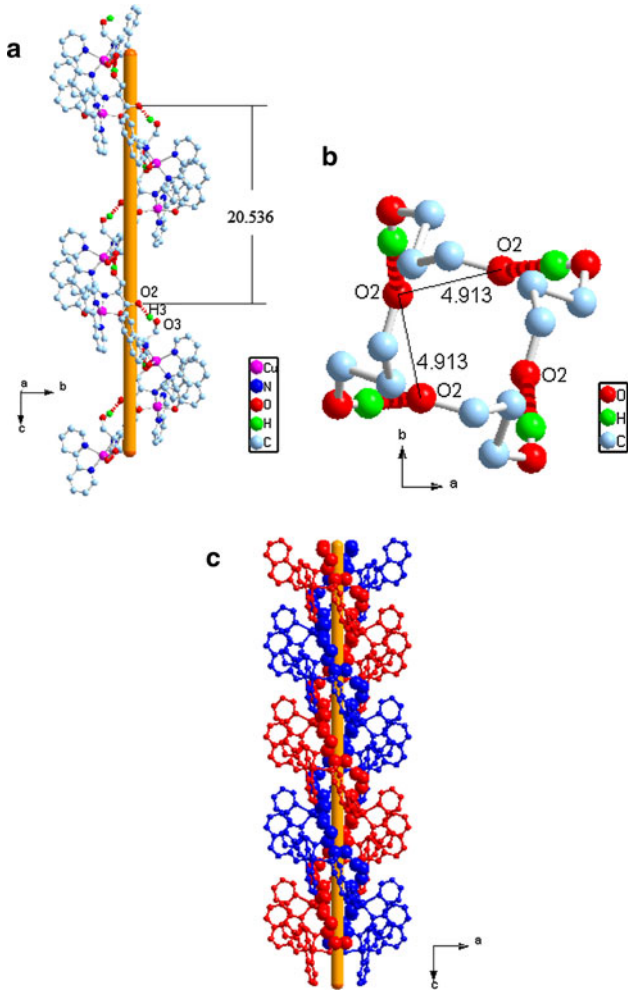

Fig. 2 **a** View of intermolecular O–H···O hydrogen bonding interactions between adjacent molecules that lead to the 1D helical chain. All the hydrogen atoms, except those involved in hydrogen bonding, have been omitted for clarity. **b** Space-filling model (helical backbone) view of the inner channel running parallel to the helical axis. **c** Perspective view of the left-handed, double-helical chains. In order to observe the helices for clarity, the irrespective hydrogen atoms were omitted

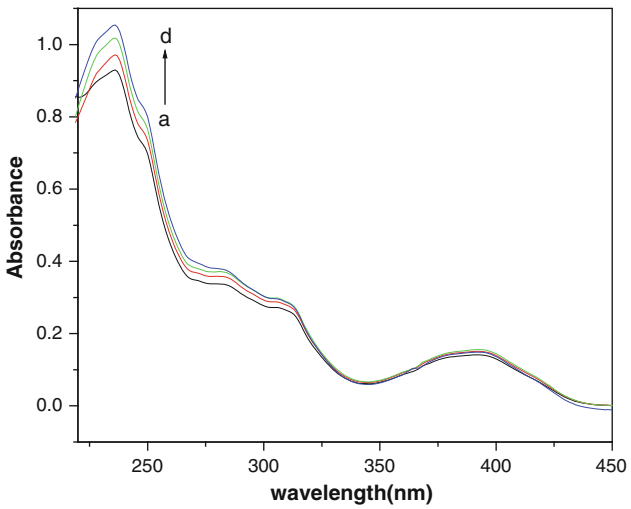

Fig. 3 UV–Vis spectra of **1** in the absence and presence of CT-DNA. [complex **1**] = 1.0×10^{-5} M, [DNA] (*a–d*) = 0, 1.0×10^{-5}, 6.0×10^{-5}, 1.2×10^{-4} M

DNA-binding studies

In order to investigate the specificity of the binding of the copper(II) complex to nucleobases, the DNA-binding experiments for the copper(II) complex with CT-DNA have been carried out by using UV–Vis, fluorescence and CD spectra. Electronic absorption spectroscopy is an effective method to examine the binding mode of DNA with metal complexes [31, 32]. The absorption spectra of the copper(II) complex in the absence and presence of CT-DNA are shown in Fig. 3. In the UV region, the complex presents two bands at 236 and 279 nm, which can be attributed to the π–π^* transition of the coordinated bipyridine ligand. The absorbance at 236 nm of the copper(II) complex increased (hyperchromism) obviously after the addition of DNA, which indicates the interactions between DNA and the copper(II) complex. A similar hyperchromism was also observed for the copper(II) complexes with ligands bearing an –OH group [33, 34]. As the DNA double helix possesses many hydrogen bonding sites that are accessible both in the minor and in the major grooves, it is likely that the –OH group of the ternary complex forms hydrogen bonds with DNA, which may contribute to the hyperchromism observed in the absorption spectra [34].

The fluorescence measurement for the copper(II) complex showed that no emission band was observed whether with or without CT-DNA at ambient temperature in aqueous solution. Hence, competitive EB (EB = 3,8-diamino-5-ethyl-6-phenylphenanthridinium bromide) binding studies were undertaken to gain support for the extent of

binding of the copper(II) complex with DNA, which can provide indirect evidence for the DNA-binding mode [35]. As shown in Fig. 4, the fluorescence intensity at 593 nm of the DNA–EB system decreased with the increase in the copper(II) complex concentration, reaching minimum 51.1% at the ratio of [complex]/[DNA] = 1:1.8, which indicates that the copper(II) complex can displace EB from the DNA–EB system. The resulting decrease in fluorescence may be caused by EB changing from a hydrophobic environment to an aqueous environment, which is often observed in interacalative complex-DNA mode [36, 37]. According to the linear Stern–Volmer equation [38], $I_0/I = 1 + K_{sq}\, r$, where I_0 and I represent the fluorescence intensities in the absence and presence of the complex, respectively, and r is the concentration ratio of the complex to DNA. K_{sq} is a linear Stern–Volmer quenching constant (seen in Fig. 4 inset). The K_{sq} value for the copper(II) complex is 0.53, which indicates that the interaction of the copper(II) complex with DNA is weaker than that of reported complex [CuL]Cl(L = 3,10-bis(2-methylpyridine)-1, 3, 5, 8, 10, 12-hexaazacyclotetradecane) (K_{sq} = 1.34) [33].

To further clarify the nature of the interaction between the copper(II) complex and DNA, CD spectra of CT-DNA in the presence of the copper(II) complex were measured because CD signals are quite sensitive to the mode of DNA interactions with small molecules in complex-DNA systems [39]. The CD spectra of CT-DNA after additions of the copper(II) complex are shown in Fig. 5, which exhibits a positive band at 275 nm (due to base stacking) and a negative band at 245 nm (due to right-handed helicity of DNA). The positive band showed increase in ellipticity with a slight red shift of the band maximum when the complex concentration was increased. These observations are supportive of the intercalative mode of binding of the copper(II) complex, where in the complex, molecules stack in between the base pairs of DNA, thus leading to an enhancement in the positive band [40, 41], which is consistent with the results of fluorescence spectral analyses.

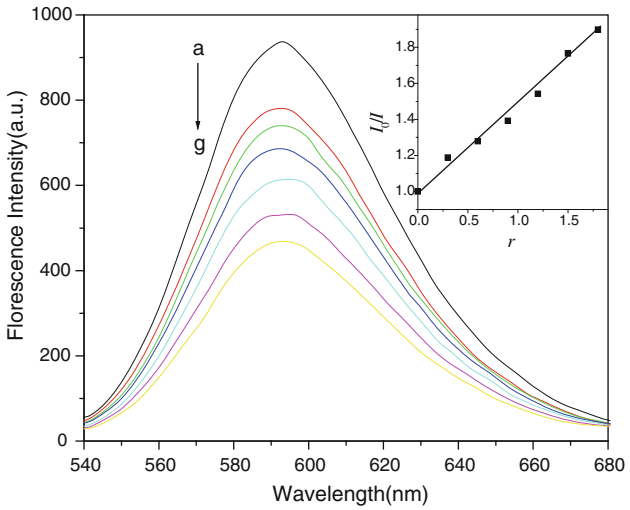

Fig. 4 Emission spectra of DNA–EB system in the absence and presence of **1**, [EB] = 2.0 (M, [DNA] = 25 (M, with r = 0.3, 0.6, 0.9, 1.2, 1.5, 1.8, respectively; the arrow shows the intensity changes on increasing the complex concentration. Inset: plot of I_0/I vs. r

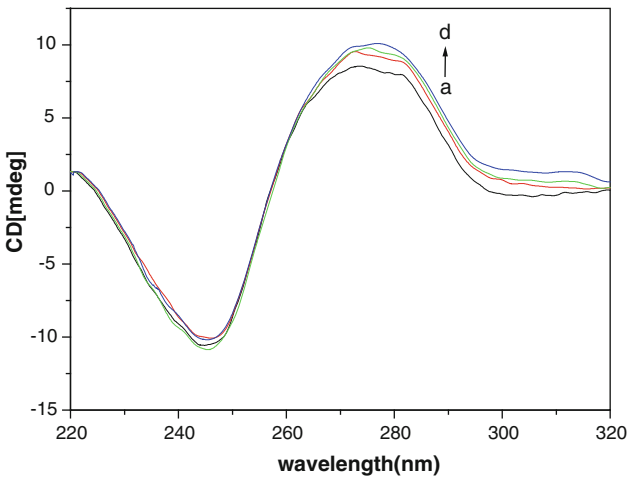

Fig. 5 CD spectra of CT-DNA (1.0×10^{-4} M) in the absence (*line a*) and presence (*line b–d*) of **1** at different r value. The *arrow* shows the intensity changes on increasing the complex concentration

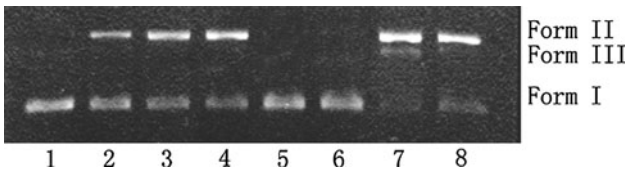

Fig. 6 Cleavage of pBR322 DNA (0.2 μg) by **1** in the absence or presence of MPA and DMSO. *Lane 1*, DNA control; *lane 2*, DNA + **1** (80 μM); *lane 3*, DNA + **1** (120 μM); *lane 4*, DNA + **1** (160 μM); *lane 5*, DNA + MPA (250 μM); *lane 6*, DNA + DMSO (500 μM); *lane 7*, DNA + **1** (160 μM) + MPA (250 μM); *lane 8*, DNA + **1** (160 μM) + MPA (250 μM) + DMSO (500 μM)

DNA-cleavage studies

It is reported that many antitumor agents can interact with DNA and cause DNA strand scission [42], for this reason we have also studied the capacity of the complex to cleave DNA by agarose gel electrophoresis using plasmid pBR322 DNA. As shown in Fig. 6, control experiments of only DNA and in the presence of MPA (3-mercaptopropionic acid) or DMSO do not have any apparent DNA cleavage (lane 1, lane 5, and lane 6). With the increase of complex concentration (from 80 to 160 μM), the Form I

(supercoiled DNA) decreased and was converted to Form II (nicked DNA) gradually (lane 2–4). The results indicate that the complex can cleave DNA hydrolytically efficiently in the absence of any reducers. Furthermore, in the presence of MPA, the Form I disappeared and the Form III (linear DNA) appeared (lane 7), which indicates that the complex is a potent DNA-cleavage agent in the presence of MPA as a reducing agent under the present experimental conditions. However, the addition of hydroxyl radical scavenger DMSO can inhibit the cleavage activity (lane 8), which suggests that its cleavage mechanism is possibly involving hydroxyl radical species in the strand oxidative cleavage reactions [43].

Conclusions

In summary, a ternary copper(II) complex coordinated by L-serine Schiff base and 2,2′- bipyridine has been synthesized and structurally characterized by X-ray single-crystal diffraction. In the crystal structure, a supramolecular assembly with left-handed double helices was formed by O–H···O hydrogen bonding interaction. The DNA-binding properties and DNA-cleavage activity of the copper(II) complex with DNA have been investigated by UV–Vis, fluorescence, and CD spectra, as well as agarose gel electrophoresis. Results indicate that the copper(II) complex can bind to CT-DNA via an intercalative mode and show efficient cleavage activity in the absence or presence of reducer.

Supplementary materials

Crystallographic data for the structural analysis of the title complex has been deposited with the Cambridge Crystallographic Data Center, CCDC No. 780634. Copies of this information may be obtained free of charge from www.ccdc.cam.ac.uk/ conts/retrieving.html or from the CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44(0)1222-336033; email: deposit@ccdc.cam.ac.uk).

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