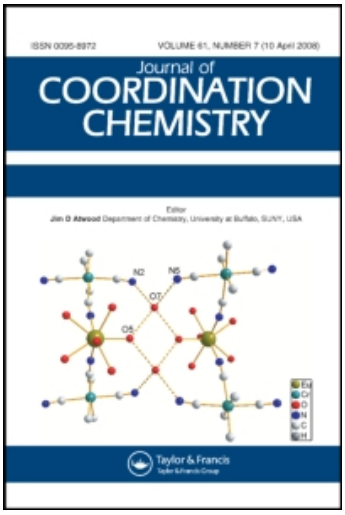

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Synthesis, crystal structure, DNA binding, and oxidative cleavage activity of copper(II)-bipyridyl complexes containing tetraalkylammonium groups

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First published on: 29 July 2010

To cite this Article Li, Ji-Hui , Wang, Jin-Tao , Zhang, Li-Yi , Chen, Zhong-Ning , Mao, Zong-Wan and Ji, Liang-Nian(2009) 'Synthesis, crystal structure, DNA binding, and oxidative cleavage activity of copper(II)-bipyridyl complexes containing tetraalkylammonium groups', Journal of Coordination Chemistry, 62: 11, 1775 — 1783, First published on: 29 July 2010 (iFirst)
To link to this Article: DOI: 10.1080/00958970902721550
URL: http://dx.doi.org/10.1080/00958970902721550

Journal of Coordination Chemistry
Vol. 62, No. 11, 1 June 2009, 1775–1783

Synthesis, crystal structure, DNA binding, and oxidative cleavage activity of copper(II)-bipyridyl complexes containing tetraalkylammonium groups

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(*Received 2 July 2008; in final form 10 September 2008*)

Two copper(II) complexes of disubstituted 2,2′-bipyridine (bpy = 2, 2′-bipyridine) with tetraalkylammonium groups, $[Cu(L^1)_2Br](ClO_4)_5 \cdot 2H_2O$ (**1**) and $[Cu(L^2)_2Br](ClO_4)_5 \cdot H_2O$ (**2**) ($L^1 = [4,4'\text{-}(Et_3NCH_2)_2\text{-bpy}]^{2+}$, $L^2 = [4,4'\text{-}((n\text{-}Bu)_3NCH_2)_2\text{-bpy}]^{2+}$), have been synthesized and characterized. X-ray crystallographic study of **1** indicates that Cu(II) is a distorted trigonal bipyramidal or square pyramid. DNA binding of both complexes was studied by UV spectroscopic titration. In the presence of reducing reagents, the cleavage of plasmid pBR322 DNA mediated by both complexes was investigated and efficient oxidative cleavage of DNA was observed. Mechanistic study with reactive oxygen scavengers indicates that hydrogen peroxide and singlet oxygen participate in DNA cleavage.

Keywords: Copper(II) complexes; 2,2′-Bipyridine; Tetraalkylammonium groups; Artificial nucleases; Oxidative DNA cleavage

1. Introduction

Inspired by natural nucleases, introduction of organic groups to the structure of the ligands has been a frequent and important strategy in the design of artificial nucleases. The first such example was reported by Krämer and co-workers, who designed zinc and Cu(II) complexes of bipyridine containing ammonium groups to serve as phosphoryl transfer enzymes [1–3]. Since then, some metal complexes whose ligands contain functional groups (e.g. thiophenyl [4], amino [5–7], guanidino [8], hydroxyalkyl [7, 9, 10], etc.) have been reported to act as artificial nucleases or hydrolases.

Our group has been involved in synthesis and DNA cleavage of transition metal complexes of 2,2′-bipyridyl ligands containing positively charged functional groups, tetraalkylammonium [11–13], protonated amino [13–15] and guanidino groups [15]. Recently, we studied nuclease activities of two zinc complexes of disubstituted

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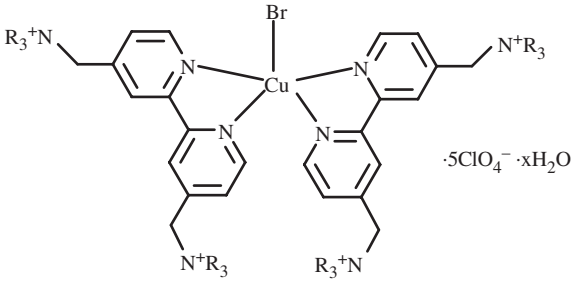
Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online © 2009 Taylor & Francis
DOI: 10.1080/00958970902721550



R = Et: **1**
n-Bu: **2**

Scheme 1. Schematic structure of complexes **1** and **2**.

2,2′-bipyridyl ligands (L^1 and L^2) containing tetraalkylammonium groups ($L^1 = [4,4'\text{-}(Et_3NCH_2)_2\text{-bpy}]^{2+}$, $L^2 = [4,4'\text{-}((n\text{-}Bu)_3NCH_2)_2\text{-bpy}]^{2+}$) [16]. In our previous study, DNA cleavages mediated by the complexes have a hydrolytic mechanism.

In this work, Cu(II) complexes of L^1 and L^2, $[Cu(L^1)_2Br](ClO_4)_5 \cdot 2H_2O$ (**1**) and $[Cu(L^2)_2Br](ClO_4)_5 \cdot H_2O$ (**2**) were synthesized (scheme 1) and characterized, and the structure of **1** was determined by X-ray diffraction analysis. Due to the potential pathobiological significance of DNA damage induced by reactive oxygen species (ROS) [17], the present work focuses on oxidative cleavage of pBR322 DNA by these two Cu(II) complexes in the presence of reducing reagents. The DNA binding of both complexes is also described.

2. Experimental

2.1. *Chemicals and reagents*

4,4′-Dimethyl-2,2′-bipyridine, (bpy = 2, 2′-bipyridine) ascorbic acid (ASC), and 3-mercaptopropionic acid (MPA) were purchased from Alfa Aesar Co., Ltd; calf thymus DNA (CT-DNA) was purchased from Sino-American Biotechnology; pBR322 DNA was purchased from MBI Co.; superoxide dismutase (SOD) was purchased from Sigma-Aldrich Co., Ltd; catalase (CAT) and tris(hydroxymethyl)aminomethane (Tris) were purchased from Shanghai Sangon Co. Other reagents of analytical grades were obtained from commercial sources and used as received. Milli-Q water was used in all physical measurement experiments.

Caution! Perchlorate salts are potentially explosive and should always be handled with care and in small scale.

2.2. *Physical methods*

UV-Vis spectra were scanned on a Varian Cary 300 UV-Vis spectrophotometer. Elemental analysis was carried out on an Elementar Vario EL elemental analyzer. X-ray crystal diffraction was performed with an Oxford Gemini S Ultra CCDC diffractometer. Electrophoresis was carried out using a Beijing Liuyi DYY-12 electrophoresis cell.

2.3. *Preparation of Cu(II) complexes*

4,4′-Bis(triethylaminomethyl)-bpy dibromide (L^1Br_2) and 4,4′-bis(tri-(*n*-butyl)aminomethyl)-bpy dibromide (L^2Br_2) were prepared according to Li *et al.* [16].

2.3.1. $[Cu(C_{24}H_{40}N_4)_2Br](ClO_4)_5 \cdot 2H_2O$ (1). To a stirred ethanol solution (3 mL) of L^1Br_2 (0.100 g, 0.165 mmol), 2 mL ethanol solution of $Cu(ClO_4)_2 \cdot 6H_2O$ (0.150 g, 0.405 mmol) was added. Brown precipitate appeared immediately, was filtered, washed with ethanol, and dried to give 0.130 g brown powder. The powder was recrystallized from 1 : 4 water–ethanol solution, and **1** was obtained as green powder (0.085 g, 68.7%). Single crystals suitable for X-ray diffraction were prepared by slow evaporation of ethanol solution of **1** at room temperature. UV (Tris buffer): $\lambda_{max} = 236.0$ nm ($\varepsilon = 3.53 \times 10^4\ M^{-1}\ cm^{-1}, \pi \rightarrow \pi^*$); 290.0 ($\varepsilon = 3.06 \times 10^4, n \rightarrow \pi^*$); 318.5 ($\varepsilon = 1.83 \times 10^4$, LMCT). IR (KBr, cm^{-1}): 2986.26 (ν_{CH_3}, w); 1621.02 ($\nu_{C=C}$, m); 1474.01 ($\nu_{C=N}$, m); 1403.76 (δ_{CH_3}, m); 1143.03 (δ_{ring}, s); 1115.79 (δ_{ring}, s); 1083.72 (δ_{ring}, s); 798.60 ($\delta_{Cring\text{-}H}$, m); 630.00 ($\delta_{Cring\text{-}H}$, m). Anal. Calcd for $C_{48}H_{84}N_8BrCl_5O_{22}Cu$ (%): C, 39.87; H, 5.86; N, 7.75. Found: C, 39.65; H, 5.95; N, 7.58.

2.3.2. $[Cu(C_{36}H_{64}N_4)_2Br](ClO_4)_5 \cdot H_2O$ (2). To a stirred solution of L^2Br_2 (0.150 g, 0.203 mmol) in water (3 mL), 2 mL aqueous solution of $Cu(ClO_4)_2 \cdot 6H_2O$ (0.200 g, 0.540 mmol) was added and green precipitate produced immediately. The precipitate was filtered, washed with cold water and dried to yield green powder (0.170 g, 94.9%). UV (Tris buffer, trace CH_3CN): $\lambda_{max=}$ 236.5 nm ($\varepsilon = 2.89 \times 10^4\ M^{-1}\ cm^{-1}, \pi \rightarrow \pi^*$); 290.5 ($\varepsilon = 2.78 \times 10^4, n \rightarrow \pi^*$); 319.0 ($\varepsilon = 1.22 \times 10^4$, LMCT). 2963.59 ($\nu_{CH_3}$, w); 2875.48 ($\nu_{CH_2}$, w); 1621.89 ($\nu_{C=C}$, m); 1470.47 ($\nu_{C=N}$, m); 1419.82 ($\delta_{CH_3}$, m); 1382.95 ($\delta_{CH_2}$, w); 1145.00 ($\delta_{ring}$, s); 1116.17 ($\delta_{ring}$, s); 1086.31 ($\delta_{ring}$, s); 627.15 ($\delta_{Cring\text{-}H}$, m). Anal. Calcd for $C_{72}H_{130}N_8BrCl_5O_{21}Cu$ (%): C, 49.01; H, 7.43; N, 6.35. Found: C, 49.09; H, 7.58; N, 6.29.

2.4. *X-ray crystallography*

A green single crystal of **1** ($0.4 \times 0.4 \times 0.3\ mm^3$) was used for X-ray diffraction analysis. Data collection was performed with Cu-Kα radiation ($\lambda = 1.54178$ Å) on an Oxford Gemini S Ultra CCDC diffractometer at 293(2) K. An absorption correction by multi-scan was applied to the intensity data. The structure was solved by direct methods and the heavy atoms were located from E-map. The remaining non-hydrogen atoms were determined from successive difference Fourier syntheses. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were generated geometrically with isotropic thermal parameters. The structure was refined on F^2 by full-matrix least-squares using the SHELXTL-97 program package [18].

2.5. *UV spectroscopic titration*

Stock solution (2.0 mM) of **1** in buffer solution (5 mM Tris-50 mM NaCl, pH 7.5) and **2** in 1 : 1 CH_3CN-buffer were used. CT-DNA was dissolved in buffer and stored at 4°C as stock solution. The concentration of DNA was determined according to the

literature method [19]. Stock solution of complexes was diluted into 30 μM with buffer solution. To the test solution of complexes (30 μM, initial volume 3.0 mL), 10 μL stock solution of CT-DNA (3.62 mM) was added every time, then the solution was scanned in the range of 400–200 nm. The change in solution volume was taken into account. Trace CH_3CN has no effect on the UV spectra.

2.6. *DNA cleavage*

The cleavage of pBR322 DNA was carried out in 20 mM Tris buffer (pH 7.5). The total volume of 10 μL reaction solution contains 38 μM bp DNA, a certain concentration of tested complex, and 250 μM reducing reagents (H_2O_2, MPA, ASC or 1 : 1 ASC : H_2O_2). The reaction mixture was incubated in a sealed plastic vessel and the cleavage was carried out at 37°C for a defined time. Then 4 μL loading buffer (bromophenol blue, 50% glycerol, and 2 mM EDTA) was added, the sample stored at −20°C was loaded onto a 0.9% agarose gel and electrophoresed at a constant voltage of 120 V for 100 min in TBE buffer (100 mM Tris/2 mM EDTA/HBO_3, pH 8.3). DNA bands were visualized in an electrophoresis documentation and analysis system 120. Densitometeric calculations were made using the analysis method in Image Tools 3.00. A correction factor of 1.47 was used for supercoiled DNA taking into account its weaker staining capacity by ethidium bromide compared to nicked and linear DNA [20].

The mechanism of DNA cleavage, i.e., the identification of ROS inducing DNA cleavage, was studied using inhibiting reagents. Hydroxyl radical ($HO^{\cdot}$) scavengers (DMSO and *t*-BuOH, 0.5 M), peroxide scavenger (CAT, 500 U mL^{-1}), singlet oxygen ($^1O_2$) scavenger (NaN_3, 0.1 M) or superoxide (O_2^-) scavenger (SOD, 500 U mL^{-1}) were added to the above-mentioned reaction mixtures. Samples were treated as described above.

3. Results and discussion

3.1. *Crystal structure of 1*

Details of the X-ray data collection and refinement are given in table 1. Selected bond lengths (Å) and angles (°) are listed in table 2. Complex **1** consists of a $[Cu(L^1)_2Br]^{5+}$ cation, five ClO_4^- anions and two H_2O molecules. The Cu(II) center is coordinated by four nitrogens from two chelating 2,2′-bipyridyls and a Br^- to construct a five-coordinate configuration (CuN_4Br). Calculated τ value of 0.47 according to the literature method [21] indicates the degree of distortion is almost the midpoint of ideal trigonal-bipyramid ($\tau = 1$) and square pyramid ($\tau = 0$). An ORTEP drawing of the cation in **1** is shown in figure 1. Bond lengths of Cu–N range from 1.998(2) to 2.134(2) Å and Cu–Br of 2.419(1) Å. The coordinated environment in **1** is very similar to analogues [11, 13, 22].

3.2. *DNA binding*

DNA binding of these complexes was studied by UV spectroscopic titration; the absorption spectra are shown in figure 2. Electronic spectra are characterized by two

Table 1. Summary of X-ray data collection and refinement for **1**.

Empirical formula	$C_{48}H_{84}BrCl_5CuN_8O_{22}$
Formula weight	1445.93
Temperature (K)	293(2)
Wavelength (Å)	1.54178
Crystal system, space group	Monoclinic, $P(1)/n$
Unit cell dimensions (Å, °)	
a	14.9551(2)
b	16.2151(3)
c	25.9088(4)
β	95.934(2)
Volume (Å^3)	6249.2(2)
Z	4
D_{Calcd} (g cm^{-3})	1.537
μ (mm^{-1})	3.899
$F(000)$	3012
Crystal size (mm^3)	$0.4 \times 0.4 \times 0.3$
θ range for data collection (°)	3.22–62.30
Limiting indices	$-17 \le h \le 16$, $-16 \le k \le 18$, $-28 \le l \le 28$
Reflections collected	28309
Independent reflections	9639 ($R_{int} = 0.0294$)
Goodness-of-fit on F^2	0.989
R_1/wR_2 [$I > 2\sigma(I)$][a]	0.0384/0.1037
R_1/wR_2 (all data)	0.0467/0.1075
Largest difference peak (eÅ^{-3})	0.662/−0.524

Note: [a] $R_1 = \sum \|F_o| - |F_c\| / \sum |F_o|$, $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$.

Table 2. Selected bond lengths (Å) and angles (°) for **1**.

Cu–N(1)	2.009(2)	Cu–N(6)	2.050(2)
Cu–N(2)	2.134(2)	Cu–Br	2.419(1)
Cu–N(5)	1.998(2)		
N(1)–Cu–N(2)	79.65(8)	N(5)–Cu–N(6)	80.55(9)
N(1)–Cu–N(5)	174.50(9)	N(1)–Cu–Br	90.49(7)
N(1)–Cu–N(6)	95.32(8)	N(2)–Cu–Br	108.00(6)
N(2)–Cu–N(5)	97.89(9)	N(5)–Cu–Br	94.97(7)
N(2)–Cu–N(6)	105.77(9)	N(6)–Cu–Br	146.23(7)

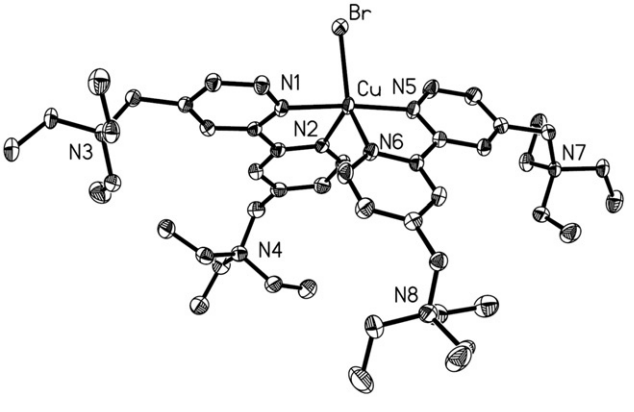


Figure 1. ORTEP drawing (50% probability) of the cation in **1**.

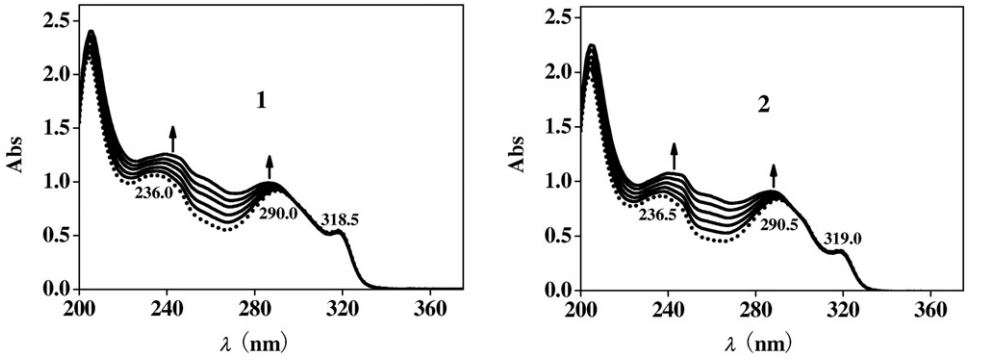


Figure 2. Absorption spectra of 3.0×10^{-5} M **1** and **2** in the absence (dotted line) and presence (solid line) of increasing amount of CT-DNA (0–5.93×10^{-5} M) in 5 mM Tris-50 mM NaCl buffer (pH 7.5) at 25°C.

ligand-centered transitions (LC) at ~236 and 290 nm, corresponding to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions, respectively, and a ligand-to-metal charge transfer (LMCT) at ~319 nm. With the addition of CT-DNA (0–5.93×10^{-5} M) to the complex solution (3.0×10^{-5} M), hyperchromicity was observed. The intrinsic binding constants (K_b) of these complexes towards CT-DNA were determined by equation (1) [23],

$$\frac{[\mathrm{DNA}]}{(\varepsilon_A - \varepsilon_F)} = \frac{[\mathrm{DNA}]}{(\varepsilon_B - \varepsilon_F)} + \frac{1}{K_b}(\varepsilon_B - \varepsilon_F) \quad (1)$$

where ε_A, ε_F, and ε_B represent apparent DNA free and fully bound extinction coefficients. The K_b values of **1** and **2** were calculated as 5.93×10^3 and 4.20×10^3 M^{-1}, respectively, higher than K_b values of corresponding zinc complexes of the same ligands [16]. The obtained K_b values are lower than those of typical intercalators (e.g. EB-DNA, ~10^6 M^{-1}) [24, 25] by several orders of magnitude and are comparable with some non-intercalators [14, 26, 27]. The hyperchromicity in absorbance and quite low K_b values indicate these complexes bearing positive functional groups would rather interact with DNA via outside electrostatic binding rather than intercalation [25], which are consistent with the results in our previous studies [13, 14, 16]. The value of K_b for **2** is lower than **1**, which indicates that steric hindrance has an effect on the interaction of complexes with DNA [16], similar to the corresponding zinc complexes [16].

3.3. *DNA cleavage activity*

Both complexes were applied to cleavage of pBR322 DNA in the presence of reducing reagents, and their DNA cleavage activities were assessed by conversion of supercoiled DNA (form I) to nicked circular (form II) or linear DNA (form II). The ability of Cu(II) complexes to induce oxidative DNA cleavage depends on the reducing reagents used for initiating the redox reaction [17]. To choose suitable activator, we tested the activity of **1** in the presence of H_2O_2, MPA, ASC, and 1 : 1 ASC : H_2O_2. Control experiments with these activators in the absence of **1** were also carried out. The results, shown in figure 3 (lanes 6–9), indicate the efficiency of these activators follow the order: $H_2O_2 <$ MPA $<$ ASC $\approx$ ASC/H_2O_2, which is similar to the literature [17, 28–30]. Although ASC and ASC/H_2O_2 exhibited higher efficiency in inducing DNA cleavage

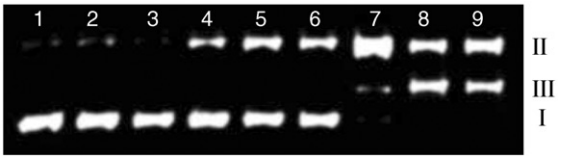


Figure 3. The cleavage of pBR322 DNA (38 μM bp) treated with different reducing reagents (250 μM) in the absence or presence of **1** (30 μM) at 37°C for 1 h. Lane 1: DNA control; lanes 2–5: DNA + H_2O_2, MPA, ASC, and ASC/H_2O_2, respectively; lanes 6–9: DNA + **1** + H_2O_2, MPA, ASC, and ASC/H_2O_2, respectively.

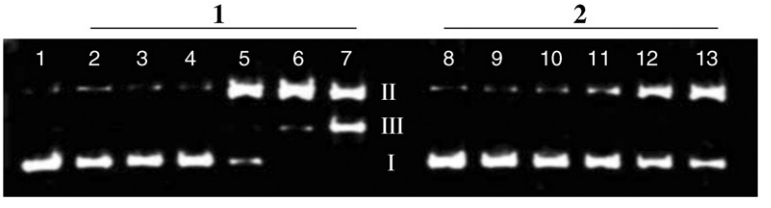


Figure 4. The cleavage of pBR322 DNA treated with indicated concentration of **1** and **2** in the presence of MPA (250 μM) at 37°C for 1 h. Lane 1: DNA control; lane 2: DNA + **1** (50 μM); lanes 3–7: DNA + MPA + **1** (5, 10, 20, 30, and 50 μM, respectively); lane 8: DNA + **2** (50 μM); lanes 9–13: DNA + MPA + **2** (5, 10, 20, 30, and 50 μM, respectively).

than MPA, they produced remarkable background DNA cleavage (lanes 4 and 5), while MPA produced nearly no background (lane 3). So MPA was used as activator in rest of the experiments.

The dependence of DNA cleavage on complex concentration is shown in figure 4. To eliminate the contribution of hydrolytic cleavage of DNA under experimental conditions, DNA cleavage activity of these complexes was assayed in the absence of MPA. Only very little form II DNA was observed (lanes 2 and 8), which indicates that hydrolytic mechanism can be excluded. For **1**, when complex concentration is less than 20 μM, only little form I DNA was converted to form II DNA (lanes 3 and 4); with increase of complex concentration, the percent of form II DNA increased markedly. When the concentration is higher than 30 μM, all form I DNA was converted to form II and form III DNA (lanes 6 and 7). Complex **2** is very similar to **1** (lanes 8–13), except that DNA cleavage activity of **2** is much lower than that of **1** and form I DNA always exists even when the concentration is increased to 50 μM. The difference in activity between **1** and **2** can be attributed to the difference in steric hindrance caused by functional groups in these complexes. Bearing larger functional groups, the steric hindrance of **2** is bigger than that of **1**, shown by lower K_b value of **2** than that of **1**.

Time-dependent DNA cleavage was also investigated. As shown in figure 5, DNA cleavage by both complexes exhibited similar time-dependence. Most cleavage was accomplished in about 30 min. To investigate which ROS induce DNA cleavage, DNA cleavage was carried out in the presence of some inhibiting reagents. DMSO, *t*-BuOH, and SOD did not inhibit DNA cleavage (figure 6, lanes 3, 4, 7 and 9, 10, 13), which indicates that $HO^{\cdot}$ and O_2^- are not involved in the cleavage. Inhibition was observed when CAT and NaN_3 were used (lanes 5, 6 and 11, 12), indicating that H_2O_2 and $^1O_2$ (or singlet-oxygen-like species) are responsible for DNA cleavage.

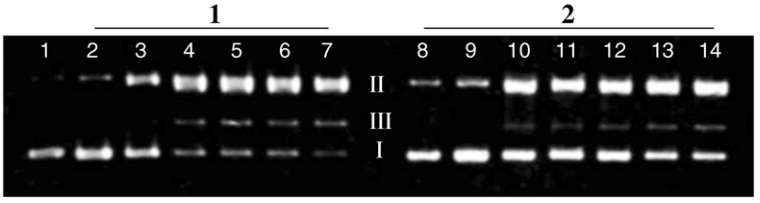


Figure 5. The time-dependent cleavage of pBR322 DNA by **1** (30 μM) and **2** (50 μM) in the presence of MPA (250 μM) at 37°C. Lane 1: DNA control; lanes 2–7: DNA + **1** + MPA for 10, 20, 30, 40, 50, and 60 min, respectively; lanes 8–14: DNA + **2** + MPA for 10, 20, 30, 40, 50, 60, and 80 min, respectively.

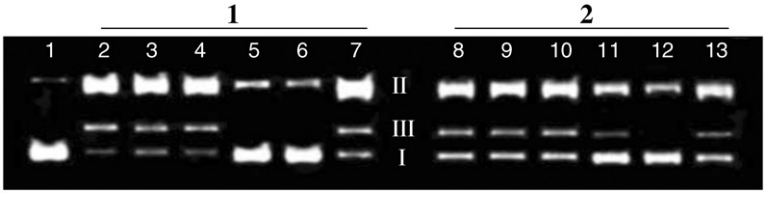


Figure 6. The cleavage of pBR322 DNA treated with **1** (30 μM)/**2** (50 μM) + MPA (250 μM) in the presence of different radical scavengers at 37°C for 1 h. Lane 1: DNA control; lane 2: DNA + **1** + MPA; lanes 3–7: DNA + **1** + MPA + DMSO (0.5 M), *t*-BuOH (0.5 M), CAT (500 U mL^{-1}), NaN_3 (0.1 M) and SOD (500 U mL^{-1}), respectively; lane 8: DNA + **2** + MPA; lanes 9–13: DNA + **2** + MPA + DMSO (0.5 M), *t*-BuOH (0.5 M), CAT (500 U mL^{-1}), NaN_3 (0.1 M) and SOD (500 U mL^{-1}), respectively.

4. Conclusion

Two new Cu(II)-bipyridyl complexes with tetraalkylammonium groups were synthesized and characterized. X-ray diffraction analysis of **1** indicates distorted trigonal bipyramidal or square pyramid at Cu(II). The UV spectroscopic titrations indicate that these complexes interact with DNA via outside electrostatic binding and the intrinsic binding constants were determined. In the presence of reducing reagents, both complexes induce efficient cleavage of pBR322 DNA; DNA cleavage activity of **1** with smaller functional groups is much higher than that of **2** with bigger functional groups. Using ROS scavengers CAT and NaN_3, obvious inhibition of DNA cleavage was observed, indicating that H_2O_2 and $^1O_2$ are responsible for DNA cleavage.

Supplementary material

CCDC 691652 contains the supplementary crystallographic data for **1**. This data can be obtained free of charge from the Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/conts/retrieving.html

Acknowledgments

This work was supported by the National Natural Science Foundation of China (No. 20725103, 30770494, 20671098, and 20529101), Guangdong provincial Natural

Science Foundation (No. 07117637) and National Basic Research Program of China (No. 2007CB815306).

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