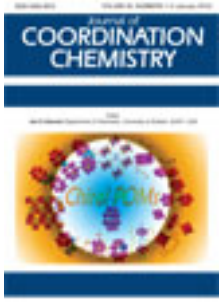

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A copper(II) complex of 1,4,7-triazacyclononane featuring acetate pendant: an efficient DNA cleavage agent

Jing Qian [a], Li-Ping Wang [b], Jin-Lei Tian [c], Cheng-Zhi Xie [d] & Shi-Ping Yan [c]

[a] College of Chemistry, Tianjin Normal University, Tianjin 300387, P.R. China

[b] Department of Chemistry, Baoding College, Baoding 071000, P.R. China

[c] Department of Chemistry, Nankai University, Tianjin 300071, P.R. China

[d] College of Pharmacy, Tianjin Medical University, Tianjin 300070, P.R. China

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A copper(II) complex of 1,4,7-triazacyclononane featuring acetate pendant: an efficient DNA cleavage agent

JING QIAN*†, LI-PING WANG‡, JIN-LEI TIAN§, CHENG-ZHI XIE¶ and SHI-PING YAN*§

†College of Chemistry, Tianjin Normal University, Tianjin 300387, P.R. China
‡Department of Chemistry, Baoding College, Baoding 071000, P.R. China
§Department of Chemistry, Nankai University, Tianjin 300071, P.R. China
¶College of Pharmacy, Tianjin Medical University, Tianjin 300070, P.R. China

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A new water-soluble copper(II) complex, Cu(**TACNA**)Br · 0.375H_2O (**1**) [**TACNA** = 1,4,7-triazacyclononane-*N*-acetate], has been synthesized to serve as artificial nucleases. The X-ray crystal structure of **1** indicates that one bromide and an oxygen from acetate pendant coordinate to copper(II) in addition to the nitrogen atoms in the **TACN** macrocycle, resulting in a five-coordinate complex with square-pyramidal geometry. The interaction of **1** with calf thymus DNA (ct-DNA) has been investigated by UV absorption and fluorescence spectroscopies, and the mode of ct-DNA binding for **1** has been proposed. In the absence of external agents, supercoiled plasmid DNA cleavage by **1** was performed under aerobic condition; the influences on DNA cleavage of different complex concentrations and reaction times were also studied. The cleavage of plasmid DNA likely involves oxidative mechanism.

Keywords: Copper(II) complex; 1,4,7-Triazacyclononane; DNA-binding; DNA cleavage

1. Introduction

Since discovery of the first chemical nuclease [1], design of DNA cleavage agents has been of interest due to their potential use as drugs, tools for molecular biology, and regulators of gene expression [2]. Low molecular weight metal complexes are attractive mimic reagents because of their inherently diverse electronic structures [3] and the studies can help us understand the role of metal ions in natural nucleases. Numerous other ligands coordinated with copper ions promoting degradation of DNA. Although they show good activity, most complexes have, to some extent, poor solubility in water, which complicate application and DNA cleavage activity.

The coordination chemistry of the small tridentate macrocycle 1,4,7-triazacyclononane (**TACN**) has attracted interest for a number of decades. Applications rely on the

*Corresponding authors. Email: qianjinger@yahoo.com.cn; yansp@nankai.edu.cn

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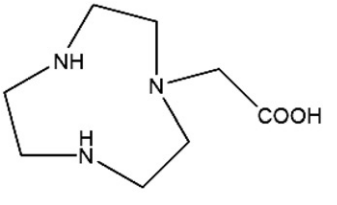
high thermodynamic stability of **TACN** complexes (for copper(II) log $K_f = 15.5$) [4]. Cu(**TACN**)Cl_2 is, an example of metal complexes, able to hydrolyze the inactive dipeptide glycyl-glycine and also the protein bovine serum albumin (BSA), at near physiological pH. This was the first complex able to cleave not only peptide bonds but also phosphodiester bonds, including DNA [5–8]. **TACN** complexes have been synthesized to serve as artificial nucleases, because transition metal complexes bearing macrocyclic ligands are highly soluble in water [9] and have effective DNA cleavage and catalytic hydrolysis phosphodiester abilities [10, 11]. Many of the first generation enzyme mimics were simple mononuclear chelate complexes featuring **TACN** derivatives [12]. Burstyn and co-workers studied a series of macrocyclic copper(II) complexes and proposed a mechanism of *bis*(p-nitrophenyl)phosphate and DNA hydrolysis showing importance of macrocyclic ring size and substituents on the ring for reactivity [13, 14]. Increasing attention has been paid to the design and synthesis of more sophisticated supporting ligand structures featuring auxiliary amino [15], guanidine [16], and anthraquinone [17] pendants. Investigations have also focused on the coordination chemistry of assemblies consisting of two or more **TACN** macrocycles connected *via* organic backbones, such as N-alkyl and N-benzyl derivatives, used in the synthesis of metal complexes in biomimic studies [17].

Our research focuses on artificial nucleases and we have obtained some species which can cleave DNA *via* hydrolysis mode [18, 19] and/or redox [20–23]. For instance, we have synthesized a novel *bis*-**TACN** macrocyclic ligand bridged by *bis*-4-methylphenol (where *bis*-**TACN** is $1^4,5^4$-dimethyl-$1^2,5^2$-dihydroxy-1(1,3),5(1,3)-dibenzene3(1,4),7(1,4)-di1,4,7-triazacyclononane) and reported binuclear zinc(II) hydrolytic cleavage agents and a binuclear copper(II) oxidative cleavage agent [24]. To further study the DNA cleavage behavior of **TACN** complexes, we have synthesized another macrocyclic ligand **TACNA**, which has one carboxylate and is highly soluble in water, and its binuclear cobalt(III) complexes. DNA cleavage mechanism studies, especially the T4 ligation experiment, show that the cleavage reaction proceeds *via* a hydrolytic pathway under anaerobic condition [25].

In an attempt to obtain more insight into the selectivity and efficiency of DNA recognition and cleavage by different complexes, we selected copper(II) due to its stronger Lewis acidity and rapid ligand exchange ability [26]. In this article, **TACNA** as ligand (scheme 1) and copper(II) produced a new five-coordinate complex to serve as nuclease mimic. Spectroscopic and detailed kinetic investigation into the nucleases activity of **1** are also presented.



TACNA

Scheme 1. Structures of ligand.

2. Experimental

2.1. *Materials and instrumentation*

1,4,7-Triazacyclononane-*N*-acetate (**TACNA · HCl**) was prepared following the procedure of Wieghardt *et al*. [27]. Ethidium bromide (EB), calf thymus DNA (ct-DNA), and pBR322 plasmid DNA were obtained from Sigma. Unless stated, all other reagents used in this research were obtained from commercial sources and used without purification. Solvents were purified by standard procedures. Tris-HCl buffer solution was prepared by using deionized, sonicated triply distilled water. Solution of the complex and other reagents used for strand scission were freshly prepared in triply distilled water before use.

Elemental analyses for C, H, and N were obtained on a Perkin-Elmer analyzer model 240. Infrared spectroscopy on KBr pellets was performed on a Bruker Vector 22 FT-IR spectrophotometer from 4000 to 400 cm^{-1}. Electronic spectra were measured on a JASCO V-570 spectrophotometer. Fluorescence spectra were recorded on a Cary 300 fluorescence spectrophotometer. The Gel Imaging and Documentation DigiDoc-It System (UVI, England) were assessed using Labworks Imaging and Analysis Software (UVI, England). Anaerobic condition was obtained using a MBraun LABStar glove box.

2.2. *Preparation of 1*

TACNA · HCl (0.099 g, 0.5 mmol) and Li(OH) (0.041 g, 1 mmol) in 15 mL H_2O were added dropwise to 5 mL of methanolic solution of $CuBr_2$ (0.112 g, 0.5 mmol). The mixture was refluxed for 3 h in air, filtered, giving black-green block microcrystals which were collected by filtration, washed with diethyl ether, and dried in air. The obtained microcrystals were dissolved in CH_3OH/DMF (1 : 2) mixture. Blue block crystals of **1** suitable for X-ray diffraction were obtained by slow evaporation of the filtrate, collected by filtration, washed with diethyl ether, and dried in air. Yield (0.124 g, 37%, based on the copper salt). Elemental analysis data: Cald for $C_{16}H_{29.50}Br_2Cu_2N_6O_{4.75}$ (668.86) (%): C, 28.71; H, 4.41; N, 12.56. Found (%): C, 28.43; H, 4.89; N, 12.31. FT-IR (KBr phase) (cm^{-1}): 3308, 3184, 2951, 2890, 1665, 1600. UV: 230 nm (π–π^*), 692 nm (d–d) (figure S1).

2.3. *X-ray crystallographic procedure*

Suitable single crystals were used for X-ray diffraction analyses by mounting on the tip of a glass fiber in air. Data were collected on a Bruker APEX-II CCD diffractometer with Mo-Kα ($\lambda = 0.71073$ Å) radiation at 294(2) K. The structures were solved by direct methods using the program SHELXS-97 and refined with full-anisotropically by full-matrix least-squares on F^2 using SHELXL-97 [28]. All non-hydrogen atoms were refined anisotropically and all hydrogen atoms were generated geometrically. Molecular graphics were drawn with the program package Diamond.

2.4. *DNA-binding experiments*

By the electronic absorption spectral method, the relative binding of **1** to ct-DNA was studied in 5 mmol L^{-1} Tris-HCl/NaCl buffer at pH = 7.4 (where Tris is tris-hydroxy methyl-amino-methane). The solution of ct-DNA gave a ratio of UV absorbance at 260 nm and 280 nm, A_{260}/A_{280}, of 1.89, indicating that the DNA was sufficiently free of protein [29]. The ct-DNA stock solutions of 5 mmol L^{-1} were prepared in Tris-HCl/NaCl buffer, pH = 7.4 (stored at 4°C and used within 4 days after preparation). The concentration of ct-DNA was determined from its absorption intensity at 260 nm with a molar extinction coefficient of 6600 $(mol\,L^{-1})^{-1}\,cm^{-1}$ [30].

By the fluorescence spectral method, the relative binding of **1** to ct-DNA was studied with an EB-bound DNA solution in 5 mmol L^{-1} Tris-HCl/NaCl buffer (pH = 7.4). The excitation wavelength was fixed at 510 nm and the emission range was adjusted before measurement. Fluorescence intensities at 602 nm were measured at different complex concentrations [31].

2.5. *DNA cleavage experiments*

Cleavage of SC pBR322 DNA by **1** was studied by agarose gel electrophoresis. The reaction was carried out following a literature method [24]. After electrophoresis, bands were visualized by UV light and photographed. The extent of cleavage of SC DNA was determined by measuring the intensities of the bands using Gel Documentation System [32]. SC DNA values were corrected by a factor 1.22, based on average literature estimate of lowered binding of ethidium [33].

The reaction was carried out by adding scavengers of SOD, KI, catalase, DMSO, L-histidine, SYBR Green, and methyl green to SC DNA alternatively. Cleavage was initiated by the addition of complex and quenched with 2 μL of loading buffer. Further analysis was carried out by the above standard method.

Deoxygenated solutions were prepared by four freeze-pump-thaw cycles. Before the final two cycles, the solutions were equilibrated with argon to aid in the deoxygenation process. The deoxygenated solutions were stored under an argon atmosphere prior to use. Reaction mixtures were prepared in the glove box by addition of the appropriate volumes of stock solutions to the reaction tubes. The reactions were initiated by quick centrifugation, incubated at room temperature and quenched by addition to the loading buffer in the glove box. All other conditions were the same as those listed for the aerobic cleavage reactions.

3. Results and discussion

3.1. *X-ray structure characterization*

Complex **1** has been structurally characterized by X-ray crystallography. To deal with non-coordinated water molecules, we refined the crystal data using the SQUEEZE program. The occupancy of the disordered water molecules is consistent with the result of elemental analysis. The data collection and refinement parameters are given in table S1, selected bond lengths and angles are given in table S2.

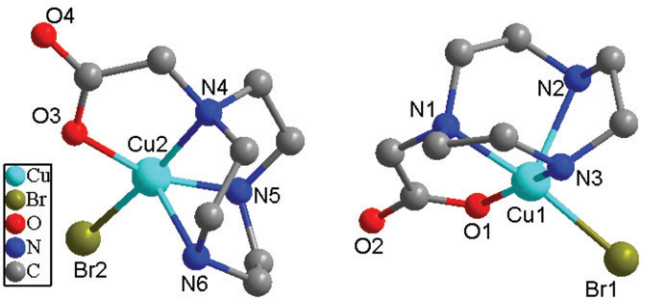


Figure 1. The labeling scheme of Cu(**TACNA**)Br; hydrogen atoms and H_2O are omitted for clarity.

For **1**, the crystallographic asymmetric unit consists of two neutral mononuclear [Cu(**TACNA**)Br] units and some lattice water molecules, as shown in figure 1. Each copper is five-coordinate with an N_3OBr ligand donor set including N_3O from a tetradentate **TACNA** and one bromide. The trigonality τ-values of Cu1 and Cu2 are calculated to be 0.157 and 0.170, respectively. According to the Addison–Reedijk geometric criterion [34–36], the geometry can be described as a distorted square-pyramidal configuration. This is indeed a feature of five-coordinate copper(II) complexes of **TACN** derivatives [37–40]. For Cu1, the basal plane is defined by Cu1, N1, N3, O1, Br1 with Cu1 lying 0.209 Å out of the plane. The axial Cu1–N2 distance (2.232 Å) is considerably longer than the planar Cu1–N distances (Cu1–N1, 2.059 Å and Cu1–N3, 2.022 Å).

3.2. *DNA-binding properties*

DNA-binding is the critical step for DNA cleavage in most cases. Therefore, the binding ability of **1** to ct-DNA was studied by various techniques. First, the potential binding ability of **1** to ct-DNA was studied by UV spectroscopy. Complex **1** exhibits weak d–d transition at 692 nm, but not a charge transfer band to monitor its interaction with DNA. So the interaction of **1** with ct-DNA was performed by following the intensity change of the intraligand π–π^* transition band, as shown in figure 2. The absorption at 268 nm for **1** is attributed to intraligand π–π^* transition; with increasing concentration of ct-DNA, hypochromism of 27% and red-shift of 20 nm for **1** were observed. Although this is not definitive, hypochromism and red shifts observed for other complexes in the presence of ct-DNA are taken as a sign of an intercalative binding mode, where stacking interactions between the aromatic chromophore of the complex and the base pairs of DNA modulate the absorption characteristics of the metal complexes [41]. Previously, we reported a mononuclear complex with bpma, $[Cu(bpma)(Ph\text{-}COO)(H_2O)]\cdot ClO_4$ [42], and selected a similar reported mononuclear complex as its comparison object, $[Cu(bpea)Cl]\cdot ClO_4$ (bpea, *N*,*N*-*bis*(2-pyridylmethyl)ethylamine) [42, 43]. We proposed that the lower red shifts observed in UV spectra were due to the partial/moderate intercalation of pyridine. The extent of the hypochromism is commonly consistent with the strength of intercalative interaction. Our results imply that **TACN** is similar to bpa-R ligands, classical tridentate nitrogen donors, which do not intercalate very strongly or deeply between the DNA base pairs.

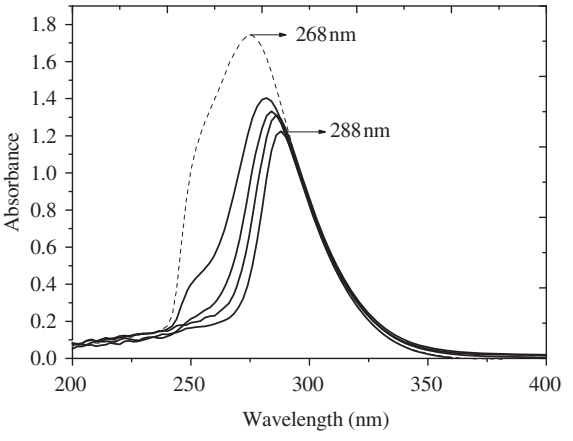


Figure 2. Absorption spectrum of **1** (6.23×10^{-5} mol L^{-1}) in the absence and presence of increasing amounts of ct-DNA 0–7.84×10^{-4} mol L^{-1} of **1** at room temperature in 5 mmol L^{-1} Tris-HCl/NaCl buffer (pH 7.4). The dashed line indicates the free complex.

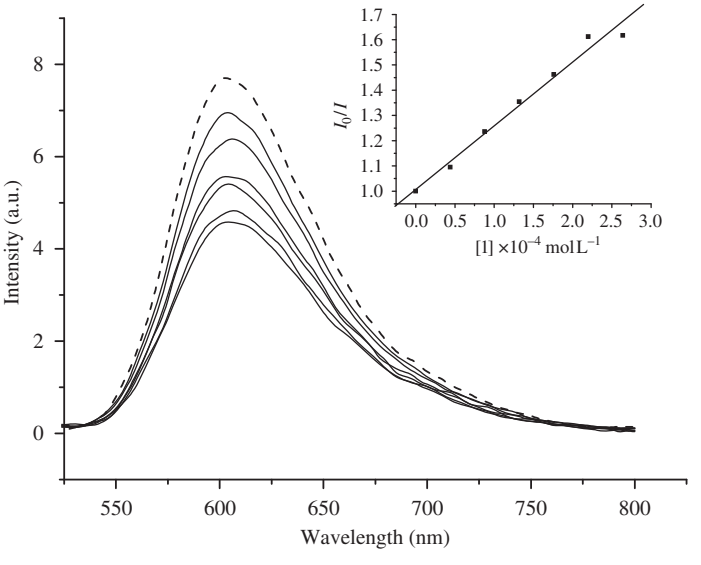


Figure 3. Emission spectrum of EB ct-DNA in the absence and presence of **1** at room temperature. Inset: the plot of I_0/I *vs.* [1]. The dashed lines indicate the free complex.

As a means for further clarifying the binding of **1**, fluorescence spectral measurement was carried out. No luminescence was observed for **1** at room temperature in aqueous solution or in the presence of ct-DNA, so binding of **1** cannot be directly observed in the emission spectra. The relative binding of **1** to ct-DNA was studied with an EB bound ct-DNA solution in Tris-HCl buffer (pH 7.4). Fluorescence intensities at 602 nm (526 nm excitation) were measured at different complex concentrations. Figure 3 shows that the fluorescence intensity of EB bound ct-DNA decreased with addition of **1**,

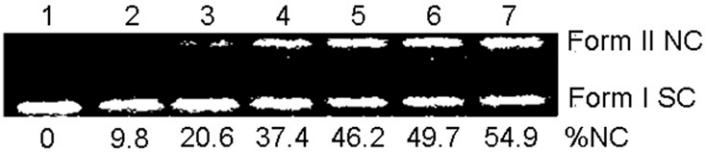


Figure 4. Gel electrophoresis diagrams showing the cleavage of pBR322 DNA (33 μmol L^{-1}) at different complex concentrations in 50 mmol L^{-1} Tris-HCl/NaCl buffer (pH 7.4) and 37°C. Lane 1: DNA control (3 h); Lanes 2–7: DNA + **1** (2 μmol L^{-1}; 30 μmol L^{-1}; 60 μmol L^{-1}; 120 μmol L^{-1}; 240 μmol L^{-1}; 480 μmol L^{-1}), respectively.

indicating that **1** binds to ct-DNA and replaces EB from the EB bound ct-DNA system. Such a feature is often found in intercalative DNA interactions [44]. According to the classical Stern–Volmer equation [45], the quenching plot illustrates that quenching of EB bound to ct-DNA by **1** is in agreement with the linear Stern–Volmer equation, indicating **1** binds to DNA. In the plot of I_0/I *versus* [1] (inset of figure 3), K_{app} is given by the ratio of the slope to intercept. According to the equation $K_{EB}[EB] = K_{app}[1]$, where the complex concentration was the value at 50% reduction of fluorescence intensity of EB and $K_{EB} = 1.0 \times 10^7$ $(\text{mol L}^{-1})^{-1}$ ($[EB] = 4.0\,\mu\text{mol L}^{-1}$), the apparent binding constant (K_{app}) at room temperature is calculated to be 1.02×10^4 $(\text{mol L}^{-1})^{-1}$ for **1**, less than the binding constant of the classical intercalators and metallointercalators (10^7 $(\text{mol L}^{-1})^{-1}$) [46] and suggesting that the interaction of **1** with DNA is a partial intercalative mode.

3.3. *Nuclease activity*

The DNA cleavage activity of **1** has been studied under physiological pH and temperature by gel electrophoresis by using supercoiled pBR322 plasmid DNA as the substrate. Figure 4 shows the results obtained at pH 7.4 and 37°C for 3 h. In the absence of external agents, **1** can cleave supercoiled DNA (form I) to nicked (form II), converting form I DNA to form II at 240 μmol L^{-1} concentration up to ~50% (lane 6). Complex **1** was found to perform DNA cleavage in a concentration-dependent manner, indicating that it is a potent chemical nuclease with nuclease activity, but less than that of binuclear copper complex [24].

Reactive oxygen species (ROS) generated during the interaction between copper complex and dioxygen or redox reagents are believed to be a major cause of DNA damage [47]. The implication of ROS (hydroxyl, singlet oxygen-like species, superoxide, and hydrogen peroxide) in the nuclease mechanism can be inferred by monitoring the quenching of DNA cleavage in the presence of ROS scavengers. To probe the potential mechanism of DNA cleavage mediated by **1**, experiments with radical scavengers were carried out under anaerobic conditions similar to those described in the caption of figure S2A. DMSO as a hydroxyl radical scavenger (lane 3) was completely ineffective in inhibiting the DNA strand scission mediated by **1**, ruling out the possibility of DNA cleavage by $^{\cdot}OH$. The addition of L-histidine (lane 4) scarcely protects against the DNA strand breakage induced by **1**, suggesting that neither singlet oxygen nor any other singlet oxygen-like entity participates in the oxidative cleavage [48]. SOD (lane 5) was ineffective in inhibiting complex activities, indicating that superoxide is not one of the

reactive species required for the breakdown of DNA in this case [49]. To examine whether H_2O_2 is the key factor responsible for DNA cleavage in this case, KI (lane 6) and catalase (lane 7) were also used to capture the active oxygen species involved in the cleavage process [50, 51]. The addition of catalase inhibits the DNA strand scission mediated by **1**, demonstrating that H_2O_2 is the active oxygen species involved in the cleavage process.

To clarify other aspects of the mechanism, groove binders such as methyl green (major-groove binder) and/or SYBR Green (minor-groove binder) can also be used (figure S2B). In the presence of the major-groove binder methyl green and the minor-groove binder SYBR Green, apparent inhibition of DNA damage was observed, a finding that implies groove binding preferences for **1** (lanes 4 and 5), which is also in accord with the conclusions drawn from the DNA-binding and kinetic studies [52]. In the absence of external agent at pH 7.4 (50 mmol L^{-1} Tris-HCl/NaCl buffer) and 21°C, DNA degradation is invisible for copper(II) and copper(I) salts (figure S2C). On the basis of all of these results, we propose that the copper(II) complex promotes DNA cleavage through an oxidative DNA damage pathway, in which giving active oxygen species O_2^-, that cleaves DNA.

4. Conclusion

TACNA with copper(II) gives a new five-coordinate complex which serves as a nuclease mimic. The interaction of **1** with ct-DNA has been studied using UV absorption and fluorescence spectroscopy, and the mode of ct-DNA binding to the complex proposed. DNA cleavage promoted by **1** was demonstrated to occur by an oxidative pathway, with O_2^- active species. The synthesis of higher affinity and reactivity of **TACN** metal complexes and their kinetic and theoretical studies are our attempts in progress.

Supplementary material

Crystallographic data for the structure analysis in this article have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC No. 602627.

Acknowledgments

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