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新型三联吡啶铜配合物的晶体结构及 DNA 切割活性

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摘要:本文合成了新型三联吡啶铜配合物[Cu(ttpy)(acetone)Cl]·$(NO_3)(H_2O)_3$(ttpy=4′-p-tolyl-2,2′:6,2″-terpyridine),通过元素分析和X-射线单晶衍射进行结构表征。该配合物属三斜晶系,空间群为 $P\bar{1}$,晶胞参数为 a=0.847 6(3) nm,b=1.265 0(5) nm,c=1.422 7(5) nm,α=111.017(7)°,β=92.174(7)°,γ=90.562(7)°,V=1.422 5(9) nm^3,Z=2,D_c=1.309 Mg·m^{-3},μ(Mo $K\alpha$)=9.00 cm^{-1},F(000)=578,R_1=0.063 3,wR=0.141 4。在配合物中,中心铜原子的配位环境为变形四方锥,并通过分子内和分子间的 C–H…Cl 和 C–H…O 氢键作用形成三维梯状结构。凝胶电泳结果表明,在 pH=7.4,温度 37°,以抗坏血酸为还原剂的条件下,该配合物对超螺旋 pUC19 DNA 表现出一定的切割活性。紫外–可见光谱结果显示,该配合物与四种核苷的反应活性顺序为:5′-GMP>5′-AMP>5′-TMP≈5′-CMP。

关键词:三联吡啶铜配合物;晶体结构;DNA 切割
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Crystal Structure and DNA Nuclease Activity of a Copper(Ⅱ) Complex of 4′-*p*-Tolyl-2,2′:6,2″-Terpyridine

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Abstract: A novel copper(Ⅱ) terpyridine complex [Cu(ttpy)(acetone)Cl]$(NO_3)(H_2O)_3$ (ttpy=4′-*p*-tolyl-2,2′:6,2″-terpyridine) had been synthesized and structurally characterized. The complex crystallized in the triclinic system, space group $P\bar{1}$ with cell parameters: a=0.847 6(3) nm, b=1.265 0(5) nm, c=1.422 7(5) nm, α=111.017(7)°, β=92.174(7)°, γ=90.562(7)°, V=1.422 5(9) nm^3, Z=2, D_c=1.309 Mg·m^{-3}, μ(Mo $K\alpha$)=9.00 cm^{-1}, F(000)=578, the final R_1=0.063 3, wR_2=0.141 4. The copper center was situated in a distorted square pyramidal (4+1) CuN_3X_2 coordination geometry with terpyridine acting as an equatorial tridentate ligand. The 3D ladder-like structure was connected by intra- and intermolecular C–H…Cl and C–H…O hydrogen bonds. The complex was able to cleave pUC19 DNA at micromole concentration in the presence of ascorbic acid. The reactivity of the complex towards four mononucleotides with the order: 5′-GMP>5′-AMP>5′-TMP≈5′-CMP, was determined by UV-Vis spectroscopy. CCDC: 625295.

Key words: terpyridine-copper(Ⅱ) complex; crystal structure; DNA cleavage

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0 Introduction

In the past decade, DNA-targeting metal complexes had been intensively explored due to their potential applications in gene regulation, probing of DNA specific structures, and cancer therapy[1]. Most of the attentions were focused on the rational design of metal complexes that can bind and cleave duplex DNA with high efficiency and sequence or structure selectivity. Both the metal centers and the ligands were found to be crucial for the interaction of a specific complex with DNA. The metal centers largely controlled the redox potential, the formation of reactive species and DNA binding ability while the ligands acted as the unit of functional regulation[2].

For example, the typical Fenton-type reaction produced hydroxyl radicals which were responsible for the non-selective DNA scission induced by $[Fe(EDTA)]^{2-}$ (EDTA =ethylenediamine tetraacetic acid)[3], while Fe-BLMs (BLM =bleomycin) can promote DNA-cleavage through the reaction of $Fe^{Ⅲ}$-OOH or $Fe^{Ⅳ}$=O with C′4-H in the minor groove[4,5]. The attachment of 1,10-phenanthroline-Cu(Ⅰ) chelate ($[Cu(OP)_2]^+$) to different site of oligoribonucleotides (ORNs) could form a series of OP-linked ORNs with template-specific DNA cleavage ability[6]. However, a $Ni^{Ⅱ}$salen-DNA hybrid [salen =*N*, *N*′-ethylenebis (salicylidene aminato)] was proved to only target at the dG sites of the complementary strand[7]. Several ternary copper complexes of terpyridine exhibited promise oxidative DNA cleavage activity in the presence of H_2O_2, ascorbic acid or glutathione[8~10], and the formation of nucleobase radical cations could be controlled by tuning their gas phase redox properties[10].

In our previous work, we had reported the synthesis and DNA binding property of two novel copper(Ⅱ) terpyridine complexes, revealing the remarkable biological effects induced by the modification of the ligands[11]. To continue our investigation on the structure-activity relationship of metal-terpyridine complexes[11,12], we described here the structure and the biological activity of another new copper(Ⅱ) terpyridine complex $[Cu(ttpy)(acetone)Cl]\cdot(NO_3)(H_2O)_3$ (ttpy =4′-*p*-tolyl-2,2′:6,2″-terpyridine). The nuclease activity of the complex had been studied and the preliminary cleavage mechanism of the complex was discussed. Moreover, its reactivity with four biomolecules (5′-GMP, 5′-AMP, 5′-TMP and 5′-CMP) had also been investigated by the UV-Vis spectroscopy.

1 Experimental

1.1 Materials and characterizations

Reagents such as methanol, ethanol, acetone, anhydrous DMF, $Cu(NO_3)_2\cdot 3H_2O$ were of analytical grade and were used without further purification. The 4′-*p*-tolyl-2,2′:6,2″-terpyridine were prepared according to the reported procedures[13]. The elemental analysis was performed on a Perkin-Elmer 240C analytical instrument.

1.2 Synthesis of $[Cu(ttpy)(acetone)Cl]\cdot(NO_3)(H_2O)_3$

A mixture of $Cu(NO_3)_2\cdot 3H_2O$ (0.241 g, 1 mmol) and ttpy (0.323 g, 1 mmol) in methanol (25 mL) was stirred for 2 h at 60 ℃, then the solids were filtered and washed with acetone and diethyl ether, and dried in vacuum. Yield: 0.363 g, 71.0%. Green crystals suitable for X-ray diffraction were obtained by vapor diffusion of acetone into a water solution of the solid (pH ≈6, HCl). Elemental analysis: calcd. for $C_{22}H_{17}N_5O_6Cu$ (510.5)(%): C 51.71, H 3.33, N 13.71; found (%): C 51.73, H 3.51, N 13.63. m.p.:>300 ℃.

1.3 X-ray crystallography

A single crystal of the complex was mounted on a glass fiber. The intensity data were collected at 293 K on a Bruker SMART Apex CCD area detector diffractometer operating in the φ-ω scan mode with graphite-monochromated Mo $K\alpha$ radiation (λ =0.071 073 nm). Empirical absorption corrections were carried out by using a multi-scan program. The SMART software was used for data acquisition and the SAINT software for data extraction. Absorption correction was made using SADABS[14]. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares methods by using the SHELXTL program[15]. All non-hydrogen atoms were refined anisotropic. All the hydrogen atoms were geometrically fixed at calculated positions.

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1.4 DNA cleavage experiments

The DNA cleavage activity of the complex was studied by agarose gel electrophoresis. Supercoiled pUC19 DNA (200 ng) in Tris-HCl buffer (50 mmol·L^{-1}) containing 50 mmol·L^{-1} NaCl (pH=7.4) was treated with copper complexes and 1 μL of ascorbic acid (Asc) at a 100-fold molar excess relative to the complex to yield a total volume of 10 μL and then incubated in dark for 60 min at 37 ℃. The reaction was quenched by the addition of 1 μL loading buffer, and then the resulting solutions were loaded on a 0.7% agarose gel. Electrophoresis was carried out at 50 V for 2 h in TAE buffer (40 mmol·L^{-1} Tris acetate / 1 mmol·L^{-1} EDTA). DNA bands were visualized under UV light and photographed. The quantification of each form of DNA was made by densitometric analysis of ethidium bromide containing agarose gel. A correction factor of 1.47 was used for supercoiled DNA (form Ⅰ) taking into account the weaker intercalation of EB to SC compared to nicked (form Ⅱ) and linear DNA (form Ⅲ).

The cleavage of pUC19 plasmid DNA in the presence of standard radical scavengers and reaction inhibitors had also been carried out. In these experiments, 1 mol·L^{-1} DMSO, 100 mmol·L^{-1} *t*-BuOH (as a hydroxyl radical scavenger), or 100 mmol·L^{-1} NaN_3 (as a singlet oxygen scavenger) or 100 mmol·L^{-1} KI (as hydrogen peroxide scavenger) was added respectively to the solution of supercoiled DNA and the copper complexes. The mixture was incubated at 37 ℃ for 20 min prior to the addition of an ascorbic acid to initiate the reaction. Subsequent treatment and analysis followed the same procedure as described above.

1.5 Interactions with biomolecules

The reactions of [Cu(ttpy)(acetone)Cl]·$(NO_3)(H_2O)_3$ with 5′-GMP, 5′-CMP, 5′-AMP or 5′-TMP at 1∶1 and 1∶2 molar ratio ($c_{complex}$ / $c_{biomolecule}$) in 5 mmol·L^{-1} Tris-HCl/50 mmol·L^{-1} NaCl (pH=7.4) were monitored by the UV-Vis spectroscopy.

2 Results and discussion

2.1 Synthesis

The reaction of 4′-*p*-tolyl-2,2′:6,2″-terpyridine and $Cu(NO_3)_2$, and crystallization of raw product by vapor diffusion of acetone into a water solution of the solid (pH≈6) resulted in the mononuclear copper(Ⅱ) terpyridine complex, [Cu(ttpy)·(acetone)Cl]·$(NO_3)(H_2O)_3$. The appearance of chloride and acetone in the crystal structure of the complex is interesting, which supported the evident solvent-effect in the crystallization of the title complex. Similar case occurred for the similar copper(Ⅱ) terpyridine complexes, [Cu(atpy)$(NO_3)(H_2O)$]$(NO_3)\cdot 3H_2O$ and Cu(atpy)$(NO_3)_2$, in which the coordinated nitrates could be readily displaced by one or more H_2O[11].

2.2 Crystal structure

The crystal data and structure refinement parameters are given in Table 1. Selected bond lengths and angles were given in Table 2. Selected hydrogen bond lengths and angles were given in Table 3.

As shown in Fig.1, the title complex consisted a

Table 1　Crystallographic data of [Cu(ttpy)(acetone)Cl]·$(NO_3)(H_2O)_3$

Formula	$C_{25}H_{25}ClCuN_4O_5$	*Z*	2
Formula weight	560.48	D_c / (Mg·m^{-3})	1.309
T / K	291(2)	*F*(000)	578
Crystal system	Triclinic	Goodness-of-fit on F^2	1.075
Space group	$P\bar{1}$	μ / mm^{-1}	0.900
a / nm	0.847 6(3)	θ range for data collection	1.85~26.00
b / nm	1.265 0(5)	Reflections collected	7 603
c / nm	1.422 7(5)	Independent reflections	5424
α / (°)	111.017(7)	Independent reflections ($I>2\sigma(I)$)	4 169
β / (°)	92.174(7)	R_1 ($I>2\sigma(I)$)	0.070 0
γ / (°)	90.562(7)	wR_2 ($I>2\sigma(I)$)	0.154 2
V / nm^3	1.422 5(9)		

Table 2 Selected bond lengths (nm) and angles (°) of [Cu(ttpy)(acetone)Cl]·(NO$_3$)(H$_2$O)$_3$

Cu(1)-N(1)	0.206 1(3)	Cu(1)-N(3)	0.204 0(3)	Cu(1)-Cl(1)	0.255 5(2)
Cu(1)-N(2)	0.194 9(3)	Cu(1)-O(1)	0.193 7(3)		
O(1)-Cu(1)-Cl(1)	103.8(1)	N(2)-Cu(1)-N(1)	79.1 (1)	N(3)-Cu(1)-Cl(1)	96.3(1)
N(1)-Cu(1)-Cl(1)	94.1(1)	N(2)-Cu(1)-N(3)	79.0 (1)	N(3)-Cu(1)-N(1)	156.9(1)
N(1)-Cu(1)-O(1)	101.7(1)	N(2)-Cu(1)-Cl(1)	98.1(1)		
N(2)-Cu(1)-O(1)	158.0(1)	N(3)-Cu(1)-O(1)	95.8(1)		

Table 3 Hydrogen bonding data for [Cu(ttpy)(acetone)Cl]·(NO$_3$)(H$_2$O)$_3$

D–H···A	Distance of D···A / nm	Angle of D-H-A / (°)
C(4)–H(4)···Cl(1)#1	0.363 9(5)	162
C(7)–H(7)···Cl(1)#1	0.369 3(4)	166
C(18)–H(18)···O(2)#2	0.338 1(6)	159
C(23)–H(23B)···O(3)#3	0.330 2(7)	139
C(25)–H(25B)···O(2)#3	0.315 8(6)	128
C(25)–H(25B)···O(3)#3	0.322 7(7)	127
C(25)–H(25A)···Cl(1)	0.319 2(6)	168
C(23)–H(23C)···O(4)	0.324 2(7)	133

Symmetry transformation used to generate equivalent atoms: #1: 1–x, 2–y, –z; #2: 2–x, 2–y, –z; #3: –1+x, y, z.

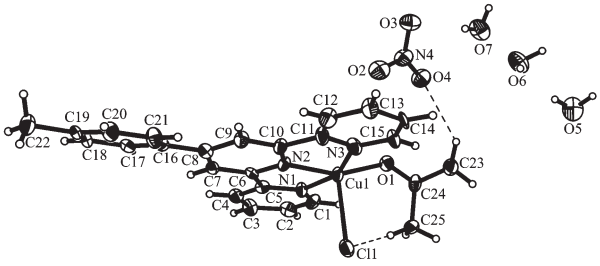
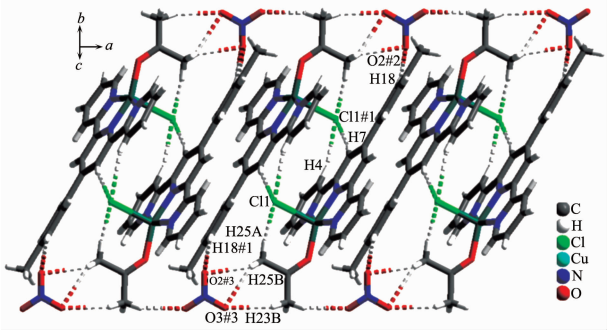


Fig.1 ORTEP drawing of [Cu(ttpy)(acetone)Cl]·(NO$_3$)(H$_2$O)$_3$ along with the atom numbering scheme, probability level of 30%

cation of [Cu(ttpy)(acetone)Cl]$^+$, the counter anion NO$_3$ and three H$_2$O solvent molecules. The cation had a distorted square pyramidal (4+1) CuN$_3$X$_2$ coordination geometry with the chloride located at the apical position. The axial bond Cu-Cl was nearly perpendicular to the basal plane with the bond length of 0.255 5(2) nm. The copper center, three nitrogen atoms from ttpy and one oxygen atom from acetone formed the basal plane. The central Cu-N bond of ttpy [0.194 9(3) nm] was shorter than those of the outer ones [0.204 0(3) and 0.206 1(3) nm], and the bond angles subtended by the terpyridyl unit [79.1(1)° and 79.0(1)°] were also deviated from the ideal value of 90°, showing the common characteristics for terpyridyl-containing complexes[9,11,16]. The dihedral angle of the two planes of phenyl and terpyridine was 15°, which was quite similar to that of Cu(ttpy)(NO$_3$)$_2$[11]. It is worthy to note that two intramolecular hydrogen bonds, C(25)–H(25A)···Cl(1) [C(25)···Cl(1): 0.319 2(6) nm] and C(23)–H(23C)···O(4) [C(23)···O(4): 0.324 2(7) nm], were found within the cations and between the cations and anions, respectively (Table 3).

The cations, [Cu (ttpy)(acetone)Cl]$^+$, were apt to form dimmer by two intermolecular C–H···Cl hydrogen bonds, C(4)–H(4)···Cl(1)#1 and C(7)–H(7)···Cl(1)#1, which are between the chloride and neighboring terpyridyl group[17]. In addition, the C–H···O hydrogen bonds derive from the NO$_3$ anion and coordinated acetone linked the dimmers to generate a 3D ladder-like framework (Fig.2). Hydrogen bonding data were shown in Table 3.



Element name and symmetry code of those atoms involved were labelled but H$_2$O molecules were omitted for clarity, Symmetry transformation used to generate equivalent atoms: #1: 1–x, 2–y, –z; #2: 2–x, 2–y, –z; #3: –1+x, y, z

Fig.2 3D ladder-like structure of [Cu(ttpy)(acetone)Cl]·(NO$_3$)(H$_2$O)$_3$ linked by C–H···Cl and C–H···O hydrogen binding

2.3 DNA nuclease activity

The oxidative cleavage of supercoiled pUC19 DNA

by the title complex was investigated in the presence of 100-fold excess ascorbic acid at 37 ℃. The concentration dependence of the DNA cleaving efficiency was studied when the reaction time is 60 min (Fig.3a) and 120 min (Fig.3b), respectively. The quantified data were shown in Table 4. As shown in Fig.3, the title complex showed more efficient DNA cleavage activity than its analogue [8]. Supercoiled DNA (Form Ⅰ) decreased while nicked DNA (Form Ⅱ), liner DNA (Form Ⅲ) and even fragmented DNA increased evidently when the concentration changed from 5 μmol·L^{-1} to 25 μmol·L^{-1}. Moreover, the influence of the reaction time on the cleavage activity of the title complex was also illustrated in Fig.3. The increase of reaction time produced a significant increase of the Form Ⅱ or Form Ⅲ DNA. When the time reaction varied from 60 to 120 min, Form Ⅰ DNA disappeared while the content of form Ⅱ DNA increased from 51% (Fig.3(a), lane 3) to 76% (Fig.3 (b), lane 3) in the presence of the title complex (10 μmol·L^{-1}). At higher concentration (≥20 μmol·L^{-1}), some smears corresponding to multi-fragmented DNA were observed when the reaction time was 120 time, while Form Ⅰ DNA (30%) still existed when the time was 60 min. These results suggested that the optimum reaction concentration may be 15~20 μmol·L^{-1} when the reaction time was 120 min.

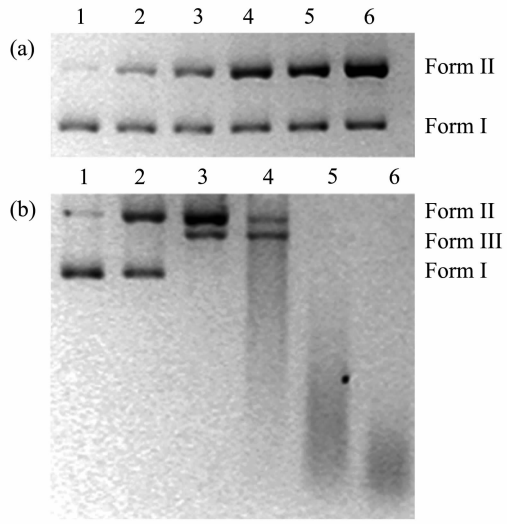


Fig.3 Agarose gel electrophoresis patterns for the cleavage of SC pUC19 plasmid DNA (0.02 mg·mL^{-1}, 30 μmol·L^{-1} base pair) by the title complex in the presence of 100-fold excess of ascorbic acid in the dark for (a) 60 min and (b) 120 min in Tris-HCl buffer (50 mmol·L^{-1}, pH 7.4) at 37 ℃: Lane 1, DNA control; lane 2~6, DNA+ascorbic acid + (5, 10, 15, 20 and 25 μmol·L^{-1}) of complex

Table 4 Data of pUC 19 DNA cleavage at different conditions

Lane	*T* / h	Reaction condition	Form / %		
			Ⅰ	Ⅱ	Ⅲ
(a)1	1	DNA control	90	10	
(a)2	1	DNA+Asc+[Cu(ttpy)(acetone)Cl]·$(NO_3)(H_2O)_3$ (5 μmol·L^{-1})	66	34	
(a)3	1	DNA +Asc+[Cu(ttpy)(acetone)Cl]·$(NO_3)(H_2O)_3$ (10 μmol·L^{-1})	49	51	
(a)4	1	DNA+Asc+[Cu(ttpy)(acetone)Cl]·$(NO_3)(H_2O)_3$ (15 μmol·L^{-1})	33	67	
(a)5	1	DNA+Asc+[Cu(ttpy)(acetone)Cl]·$(NO_3)(H_2O)_3$ (20 μmol·L^{-1})	30	70	
(a)6	1	DNA+Asc+[Cu(ttpy)(acetone)Cl]·$(NO_3)(H_2O)_3$ (25 μmol·L^{-1})	24	76	
(b)1	2	DNA control	90	10	
(b)2	2	DNA+Asc+[Cu(ttpy)(acetone)Cl]·$(NO_3)(H_2O)_3$ (5 μmol·L^{-1})	37	63	
(b)3	2	DNA +Asc+[Cu(ttpy)(acetone)Cl]·$(NO_3)(H_2O)_3$ (10 μmol·L^{-1})		76	24
(b)4	2	DNA+Asc+[Cu(ttpy)(acetone)Cl]·$(NO_3)(H_2O)_3$ (15 μmol·L^{-1})		41	59
(b)5	2	DNA+Asc+[Cu(ttpy)(acetone)Cl]·$(NO_3)(H_2O)_3$ (20 μmol·L^{-1})			
(b)6	2	DNA+Asc+[Cu(ttpy)(acetone)Cl]·$(NO_3)(H_2O)_3$ (25 μmol·L^{-1})			

2.4 Reactivity towards nucleotides

To further understand the DNA cleavage activity of the title complex, the reactions of the complex with four mononucleotides (5′-GMP, 5′-AMP, 5′-TMP and 5′-CMP) at 1:1 and 2:1 molar ratios ($c_{mononucleotide}$ / $c_{complex}$) were performed by UV-Vis spectroscopy, respectively. As shown in Fig.4 (a) and 4 (c), the UV-Vis absorption spectra of the solution of [Cu(ttpy)(acetone)Cl]·$(NO_3)(H_2O)_3$ (2×10^{-5} mol·L^{-1}, 5 mmol·L^{-1} Tris, 50 mmol·L^{-1} NaCl, pH=7.4) changed significantly as a result of its

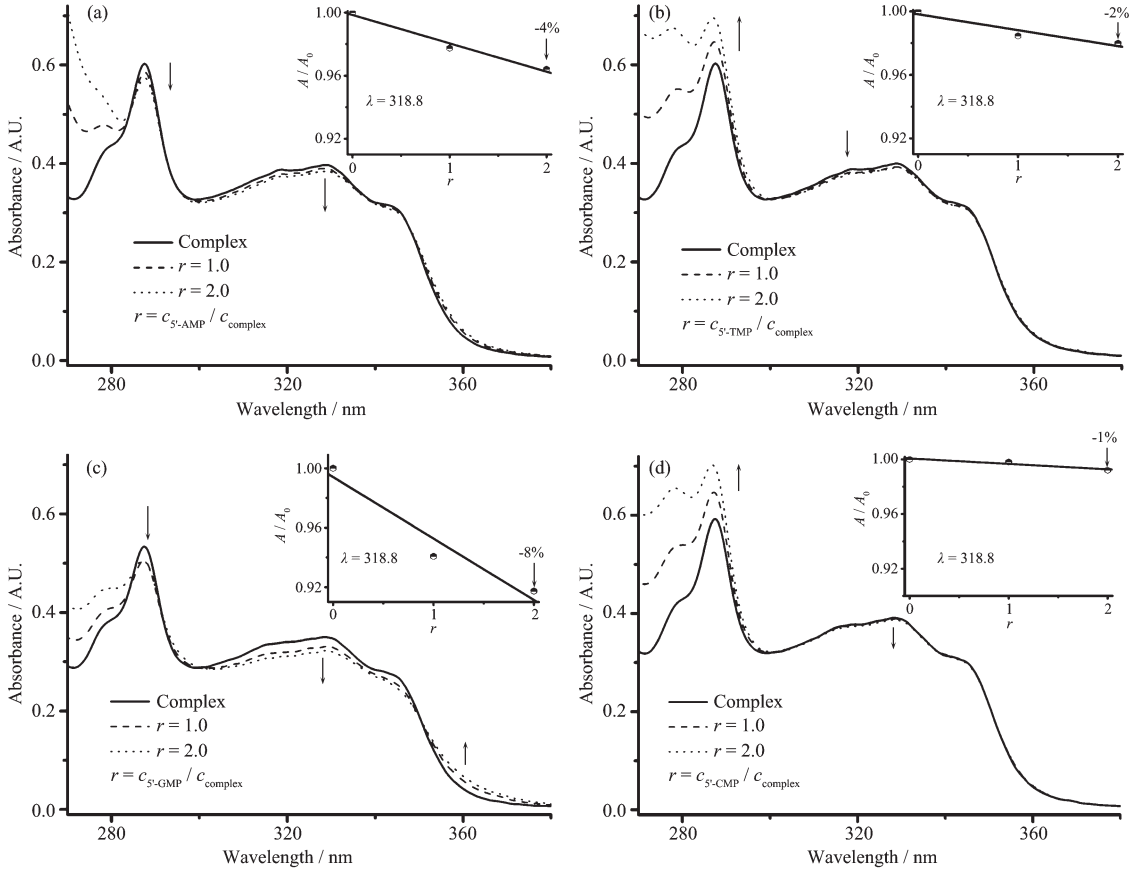


Fig.4 UV-Vis spectra of $[Cu(ttpy)(acetone)Cl]\cdot(NO_3)(H_2O)_3$ (2×10^5 mol·L^{-1}) in the buffer solution (5 mmol·L^{-1} Tris-HCl, 50 mmol·L^{-1} NaCl, pH 7.4) with increasing concentration of mononucleotides: (a) 5′-AMP; (b) 5′-TMP; (c) 5′-GMP; (d) 5′-CMP at r value ($c_{mononucleotides}/c_{complex}$) from 1 to 2

binding to 5′-GMP or 5′-AMP. The complex exhibited pronounced hypochromism of the $\pi \rightarrow \pi^*$ transition (tpy) at about 288 nm when reacted with 5′-GMP or 5′-AMP (Fig.4(a) and 4(c)), while evident hyperchromism of the same peak was observed when 5′-TMP or 5′-CMP was added (Fig.4(b) and Fig.4(d)). In addition, different change of the LMCT transition was also observed for the LMCT transition (centered at 318.8 nm) with the increase of 5′-GMP or 5′-AMP. When the ratio reached 2∶1, the hypochromicity of the system containing 5′-GMP is 8% while that containing 5′-AMP is 4%. For the system containing 5′-TMP or 5′-CMP, however, the hypochromism was not evident. Thus, it can be speculated that the reactivity of the complex towards four mononucleotides followed the order: 5′-GMP>5′-AMP>5′-TMP≈5′-CMP. The possible reason may be that the copper(Ⅱ) complex could covalently bind to the N7 of guaninyl or adeninyl and induced their conformational change[18,19].

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