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含 2,4-二氨基-6-(2′-吡嗪)-均三嗪及甘氨酸的铜(Ⅱ)配合物的合成、晶体结构及与 DNA 作用

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摘要:以 2,4-二氨基-6-(2′-吡嗪)-均三嗪(PZTA)及甘氨酸为配体与高氯酸铜作用合成了配合物[Cu(H_2O)(Gly)(PZTA)]ClO_4(Gly=甘氨酸根)。通过元素分析、测定摩尔电导率、红外光谱和紫外可见光谱进行表征,并用单晶 X-射线衍射方法测定了该配合物的晶体结构。配合物晶体属于单斜晶系,空间群 *C*2/*c*,晶胞参数:*a*=2.189 6(3) nm,*b*=1.308 3(2) nm,*c*=1.465 4 (4) nm,*β*=131.467(3)°,晶胞体积:*V*=3.145 6(9) nm^3,晶胞内结构基元数:*Z*=8,D_c=1.876 g·cm^{-3},最后的残差因子:R_1=0.037 4,wR_2=0.100 9。应用紫外光谱、溴化乙锭荧光探针及粘度测定等方法研究了配合物与 DNA 的作用。结果表明,主题配合物以部分插入方式与 DNA 作用。

关键词:铜(Ⅱ)配合物;2,4-二氨基-6-(2′-吡嗪)-均三嗪;甘氨酸;晶体结构;脱氧核糖核酸
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Synthesis, Crystal Structure and DNA-Binding Properties of Copper(Ⅱ) Complex with 6-(Pyrazin-2′-yl)-1,3,5-triazine-2,4-diamine and Glycinate

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Abstract: The copper(Ⅱ) complex [Cu(H_2O)(Gly)(PZTA)]ClO_4 (Gly=glycinate) was prepared by the reaction of 6-(pyrazin-2′-yl)-1,3,5-triazine-2,4-diamine (PZTA) and glycine (Gly) with copper(Ⅱ) perchlorate, and characterized by elemental analysis, infrared radiation, UV-Vis, and molar conductance. Its crystal structure was determined by single crystal X-ray diffraction method. The complex crystallizes in the monoclinic system, space group *C*2/*c*, with cell parameters: *a*=2.189 6(3) nm, *b*=1.308 3(2) nm, *c*=1.465 4(4) nm, *β*=131.467(3)°, cell volume: *V*=3.145 6(9) nm^3, number of molecules inside the cell: *Z*=8, final *R* indices ($I>2\sigma(I)$): R_1=0.037 4, wR_2=0.100 9. The interaction of the complex to DNA was studied by UV spectroscopy, EtBr fluoescent probe and viscosity measurement. The results indicate that the complex could interact with DNA by partial intercalative mode. CCDC: 848150.

Key words: copper(Ⅱ) complex; 6-(pyrazin-2′-yl)-1,3,5-triazine-2,4-diamine; glycine; crystal structure; DNA

Recent years have found a great deal of attention for the studies on the interaction of transition-metal complexes with DNA. Transition metal complexes can be utilized as probes of DNA structure, chemical nucleases, SOD mimics, and chemtherapeutic agents[1-10]. Among the metal complexes so far investigated,

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copper(Ⅱ) complexes with aromatic amines have attracted much attention for their numerous functions. It is well known that the aromatic amine copper complexes can bind and cleave DNA efficiently under physiological conditions in the presence of a reductant or on irradiation with UV or visible light[5,11-12], which would contribute to the development of new classes of chemical nucleases and anticancer medicines. Unfortunately, compared with the number of studies dealing with copper complexes of 1,10-phenanthroline and its derivatives complexes, relatively few studies on copper complexes with DNA base-like ligands have been reported to date. Therefore, extensive studies using different structural DNA base-like ligands to evaluate and understand the factors that determine the mode of the binding interaction with DNA and mechanism are necessary.

In this paper, a new ternary copper(Ⅱ) complex $[Cu(H_2O)(Gly)(PZTA)]ClO_4$ has been synthesized and structurally characterized, by using 6-(pyrazin-2′-yl)-1,3,5-triazine-2,4-diamine (PZTA), glycine (Gly) and copper(Ⅱ) perchlorate. The DNA-binding properties of the copper(Ⅱ) complex were explored by using electronic absorption spectroscopy, fluorescence spectroscopy, and viscosity measurement. The results indicate that the complex binds to CT-DNA through partial intercalative mode. The results should be valuable in understanding the mode of the copper complex with DNA as well as laying a foundation for the rational design of novel, powerful agents for probing and targeting nucleic acids.

1 Experimental

1.1 Materials and apparatus

All materials and reagents of analytical grade were commercially purchased and used without further purification, and $Cu(ClO_4)_2\cdot 6H_2O$ was synthesized according to the literature[13], and 6-(pyrazin-2′-yl)-1,3,5-triazine-2,4-diamine (PZTA) by the reaction of 2-cyano-pyrazine with dicyandiamide in the presence of KOH in 2-methoxyethanol on the basis of the method for 1,3,5-triazine-2,4-diamine ring preparation established by Case[14]. Calf thymus DNA (CT-DNA) was obtained from the Sino-American Biotechnology Company and pBR322 DNA from the MBI Fermentas (Lithuania). Agarose (molecular biology grade) and ethidium bromide (EB) were purchased from Sigma (USA). Tris (hydroxymethyl) aminomethane-HCl (Tris-HCl) buffer solution was prepared by using doubly distilled water . The UV absorbance at 260 and 280 nm of the CT-DNA solution in 5 $mmol\cdot L^{-1}$ Tris-HCl buffer (pH 7.2) gave a ratio of 1.9, indicating the DNA was sufficiently free of protein[15]. The concentration of CT-DNA was measured from the band intensity at 260 nm with a known ε value (6 600 $mol^{-1}\cdot L\cdot cm^{-1}$)[16].

Elemental analyses for C, H and N were performed using a Vario EL elemental analyzer and infrared spectra (KBr pellets) were taken on Bruker Equinoxo 55 spectrometer. Molar conductivity was performed on a DDS-12A conductometer. UV-Vis and fluorescence spectra were recorded on a Pharmacia 4000 UV-Vis, and Hitachi F-4500 spectrophotometers at room temperature, respectively.

1.2 Synthesis

Glycine (0.5 mmol) and $Cu(ClO_4)_2\cdot 6H_2O$ (0.5 mmol) were dissolved in 15 mL 80% (*V*/*V*) ethanol-water solution. To this solution was added PZTA (0.5 mmol) under heating and stirring for an hour. Then the solution was left for ten days at room temperature until the precipitate was formed, followed by recrystallization. The crystals were collected and washed with water and ethanol, respectively, then dried in the open air. Anal. Calcd for $C_9H_{13}CuN_8O_7Cl$(%): C, 24.33; H, 2.95; N, 25.22. Found (%): C, 24.62; H, 2.95; N, 25.24. IR ν/cm^{-1} 3 564m, 3 297m, 3 144m, 1 628vs, 1 382m, 1 584 m, 1 090m; UV-Vis (H_2O) λ/nm (ε/($L\cdot mol^{-1}\cdot cm^{-1}$)) 216 (37 488), 280 (11 389), 634 (66); Molar conductivity (methanol)/($S\cdot cm^2\cdot mol^{-1}$) 93.

Caution! Perchlorate compounds are potentially explosive. Only small quantity of material should be prepared and handled carefully.

1.3 Crystal structure determination

All geometric and intensity data for the complex were collected at room temperature on a Bruker Smart 1K CCD system diffractometer with graphite monochromatized Mo $K\alpha$ radiation at λ=0.071 073 nm. The

Table 1 Crystallographic data for $[Cu(H_2O)(Gly)(PZTA)]ClO_4$

Empirical formula	$C_9H_{13}CuN_8O_7Cl$	Absorption coefficient μ / mm^{-1}	1.616
Formula weight	444.27	Crystal size / mm	0.45×0.44×0.42
Crystal system	Monoclinic	θ range for data collection / (°)	2.0 to 27.1
Temperature / K	293(2)	Index ranges	$-24 \leqslant h \leqslant 28, -11 \leqslant k \leqslant 16, 18 \leqslant l \leqslant 17$
λ / nm	0.071 073	Reflections collected	8 586
Space group	*C*2/*c*	Independent reflections	3 394
a / nm	2.189 6(3)	R_{int}	0.015
b / nm	1.308 3(2)	Refinement method	Full-matrix least-squares on F^2
c / nm	1.465 4(2)	Data / restraints / parameters	3 394 / 0 / 236
β / (°)	131.467(8)°	Goodness-of-fit on F^2	1.06
V / nm^3	3.145 6(9)	Final *R* indices ($I>2\sigma(I)$)	R_1=0.037 4, wR_2=0.100 9
Z	8	*R* indices (all data)	R_1=0.045 4, wR_2=0.107 3
D_c / (g·cm^{-3})	1.876	$\Delta\rho_{max}$, $\Delta\rho_{min}$ / (e·nm^{-3})	870, −560
F(000)	1 800		

SMART program was used for data acquisition, and the SAINT+ soft ware for data extraction. Absorption correction was carried out using the SADABS program[17]. The structure was solved and refined by full-matrix least-squares method using the SHELX system of programs[18]. All non-hydrogen atoms refined anisotropically. The hydrogen atoms were placed in calculated positions and refined using a riding model. Details of the crystal parameters, data collection and refinements are listed in Table 1.

CCDC: 848150.

1.4 DNA binding experiments

The electronic absorption spectra of the complex (5.0×10^{-5} mol·L^{-1}) were recorded at room temperature before and after addition of CT-DNA in the Tris-HCl/NaCl buffer.

Fluorescence spectra were recorded with excitation at 525 nm and emission at 600 nm. The experiment was performed by titrating the complex (1.0×10^{-3} mol·L^{-1} in Tris-HCl/NaCl buffer) into samples containing 5.5×10^{-5} mol·L^{-1} CT-DNA and 4.8×10^{-5} mol·L^{-1} ethidium bromide (EB).

Viscosity measurements were carried out in Tris-HCl/NaCl buffer using an Ubbelodhe viscometer at (29.0±0.1) ℃. The results were presented as $(\eta/\eta_0)^{1/3}$ versus the complex concentration (2.0×10^{-5}~6.0×10^{-5} mol·L^{-1}) in 2×10^{-4} mol·L^{-1} CT-DNA solutions, where η and η_0 are the viscosity of CT-DNA solutions in the presence and absence of the complex, respectively. The viscosity values were calculated according to the relation $\eta=(t-t_0)/t_0$, where t was the flow time of CT-DNA solution in the presence or absence of the complex and t_0 is the flow time of the buffer alone.

2 Results and discussion

2.1 General aspects

The elemental analyses of the complex are in good agreement with the following formulas: $[Cu(H_2O)(Gly)(PZTA)]ClO_4$. The molar conductivy for the complex in methanol is 93 S·cm^2·mol^{-1}, indicating which the complex is 1:1 electrolyte[19].

The IR spectrum of the complex shows a band near 3 564 cm^{-1}, which is most likely ascribed to the stretching vibration $\nu_{O\text{-}H}$ of water molecules. The two broad bands near 3 297 and 3 144 cm^{-1} attributed, respectively, to asymmetric $\nu_{as}(\text{-}NH_2)$ and symmetric stretching $\nu_s(\text{-}NH_2)$ vibrations of the coordinated and uncoordinated -NH_2 groups. The absence of any band in the range of 1700~1750 cm^{-1} for the complex suggests coordination of the COO^- group of the amino acid to the central copper ion. The asymmetric $\nu_{as}(COO^-)$ and the symmetric stretching vibration $\nu_s(COO^-)$ of the coordinated carboxylate groups is 1 628 and 1 382 cm^{-1}, respectively. The difference value (246 cm^{-1}) between $\nu_{as}(COO^-)$ and $\nu_s(COO^-)$ stretching frequencies is greater than 200 cm^{-1}, which indicates

that the carboxylate groups are coordinated to the metal ion as a monodentate group[20]. The band at 1584 cm^{-1} can be attributed to the ring stretching frequencies [ν(C=C) and ν(C=N)] of 6-(pyrazin-2′-yl)-1,3,5-triazine-2,4-diamine. The band at 1 090 cm^{-1} can be assigned to ν(Cl-O) of perchlorate anions.

The electronic absorption spectra of the complex in methanol present three absorption bands, in which the very strong bands near 216 and 280 nm can be attributed to the $\pi \rightarrow \pi^*$ transitions of 6-(pyrazin-2′-yl) -1,3,5-triazine-2,4-diamine, and the weak and broad absorption band at 640 nm to the $d \rightarrow d$ transition of the central metal ion, indicating that the geometry of the complex is square pyramidal, as observed in the solid state[21].

2.2 Crystal structure

The selected bond distances and bond angles are summarized in Table 2. The coordination environment of central ion Cu(Ⅱ) is shown in Fig.1.

In the complex, the central ion copper (Ⅱ) is coordinated in a distorted square pyramidal geometry through two nitrogen atoms of 6-(pyrazin-2′-yl)-1,3,5-triazine-2,4-diamine and the amino nitrogen atom and one carboxylate oxygen atom of glycinate in the equatorial positions and one water oxygen atom at an axial position. N(1), N(5), N(8), O(1) and Cu(1) atoms for the molecule deviate by 0.010 40, −0.005 61, −0.005 20, 0.010 69 and −0.010 28 nm, respectively, from the least-squares plane (0.014 2x+0.995 9y+0.089 2z= 8.742 2) defined by the five atoms, indicating that the five equatorial atoms (N(1), N(5), N(8), O(1) and Cu (1)) are nearly coplanar. The Cu (1)-O (1) bond is shorter than Cu (1)-O (1W) bond, indicating that the coordination ability of carboxylate oxygen of glycine is stronger than that of water. The bond angles of N(5)-Cu(1)-N(8) (177.16(10)°) and O(1)-Cu(1)-N(1)(167.73 (10)°) are contracted from the ideal value of 180° for a regular square-planar structure, indicating distortion in the basal plane. The key bond lengths and bond angles (Table 2) of the complex are similar to the

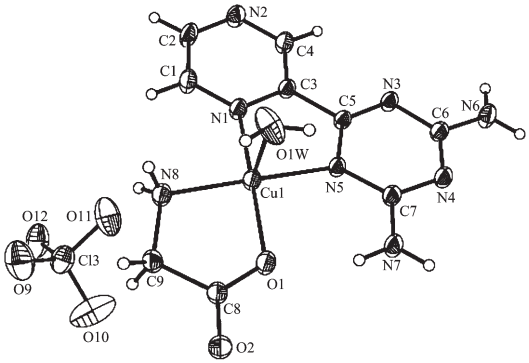


Fig.1 Molecular structure for $[Cu(H_2O)(Gly)(PZTA)]ClO_4$ with thermal ellipsoids at the 30% probability level

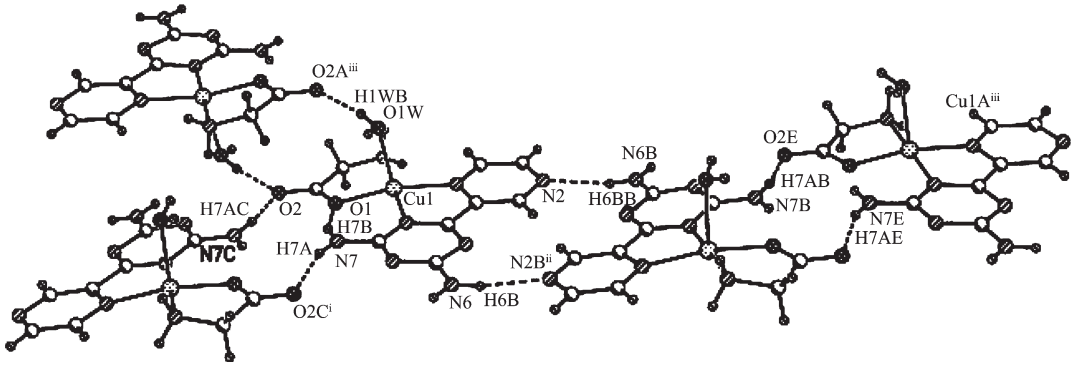
Table 2 Selected bond lengths (nm) and angles (°) for $[Cu(H_2O)(Gly)(PZTA)]ClO_4$

Cu(1)-O(1)	0.194 2(2)	Cu(1)-N(8)	0.201 1(2)	Cu(1)-N(5)	0.201 0(2)
Cu(1)-O(1W)	0.228 5(3)	Cu(1)-N(1)	0.201 7(2)		
O(1)-Cu(1)-O(1W)	92.54(10)	O(1W)-Cu(1)-O(1)	93.48(9)	N(1)-Cu(1)-N(5)	80.86(9)
O(1)-Cu(1)-N(5)	96.70(8)	O(1W)-Cu(1)-N(5)	89.33(9)	N(1)-Cu(1)-N(8)	98.23(9)
O(1)-Cu(1)-N(8)	83.62(9)	O(1W)-Cu(1)-N(8)	99.60(10)	N(5)-Cu(1)-N(8)	177.16(10)
O(1)-Cu(1)-N(1)	167.73(10)	O(1W)-Cu(1)-N(1)	92.54(10)		

Table 3 Selected hydrogen bond parameters for $[Cu(H_2O)(Gly)(PZTA)]ClO_4$

D–H···A	d(D-H) / nm	d(H···A)/ nm	d(D···A) / nm	∠DHA / (°)
N(7C)–H(7AC)···O(2)	0.086 00	0.212 00	2.947(3)	161.00
N(7)–H(7A)···O(2C)^{i}	0.086 00	0.212 00	2.947(3)	161.00
N(6B)–H(6BB)···N(2)	0.086 00	0.216 00	3.012(5)	168.00
N(6)–H(6B)···N(2B)^{ii}	0.086 00	0.216 00	3.012(5)	168.00
O(1W)–H(1WB)···O(2)	0.082 00	0.197 00	2.783(5)	170.00
O(1W)–H(1WB)···O(2A)^{iii}	0.082 00	0.197 00	2.783(5)	170.00

Symmetry transformations used to generate equivalent atoms: ^{i} 2−x, y, 3/2−z; ^{ii} 1−x, y, 1/2+z; ^{iii} 2−x, 1−y, 1−z.



Symmetry codes: ^{i} 2−x, y, 3/2−z; ^{ii} 1−x, y, 1/2+z; ^{iii} 2−x, 1−y, 1−z, ^{iiii} x−1, y, z−1

Fig.2　Hydrogen bonds in the crystal for $[Cu(H_2O)(Gly)(PZTA)]ClO_4$

related data in the literatures[22-23].

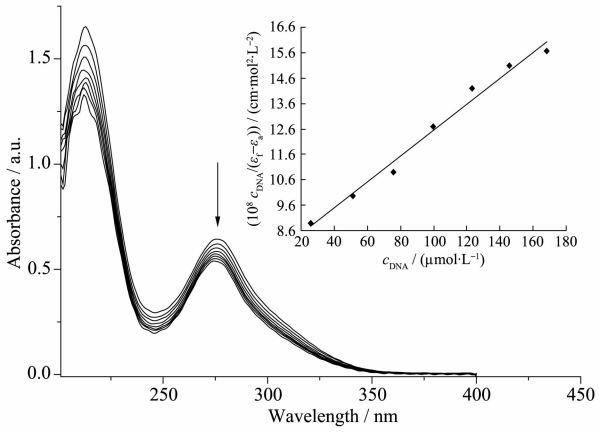
In the crystal of the complex, there are many intermolecular hydrogen-bond interactions listed in Table 3. The hydrogen bonds lead to a one dimensional network structure represented as Fig.2. Another important crystal structural feature of the complex is the existence of intermolecular PZTA-PZTA aromatic-ring stacking interaction between the neighboring $[Cu(H_2O)(Gly)(PZTA)]^+$ cations, and the interplanar distances are in the range of 0.335 0~0.337 3 nm, which is similar to those observed in many related ternary copper complexes with aromatic amines and amino acids[23-24].

2.3　Interactions of the complex with DNA

The interactions of metal complexes with DNA have been the subject of interests for the development of biotechnology and drug design as well as molecular biology. The binding modes of metal complexes to DNA would give insights into the understanding of the biochemical mechanism of action of the complexes.

2.3.1　UV spectroscopic studies

It is well known that electronic absorption spectroscopy is universally employed to determine the binding modes and binding extent of metal complexes with DNA. The hypochromism and red shift (bathchromism) are associated with the intercalative mode of the metal complexes to the DNA helix involving a strong stacking interaction between aromatic chromophore and the base pairs of DNA. The absorption spectra of the complex in the absence and presence of CT-DNA are given in Fig.3.



Arrows show the absorbance changing upon the increase in CT-DNA concentration; plots of $c_{DNA}/(\varepsilon_f-\varepsilon_a)$ vs c_{DNA} for the titration of the complex with DNA; $c_{complex}$=5.0 μmol·L^{-1}, c_{DNA}/(μmol·L^{-1}): 0, 26.0, 51.2, 75.8, 99.8, 123.1, 145.9, 168.2

Fig.3　UV Absorbance spectra of the interaction between $[Cu(H_2O)(Gly)(PZTA)]ClO_4$ and CT-DNA

On addition of CT-DNA, the complex exhibits decrease in molar absorptivity (hypochromism) of the LMCT absorption band at 275 nm as well as a slight red shift, indicating their binding to the DNA. The result led us to suspect that the complex may bind to CT-DNA by the insertion of PZTA-ring between adjacent base pairs on the DNA duplex.

The binding constant (K_b) of the complex toward CT-DNA, has been determined from the spectroscopic titration data using the following equation[25]:

$$c_{complex}/(\varepsilon_a-\varepsilon_f)=c_{DNA}/(\varepsilon_b-\varepsilon_f)+1/K_b(\varepsilon_b-\varepsilon_f)$$

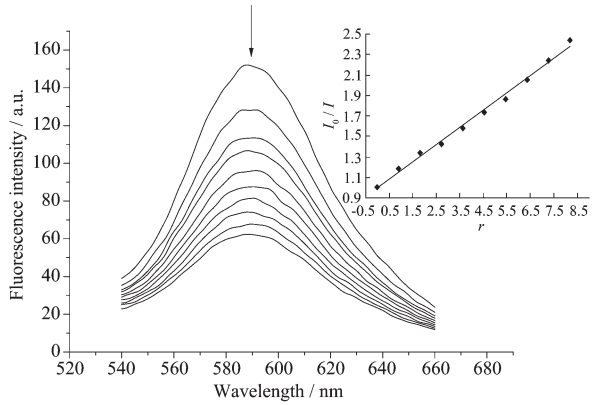
where ε_a, ε_f and ε_b correspond to $(A_{obsd}/c_{complex})$, the extinction coefficient for the free copper(Ⅱ) complex and extinction coefficient for the copper(Ⅱ) complex in

the fully bound form, respectively. From the plot of $c_{DNA}/(\varepsilon_a-\varepsilon_f)$ versus c_{DNA}, shown in the inset Fig.3, the binding constant K_b is given by the ratio of the slope to the intercept. The intrinsic binding constant K_b of the complex is 3.91×10^3 L·mol^{-1}, which is smaller than that (1.09×10^4 L·mol^{-1}) observed for complex [Cu(dppz)(*L*-val)(H_2O)]ClO_4[26], as expected from the smaller intercalative plane PZTA compared to dppz.

2.3.2 Fluorescence spectroscopic studies

Generally, the intrinsic fluorescence intensity of DNA is very weak, and that of ethidium bromide (EB) in Tris buffer is also not high due to quenching by the solvent water molecules. However, when DNA is added, the fluorescence intensity of EB will be enhanced because of its intercalation into the DNA helix. In addition, the enhanced fluoresence can be quenched by the addition of a complex molecule due to decreasing of the binding sites of DNA available for EB. Thus, EB can be used to probe the interaction of complexes with DNA[27].

The emission spectra of EB bound to CT-DNA in the absence and the presence of the copper(Ⅱ) complex are given in Fig.4. The addition of the complex to CT-DNA pretreated with EB causes appreciable reduction in emission intensity at 590 nm, indicating that some EB molecules were released into solution after an exchange with the complex which result in the fluorescence quenching of EB.



Arrows show the absorbance changing upon the increase in complex concentration; plots of I_0/I vs r for the titration of CT-DNA-EB with the complex; c_{DNA}=55 μmol·L^{-1}, c_{EB}=48 μmol·L^{-1}, $c_{complex}$/(μmol·L^{-1}): 0, 5.0, 10.0, 15.0, 19.9, 24.9, 29.8, 34.8, 39.7, 44.6

Fig.4 Change of the fluorescence intensity of CT-DNA-EB titrated with increasing [Cu(H_2O)(Gly)(PZTA)]ClO_4

In order to understand quantitatively the magnitude of the binding strength of the complex with CT-DNA, the linear Stern-Volmer equation is used[28].

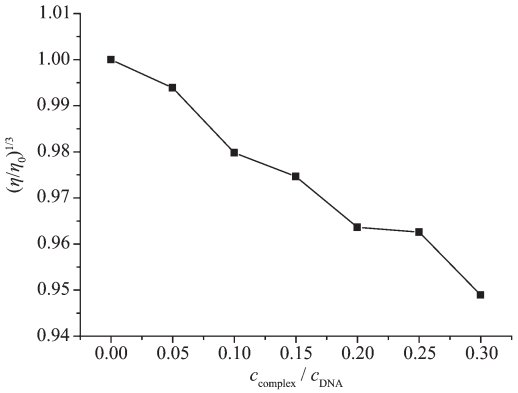
$$I_0/I=1+K_{sq}r$$

where I_0 and I are the fluorescence intensities in the absence and the presence of complex, respectively. K_{sq} is a linear Stern-Volmer quenching constant dependent on the ratio of the bound concentration of EB to the concentration of DNA. r is the ratio of total concentration of complex to that of DNA. From the inset in Fig.4, the obtained K_{sq} value for the complex is 0.169 7, and is smaller than that of [Cu(dppz)(*L*-val)(H_2O)]ClO_4 [26], which is in agreement with the obtained result by UV spectroscopic studies.

2.3.3 Viscosity studies

To clarify further the interaction mode of the copper(Ⅱ) complex with CT-DNA, viscosity measurements were carried out on CT DNA by varying the concentration of the added complex. In classical intercalation the DNA helix lengthens as base pairs are separated to accommodate the bound ligand leading to increased DNA viscosity. By contrast, complexes that bind exclusively in the DNA grooves by partial and/or nonclassical intercalation, under the same conditions, typically cause less pronounced (positive or negative) or no change in DNA solution viscosity[29]. Therefore viscosity measurement is regarded as the least ambiguous and the most critical means studying the binding mode of metal complexes with DNA in solution and provides stronger arguments for binding mode. The effects of the complex on the viscosity of CT-DNA are shown in Fig.5.

Fig.5 reveals that, on increasing the amount of the complex, the relative viscosity of CT-DNA decreases steadily and slightly, which may be explained by a binding mode which produced bends or kinks in the DNA and thus reduced its effective length and concomitantly its viscosity. A similar slight decrease in relative viscosity has been observed on the addition of $[Cu(bcp)_2]^+$, which was proposed to be bound to DNA by partial intercalation[30]. Thus, the binding mode of the copper(Ⅱ) complex with CT-DNA



c_{DNA}=2×10^{-4} mol·L^{-1} and $c_{complex}$ / c_{DNA}: 0, 0.05, 0.10, 0.15, 0.20, 0.25, 0.30

Fig.5　Effect of increasing amounts of [Cu(H_2O)(Gly)(PZTA)]ClO_4 on the relative viscosity of CT-DNA at (29.0±0.1) ℃

may be rationalized by partial intercalation.

3　Conclusions

A new ternary copper(Ⅱ) complex with 6-(pyrazin-2′-yl)-1,3,5-triazine-2,4-diamine (PZTA), glycinate (Gly) and copper(Ⅱ) perchlorate, has been synthesized and structurally characterized. The crystal structure of the complex shows a distorted square pyramidal coordination geometry in which PZTA and Gly bind at the basal positions, and one water oxygen atom at an axial position. The complex could interact with DNA by partial intercalative mode.

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