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# 含有 1,4,7-三苄基-1,4,7-三氮杂环壬烷的两个双核铜配合物的合成、表征及其与 DNA 的相互作用

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**摘要**:合成了 2 个含有 1,4,7-三苄基-1,4,7-三氮杂环壬烷($Bn_3tacn$)的双核铜配合物:$[Cu_2(Bn_3tacn)_2(m\text{-bdc})(CH_3CN)_3(H_2O)_2](ClO_4)_4$ (**1**)和$[Cu_2(Bn_3tacn)_2(OH)_2](ClO_4)_2$ (**2**)。配合物 **1** 由间苯二甲酸采取单双齿方式桥连 Cu(Ⅱ)离子,配合物 **2** 由 OH 桥连。配合物 **1** 和 **2** 晶体均属于单斜晶系,分别为 $P2_1/c$ 空间群和 $C2/c$ 空间群。分别对 2 个配合物进行了红外光谱、紫外-可见光谱和元素分析表征。研究了配合物 **1** 与 DNA 的相互作用,对配合物 **2** 进行了循环伏安测试。

**关键词**:双核铜配合物;1,4,7-三氮杂环壬烷;DNA 相互作用

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# Two Binuclear Copper(Ⅱ) Complexes Containing 1,4,7-Trisbenzyl-1,4,7-triazacyclononane ($Bn_3tacn$) Ligand: Syntheses, Characterization and Binding with DNA

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**Abstract:** Two binuclear copper(Ⅱ) complexes were prepared with ligand 1,4,7-tribenzyl-1,4,7-triazacyclononane ($Bn_3tacn$): $[Cu_2(Bn_3tacn)_2(m\text{-bdc})(CH_3CN)_3(H_2O)_2](ClO_4)_4$ (**1**) and $[Cu_2(Bn_3tacn)_2(OH)_2](ClO_4)_2$ (**2**). The copper(Ⅱ) ion in complex **1** is bridged by the *m*-benedicarboxylic acid (*m*-bdc) adopting bis(bidentate/monodentate) coordination type and is bridged by the $\mu$-OH in complex **2**. Complexes **1** and **2** crystalize in the monoclinic system, space group $P2_1/c$ and $C2/c$, respectively. IR, UV-Vis, element analysis, binding with DNA properties of the complex **1** and cyclic voltammogram of complex **2** have been studied. CCDC: 609919, **1**; 611963, **2**.

**Keywords:** binuclear copper(Ⅱ); 1,4,7-triazacyclonoane; binding with DNA

1,4,7-Triazacyclonone (tacn) and its derivatives have been progress a rapid expansion in the area of the coordination chemistry, and a stable and wide range of metal coordination compounds have been prepared as a result of the propensity of tacn for facial coordination with metal ions[1]. It has been extensively noted that tacn and its N-substituted complexes are suitable ligands forming both mono- and bi-metallic

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complexes.

Hence, many of tacn and its N-substituted complexes are found to be both structural and functional models of various metalloenzyme[2-8], capable of promoting phosphate ester degradation with DNA[9-13] or RNA[14-15] cleavage and used in oxidative catalysis[16]. 1,4,7-Tribenzyl-1,4,7-triazacyclononane ($Bn_3tacn$), as one type of their derivative, has been investigated many years[17-19]. The central role of the binding and activation of dioxygen by copper ions with a wide range of important processes in biology and catalyst areas has led to intense interest in the synthesis, characterization, and examination of the reactivity of $[Cu_2O_2]$ complexes[20]. Previously, we have reported the complexes with the same ligand [21] and another N-substituted ligand further compared their structures and spectra[22-23]. Similar ligands were also reported recently[24-25]. In this work, we prepared two binuclear copper complexes containing the ligand $Bn_3tacn$ using *m*-bdc (1,4-benzenedi-carboxylic) and $H_2O$ as bridged ligand: $[Cu_2(Bn_3tacn)_2(m\text{-bdc})(CH_3CN)_3(H_2O)_2]ClO_4$ (**1**) and $[Cu_2(Bn_3tacn)_2(OH)_2](ClO_4)_2$ (**2**) (L=$Bn_3tacn$); the syntheses, structures, spectroscopic properties and DNA binding properties will be described here.

## 1 Experimental

### 1.1 Materials and instrument

1, 4, 7-Triazacyclononane (tacn) was prepared according to the previous procedure[26-27] and the ligand $Bn_3tacn$ was prepared according to the literature[28]. All starting materials and solvents are analytical reagents.

Elemental analyses of C, H and N were carried out on Model 240 Perkin-Elemer instrument. IR spectra were measured using KBr disks with Bruker Tensor 27 FTIR spectrophotometer in the 400~4 000 $cm^{-1}$ region. The UV-Vis spectra were measured on Jasci V-570 UV-Vis spectrophotometer within 200~2 000 nm region.

### 1.2 Syntheses of the complexes

$[Cu_2(Bn_3tacn)_2(m\text{-bdc})(CH_3CN)_3(H_2O)_2]ClO_4$ (**1**). A solution of $Cu(ClO_4)_2\cdot 6H_2O$ (0.111 g, 0.3 mmol) in acetonitrile (10 mL) was added to a solution of $Bn_3tacn$ (0.024 g, 0.3 mmol) in acetonitrile (10 mL). The reaction mixture was stirred at room temperature for 30 min until all of the solid dissolved to afford a clear deep-blue solution, and then a solution of *m*-bdc piperidine hydrochloride (0.043 g, 0.15 mmol) dissolved in water (5 mL) was slowly added to the previous solution. The reaction mixture was continuously stirred for 2 h, filtered to get rid of any insoluble particles. The light yellow rhombic crystals suitable for X-ray crystallographic analysis were obtained by slow evaporation of the filtrate (Yield: 63%). Anal. Calcd. for $C_{65}H_{76}Cl_2Cu_2N_8O_{12}$ (%): C 57.43, H 5.64, N 8.24; Found(%): C 57.40, H 5.62, N 8.21.

$[Cu_2(Bn_3tacn)_2(OH)_2](ClO_4)_2$ (**2**). A suspension of $Cu(ClO_4)_2\cdot 6H_2O$ (0.111 g, 0.3 mmol) and the ligand $Bn_3tacn$ (0.024 g, 0.3 mmol) in acetonitrile (20 mL) was stirred for 30 min to give a blue solution, and then the pH value was adjusted to 8.5 and the solution was filtered. The deep blue crystal was obtained after one week evaporation of the solvent, filtered off, washed with ethanol and ether, and dried under vacuum (Yield: 42%). Anal. Calcd. for $C_{54}H_{66}Cl_2Cu_2N_6O_{10}$(%): C 56.80, H 5.69, N 7.79; Found(%): C 56.88, H 5.70, N 7.80.

**Caution!** Although no problems were encountered in this work, perchlorate complexes containing organic ligands are potentially explosive. They should be prepared in small quantities and handled with care.

### 1.3 X-ray crystallography

Diffraction data for **1** and **2** were collected at 293 K, with a Bruker SMART 1000 CCD diffractometer using Mo $K\alpha$ radiation ($\lambda$=0.071 073 nm) with the $\varphi$-$\omega$ scan technique. An empirical absorption correction (SADABS) was applied to raw intensities[29]. The structures were solved by direct methods (SHELXS-97[30]) and refined by full-matrix least-squares procedures on $F^2$ using SHELXL-97[30], the structure of complex **2** was further solved by SQUEEZE software. According to the elimination electronics, relevant $H_2O$ solvent was eliminated. The hydrogen atoms were added theoretically, and riding on the concerned atoms and refined with fixed thermal factors. Further details about crystal data and structure refinement are

**Table 1 Crystal data and structure refinements for 1 and 2**

| Complex | 1 | 2 |
|---|---|---|
| Empirical formula | $C_{66}H_{76}Cl_2Cu_2N_8O_{12}$ | $C_{54}H_{66}Cl_2Cu_2N_6O_{10}$ |
| Formula weight | 1 371.32 | 1 157.10 |
| Temperature / K | 153(2) | 294(2) |
| Crystal system | Monoclinic | Monoclinic |
| Space group | $P2_1/c$ | $C2/c$ |
| $a$ / nm | 1.028 41(16) | 2.787 5(16) |
| $b$ / nm | 3.307 9(3) | 1.534 3(7) |
| $c$ / nm | 1.116 61(18) | 2.967 4(13) |
| $\beta$ / (°) | 113.351(2) | 91.978(13) |
| $V$ / nm$^3$ | 3.487 5(9) | 12.684(11) |
| $Z$ | 2 | 8 |
| $D_c$ / (g·cm$^{-3}$) | 1.306 | 1.218 |
| $\mu$ / mm$^{-1}$ | 0.75 | 0.809 |
| Crystal size / mm | 0.16×0.14×0.10 | 0.26×0.18×0.16 |
| $\theta$ range / (°) | 2.08~27.85 | 1.52~25.02 |
| Limiting indices | $-13 \leqslant h \leqslant 13, -41 \leqslant k \leqslant 42, -11 \leqslant l \leqslant 14$ | $-33 \leqslant h \leqslant 18, -18 \leqslant k \leqslant 18, -35 \leqslant l \leqslant 35$ |
| Reflection collected, unique | 26 745, 7 536 ($R_{int}$=0.018 1) | 30 996, 11 052 ($R_{int}$=0.136 3) |
| $F$(000) | 1 432 | 4 832 |
| Goodness-of-fit on $F^2$ | 1.053 | 0.946 |
| Final $R$ indices [$I>2\sigma(I)$] | $R_1$=0.040 2, $wR_2$=0.118 7 | $R_1$=0.081 4, $wR_2$=0.256 2 |
| $R$ indices (all data) | $R_1$=0.047 7, $wR_2$=0.115 2 | $R_1$=0.175 0, $wR_2$=0.199 2 |
| $(\Delta\rho)_{max}$, $(\Delta\rho)_{min}$ / (e·nm$^{-3}$) | 866, −640 | 757, −714 |

summarized in Table 1.

CCDC: 609919, **1**; 611963, **2**.

### 1.4 Procedure for DNA binding experiments

By the electronic absorption spectral method, the relative binding of the two complexes to calf thymus (CT) DNA was studied in 10 mmol·L$^{-1}$ Tris-HCl/NaCl buffer (pH=7.5). The solution of CT-DNA gave a ratio of UV absorbance at 260 nm and 280 nm ($A_{260}/A_{280}$) of 1.8~1.9, indicating that the DNA was sufficiently free of protein[31]. The stock solution of CT-DNA was prepared in Tris-HCl/NaCl buffer, pH=7.5 (stored at 4 ℃ and used not more than 4 days). The concentration of CT-DNA was determined from its absorption intensity at 260 nm with a molar extinction coefficient of 6 600 L·mol$^{-1}$·cm$^{-1}$ [32].

## 2 Results and discussion

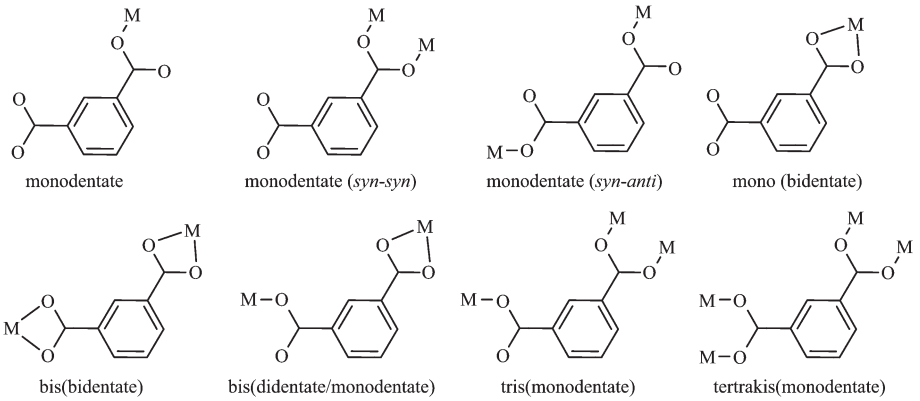
### 2.1 Crystal structure description

Selected bond lengths and angles of **1** and **2** are listed in Table 2. The structure of complex **1** is shown in Fig.1a. One Cu ion was five coordinated by three N atoms from ligand $Bn_3tacn$ and two O atoms from *m*-bdc ligand while the other Cu ion was five coordinated by three N atoms from ligand $Bn_3tacn$, one O atom from *m*-bdc ligand and the other O atom from $H_2O$. As shown in Scheme 1, complex **1** adopts an unusual bis(bidentate/monodentate) coordination type due to the steric hindrance. The intermolecular distance of the two Cu(Ⅱ) ions is 1.004 3 nm. Three benzyl groups are flatted opposite the *m*-bdc ligand, which favor atom N coordinating to copper ion. The length of Cu(1)-N(1) is 0.219 17 nm, which is slightly longer than the length of Cu(1)-N(2) of 0.201 97 nm, Cu(1)-N(3) of 0.203 75 nm, Cu(1)-O(1) of 0.200 63 nm and Cu(1)-O(2) of 0.195 91 nm as show in Fig.1a.

As shown in Fig.1b, the crystal structure is made up of $[Cu_2(Bn_3tacn)_2(\mu\text{-}OH)_2]^{2+}$ cation and $ClO_4^-$ anions. The complex crystallizes in the monoclinic $C2/c$ space group. An interesting feature of complex **2** is that the complex has a central $[Cu_2O_2]$ coordination core where

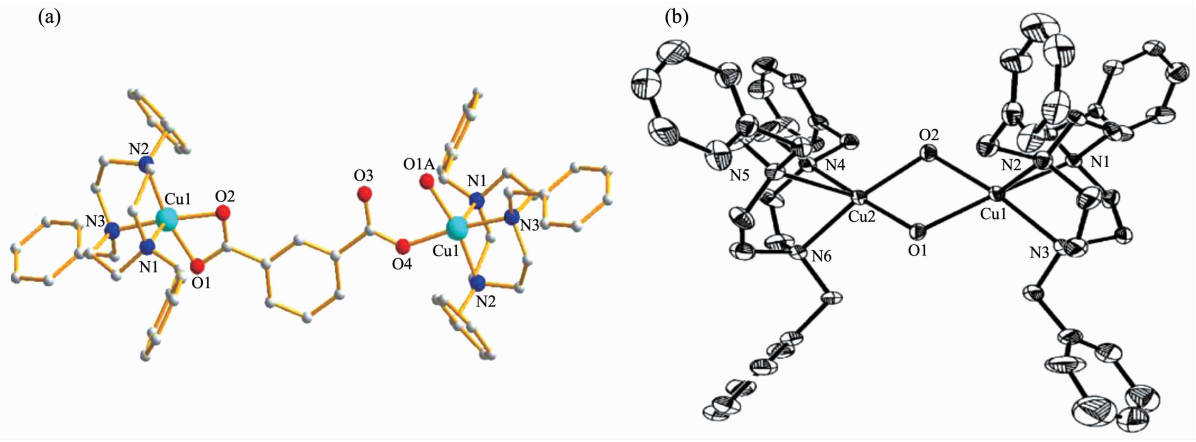
**Table 2　Selected bond lengths (nm) and angles (°) for 1 and 2**

| | | | | | |
|---|---|---|---|---|---|
| **1** | | | | | |
| Cu(1)-O(2) | 0.195 9(11) | Cu(1)-O(4) | 0.204 7(10) | Cu(1)-O(1) | 0.200 6(3) |
| Cu(1)-N(1) | 0.219 17(19) | Cu(1)-N(2) | 0.201 96(19) | Cu(1)-N(3) | 0.203 74(19) |
| O(2)-Cu(1)-O(1) | 70.69(18) | N(2)-Cu(1)-N(1) | 86.22(7) | O(2)-Cu(1)-N(2) | 101.67(17) |
| O(2)-Cu(1)-C(28) | 33.9(2) | O(1)-Cu(1)-N(2) | 168.78(11) | O(1)-Cu(1)-C(28) | 36.75(15) |
| O(2)-Cu(1)-N(3) | 167.2(2) | N(2)-Cu(1)-C(28) | 135.09(14) | O(1)-Cu(1)-N(3) | 99.35(11) |
| N(3)-Cu(1)-C(28) | 135.56(13) | N(2)-Cu(1)-N(3) | 86.90(7) | O(4)-Cu(1)-C(28) | 47.5(2) |
| O(2)-Cu(1)-O(4) | 13.6(2) | N(3)-Cu(1)-C(28) | 46.8(2) | O(1)-Cu(1)-O(4) | 84.2(2) |
| N(1)-Cu(1)-C(28) | 106.76(13) | N(2)-Cu(1)-O(4) | 88.48(19) | N(2)-Cu(1)-N(1) | 86.22(7) |
| N(3)-Cu(1)-O(4) | 172.1(3) | N(3)-Cu(1)-N(1) | 86.33(7) | O(2)-Cu(1)-N(1) | 103.6(3) |
| O(4)-Cu(1)-N(1) | 99.7(3) | O(1)-Cu(1)-N(1) | 103.38(11) | | |
| **2** | | | | | |
| Cu(1)-O(2) | 0.196 5(5) | Cu(1)-Cu(2) | 0.295 70(15) | Cu(1)-O(1) | 0.202 1(5) |
| Cu(2)-O(2) | 0.195 7(5) | Cu(1)-N(3) | 0.207 9(6) | Cu(2)-O(1) | 0.199 3(5) |
| Cu(1)-N(1) | 0.211 9(6) | Cu(2)-N(4) | 0.209 1(6) | Cu(1)-N(2) | 0.227 5(6) |
| Cu(2)-N(6) | 0.208 8(6) | Cu(2)-N(5) | 0.230 3(6) | | |
| O(2)-Cu(2)-O(1) | 81.3(2) | O(2)-Cu(1)-N(3) | 168.3(2) | O(2)-Cu(2)-N(4) | 96.4(2) |
| O(1)-Cu(1)-N(3) | 95.0(2) | O(1)-Cu(2)-N(4) | 174.2(2) | O(2)-Cu(1)-N(1) | 98.2(2) |
| O(2)-Cu(2)-N(6) | 168.0(2) | O(1)-Cu(1)-N(1) | 169.2(2) | O(1)-Cu(2)-N(6) | 96.0(2) |
| N(3)-Cu(1)-N(1) | 84.4(2) | N(4)-Cu(2)-N(6) | 85.2(2) | O(2)-Cu(1)-N(2) | 108.0(2) |
| O(2)-Cu(2)-N(5) | 108.5(2) | O(1)-Cu(1)-N(2) | 107.8(2) | O(1)-Cu(2)-N(5) | 102.9(2) |
| N(3)-Cu(1)-N(2) | 83.7(2) | N(4)-Cu(2)-N(5) | 82.9(2) | N(1)-Cu(1)-N(2) | 82.5(2) |
| N(6)-Cu(2)-N(5) | 83.5(2) | O(2)-Cu(1)-Cu(2) | 40.97(15) | O(2)-Cu(2)-Cu(1) | 41.18(14) |
| O(1)-Cu(1)-Cu(2) | 42.20(15) | O(1)-Cu(2)-Cu(1) | 42.91(16) | N(3)-Cu(1)-Cu(2) | 130.78(16) |
| N(4)-Cu(2)-Cu(1) | 133.11(16) | N(1)-Cu(1)-Cu(2) | 132.71(16) | N(6)-Cu(2)-Cu(1) | 131.84(17) |




Scheme 1　Eight coordination mode of *m*-bdc

copper and hydroxo oxygen atom are alternate to each other, constituting a cyclic four-membered ring. Noteworthily, the Cu1-O1-Cu2-O2 bridging unit is not strictly coplanar, whereas a roof shape core as the complex have been reported[15] because of the hydrogen in $H_2O$ was adopted as *syn-syn* type. Cu1-O1-Cu2 angle is 94.91°, while the angle of Cu1-O2-Cu2 is 97.85°. The geometry around both Cu atoms can best be described as an axially elongated octahedron, with the atoms N1, N2, N3, O2 constituting the basal plane




Hydrogen atoms have been omitted for clarity in (a); Hydrogen atoms, $ClO_4^-$ and $H_2O$ have been omitted for clarity in (b)

Fig.1 (a) Molecular structure of complex **1**; (b) Molecular structure of complex **2** with thermal ellipsoids at 30% probability level

and the atom O1 occupying the axial position. The essential similarity of the two independent bridging Cu-O bond lengths of 0.195 7 and 0.199 3 nm demonstrates that the oxygen atoms are asymmetrically bound to the two copper atoms. The length of Cu-Cu is 0.295 7 nm.

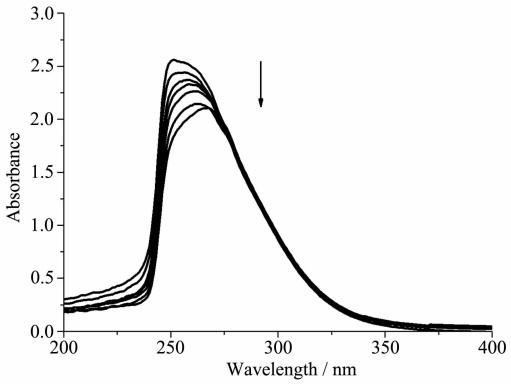
## 2.2 IR and UV-Vis spectrum

Both the two complexes have the similar IR spectra. The broad peak at 3 600~3 300 $cm^{-1}$ should be attributed to the $\nu$(O-H) stretching frequency of water molecule in the complexes. The $\nu$(C-H) stretching frequency of $Bn_3tacn$ is indicated by a shoulder band involving a split sharp peak at 2 980 and 2 850 $cm^{-1}$. Two moderate absorption, at 1 593 and 1 548 $cm^{-1}$, are ascribed to the characteristic absorption of C=O in the m-bdc. The peak at 1 121 and 625 $cm^{-1}$ should be the absorption of $ClO_4^-$. Additionally, the abundant of absorption peaks in the region of 670~840 $cm^{-1}$ strongly argues in favor of the presence of phenyl. All of these results are quite consistent with the crystal structures of complexes **1** and **2**.

The UV-Vis spectra of complexes **1** and **2** were tested in dissolving DMSO solvent at room temperature. The wide absorption band in 656 nm was attributed to the $^2B_1 \rightarrow {}^2B_2$ electronic transformation of $Cu^{2+}$ in the tetragonal pyramid $C_4$ confirmation of complex **1**[33]. The absorption of 300 nm was attributed to the charges transfer of ligand $Bn_3tacn$ in complex **2**, while the absorption at 656 nm was also observed due to $^2B_1 \rightarrow {}^2B_2$ electronic transformation of $Cu^{2+}$ ($3d^9$) with symmetric $C_4$ coordination environments[34].

## 2.3 DNA binding

In order to investigate whether DNA was the biological target of the complex, its interactions with calf thymus DNA (CT-DNA) were tested by UV-Vis, Fluorescence spectroscopy. The absorption spectra of the complex **1** in the absence and presence of CT-DNA at various concentrations are given in Fig.2. Free $Bn_3tacn$ does not have any absorption band in the ultraviolet region because of the high energy gap between LUMO and HOMO. However, copper binding lowered the gap and thus caused the transition

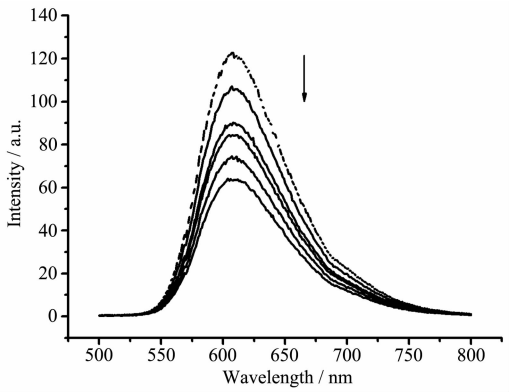



Buffer=10 mmol·$L^{-1}$ tris, 1 mmol·$L^{-1}$ $Na_2EDTA$, pH=7.50; $V_{CH_3CN}$:$V_{buffer}$=1:3; $c_{complex}$=2.0 ×$10^{-5}$ mol·$L^{-1}$, $r$=$c_{CT\text{-}DNA}$/$c_{complex}$= 0~0.6

Fig.2 UV-Vis absorption spectra of the complex in mixed solution of $CH_3CN$ and buffer with increasing concentration of CT-DNA

occurring at 256 nm. The potential CT-DNA binding ability of complexes was studied by UV spectroscopy by following the intensity changes of the intraligand $\pi$-$\pi$* transition band at 256 nm. Upon addition of an increasing amount of CT-DNA (from $1\times10^{-5}$ to $1\times10^{-4}$ mol·L$^{-1}$) to the complex **1** ($1\times10^{-5}$ mol·L$^{-1}$), a 20% hypochromism and a slight red shift (7~12 nm) were observed, which indicate strong binding of the complex to DNA.

The DNA-EB system was used to further probe the DNA binding mode of the complex **1**. Ethidium bromide (EB) is an intercalator that gives a significant increase in fluorescence emission when bound to DNA and its displacement from DNA results in decrease in fluorescence intensity[35]. Fluorescence titration spectra are shown in Fig.3. The emission intensity decreased with the increase of the concentration of the complex, which suggests that the complex can replace EB from CT-DNA and intercalate into the DNA double helix.




$\lambda_{ex}$=526 nm; $c_{EB}$=2.5×10$^{-5}$ mol·L$^{-1}$, $c_{DNA}$=1×10$^{-4}$ mol·L$^{-1}$; $c_1$=1×10$^{-4}$ mol·L$^{-1}$, 10 μL per scan

Fig.3　Fluorescence emission spectra of the EB-DNA system in the absence (dotted line) and presence (solid line) of **1**

## 2.4　Cyclic voltammetry

As shown in Fig.4, the cyclic voltammogram of the ternary complex in absolute chromatographic DMSO solution containing 0.1 mol·L$^{-1}$ [($n$-Bu)$_4$N]ClO$_4$ (Scan speed: 100 mV·s$^{-1}$) shows the ternary complex is redox-active. The cathodic peak potential ($E_{pc}$) and the anodic peak potential ($E_{pa}$) are 1 080 and 186 mV, respectively. The separation of the anodic and cathodic peak potentials ($\Delta E_p$) is 894 mV.

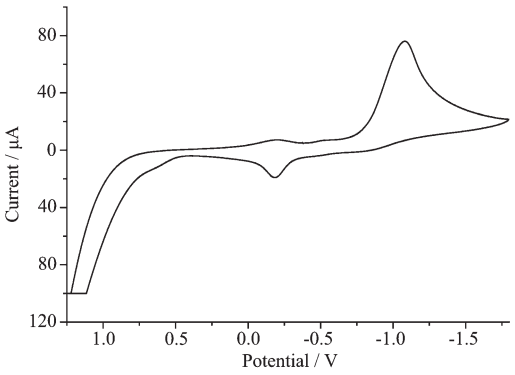



Fig.4　Cyclic voltammogram diagram of the complex **2** in DMSO

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## References:

[1] Chaudhuri P, Wieghardt K. *Prog. Inorg. Chem.*, **1987**,**35**:329-436

[2] Bossek U, Hummel H, Weyhermüller T, et al. *Angew. Chem. Int. Ed.*, **1995**,**34**:2642-2645

[3] Chin J. *Acc. Chem. Res.*, **1991**,**24**:145-152

[4] Williams N H, Takasaki B K, Wall M, et al. *Acc. Chem. Res.*, **1999**,**32**:485-493

[5] Hegg E L, Burstyn J N. *Coord. Chem. Rev.*, **1998**,**173**:133-165

[6] Tolman W B. *Acc. Chem. Res.*, **1997**,**30**:227-237

[7] Yan H L, Yan S P, Liao D Z, et al. *J. Coord. Chem.*, **2006**, **59**:493-498

[8] Chen X Y, Xia J, Zhao B, et al. *J. Coord. Chem.*, **2004**,**57**: 231-237

[9] Bim D, Svobodova E, Eigner V, et al. *Chem. Eur. J.*, **2016**, **22**:10426-10437

[10]Tjioe L, Joshi T, Forsyth C M, et al. *Inorg. Chem.*, **2012**,**51**: 939-953

[11]Longford D, Campi E, Sawford T, et al. *Biotechnol. J.*, **2015**, **10**:480-489

[12]Deal K A, Hengge A C, Burstyn J N, et al. *J. Am. Chem. Soc.*, **1996**,**118**:1713-1718

[13]Hirohama T, Arii H, Chikira M, et al. *J. Inorg. Biochem.*, **2004**,**98**:1778-1786

[14]Zeng Z, Torriero A A J, Bond A M, et al. *Chem Eur. J.*, **2010**,**16**:9154-9163

[15]Belousoff M J, Duriska M B, Graham B, et al. *Inorg. Chem.*, **2006**,**45**:3746-3755

[16]Sibbons K F, Shastri K, Watkinson M, et al. *Dalton Trans.*, **2006**,**5**:645-661

[17]Enomoto M, Aida T, et al. *J. Am. Chem. Soc.*, **1999**,**121**:874-875

[18]Mahapatra S, Halfen J, Wilkinson A E C, et al. *J. Am. Chem. Soc.*, **1996**,**118**:11555-11574

[19]Mahapatra S, Halfen J A, Tolman W B, et al. *J. Am. Chem. Soc.*, **1996**,**118**:11575-11586

[20]Kitajima N, Moro-oka Y, et al. *Chem. Rev.*, **1994**,**94**:737-758

[21]Yang Y S, Gu W, Qiang J, et al. *J. Coord. Chem.*, **2007**,**60**:1681-1690

[22]Yang Y S, Gu W, Zhang L Z, et al. *J. Coord. Chem.*, **2007**, **60**:1913-1921

[23]Yang Y S, Gu W, Zhang L Z, et al. *J. Coord. Chem.*, **2008**, **61**:571-578

[24]LI Xiu-Min(李秀敏), YANG Yu(杨雨), ZHANG Zong-Yao(张宗尧), et al. *Chinese J. Inorg. Chem.*(无机化学学报), **2017**,**33**(7):1299-1304

[25]LI Qing-Xiang(李庆祥), XIANG Ai-Hua(向爱华), MENG Xiang-Gao(孟祥高), et al. *Chinese J. Inorg. Chem.*(无机化学学报), **2013**,**29**(7):1428-1432

[26]Richman J E, Atkins T J, et al. *J. Am. Chem. Soc.*, **1974**, **96**:2268-2271

[27]Wieghardt K, Hahn M, Swiridoff W, et al. *Inorg. Chem.*, **1984**,**23**:94-99

[28]Beissel T, Beatriz S P, Vedova D, et al. *Inorg. Chem.*, **1990**, **29**:1736-1741

[29]Sheldrick G M. *SADABS, Program for Empirical Absorption Correction of Area Detector Data*, University of Göttingen, Germany, **1996**.

[30]Sheldrick G M. *SHELX*-97, *Program for the Solution and the Refinement of Crystal Structures*, University of Göttingen, Germany, **1997**.

[31]Kumar C V, Barton J K, Turro N J, et al. *J. Am. Chem. Soc.*, **1985**,**107**:5518-5523

[32]Marmur J. *J. Mol. Biol.*, **1961**,**3**:208-218

[33]Hathaway B J. *Struct. Bond.*, **1984**,**57**:55-118

[34]Ballhausen C J. *Introduction to Ligand Field Theory*. New York: McGraw-Hill, **1962**.

[35]Reichmann M E, Rice S A, Thomas C A, et al. *J. Am. Chem. Soc.*, **1954**,**76**:3047-3053