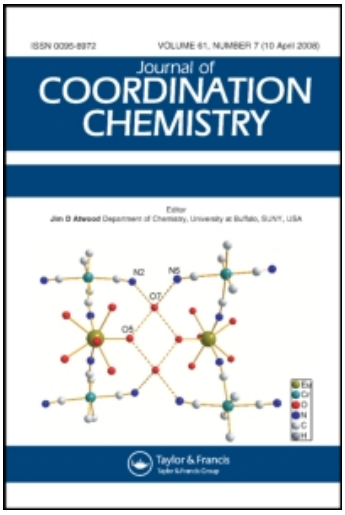

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A new two-dimensional polymeric copper(II) complex bridged both by oxamidate and azide groups: synthesis, structure and DNA binding properties

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A new two-dimensional polymeric copper(II) complex bridged both by oxamidate and azide groups: synthesis, structure and DNA binding properties

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A new two-dimensional polymeric copper(II) complex, $[Cu_2(heae)(N_3)_2]_n$, where heae stands for the dianion of *N*,*N*′-*bis*(*N*-hydroxyethylaminoethyl)oxamide, has been synthesized and characterized by elemental analysis, molar conductivity measurement, IR, electronic spectral studies and single-crystal X-ray diffraction. The compound crystallizes in the monoclinic system, $P2_1/c$ space group with crystallographic data: $a = 9.1588(18)$ Å, $b = 6.6238(13)$ Å, $c = 14.602(3)$ Å and $Z = 2$. The X-ray analysis reveals a two-dimensional copper(II) polymeric coordination network constructed by *bis*-tridentate chelated $[Cu(trans\text{-}heae)Cu]^{2+}$ building blocks and end-on azido ligands. The environment around the copper(II) atom can be described as a square-based pyramid. The azido bridge is very asymmetric with one Cu–N bond distance short and the other long. The Cu···Cu separations through μ-*trans*-oxamidate and μ-azido bridges are 5.2996(13) Å and 4.2464(7) Å, respectively. The copper(II) complex is a polymer in the solid state, whereas in solution it exists as discrete neutral binuclear copper(II) species. Coordination mode of the azide in solution is proved by electronic spectra. The DNA-binding properties of the binuclear copper(II) species were investigated by emission spectral and electrochemical techniques, indicating the binuclear copper(II) complex binds to *HS*-DNA via a groove mode.

Keywords: Two-dimensional polymeric copper(II) complex; Crystal structure; Oxamido-bridge; Azido-bridge; DNA-binding properties

1. Introduction

Studies on polymer-metal complexes have been an active field of research [1, 2] for models for metalloenzymes [3, 4] and for developing highly efficient catalysts [5]. An effective method to construct polymer-metal complexes is self-assembly of ligands with versatile coordination modes [6]. *N*,*N*′-*bis*(substituent)oxamides have played a key role in design of polymetallic systems because their coordinating ability toward transition-metal ions can be modified by changing the nature of the amide substituent [7]. The easy *cis-trans* conformational change affords symmetric or antisymmetric oxamidato

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bridges, which makes it practical to design tunable molecular materials with extended structures and desired properties [8]. The *bis*-tridentate character of *trans*-oxamidates favors formation of *trans*-oxamidato-bridged binuclear building blocks. Spacers with versatile coordination modes are also indispensable to construct polymetallic networks. Azide is a good building block linking two or more metal ions in the μ-1,1 (end-on, EO), μ-1,3 (end-to-end, EE), or still other modes, yielding various polynuclear and one- (1-D), two- (2-D), or three-dimensional (3-D) species of different topologies, depending on the metal ion and the coligand [9]. Following this synthetic approach, a series of new metal polymers based on the bridging azide and *N*,*N*′-*bis*(substituent)oxamides with interesting structures and magnetic properties have been reported [6, 10]. However, studies on DNA binding properties of such complexes in solution are rare.

DNA is a useful target for antitumor reagents in the organism. These reagents react with DNA, changing the replication of DNA and inhibiting the growth of the tumor cell [11]. Transition metal complexes interact with DNA through covalent binding, electrostatic interaction, groove binding, or intercalation [12, 13]. Many copper(II) [14, 15] and ruthenium(II) [16, 17] complexes have been synthesized and their interactions with DNA studied, revealing that modification of the ligands lead to subtle or substantial changes in the binding modes. This provides valuable information to explore potential chemotherapeutical agents. Such studies focus on the interaction of complexes containing aromatic rings which bind DNA primarily via base-pair intercalation, and reports on the other complexes without aromatic rings are limited. To the best of our knowledge, no DNA-binding studies of complexes containing both oxamido and azido groups have been reported, prompting us to synthesize and study such complexes to gain insight into DNA-binding properties.

In this article, we report the synthesis, structure of a new two-dimensional polymeric copper(II) complex, $[Cu_2(heae)(N_3)_2]_n$, bridged both by *N*,*N*′-*bis*(*N*-hydroxyethylaminoethyl)- oxamide (H_2heae) and end-on azido groups, and the DNA binding properties in solution.

2. Experimental

The ligand *N*,*N*′-*bis*(*N*-hydroxyethylaminoethyl)oxamide (H_2heae) was synthesized according to literature method [18]. All chemicals used were of reagent grade.

2.1. *Physical measurements*

Carbon, hydrogen and nitrogen elemental analyses were performed with a Perkin-Elmer elemental analyzer Model 240. Molar conductance was measured with a Shanghai DDS-11A conductometer. The infrared spectrum was recorded with samples as KBr pellets in a Nicolet model Impact 470 FTIR spectrophotometer in the spectral range 4000–400 cm^{-1}. The UV–Visible spectrum was recorded in a 1-cm-path length quartz cell on a Cary 300 spectrophotometer. Fluorescence was tested on an Fp-750w Fluorometer. A CHI 832 electrochemical analyzer (Shanghai CHI Instrument, Shanghai, China) in connection with a glassy carbon working electrode (GCE), a saturated calomel reference electrode (SCE) and a platinum wire counter electrode was

used for the electrochemical measurement. The GCE surface was freshly polished to a mirror prior to each experiment with 0.05 μm α-Al_2O_3 paste and then cleaned in water for 5 min.

2.2. *DNA-binding studies*

All experiments involving *HS*-DNA (*HS*-DNA stands for Herring Sperm DNA) were performed in *tris*-HCl buffer solution (pH = 7.86). Solutions of *HS*-DNA in *tris*-HCl buffer gave a ratio of UV absorbance at 260 and 280 nm, A_{260}/A_{280}, of ≈1.9, indicating that the DNA was sufficiently free of protein [19]. The concentration of DNA was determined by UV absorbance at 260 nm. The molar absorption coefficient, ε260, was taken as 6600 $mol^{-1}\,L\,cm^{-1}$ [20]. Stock solution of DNA was stored at 4°C and used after no more than 4 days. The electrochemical titration experiments were performed by keeping the concentration of the complex constant while varying the *HS*-DNA concentration. In the ethidium bromide (EB) fluorescence displacement experiment, stock solution of the complex (2×10^{-3} mol L^{-1}) in *tris*-HCl buffer solution was freshly prepared before use. 5 μL of the EB *tris*-HCl buffer solution (1 mmol L^{-1}) was added to 1 mL of DNA solution (at saturated binding levels) [21], stored in the dark for 2 h. The solution of complex was titrated into the DNA/EB mixture and then diluted in *tris*-HCl buffer to 5 mL, producing solutions with varied mole ratio of complex to *HS*-DNA. Before measurements, the mixture was shaken and incubated at room temperature for 30 min. The fluorescence spectra were obtained at an excitation wavelength of 522 nm and an emission wavelength of 584 nm in the Fluorometer.

2.3. *Synthesis of* $[Cu_2(heae)(N_3)_2]_n$

To a stirred methanol solution (5 mL) containing $Cu(NO_3)_2 \cdot 6H_2O$ (59.2 mg, 0.2 mmol) was added dropwise a methanol solution (10 mL) of H_2heae (26.2 mg, 0.1 mmol) and piperidine (17.0 mg, 0.200 mmol) at room temperature. The mixture was stirred rapidly for 30 min. A methanol solution (5 mL) of NaN_3 (13.0 mg, 0.2 mmol) was then added dropwise to the mixture. After stirring continuously at 333 K for 6 h, the resulting blue solution was filtered and blue cube crystals of the complex suitable for X-ray analysis were obtained by slow evaporation at room temperature. Yield: 0.034 g (72%). Anal. Calcd for $Cu_2C_{10}H_{20}N_{10}O_4$: C, 25.48; H, 2.14; N, 29.71%. Found: C, 25.60; H, 2.22; N, 29.77%.

2.4. *X-ray crystallography*

The crystal structure analyses were carried out on a Bruker APEX area-detector diffractometer with graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). The crystal structure was solved by direct methods followed by Fourier syntheses. Structure refinement was performed by full matrix least-squares procedures using SHELXL-97 on F^2 [22]. H atom of the hydroxy group was located in a difference Fourier map and was treated as riding, with refined Uiso(H) = 0.066(10) $Å^2$. Other H atoms were placed in calculated positions, with C–H = 0.97 Å and N–H = 0.91 Å, and included in the final cycles of refinement in the riding mode, with Uiso(H) = 1.2 Ueq of the carrier atoms.

Table 1. Crystallographic data and structure refinement for the copper(II) polymer.

Empirical formula	$Cu_2C_{10}H_{20}N_{10}O_4$
Formula weight	471.44
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions (Å, °)	
a	9.1588(2)
b	6.6238(1)
c	14.602(3)
α	90.00
β	102.56(3)
γ	90.00
V (Å^3)	864.6(3)
Z	2
D_{Calcd} (g cm^{-3})	1.811
μ (Mo-Kα)(mm^{-1})	2.501
F(000)	480
Crystal size (mm^3)	$0.09 \times 0.10 \times 0.23$
Temperature (K)	293
Radiation (Å)	Mo-Kα 0.71073
Limiting indices	$-10 \le h \le 10$, $-7 \le k \le 7$, $-17 \le l \le 14$
Tot., Uniq. data, $R_{(int)}$	4148, 1557, 0.019
θ range	2.28, 25.23
Observed data [$I > 2\sigma(I)$]	1305
R, wR_2, S	0.0267, 0.0730, 1.102
Max., av. shift/error	0.000, 0.000

A nitrogen atom in the azido ligand was disordered at two positions (N5a, N5b) with the occupancy of 0.5. Crystal data and refinement conditions are summarized in table 1.

3. Results and discussion

3.1. *General properties of the complex*

The polymeric copper(II) complex is very soluble in DMSO and DMF, giving stable solution at room temperature and is moderately soluble in water, methanol and acetone, and practically insoluble in carbon tetrachloride, chloroform and benzene. In the solid state the complex is fairly stable in air, allowing physical measurements. For the complex, the observed molar conductance value ($\Lambda = 36\,\Omega^{-1}\,cm^2\,mol^{-1}$ DMF solution) falls in the expected range for non-electrolytes [23], consistent with the following spectroscopic analyses and the structure of the complex.

3.2. *IR and electronic spectra*

In the IR spectrum of the complex, the N–H and O–H stretching vibrations of the bridging ligand (heae) appear in the region 3223–3422 cm^{-1}. Strong bands observed at 1655 cm^{-1} and 2050 cm^{-1} are characteristics of the N = C–O stretching vibration of the bridging oxamido [18] and the stretching vibration of the end-on bridging azide [9], respectively.

To clarify the mode of bonding of the copper(II) polymer in solution, the electronic spectrum of the complex was measured in the UV–Vis region (200 ~ 800 nm) using methanol as the solvent. Three absorption bands with varied intensity can be observed.

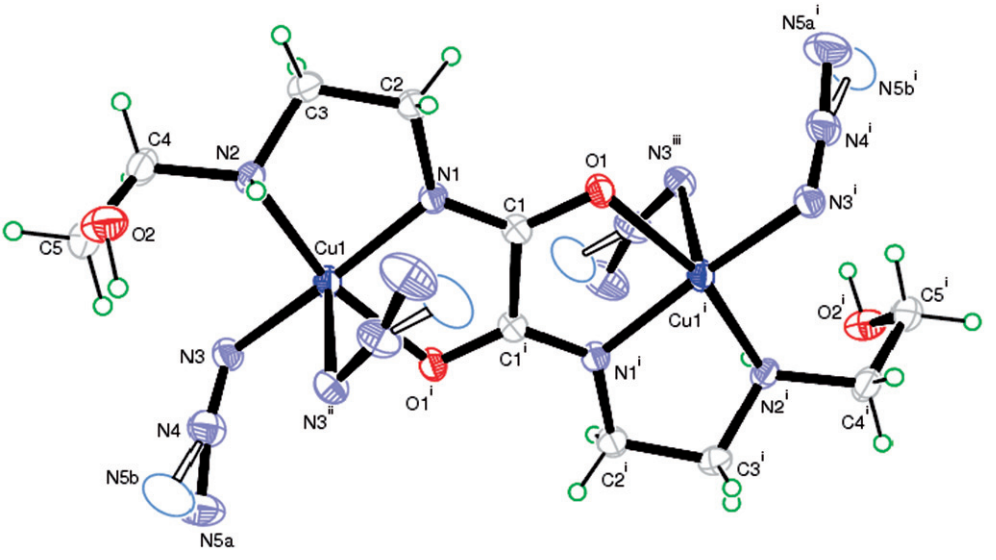

Figure 1. ORTEP drawing of the unit of $[Cu_2(heae)(N_3)_2]_n$ with 30% probability displacement ellipsoids (symmetry code: i $= -x, 1-y, -z$; ii $= -x, y-1/2, -z+1/2$; iii $= x, -y+3/2, z-1/2$).

The broad, less intense band at 617 nm ($\varepsilon = 250\,mol^{-1}\,L\,cm^{-1}$) in the spectrum corresponds to the d-d transition of copper(II) in a square-based pyramid [24], while the strong absorption centered at 362 nm ($\varepsilon = 2344\,mol^{-1}\,L\,cm^{-1}$) is typical for the azido-to-copper charge transfer transition (LMCT) [25–27], indicating that the copper(II) polymer is a discrete neutral binuclear copper(II) species in solution with a solvent molecule probably occupying the axial position in the coordination sphere. The strong absorption centered at 260 nm ($\varepsilon = 13500\,mol^{-1}\,L\,cm^{-1}$) may be due to the spin-exchange interaction between the copper(II) ions through the Π-path orbital of an oxamido bridge [18]. Further investigation of this and similar systems is required to obtain more detailed assignment for the charge transfer.

3.3. *Description of the structure*

A plot and atom numbering scheme of $[Cu_2(heae)(N_3)_2]_n$ is given in figure 1 and selected geometric parameters are summarized in table 2. Single-crystal X-ray analysis reveals that the complex contains an inversion center at the mid-point of the C1–C1^{i} bond (i $= -x, 1-y, -z$). The copper(II) has a square-pyramidal coordination geometry, which is completed by two nitrogen atoms (N1, N2) and one oxygen (O1^{i}) from the oxamide ligand and one azido nitrogen (N3) in the basal plane, and another azido nitrogen (N3^{ii}, ii $= -x, y-1/2, -z+1/2$) at the apical position. The maximum displacement of the four atoms N1, N2, O1^{i}, N3 from the basal plane is 0.1615(12) Å at N1, and the copper(II) atom lies 0.0770(11) Å out of the plane, which forms a dihedral angle of 6.7(2)° with the oxamido plane N1C1O1N1^{i}C1^{i}O1^{i}.

The *trans*-oxamidate is a *bis*-tridentate ligand chelating and bridging copper(II) atoms to form [Cu(*trans*-heae)Cu]$^{2+}$ building blocks. The bond distances of C1–N1 [1.287(3) Å] and C1–O1 [1.281(3) Å] indicate that the bond order of C1–O1 is almost 1,

Table 2. Selected bond distances (Å) and angles (°) for the complex.

Cu1–N1	1.931(2)	C2–C3	1.521(4)
Cu1–N3	1.963(2)	C3–N2	1.491(3)
Cu1–O1^{i}	2.0378(19)	C4–N2	1.489(3)
Cu1–N2	2.051(2)	C4–C5	1.504(4)
O1–C1	1.281(3)	N3–N4	1.185(3)
O2–C5	1.417(4)	N4–N5a	1.15(2)
C1–N1	1.287(3)	N4–N5b	1.19(2)
C1–C1^{i}	1.525(5)	Cu1–N3^{ii}	2.616(2)
C2–N1	1.454(3)		
N1–Cu1–N3	166.78(9)	N2–C4–C5	109.9(2)
N1–Cu1–O1^{i}	82.53(8)	O2–N5–N4	108.8(2)
N3–Cu1–O1^{i}	94.51(8)	C1–N1–C2	124.7(2)
N1–Cu1–N2	81.72(8)	C1–N1–Cu1	116.84(17)
N3–Cu1–N2	102.08(9)	C2–N1–Cu1	118.32(16)
O1–Cu1–N2	163.31(8)	C4–N2–C3	113.4(2)
C1–O1–Cu1	109.99(14)	C4–N2–Cu1	121.12(17)
O1–C1–N1	129.5(2)	C3–N2–Cu1	106.27(15)
O1–C1–C1^{i}	118.3(3)	N4–N3–Cu1	117.96(18)
N1–C1–C1^{i}	112.2(3)	N5a–N4–N3	164.9(8)
N1–C2–C3	106.3(2)	N5a–N4–N5b	29.5(10)
N2–C3–C2	108.7(2)	N3–N4–N5b	165.1(8)

Symmetry code: i = $-x$, $1-y$, $-z$; ii = $-x$, $y-1/2$.

whereas that of C1–N1 is 2, suggesting that the ligand is an iminoalcohol form [28], although other papers refer to O1 as a carbonyl oxygen [29]. Therefore, H_2heae is deprotonated at the hydroxy groups and adopts a *bis*-tridentate *trans* conformation to form two five-membered chelate rings around each Cu(II) ion. The ring Cu1–O1^{i}–C1^{i}–C1–N1 is almost planar, whereas Cu1–N1–C2–C3–N2 takes a twist conformation with the corresponding puckering parameters [30] of $\varphi = 123.9(3)^\circ$, $Q = 0.431(3)$ Å. The Cu1 $\cdots$ Cu1^{i} separation is 5.2996(13) Å. The three bond distances of Cu1–N1 [1.931(2) Å], Cu1–N2 [2.051(2) Å] and Cu1–O1^{i} [2.038(2) Å] are close to those found in other oxamidato-bridged copper(II) complexes [28, 29, 31–33]. The Cu1–N1 (amido) bond is shorter than the Cu1–N2 (imine) bond, consistent with stronger donor ability of the nitrogen in imine compared with amine.

The [Cu(*trans*-heae)Cu]$^{2+}$ building blocks are linked by the spacers (azido groups) in end-on mode to form a 2-D polymer parallel to the plane (1 0 0) (figure 2). The bridging N3 coordinates to Cu1 in the basal plane while to Cu1^{iv} on the apical position, in a very asymmetric bridge with one Cu–N bond distance short [Cu1–N3, 1.963(2) Å] and the other long [Cu1^{iv}–N3, 2.616(2) Å, iv = $-x$, $y+1/2$, $-z+1/2$]. Such a disposition is typical for EO azide bridges [8, 9]. The uncoordinated terminal nitrogen atom of the azido bridge is disordered at two positions (N5a and N5b) with occupancy of 0.5; the angles of N3–N4–N5a and N3–N4–N5b are 164.9(8)° and 165.1(8)°, respectively. The Cu1 $\cdots$ Cu1^{iv} separation through the μ-azido bridge is 4.2464 (7) Å and the Cu–N–Cu bridging angle is 135.5(1)°.

3.4. *DNA binding studies*

Due to the very asymmetric azide bridge with one Cu–N bond distance short and the other long, we consider the copper(II) polymer a discrete neutral binuclear copper(II)

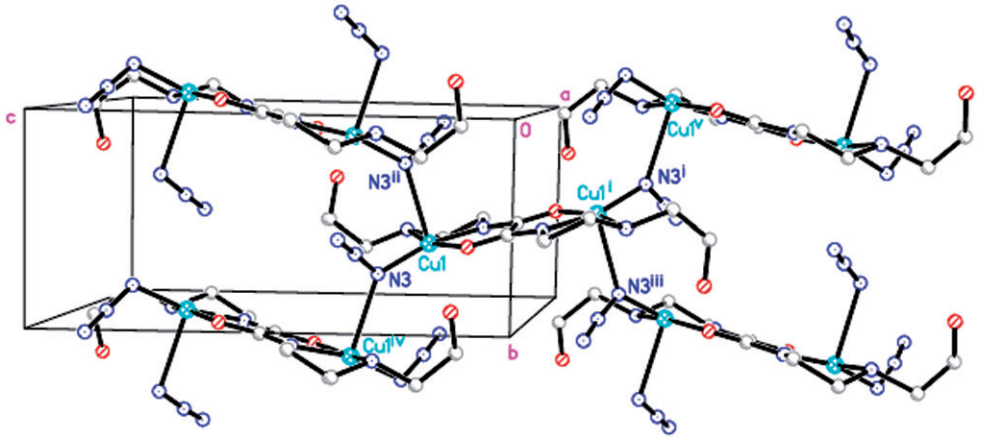

Figure 2. The two-dimensional polymer structure of $[Cu_2(heae)(N_3)_2]_n$ parallel to the (1 0 0) plane; hydrogen atoms are omitted for clarity (symmetry code: i = $-x$, $1-y$, $-z$; ii = $-x$, $y-1/2$, $-z+1/2$; iii = x, $-y+3/2$, $z-1/2$; iv = $-x$, $y+1/2$, $-z+1/2$; $v = x$, $-y+1/2$, $z-1/2$).

species in solution, confirmed by the electronic spectrum and the solubility of the copper(II) polymer. The binding properties of the binuclear copper(II) complex with DNA was explored by the EB fluorescence displacement experiment and electrochemical measurements (*vide infra*).

3.4.1. Competitive binding between EB and the complex. Ethidium bromide fluorescence displacement experiments were used to investigate the DNA binding of the binuclear copper(II) complex. The intrinsic fluorescence intensity of DNA is very low, and that of EB in *tris* buffer is also not high due to quenching by solvent. However, on addition of DNA, the fluorescence intensity of EB is enhanced by intercalation into DNA. Thus, EB can be used to probe the interaction of complexes with DNA. The fluorescence intensity of EB can be quenched by addition of another molecule due to decreasing of the binding sites of DNA available for EB [34]. In our experiment, as illustrated in figure 3, the fluorescence intensity of EB bound to DNA at 584 nm shows a decrease with increasing concentration of the binuclear copper(II) complex. Considering the non-planarity of the ligands in the complex lead us to suspect that the binuclear copper(II) complex interacts with DNA through the groove binding mode, releasing some EB molecules from the EB-DNA system [35].

In order to understand quantitatively the magnitude of the binding strength of the binuclear copper(II) complex with *HS*-DNA, the linear Stern-Volmer equation is employed [36]:

$$\frac{I_0}{I} = 1 + K_{sv}[Q] \tag{1}$$

where I_0 and I represent the fluorescence intensities in the absence and presence of quencher, respectively. Q is the concentration of quencher. K_{sv} is a linear Stern-Volmer quenching constant. In the quenching plot (figure 4) of I_0/I *versus* [complex], K_{sv} is given by the slope. The K_{sv} value for the binuclear copper(II) complex is 5.32×10^3

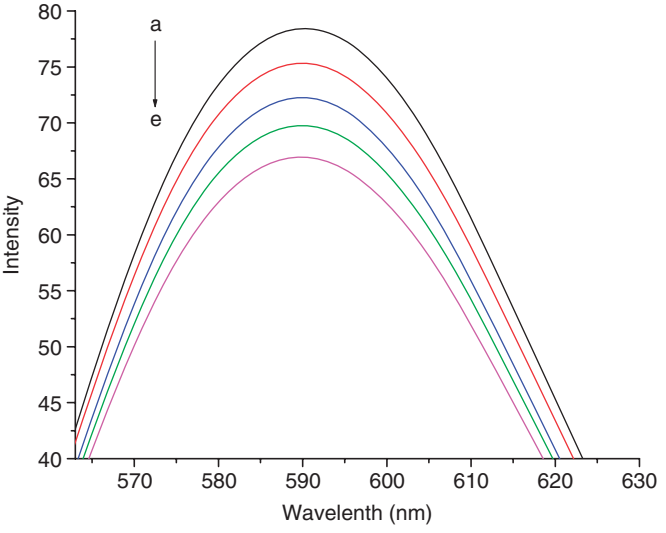

Figure 3. Fluorescence changes that occur when the *HS*-DNA-EB system is titrated with the binuclear copper(II) complex: $\lambda_{ex} = 522$ nm; [EB] = 4×10^{-6} M, [DNA] = 1.2×10^{-4} M; [complex] = (a) 0, (b) = 8×10^{-6} M, (c) = 1.6×10^{-5} M, (d) = 2.4×10^{-5} M, (e) = 3.2×10^{-5} M. Arrow shows the intensity change upon increasing the complex concentrations.

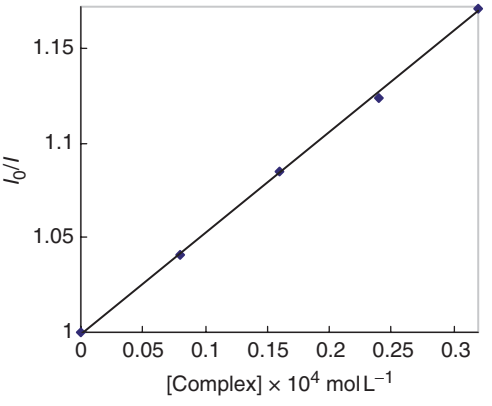

Figure 4. Plot of I_0/I *vs.* [complex] for the titration of the binuclear copper(II) complex to *HS*-DNA-EB system.

($R = 0.9993$ for five points), suggesting weak affinity of the binuclear copper(II) complex to *HS*-DNA.

3.4.2. Cyclic voltammetry. Application of cyclic voltammetry to study interaction between metal complexes and DNA provides a useful complement to the spectral studies. As can be seen in figure 5, in the absence of DNA (curve 1), the complex has a quasi-reversible redox process corresponding to Cu(II)/Cu(I) with the cathodic (E_{pc}) and anodic peak potential (E_{pa}) being −0.176 V and −0.058 V, respectively

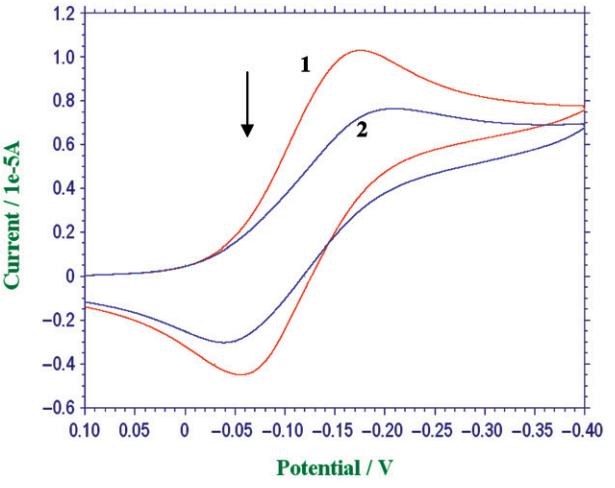

Figure 5. Cyclic voltammograms of the binuclear copper(II) complex in the absence (curve 1) and the presence (curve 2) of DNA (1.0×10^{-4} moL L^{-1}) in the solution of *tris*-HCl buffer (pH = 7.86) with the scan rate of 0.1 Vs^{-1}.

($\Delta E_p = 0.118$ V). The formal potential $E^{o\prime}$ was found to be −0.117 V. In the presence of DNA (curve 2) with $R = 10$ ($R = [DNA]/[complex]$), the voltammetric peak currents decreased, indicating that there exists an interaction between the complex and DNA [37]. The drop of the voltammetric current in the presence of DNA may be attributed to slow diffusion of the complex bound to *HS*-DNA. The peak-to-peak separation becomes larger with $\Delta E_p = 0.166$ V, suggesting that in the presence of DNA the electron-transfer process becomes less reversible. The shift in E° can be used to estimate the ratio of binding constants for reduced and oxidized forms to DNA using equation 2 [38]:

$$E_b^{o'} - E_f^{o'} = 0.059 \log \left(K_{Cu(I)}/K_{Cu(II)}\right) \quad (2)$$

where $E_b^{o'}$ and $E_f^{o'}$ are the formal potentials of the Cu(I)/Cu(II) couple in the binding and free forms, respectively, and $K_{Cu(I)}$ and $K_{Cu(II)}$ are the binding constants of Cu(I) and Cu(II) forms to DNA. The ratio of constants for the binding of the Cu(I) and Cu(II) ions to DNA was estimated to be 1.0, which indicates that both Cu(I) and Cu(II) forms interacted with DNA to the same extent. Hence, we deduce that the complex binds DNA in groove binding mode [37, 39], in agreement with the above spectral result.

Further investigations on this and similar systems are required to get deeper insight into this exciting field of DNA binding and are in progress in our laboratory.

Supplementary materials

CCDC 641250 contains the supplementary crystallographic data for this article. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre,

12 Union Road, Cambridge CB2 1EZ, UK [Fax: (+44) 1223-336-033; or E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgements

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