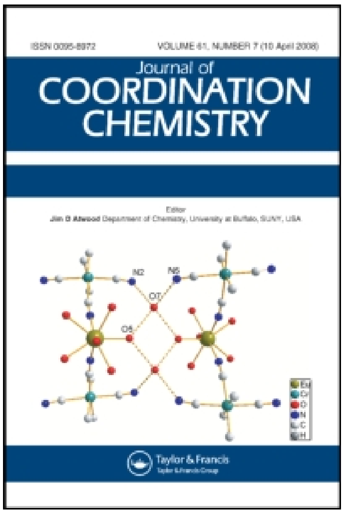

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Synthesis, structure and properties of a 4,4'-bipyridine bridged dinuclear Cu(II) complex: $\{Cu_2(4,4'\text{-bipy})[HOCH_2CH_2N(CH_2CH_2NH_2)_2]_2\}\cdot(ClO_4)_4\cdot 1/2(4,4'\text{-bipy})\cdot 4H_2O$

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To cite this Article Gao, Jian , Xu, Xing-You , Wang, Ming-Yan , Liu, Qing-Liang and song, Hai-Bing(2005) 'Synthesis, structure and properties of a 4,4'-bipyridine bridged dinuclear Cu(II) complex: $\{Cu_2(4,4'\text{-bipy})[HOCH_2CH_2N(CH_2CH_2NH_2)_2]_2\}\cdot(ClO_4)_4\cdot 1/2(4,4'\text{-bipy})\cdot 4H_2O$', Journal of Coordination Chemistry, 58: 15, 1351 — 1360
To link to this Article: DOI: 10.1080/00958970500237546
URL: http://dx.doi.org/10.1080/00958970500237546

Journal of Coordination Chemistry
Vol. 58, No. 15, October 2005, 1351–1360

Synthesis, structure and properties of a 4,4′-bipyridine bridged dinuclear Cu(II) complex: $\{Cu_2(4,4'\text{-bipy})[HOCH_2CH_2N(CH_2CH_2NH_2)_2]_2\} \cdot (ClO_4)_4 \cdot 1/2(4,4'\text{-bipy}) \cdot 4H_2O$

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(*Received in final form 27 June 2005*)

A new bicopper(II) complex was synthesized and characterized by X-ray crystallography. Crystals of the complex were monoclinic, space group $C2$ with $a = 33.717(10)$, $b = 12.078(4)$, $c = 11.386(3)$ Å and $\beta = 103.980(6)°$. The two Cu(II) atoms are bridged by 4,4′-bipyridine and each Cu(II) is five-coordinate in a distorted trigonal-bipyramid geometry. Magnetic investigation shows that the complex has a weak ferromagnetic interaction between the two metal ions. A cyclic voltammogram of the complex shows two quasi-reversible peaks for the couples $Cu^{II}Cu^{II}/Cu^{I}Cu^{II}$ and $Cu^{I}Cu^{II}/Cu^{I}Cu^{I}$. Study of the antimicrobial activity showed the complex was active against *Candida albican*, *Staphylococcus aureu*, *Bacillus pumilus* and *Eschierichia coli*.

Keywords: Bicopper(II) complex; Crystal structure; Magnetic property; Redox property; Antimicrobial activity

1. Introduction

Since the pioneering work of Robson and coworkers in 1990 [1], 4,4′-bipyridine is widely used as a building block in designing coordination polymers [2], which possess potentially useful properties such as magnetism, fluorescence, non-linear optical activity and catalysis [3–7]. Strong coordination of the amine nitrogen atoms to transition metal ions and the role of such complexes in catalysis, redox, antimicrobial activity and mimic studies on superoxide dismutase [8–14], encourages efforts in designing and

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Journal of Coordination Chemistry
ISSN 0095-8972 print: ISSN 1029-0389 online © 2005 Taylor & Francis
DOI: 10.1080/00958970500237546

constructing 4,4′-bipyridine-based self-assemblies with tripodal polyamine and Cu(II) centers. Described herein is the synthesis, structure, redox, antimicrobial activity and magnetic properties of a new five-coordinate copper(II) complex obtained from self-assembly of 2-[bis(2-aminoethy)amino]ethanol, 4,4′-bipyridine and Cu(II).

2. Experimental

2.1. *Materials and physical measurements*

4,4′-Bipyridine was obtained from Aldrich Company. 2-[Bis(2-aminoethy)amino] ethanol (OH22) was prepared according to the literature [15]. Elemental analysis was determined with a Perkin–Elmer 240 c instrument. IR spectra were measured as KBr discs using a Nicolet 5DX FT-IR spectrophotometer. Solution conductivities were measured by a BSD-A numerical conductometer (Jiangsu, China) with solution concentration of $\sim 1.0 \times 10^{-3}\,\mathrm{mol\,dm^{-3}}$ in methanol at 279 K. The cyclic voltammograms were obtained on a CHI660 electrochemical analyzer. The ES mass spectral measurement was carried out on a LCQ System (Finngann MAT, USA) using methanol as the mobile phase. X-band electron spin resonance (ESR) spectra of the complex in CH_3CN solution as a function of temperature were recorded on a Bruker ER 200D-SRC spectrometer. Variable-temperature magnetic susceptibility data were obtained with a CHAN-2000 Faraday-type magnetometer in the temperature range 75.8–300.5 K. Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were obtained under flowing N_2 with a heating rate of $5^{\circ}\mathrm{C\,min^{-1}}$.

2.2. *Synthesis of complexes*

2.2.1. [Cu(OH22)](ClO_4)$_2$ (b). A solution of $Cu(ClO_4)_2 \cdot 6H_2O$ (0.371 g, 1 mmol) in methanol (20 cm^3) was added in portions to 15 cm^3 of a methanol solution containing OH22 (0.147 g, 1 mmol). After stirring for an hour, the resulting blue precipitate was filtered off, washed with methanol and dried in vacuum.

2.2.2. [(OH22)Cu(4,4′-bpy)Cu(OH22)](ClO_4)$_4$ (a). To a solution containing **b** (0.164 g, 0.4 mmol) in 30 cm^3 of methanol was added to a methanol solution of 4,4′-bipyridine (0.031 g, 0.2 mmol). After reflux for 2 h, the solution was filtered. The filtrate was placed in an ambient environment and blue single crystals suitable for X-ray structure determination were obtained by slow evaporation after 2 weeks. Yield 46%, m.p. >231°C (dec.). Anal. Calcd for $C_{27}H_{54}Cl_4Cu_2N_9O_{22}$ (%): C, 28.78; H, 4.80; N, 11.19. Found: C, 28.71; H, 4.76; N, 11.06. IR (cm^{-1}): 3430s ν(OH); 3210, 3200m ν(NH_2); 1612, 1420m ν(py); 1088s ν(ClO_4); *m*/*z* (%) 208.9(48), 240.7(64), 268.0(100), 310.0(24). Λ_M (CH_3OH, 279 K): 406 S cm^2 mol^{-1}.

Caution: Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small amounts of material should be prepared, and these should be handled with caution.

2.3. *Crystal structure determination for the title complex*

A blue single crystal of dimensions $0.22 \times 0.18 \times 0.14\,\mathrm{mm}^3$ was mounted on a glass fibre. The crystal data were collected at 293(2) K on a Siemens Smart/CCD

Table 1. Crystal data collection parameters.

Empirical formula	$C_{27}H_{54}Cl_4Cu_2N_9O_{22}$
Formula weight	1125.67
Radiation (Å)	0.71073
Crystal system	Monoclinic
Space group	$C2$
a (Å)	33.717(10)
b (Å)	12.078(4)
c (Å)	11.386(3)
α (°)	90.00
β (°)	103.980(6)
γ (°)	90.00
V (Å^3)	4499(2)
Z	4
D_{calcd} (Mg m^{-3})	1.662
Absorption coefficient (mm^{-1})	1.272
θ range (°)	$1.24° \leq \theta \leq 25.00°$
Index ranges	$-37 \leq h \leq 40$, $-14 \leq k \leq 11$, $-13 \leq l \leq 10$
Reflections collected	11742
Independent reflections	7358
Independent reflections ($>2\sigma$)	5234
Absorption Correction	Semi-empirical from equivalents
Max/min transmissions	1.000000/0.646570
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	7358/1/577
Goodness-of-fit on F^2	1.024
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0638$, $wR_2 = 0.1347$
R indices (all data)	$R_1 = 0.1001$, $wR_2 = 0.1597$
Largest diff. peak and hole (e Å^{-3})	1.187 and −0.422

area-detector diffractometer with Mo-K_α radiation ($\lambda = 0.71073$ Å) over the range $1.24° \leq \theta \leq 25.00°$ with a ω scan mode. Data reductions and cell refinements were performed with Smart-CCD software. An absorption correction by using SADABS software was applied. The structures were solved by direct methods and refined by full-matrix least squares on F^2 using SHELXL-97 [16]. The details of data collection, refinement and crystallographic data are summarized in table 1.

2.4. *Antimicrobial activity determination*

The antimicrobial activity for the complex was evaluated by testing antimicrobial activity to bacterial strands using the agar diffusion method as described in the literature [17]. Complex dissolved in dimethylformamide (DMF) was tested against standard strains of *Candida albicans* CMCC (F) 98 001, *Staphylococcus aureus* CMCC (B) 26 003, *Bacillus pumilus* CMCC (B) 63 202 and *Eschierichia coli* CMCC (B) 44 102. Nutrient agar thawed by heating in a water bath was transferred to glass plates and frozen at 37°C. After test strains were spread on the solid nutrient agar surface, stainless steel tubes ($7.8 \times 6 \times 10$ mm^3) were placed vertically on the surface. 0.04 mL samples with certain concentrations were injected into the steel tubes. They were allowed to incubate at 37°C for 24 h. The inhibition zone around the disc was calculated as zone diameter in millimeters. Blank tests showed that DMF in the preparation of the test solutions does not affect the test organisms. All tests were repeated three times and average data were taken as the final result.

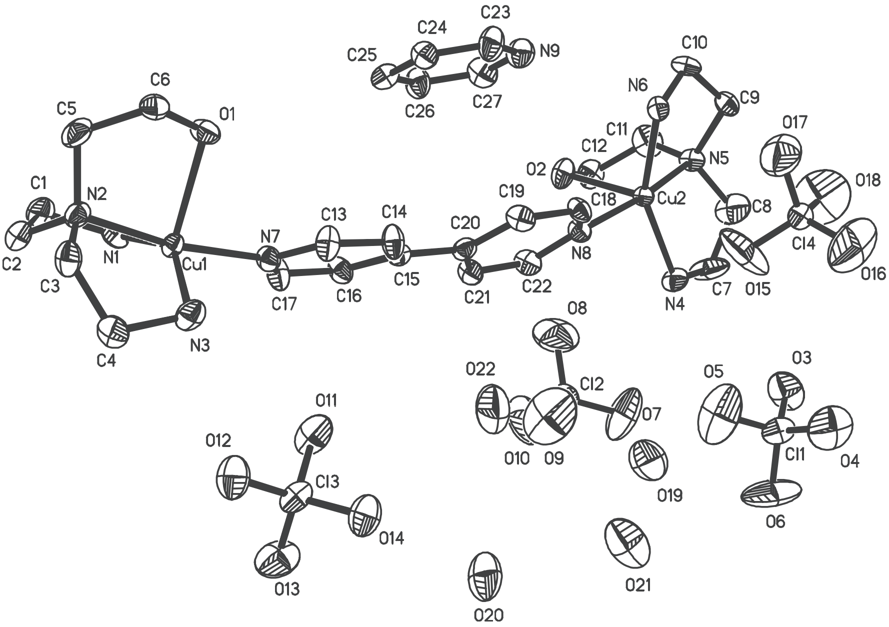

Figure 1. Molecular structure of the title complex (ellipsoids at 30% probability).

3. Results and discussion

3.1. *Characterization of the complex*

The structure of the title complex is confirmed by elemental analysis, IR, electron impact/ionization mass spectrometry (EI-MS) and electrical conductivity. IR spectra exhibit the main absorption bands of bipy, –NH$_2$ and –OH, which were found to be red-shifted relative to the free ligand [18], indicating coordination though the pyridine nitrogen, primary amine nitrogen and hydroxyl oxygen. The strong peak at 1088 cm^{-1} without splitting showed that the ClO_4^- did not take part in coordination with Cu. This is also confirmed by molar conductivity of the complex [Λ_M (CH_3CN, 289 K) $= 406\,S\,cm^2\,mol^{-1}$], which is attributable to a 1 : 4 electrolyte. The main peaks at m/z 208.9, 240.7, 268.0 and 310.0 are observed in the ES-MS spectra, corresponding to the species of [(OH22)Cu(4,4′-bpy) + CH_3OH + H_2O]$^{2+}$, [(OH22)Cu(4,4′-bpy) + 3CH_3OH + H_2O]$^{2+}$, [(OH22)Cu(4,4′-bpy) + 3CH_3OH + 4H_2O]$^{2+}$and [(OH22) Cu(ClO_4)]$^+$, respectively.

3.2. *Crystal structure of the title complex*

The crystal structure consists of cationic [(OH22)Cu(4,4′-bipy)Cu(OH22)]$^{4+}$, ClO_4^- anion, H_2O molecule and non-coordinated 4,4′-bipy. The molecular structure of the title complex showing the atomic numbering scheme is indicated in figure 1. Selected bond lengths and bond angles relevant to the Cu coordination sphere are listed in table 2. In the cation, two Cu(II) atoms ($Cu\cdots Cu = 10.934$ Å) are bridged by 4,4′-bipy in a N(4)O coordination environment forming two distorted trigonal bipyramids. The distortion (Δ) of the coordination polyhedron has been calculated

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

Cu(1)–N(7)	1.992(7)	Cu(1)–N(3)	2.019(7)
Cu(1)–N(2)	2.028(8)	Cu(1)–N(1)	2.032(7)
Cu(1)–O(1)	2.254(6)	Cu(2)–N(8)	2.002(8)
Cu(2)–N(4)	2.014(8)	Cu(2)–N(5)	2.025(7)
Cu(2)–N(6)	2.032(7)	Cu(2)–O(2)	2.275(6)
N(7)–Cu(1)–N(3)	96.0(3)	N(7)–Cu(1)–N(2)	170.3(3)
N(3)–Cu(1)–N(2)	85.5(3)	N(7)–Cu(1)–N(1)	98.8(3)
N(3)–Cu(1)–N(1)	142.0(3)	N(2)–Cu(1)–N(1)	85.6(3)
N(7)–Cu(1)–O(1)	90.5(3)	N(3)–Cu(1)–O(1)	106.5(3)
N(2)–Cu(1)–O(1)	79.9(3)	N(1)–Cu(1)–O(1)	108.1(3)
N(8)–Cu(2)–N(4)	97.5(3)	N(8)–Cu(2)–N(5)	170.5(3)
N(4)–Cu(2)–N(5)	85.2(3)	N(8)–Cu(2)–N(6)	96.2(3)
N(4)–Cu(2)–N(6)	151.3(3)	N(5)–Cu(2)–N(6)	85.4(3)
N(8)–Cu(2)–O(2)	89.5(3)	N(4)–Cu(2)–O(2)	104.5(3)
N(5)–Cu(2)–O(2)	81.0(3)	N(6)–Cu(2)–O(2)	100.7(3)

using the Muetterties description [19] by comparison of the observed dihedral angles formed by the normal to adjacent polytopal faces with the ones of the ideal trigonal bipyramid ($\Delta = 1$). The values of Δ for Cu(1) and Cu(2), 0.32 and 0.31, respectively, indicate that Cu(1) and Cu(2) polyhedra are close to trigonal bipyramid (TBP). The Cu(1) atom lies 0.2084 Å below the trigonal equatorial plane formed by the terminal N and O atoms of the tripod with N(3)–Cu(1)–N(1) = 142.0(3)°, N(3)–Cu(1)–O(1) = 106.5(3)° and N(1)–Cu(1)–O(1) = 108.1(3)°. The two axial sites are occupied by the tertiary nitrogen atom N(2) from diethylenetriamine and N(7) of 4,4′-bipy with N(2)–Cu(1)–N(7) = 170.3(3)°. The Cu(2) atom lies 0.1983 Å above the trigonal equatorial plane formed by N(4), N(6) and O(2) with N(4)–Cu(2)–N(6) = 151.3(3)°, N(4)–Cu(2)–O(2) = 104.5(3)° and N(6)–Cu(2)–O(2) = 100.7(3)°. The two axial sites are occupied by the tertiary nitrogen atom N(5) from diethylenetriamine moiety and N(8) atom of 4,4′-bipy with a N(5)–Cu(2)–N(8) = 170.5(3)°. The centroid–centroid distance of the two equatorial planes mentioned earlier are 11.103 Å, and the dihedral angle is 36.4°. The shorter Cu–N(4,4′-bipy) distances (average 1.997 Å) compared to the Cu–N(OH22) distances (average 2.025 Å) are consistent with the hybridization of the ligating nitrogen atoms (sp^2 for 4,4′-bipy, sp^3 for OH22), in agreement with a previously reported structure [7]. The two pyridyl rings of the cation exhibit a distinct twist with a dihedral angle of 14.2°, and the mean deviations from their least square planes for the pyridyl rings are 0.0167 and 0.0097 Å, respectively. The deviation from linearity gives the cation an obvious bower feature. The non-coordinating 4,4′-bipy molecules lie between the adjacent concaves.

Hydrogen bonds are extensive. The hydroxyethyl O(1) and O(2) atoms form two strong hydrogen bonds with O(19) and O(20) of two water molecules, respectively [O(1)···O(19) = 2.760 Å and O(1)–H(1)···O(1)9 = 133.1°; O(2)···O(20) = 2.703 Å and O(2)–H(2C)···O(20) = 132.3°], and the two water molecules are donors for hydrogen bonds with O(19), O(21) and O(22) of water molecules [O(20)···O(22) = 3.194 Å and O(20)–H(20B)···O(22) = 124.1°; O(20)···O(21) = 2.98 Å and O(20)–H(20A)···O(21) = 167.4°; O(19)···O(21) = 3.098 Å and O(19)–H(19B)···(21) = 143.7°; O(19)···O(19) = 2.877 Å and O(19)–H(19A)···O(19) = 135.3°]. The latter water molecules as donors can also form hydrogen bonds with perchlorate. Each perchlorate anion is an acceptor of hydrogen bonds with the amino group of an adjacent complex cation. In addition, two pyridyl rings [N(8), C(18)–C(22) and N(9), C(23)–C(27)] are almost parallel with

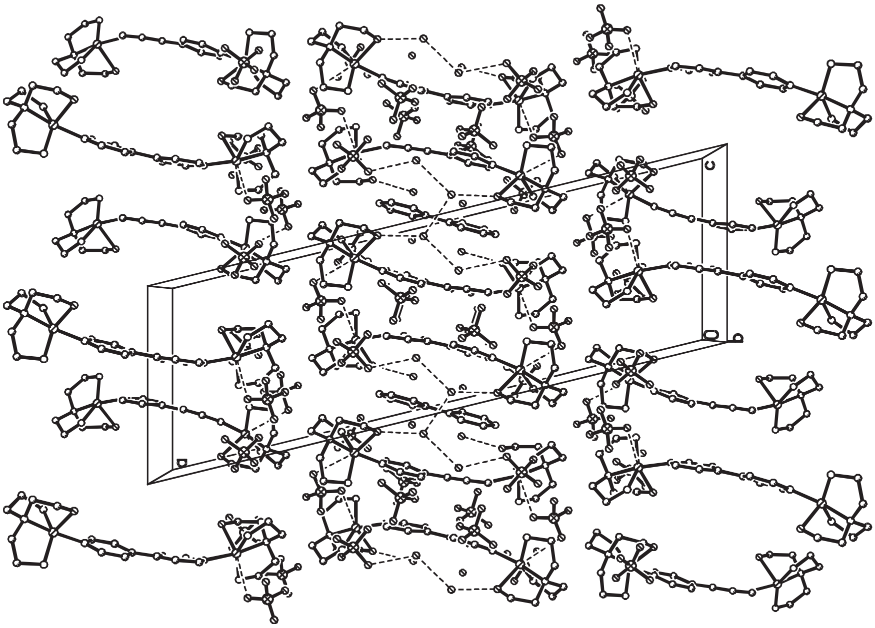

Figure 2. Perspective view of cell packing in the complex.

a dihedral angle of 14.4° and the center distance of 3.832 Å, indicating the presence of a weak face–face π–π stacking interaction [2]. All the above intermolecular interactions are responsible for formation of the supermolecular structure, which is shown in figure 2.

3.3. *Magnetic properties*

The magnetic moment for the binuclear copper(II) complex measured at room temperature is 2.52 B.M., somewhat higher than the spin-only value indicating a weak ferromagnetic exchange coupling between copper(II) ions. To determine the extent of magnetic interaction between the metal ions, magnetic susceptibilities at various temperatures (300–75 K) were measured. The temperature variation of molar magnetic susceptibility (χ_m) and effective susceptibility (μ_{eff}) for the complex are shown in the figure 3. The experimental data fit well with the Curie–Weiss formula, $\chi_m = C/(T - \theta)$, which gives the best-fit parameters: $C = 0.63045$, $\theta = 1.37557 > 0$, and the fitting constant $F = 2.0 \times 10^{-9}$, with a correlation coefficient $R = 0.99946$.

X-ray band spectra measured in the solid state and in CH_3CN solution at various temperatures are shown in figure 4. The presence of hyperfine structure at 288, 250 and 230 K suggests some interaction between Cu(1) and Cu(2), but the lack of hyperfine splitting in the parallel portion prevented determination of $g_{\parallel}$ and $A_{\parallel}$. The g factor values of $g = 2.11$ (solid state), $g = 2.13$ (107, 150, 200 K) and $g = 2.06$ (288, 250, 230 K) in CH_3CN solution are consistent with five-coordinate systems involving a distorted TBP conformation. Compared with ESR spectra of a similar compound reported by Xing-You Xu *et al.* [7], there is a basic similarity in appearance, but somewhat different parameters such as g values, associated with the similar structure and the substitution of the hydroxyethyl pendant for an aminoethyl group in the complex.

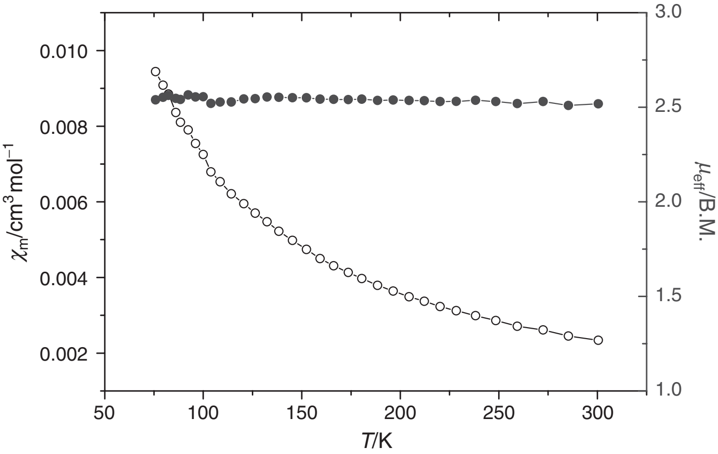

Figure 3. Temperature dependence of the magnetic susceptibility in the form χ_m (○) and μ_{eff} (●) versus T.

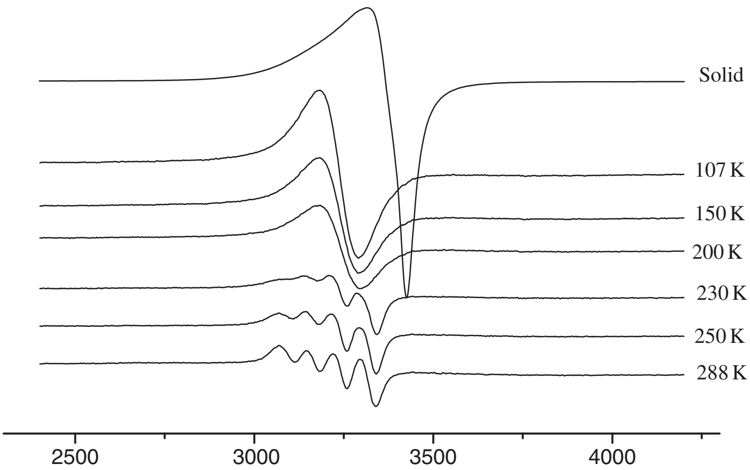

Figure 4. ESR spectra of CH_3CN solution at various temperatures.

3.4. *Cyclic voltammetric study*

Measurements were carried out in mixed water solution of sodium dihydrogen phosphate and disodium hydrogen phosphate with a pH value of 6.8 and using a three-electrode cell in which a glassy carbon electrode was the working electrode, saturated calomel electrode was the reference electrode and platinum wire was used as the counter electrode. The working electrode was polished with fine emery paper and aluminum oxide powder on chamois leather. The electrode was activated in 0.01 M H_2SO_4 solution and then sonicated in water for 20 s after polishing. Adsorption of the Cu(II) complex on the pyrolytic graphite (PG) electrode was obtained by depositing a solution containing the complex onto the freshly polished PG. The cyclic voltammograms for the copper(II) complex were recorded in the potential

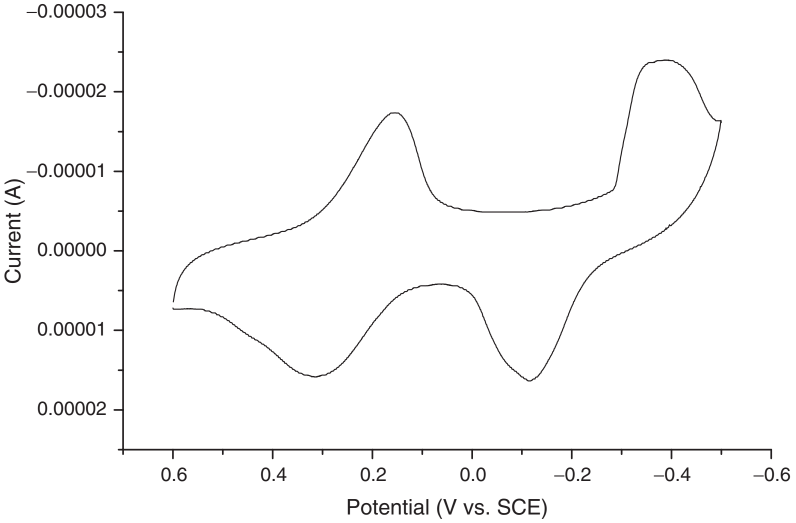

Figure 5. Cyclic voltammogram of the title complex at scan rate of $1\,\mathrm{mV\,s^{-1}}$.

Table 3. Cyclic voltammetric data of the title complex.

Redox couple	E_{pa} (V)	E_{pc} (V)	ΔE (mV)	$E_{1/2}$ (V)	I_{pa}/I_{pc}	$\Delta E_{1/2}$ (V)
$Cu^{II}Cu^{II}/Cu^{I}Cu^{II}$	0.316	0.155	161	0.236	1.01	0.489
$Cu^{I}Cu^{II}/Cu^{I}Cu^{I}$	−0.116	−0.389	273	−0.253	0.61	

range of −0.1 to 0.5 V with scan rate of $1\,\mathrm{mV\,s^{-1}}$. As shown in figure 5, two reduction waves are obtained in the cathodic region corresponding to stepwise one-electron reductions through a $Cu^{I}Cu^{II}$ intermediate to give a binuclear Cu^{I} species. The two redox processes are assigned as follows: $Cu^{II}Cu^{II} \overset{e}{\rightleftharpoons} Cu^{II}Cu^{I} \overset{e}{\rightleftharpoons} Cu^{I}Cu^{I}$. The cyclic voltammetric data of the two redox couples are summarized in table 3. In the redox couple $Cu^{II}Cu^{II}/Cu^{I}Cu^{II}$, the peak separation ΔE [20] and I_{pa}/I_{pc} value of 161 mV and 1.01, respectively, indicate a quasi-reversible electrode reaction. For the other redox couple, ΔE was 273 mV, and I_{pa}/I_{pc} value was 0.61, so the electrode reaction was also quasi-reversible, corresponding to the redox couple $Cu^{II}Cu^{I}/Cu^{I}Cu^{I}$. The large separation between the potentials of the couple also suggests high stability of the mixed-valence species. It could be related to the exchange interaction between the metal centers though a 4,4′-bipy bridge [21].

3.5. *Antimicrobial activity*

The title complex $[(OH22)Cu(4,4'\text{-bpy})Cu(OH22)](ClO_4)_4$ (**a**) was active against four test organisms with no exception (see table 4). The values of the antimicrobial activity of the similar bicopper complex $[(tren)Cu(4,4'\text{-bpy})Cu(tren)](ClO_4)_4$ (**a′**) [7] was also tested for comparison. In the range 15.0–1.9 $\mathrm{mg\,mL^{-1}}$, these compounds were more active against the test strains with increase of concentration. The highest antimicrobial activity among the group of these organisms was observed against *Staphylococcus aureus*. Small difference in antimicrobial activity between the two complexes was

Table 4. The diameter of inhibition zone (in mm).

Complex	Conc. of complex (mg mL^{-1})	Diameter of inhibition zone (mm)			
		Candida albicans	*Staphylococcus aureus*	*Bacillus pumilus*	*Eschierichia coli*
Complex **a**	15.0	23.1	28.5	24.6	24.5
	7.5	20.3	27.1	21.6	22.8
	3.8	17.8	24.6	17.9	20.1
	1.9	15.4	23.1	14.1	18.7
Complex **a**′	15.0	21.9	27.8	24.1	23.5
	7.5	19.7	26.5	22.3	20.3
	3.8	18.9	22.3	16.5	19.7
	1.9	16.3	16.1	13.9	19.5

observed, mainly due to the substitution of –CH_2CH_2OH for –$CH_2CH_2NH_2$ in the title complex, and this result produced by group substitution is consistent with a previous study [17].

Supplementary material

Crystallographic data for the structures in this article have been deposited with the Cambridge Crystallographic Data Centre (CCDC) as supplementary publication no. CCDC 240984 for the title complex. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK.

Acknowledgement

This work was supported by the Key Laboratory of Marine Biotechnology of Jiangsu Province.

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