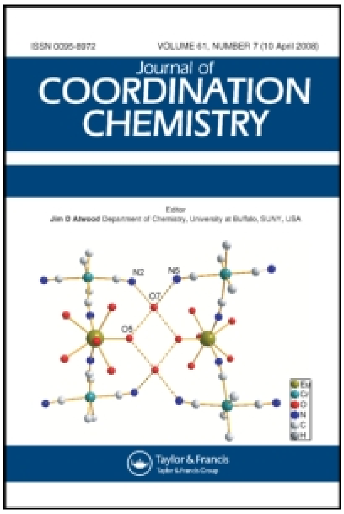

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

A tetranuclear copper(II) complex: crystal structure, assembly, EPR, electrochemistry and magnetism

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To cite this Article Zhou, Hong , Yan, Xiaofei , Peng, Zhenghe , Pan, Zhiquan , Song, You and Huang, Qimao(2009) 'A tetranuclear copper(II) complex: crystal structure, assembly, EPR, electrochemistry and magnetism', Journal of Coordination Chemistry, 62: 4, 655 — 664, First published on: 01 October 2010 (iFirst)

To link to this Article: DOI: 10.1080/00958970802251773

URL: http://dx.doi.org/10.1080/00958970802251773

Journal of Coordination Chemistry
Vol. 62, No. 4, 20 February 2009, 655–664

A tetranuclear copper(II) complex: crystal structure, assembly, EPR, electrochemistry and magnetism

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(*Received 2 February 2008; in final form 15 April 2008*)

A tetranuclear copper(II) complex, $[Cu_2L]_2(ClO_4)_2 \cdot 4H_2O$ (**1**), where $H_3L = N,N'$-*bis* (4-(3′-formyl-5′-chlorosalicyclidene)iminoethyl)-4-chloro-2,6-bimethyliminophenol, has been synthesized and structurally characterized by ES-MS, IR and X-ray crystallography. The complex is a dimer of two dinuclear copper(II) acylic enantiomorph subunits ($[Cu_2L]ClO_4 \cdot 2H_2O$), held together by π–π, coordination and hydrogen bond interactions. The Cu–Cu separation in each subunit, bridged by one phenoxide, is 3.228 Å, and the shortest distance of Cu–Cu between the two subunits is 3.252 Å. There are two crystallographically unique copper(II) environments, one (Cu1) is square-based pyramidal with O_3N_2 donor set, another (Cu2) square planar with O_2N_2 donor set. The cyclic voltammogram of the complex shows that it undergoes two stepwise reduction processes, $E_{pc} = -0.707$ and -0.850 V, respectively. Magnetic measurements in the 2–300 K range indicate strong antiferromagnetic interactions between Cu(II) ions in each subunit with the exchange constant $J = -211(2)\,cm^{-1}$. The observation has been rationalized on the basis of the effective magnetic pathway.

Keywords: Crystal structure; Self-assembly; Magnetism; EPR; Electrochemistry

1. Introduction

Schiff-base complexes, derived from condensation of 2,6-diformyl-4-R-phenol and alkylenediamine, have been extensively studied, and varieties of the dinuclear and polynuclear complexes have been synthesized and characterized [1–4]. Assembly between two macrocyclic units in these complexes is formed by coordination interactions via μ-oxo ligands [5, 6] or small molecules or anions bridging [7–9]. However, to our knowledge, no assembly derived from direct interactions between the ligands has been found in these kinds of complexes. Herein, we report the synthesis and crystal structure of a tetranuclear copper(II) Schiff-base complex $[Cu_2L]_2(ClO_4)_2 \cdot 4H_2O$ (**1**), which is obtained by [3 + 2] condensation of 2,6-diformyl-4-chloro-phenol and

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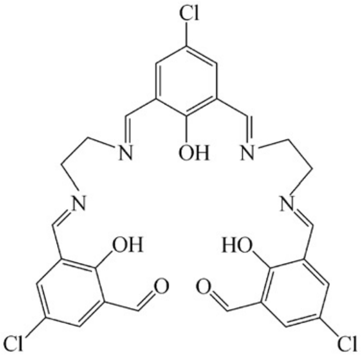
Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online © 2009 Taylor & Francis
DOI: 10.1080/00958970802251773



Scheme 1. The formula structure of the ligand.

ethenyldiamine and has special self-assembly behavior. To understand the effect of the structure on the properties, the electrochemical and magnetic properties have also been investigated. The structure of H_3L is shown in scheme 1.

2. Experimental

2.1. *Materials*

All solvents and chemicals were of analytical grade and used as received, except methanol, which was dried to absolute by general method. 2,6-Diformyl-4-chlorine-phenol and *N*,*N*′-*bis*(3-formyl-5-chloro-salicylidene) ethylenediimine (L′) were prepared according to the literature methods [10].

2.2. *Preparation of the complex*

2.2.1. *N*,*N*′-*bis*(4-(3′-formyl-5′-chloro-salicyclidene)imineethyl)4-chloro-2,6-dimethyliminophenol (H_3L). A suspension of L′ (0.294 g, 0.75 mmol) in absolute methanol (30 mL) and a solution of 2,6-diformyl-4-chlorine-phenol (0.138 g, 0.75 mmol) in absolute methanol (20 mL) were mixed and refluxed for 3 h. An absolute methanol solution (10 mL) of ethylenediamine (0.045 g, 0.75 mmol) was added dropwise, and the mixture was stirred at ambient temperature for 24 h. The resulting solution was filtered, and the orange solid was recrystallized from methanol. Yield: 0.329 g (73%). Anal. Calcd for $C_{28}H_{23}Cl_3N_4O_5$ (%): C, 55.88; H, 3.85; N, 9.31. Found: C, 55.76; H, 3.62; N, 9.54; IR (KBr, cm^{-1}): 1680 (C=O), 1633 (CH=N).

2.2.2. $[Cu_2L]_2(ClO_4)_2 \cdot 4H_2O$ (1). To a suspension of H_3L (0.15 g, 0.25 mol) in absolute methanol (30 mL), triethylenediamine (1 mL), $Cu(OAc)_2 \cdot H_2O$ (0.05 g, 0.25 mmol) and $Cu(ClO_4)_2 \cdot 6H_2O$ (0.09 g, 0.25 mmol) were added in sequence. The mixture was stirred at ambient temperature for 8 h, and then the resulting solution was filtered. Cube black crystals suitable for X-ray diffraction were obtained by slow evaporation of the mother solution. Yield 0.09 g (41%). Anal.

Calcd for $C_{56}H_{48}Cl_8Cu_4N_8O_{22}$ (%): C, 39.04; H, 2.81; N, 6.50. Found: C, 39.37; H, 2.61; N, 6.72; IR (KBr, cm^{-1}): 3446 (O–H), 1672 (C=O), 1628 (CH=N), 1099 (ClO_4^-) and 624(ClO_4^-).

2.3. *Physical measurements*

IR spectra were recorded on a Vector 22 FT-IR spectrophotometer using KBr discs. Electronic spectra were performed on an UV-2450 spectrophotometer. Elemental analyses were measured with a Perkin-Elmer 240 analyzer. Electrospray mass spectra (ES-MS) were determined on a Finnigan LCQ ES-MS mass spectrograph using methanol as the mobile phase with a concentration of $1.0\,\mathrm{mmol\,mV^{-1}}$. This diluted solution was electrosprayed at a flow rate of $5 \times 10^{-6}\,\mathrm{mV\,min^{-1}}$ with a needle voltage of 4.5 kV. The temperature of the heated capillary in the interface was set at 200°C and a fuse silica sprayer was used.

Magnetic susceptibility of a crystalline-powdered sample was measured on a SQUID-based sample magnetometer in the temperature range $2.0 \sim 300\,\mathrm{K}$, and diamagnetic corrections were made according to Pascal's constants. EPR spectra were recorded at room temperature on a Bruker EMX-10/12 spectrometer operating at 9.4 GHz with DPPH as an external calibrant. Cyclic voltammograms were run on a CHI model 750 B electrochemical analyzer in DMF solution containing tetra (*n*-butyl)ammonium perchlorate (TBAP) as the supporting electrolyte. A three-electrode cell was used, which was equipped with a glassy carbon-working electrode, a platinum wire as the counter electrode, and a Ag/AgCl electrode as the reference electrode. Scanning rates were in the range of $20 \sim 200\,\mathrm{mV\,s^{-1}}$. The solution was deaerated for 15 min before measuring. The half-wave potentials were calculated approximately from $(E_{pa} + E_{pc})/2$, and the measured error was $\pm 2\,\mathrm{mV}$.

2.4. *Crystal structure determination*

Diffraction intensity data were collected on a SMART-CCD area-detector diffractometer at 293 K using graphite monochromatic Mo-Kα radiation ($\lambda = 0.71073$ Å). Data reduction and cell refinement were performed by the SMART and SAINT programs [11]. The structure was solved by direct methods (Bruker SHELXTL) and refined on F^2 by full-matrix least squares (Bruker SHELXTL) using all unique data [12]. The non-H atoms in the structure were treated as anisotropic. Hydrogen atoms were located geometrically and refined in riding mode.

3. Results and discussion

3.1. *Synthesis of the complex*

In the preparation of the complex, the first step is to synthesize the acylic Schiff-base ligand H_3L, obtained by Schiff-base condensation of *N*,*N′*-*bis*(3-formyl-5-chloro-salicylidene) ethylenediimine (L′), 2,6-diformyl-4-chloro-phenol and ethylenediamine in 1 : 1 : 1 molar ratio. The reaction of H_3L with $Cu(OAc)_2 \cdot H_2O$ and $Cu(ClO_4)_2 \cdot 6H_2O$ in absolute methanol gives **1**. Triethylenediamine is required to avoid destruction of the Schiff base due to protonation [10].

3.2. *IR and UV-Visible spectra*

In the IR spectra of **1**, the intense absorption band at 1672 cm^{-1} is assigned to $\nu(\mathrm{C{=}O})$, which shifts to lower frequency by 8 cm^{-1} compared with C=O in the ligand. The shift can be ascribed to decreasing electron density of the C=O bond caused by hydrogen bond interaction and the electron withdrawing effect of copper(II) [13]. The band at 1628 cm^{-1} shows formation of –CH=N [9, 10, 14]. In addition, the complex is characterized by the intense perchlorate absorption at 1099 ($\nu_{\mathrm{ClO}_4^-}$) cm^{-1}, and the out-of-plane bending vibration at 624 ($\delta_{\mathrm{ClO}_4^-}$) cm^{-1}. The unsplit IR band at 1099 cm^{-1} is in accordance with the crystal structure determinations, which indicates that perchlorate is not coordinating in **1**. The strong absorption band in the electronic spectra of **1** at 269 nm was attributed to the π–π^* transition [15, 16], the band at 408 nm to the charge transition from phenol and azomethine to copper(II) [2] and the copper-based d–d band at ca 581 nm [17].

3.3. *ES-MS spectra*

The ES-MS spectrum of **1** in methanol (shown in Supplementary Material) has a fragment at m/z 202.3 ascribed to $[\mathrm{Cu_2H_2L(H_3O)(CH_3OH)}]^{4+}$ as the molecule ion peak. Peaks at $m/z = 238.3$, 504.9 and 491.0 are attributed to $[\mathrm{CuH_2L(H_3O)(CH_3OH_2)}]^{3+}$, $[\mathrm{Cu_2L(H_3O)(ClO_4)_2(CH_3OH_2)_2}]^{2+}$ and $[\mathrm{Cu_2L(H_3O)_3(ClO_4)_2}]^{2+}$, respectively. Associations between cationic complexes and counteranions are very common in ES-MS and have been tentatively attributed to electrostatic interactions. The three main peaks in the complex contain $[\mathrm{Cu_2L}]^+$, indicating that $[\mathrm{Cu_2L}]^+$ has better stability in methanol.

3.4. *Crystal structures of* $[\mathrm{Cu_2L}]_2(\mathrm{ClO_4})_2\cdot 4\mathrm{H_2O}$

The perspective view of the cation of **1** is given in figure 1, with the atom-numbering scheme. The crystal data and details of the structure determination are listed in table 1. Selected bond lengths and angles relevant to the copper coordination spheres of the complex are listed in table 2. The structure of the complex can be described as a dimer of a pair of dinuclear copper(II) $[\mathrm{Cu_2L}]\mathrm{ClO_4}\cdot 2\mathrm{H_2O}$ subunits. The coordination spheres of Cu1 and Cu2 are different; the former has a square pyramid with $\mathrm{O_3N_2}$ donor atoms while the latter is square planar with $\mathrm{O_2N_2}$ donor atoms. For Cu1 the apical O2A, bridging the two Cu(II) ions in adjacent subunits, has somewhat longer contact Cu(1)–O(2A) (2.685 Å) that is within the range observed for axial copper–oxygen bonds [7]. In the basal plane Cu-ligand distances fall in the range 1.895–1.967 Å for Cu1 and 1.892–1.946 Å for Cu2. The Cu–Cu distances are Cu1–Cu2 3.228 Å, Cu1–Cu1A 3.252 Å, Cu2A–Cu1 4.934 Å, Cu2A–Cu2 7.679 Å, and the bond angles of Cu1–O2A–Cu1A and Cu1–O1–Cu2 are 88.65 and 111.90°, respectively. The Cu1–O2A bond is almost perpendicular to the coordination plane of Cu1 (86.0°). The two coordination planes constituted by the coordination atoms in the basal planes of Cu1 and Cu1A are parallel and the distance between centroid-centroid coordination planes is 3.396 Å.

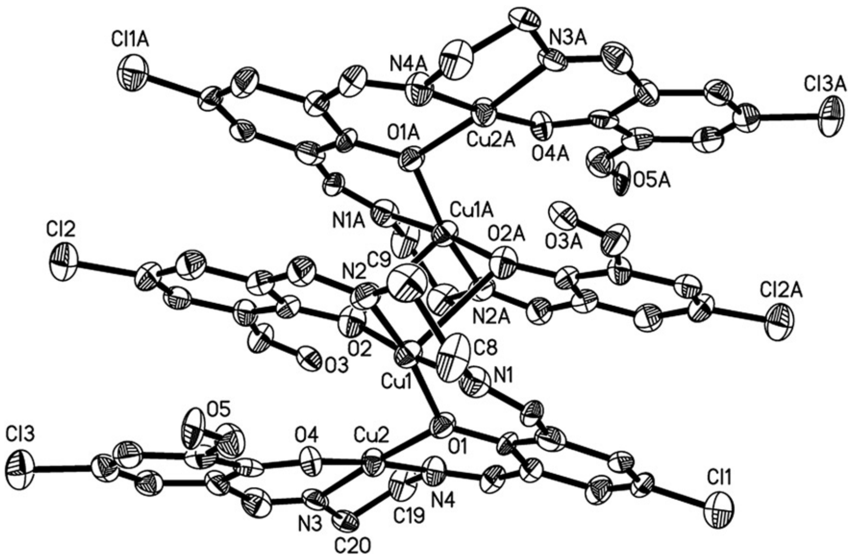


Figure 1. The cation perspective view of **1** showing 30% probability thermal ellipsoids; hydrogen atoms are omitted for clarity.

Table 1. Crystal data and details of the structure determination for **1**.

Formula (weight)	$C_{56}H_{48}Cl_8Cu_4N_8O_{22}$ (1722.82)
Crystal system	Triclinic
Space group	$P\bar{1}$ (No. 2)
Unit cell dimensions (Å, °)	
a	11.19(1)
b	11.37(2)
c	14.38(2)
α	107.279(3)
β	95.520(3)
γ	100.807(3)
V (Å ^{3})	1692.8(4)
Z	1
D_{Calcd} (g cm^{-3})	1.690
u(Mo-Kα) (mm)	1.636
F(000)	868
Crystal size (mm^3)	0.24 × 0.26 × 0.30
Temperature (K)	293
Radiation (Å)	Mo-Kα 0.71073
θ min-max (°)	2.0, 26.0
Data set	−13: 13; −14: 13; −10: 17
R, wR_2, S	0.0596, 0.1363, 1.05
Min. and max. resd.	−0.46, 0.31

Unlike previously structurally characterized dimer of the copper(II) complexes of this type, formed only through coordination interactions [5, 6], **1** is a dimer maintained by three kinds of interactions between the two subunits. One is the coordination interactions described above, another is the intramolecular hydrogen bonds of C9A–H9BA $\cdots$ O3 and C9–H9B $\cdots$ O3A (2.408 Å), and the most important ones are

Table 2. Selected bond lengths (Å) and angles (°) of **1**.

Cu1–O1	1.951(4)	Cu1–O1–Cu2	111.9(2)
Cu1–O2	1.899(4)	Cu1–O2–Cu1a	88.7(2)
Cu1–N1	1.967(5)	O1–Cu1–O2	92.5(2)
Cu1–N2	1.895(5)	O2–Cu1–N2	92.7(2)
Cu2–O1	1.946(3)	O1–Cu1–N1	90.5(2)
Cu2–O4	1.892(3)	N1–Cu1–N2	85.2(2)
Cu2–N3	1.927(4)	N3–Cu2–N4	85.0(2)
Cu2–N4	1.901(4)		

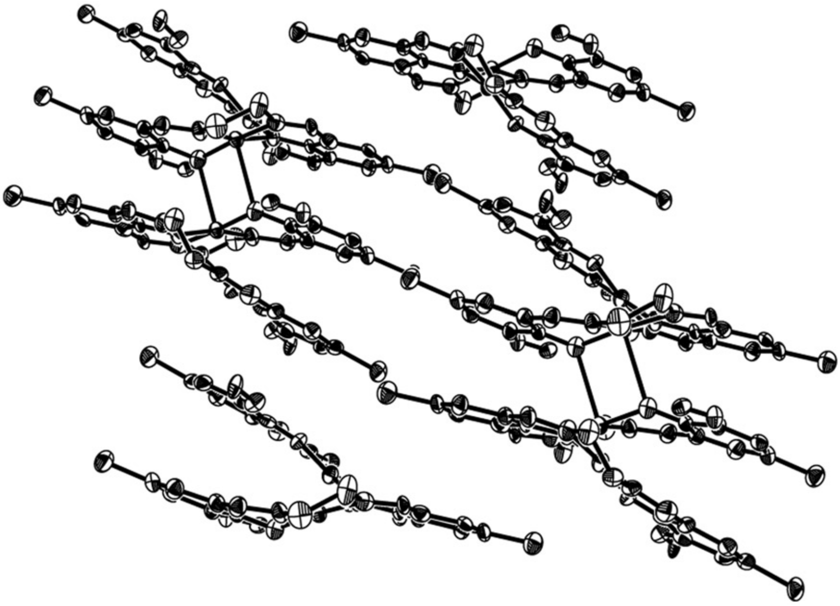


Figure 2. Molecular stacking diagram in two-dimensional sheet structure (showing dimer and one-dimensional chain, respectively).

the strong π–π aromatic interactions between the adjacent phenyl planes in the dimer. The phenyl rings located on both sides of the dimer are face to face stacked with centroid-centroid distance of 3.638 and 3.658 Å, and the angles between phenyl ring planes of 7.1 and 7.2°, respectively. The contortions of N1–C8–C9–N2 and N3–C20–C19–N4, (39.2°, 36.5°), with considerably larger twists of the two coordination planes (Cu1 and Cu2, 57.9°), contribute to the π–π interactions of the phenyl rings.

Intermolecular π–π interactions are also observed between adjacent phenyl planes of two dimers with centroid-centroid distance of 3.757 Å, weaker than the intramolecular π–π interactions (figure 2). Furthermore, the three-dimensional structure is maintained by hydrogen bond interactions between different dimers (C8–H8A ⋯ O10, 2.470 Å and C18–H18 ⋯ O10, 2.460 Å) [18].

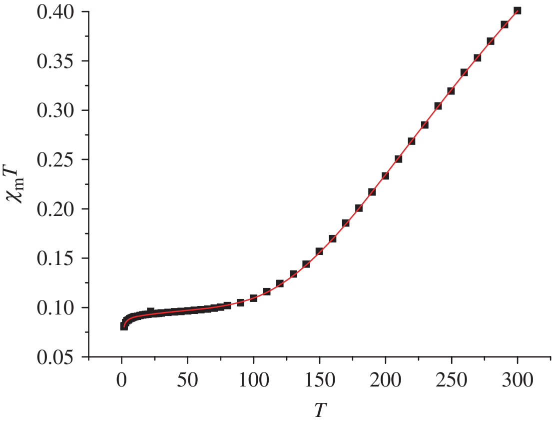


Figure 3. Plot of the temperature dependence of χ_MT (emu K mol^{-1}) *vs.* T(K) for **1**. The solid line shows the best fit with equation 1.

3.5. *Magnetic studies*

Variable-temperature (2–300 K) magnetic susceptibility data were collected for the crystalline powdered sample of **1**. Gradual decrease in $\chi_M T$ is observed as the temperature decreases (figure 3), indicating an overall antiferromagnetic interaction. From the molecular structure of **1**, the tetranuclear copper was treated as a linear tetramer system, ignoring interactions between two interval copper ions due to the long distances between them. Because of the existence of the center of symmetry in the dimer, the coupling constant of the two Cu(II) ions in each subunit is the same, defined as J_1, that of the two adjacent Cu(II) ions in different subunits is defined as J_2. However, it is not physically acceptable to model this system with the expression of χ_M for this type of linear tetranuclear copper complex [19].

In the coordination structure of the dimer, there are two kinds of the bridged phenoxides in the complex. One links two Cu(II) ions (Cu2–O1–Cu1 or Cu1A–O1A–Cu2A) with two short equatorial Cu–O bonds, Cu1–O1 (1.951 Å), Cu2–O1 (1.946 Å), and the magnetic exchange can be enhanced by the effective orbit overlap of two copper(II) through Cu2–O–Cu1 or Cu1A–O–Cu2A. Another links two Cu(II) ions with one equatorial Cu1–O2 bond (1.899 Å) and one long axial Cu1A–O2 (2.685 Å) bond. This type of equatorial-axial linking is well known to be much smaller in terms of magnetic exchange than the equatorial-equatorial one [20]. It is reasonable to consider only Cu1–Cu2 as a basic magnetic unit, and treat the very weak coupling constant (J_2) as zero, which is confirmed by Fallon *et al.* using the appropriate tetramer model [20]. The Bleaney-Bowers expression for the magnetic susceptibility [21, 22], taking into account paramagnetic impurities, is:

$$\chi = \frac{2Ng^2\beta^2}{kT} \times \frac{1}{3 + e^{-2J/kT}} \times (1 - \rho) + \rho \times \frac{Ng^2\beta^2}{2kT} \qquad (1)$$

An excellent fit of the data can be obtained with $g = 2.08(1)$, $J = -211(2)\,\mathrm{cm^{-1}}$, $\rho = 0.05(0)$, *TIP* value of $12 \times 10^{-5}\,\mathrm{cm^3\,mol^{-1}}$, which results in a coefficient of determination of $r^2 = 0.9994$ (solid lines in figure 3). The agreement factor defined as $\Sigma(\chi_M T^{\text{Calcd}} - \chi_M T^{\text{obsd}})^2/\Sigma(\chi_M T^{\text{obsd}})^2$ is equal to 5.8×10^{-6}. The J value is lower than

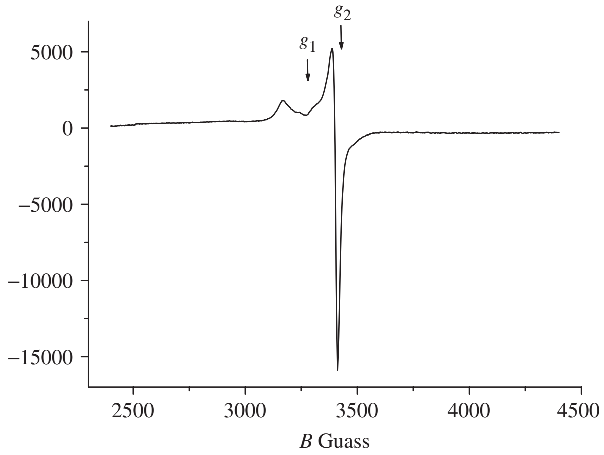


Figure 4. EPR spectra of **1** determined at room temperature on crystalline powder sample.

those of macrocyclic dinuclear copper(II) complexes [16], bridged by two phenoxide groups, partially due to more effective superexchange pathway and shorter distance between the two Cu(II) ions in macrocyclic dinuclear copper(II) complexes than those in this complex.

3.6. *EPR studies*

The X-band EPR spectrum obtained for the crystalline powdered sample of **1** at room temperature is shown in figure 4. No detectable zero field splitting or half-filled signal were observed. The calculated EPR parameters are $g = 2.13$, $g_{\perp} = 2.055$, respectively. $g_{\text{av}} = 2.08$, where $g_{\text{av}} = 1/3(g + 2g_{\perp})$, consistent with the g value derived from the calculated value from magnetism. The fact of $g > g_{\perp} > 2.0023$ indicates that the unpaired electron predominantly occupies the $d_{x^2-y^2}$ orbital [23], in agreement with the magnetic behavior.

3.7. *Electrochemistry studies*

Redox properties of **1** have been investigated by cyclic voltammetry in DMF. Cyclic voltammograms of the complex at different scan rates are shown in figure 5. When scanning from 0 to −1.2 V at a scan rate of $50\,\text{mV}\,\text{s}^{-1}$, two successive reduction waves at $E_{\text{pc}} = -0.707$ and $-0.850\,\text{V}$ are observed.

$$2[\text{Cu(II)Cu(II)L}] \xrightarrow{+2e} 2[\text{Cu(II)Cu(I)L}] \underset{-2e}{\overset{+2e}{\rightleftharpoons}} 2[\text{Cu(I)Cu(I)L}]$$

The latter appears to be very weakly pseudo-reversible ($\Delta E = 0.156\,\text{V}$, $v = 50\,\text{mV}\,\text{s}^{-1}$), whereas the first is fully irreversible. The first electron-transfer reaction in the complex can be ascribed to the square-planar Cu(II) site because it is easier to be reduced than that of Cu(II) in a square pyramid. The first reduction potential is more negative

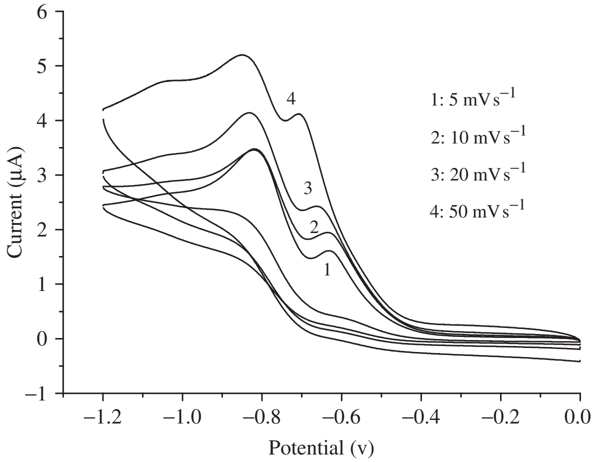


Figure 5. Cyclic voltammogram of **1** in DMF at different scan rates.

than those of related macrocyclic complexes [26], indicating that complex is more difficult to reduce. This can be ascribed to more electron density around the square-pyramidal Cu(II) in the complex because the Cu(II) in **1** only shares one phenolate oxygen with another Cu(II), while each Cu(II) in the similar macrocyclic complex shared two phenolate oxygens. The pseudo-reversible process appears at half wave potential −0.757 V. With the enhancement of the scan rates, the ratio of $i_{pc}/v^{1/2}$ increases and the value of E_{pc} becomes more negative, and an augmentation in height of the cathodic peak occurs to greater extent than the anodic peak, revealing that the reduced Cu(I)Cu(I) species is weakly adsorbed on the electrode surface [9].

4. Conclusion

The tetranuclear complex, $[Cu_2L]_2(ClO_4)_2 \cdot 4H_2O$, was formed by three interactions, π–π, coordination, and hydrogen bond between two subunits. Compared with similar macrocyclic ligands, the more flexible and longer structure of H_3L effects the assembly and properties of **1**: 1) the contortions of the structure lead to special assembly; 2) the non coplanar character of the coordination sites in each subunit results in lower antiferromagnetic interactions; 3) the complex has more negative potential of the first one-electron reduction because the Cu(II) ions have more electron density relative to those of similar macrocyclic complexes.

The CCDC number for **1** is 656513.

Acknowledgements

The authors express thanks to Local Key Foundation of the Education Department of Hubai Province, China (No. D20081503), and the National Nature Science Foundation of China (20271039).

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