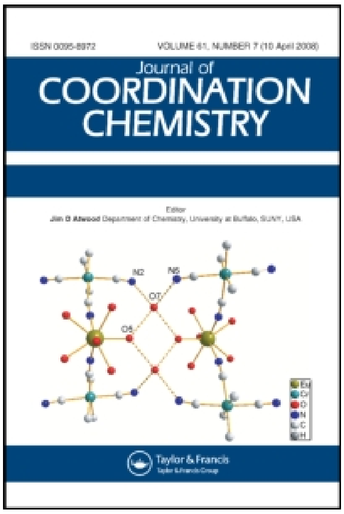

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Synthesis, X-ray crystal structure and electrochemical properties of (dithiolato)(diimine)copper(II) complexes: [Cu(mnt)(phen)]<i>n</i> and [Cu(dmit)(phen)]2

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To cite this Article Guo, Wen-Yong , Peng, Zheng-He , Wang, Cheng-Gang and Zhou, Yun-Hong(2006) 'Synthesis, X-ray crystal structure and electrochemical properties of (dithiolato)(diimine)copper(II) complexes: **[Cu(mnt)(phen)]**<i>n</i> **and [Cu(dmit)(phen)]**2', Journal of Coordination Chemistry, 59: 11, 1213 — 1223
To link to this Article: DOI: 10.1080/00958970500471103
URL: http://dx.doi.org/10.1080/00958970500471103

Journal of Coordination Chemistry
Vol. 59, No. 11, 20 July 2006, 1213–1223

Synthesis, X-ray crystal structure and electrochemical properties of (dithiolato)(diimine)copper(II) complexes: $[Cu(mnt)(phen)]_n$ and $[Cu(dmit)(phen)]_2$

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(*Received 13 April 2005; in final form 24 August 2005*)

Copper (II) complexes $[Cu(dmit)(phen)]_2$ (**1**) and $[Cu(mnt)(phen)]_n$ (**2**) (mnt^{2-} = maleonitrilemaleonitriledithiolate, $dmit^{2-}$ = 1,3-dithiole-2-thione-4,5-dithiolate, phen = 1,10-phenanthroline) have been prepared by ligand-exchange between phen and $[N(Bu)_4]_2[Cu(dmit)_2]$ or $[N(Bu)_4]_2[Cu(mnt)_2]$. Both complexes have been characterized by spectroscopic, electrochemical, and single-crystal X-ray analysis. In complex **1**, dimers are extended into a two-dimensional array by weak S5–Cu contacts. In complex **2**, monomers are extended into chains in a head-to-tail arrangement by weak Cu–S coordination bonds and π–π stacking interactions.

Keywords: Copper(II) complex; Dithiolate; Diimine; Single-crystal structure; Dimer; Cyclic voltammetry

1. Introduction

Over the past decade, polarized metal complexes with both sulfur-rich and diimine ligands have attracted interest because they, or their oxidized compounds, can be expected to form electrical conductors, molecular conductors and superconductors [1–3]. They also may be used as nonlinear optical materials [4] and solar cell dyes [5, 6] owing to their charge-transfer and spectroscopic properties. In addition, the complex (SP)Cu(mnt) (SP = (−)sparteine (6R, 11S)) with a distorted tetrahedral geometry has been studied as a model of blue copper protein [7]. In past studies, the dithiolates employed were mnt, dmit, dmid(1,3-dithiole-2-oxo-4,5-dithiolate) or others, the diimines were phen, bpy(2,2′-bipyridine) or their derivatives, and the metals were Pt, Pd, Ni, Zn, Cd and Au in the mixed-ligand complexes (dithiolato)(diimine)M.

This article reports the synthesis of two new mixed-ligand Cu(II) complexes $[Cu(dmit)(phen)]_2$ (**1**) and $[Cu(mnt)(phen)]_n$ (**2**), which were studied by IR, UV-Vis, cyclic voltammetry and X-ray structure analysis.

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Journal of Coordination Chemistry
ISSN 0095-8972 print: ISSN 1029-0389 online © 2006 Taylor & Francis
DOI: 10.1080/00958970500471103

2. Experimental

2.1. *Reagents and instrumentation*

All solvents were dried and distilled using standard methods. All reagents were obtained from Shanghai Chemical Reagents Company and used as received. The benzoyl salt dmit$(COPh)_2$ was prepared following the method of Steimeche and co-workers [8]. The dimt^{2-} anion was generated in solution by reaction of dmit$(COPh)_2$ with 2 mol equivalents of sodium methoxide at room temperature [9]. The sodium salt of maleonitriedithiolate salt (Na_2mnt) was prepared by methods previously reported [10].

The infrared spectra were recorded in the 400–4000 cm^{-1} region, using KBr pellets on a Nicolet 170SX FT-IR spectrometer. Electronic spectra were performed in the range 200–900 nm on a Shimadzu UV-240 spectrometer in N,N-dimethylformamide (DMF) solution.

Cyclic voltammetry was performed in a conventional two-compartment cell with Ohmic resistance compensation at room temperature. A glassy carbon electrode of area 0.07 cm^2 (BAS M2070) was used as the working electrode. The counter electrode was a platinum wire loop and an Ag/$AgNO_3$ (0.1 mol L^{-1} in CH_3CN) electrode was used as the reference electrode. Cyclic voltammetry was performed with a CHI potentiostat 660B (CH Instruments Inc. USA) at a scan rate of 0.100 V s^{-1}. Dry DMF was purified by distillation from CaH_2, and TBAP was recrystallizated from absolute ethanol and dried in a vacuum oven at 120°C for 24 h.

Elemental analyses were carried out on a Perkin-Elmer 2400LS II CHNSO elemental analyzer. The Cu content was measured by EDTA titration. Thermal analyses were performed with a Perkin-Elmer TGS-Z thermogravimetric analyzer in the range of 40–750°C at a rate of 10°C min^{-1} under N_2.

2.2. *X-ray data collection and structure determination*

Crystals of both compounds ($0.23 \times 0.20 \times 0.20\,mm^3$ for **1**, and $0.20 \times 0.18 \times 0.16\,mm^3$ for **2**) were mounted on a Bruker Smart/CCD area detector diffractometer and the data were collected using graphite-monochromated Mo-Kα ($\lambda = 0.71073$ Å) radiation. The structures were solved with direct methods (SHELXTL-97) [11] and refined by the full-matrix least-squares on F^2 methods (SHELXTL-97) [12]. Anisotropic thermal parameters were refined for non-hydrogen atoms. All hydrogen atoms were located from difference Fourier maps, placed at calculated positions (C–H: 0.93–0.97 Å) and refined isotropically using a riding model. The crystallographic data and the parameters of structure refinement are summarized in table 1.

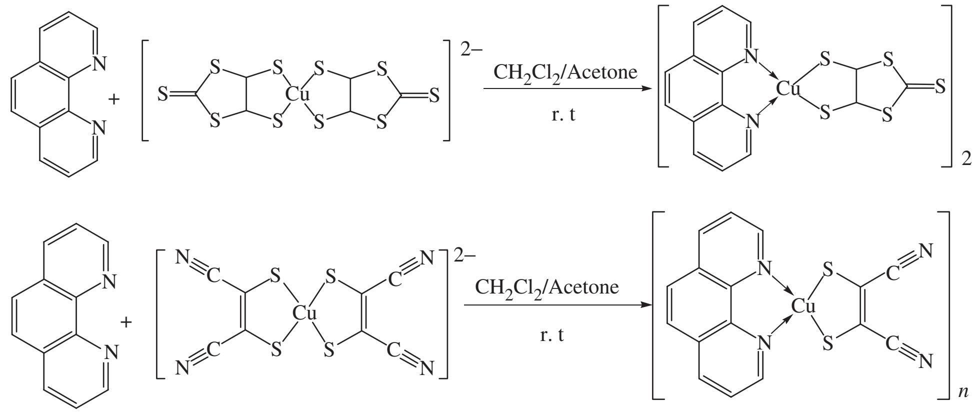
2.3. *Syntheses of copper complexes*

Bis(tetrabutylammonium)bis(maleonitriledithiolate)cuprate $[NBu_4]_2[Cu(mnt)_2]$ and Bis(tetrabutylammonium)bis(1,3-dithiole-2-thione-4,5-dimercapto)cuprate $[NBu_4]_2[Cu(dmit)_2]$ were prepared according to the literature method [10, 13].

2.3.1. $[Cu(dmit)(phen)]_2$ (1). A dichloromethane (30 mL) solution of $[N(Bu)_4]_2[Cu(dmit)_2]$ (94 mg, 0.1 mmol) was placed in a large test tube. To this solution was carefully layered a solution of phen (54 mg, 0.3 mmol) in 30 mL acetone. After the sealed test

Table 1. Crystal data and structure refinement for **1** and **2**.

Complex	**1**	**2**
Colour/Shape	Red/Prismatic	Red/Prismatic
Formular weight	880.14 (dimer)	383.92 (monomer)
Crystal size (mm^3)	$0.23 \times 0.20 \times 0.20$	$0.20 \times 0.18 \times 0.16$
Crystal system	Monoclinic	Orthorhombic
Space group	$P2(1)/n$	$Pbcn$
Temperature (K)	291(2)	293(2)
Unit cell dimensions (Å, °)		
a	9.561(2)	7.619(2)
b	13.695(3)	26.965(5)
c	12.519(3)	7.588(2)
α	90.00	90.00
β	92.50(3)	90.00
γ	90.00	90.00
Volume (Å^3)	1637.6(6)	1558.8(5)
Z	4	4
Density (calculated) ($g\,cm^{-3}$)	1.785	1.636
$F(000)$	884	772
Absorption coefficient (mm^{-1})	1.968	1.671
θ range for data collection (°)	$2.21 < \theta < 25.00$	$1.51 < \theta < 25.00$
Index ranges	$0 \le h \le 11$, $-16 \le k \le 16$, $-14 \le l \le 14$	$-9 \le h \le 0$, $-31 \le k \le 32$, $-8 \le l \le 8$
Reflections collected	3912	3880
Independent reflections	2354	1284
Data/restraints/parameters	2354/0/209	1284/0/110
Final R indices [$I > 2\delta(I)$]	$R = 0.0391$ $wR = 0.0658$	$R = 0.0877$ $wR = 0.0711$
Largest diff. peak and hole (e Å^{-3})	0.308 and −0.328	0.965 and −0.849
Absorption correction	None	None



Scheme 1. Synthesis of **1** and **2**.

tube was allowed to stand undisturbed in the dark at room temperature for 20 days, dark red crystals were obtained (scheme 1). The crystals were collected by filtration, washed with acetone and dried in vacuum. Yield: 36.5 mg (83%). $C_{15}H_8CuN_2S_5$ (440.1): Calcd. C, 40.94; H, 1.83; N, 6.37; Cu, 14.44. Found: C, 41.40;

H, 1.91; N, 6.35; Cu, 15.09. FT-IR (KBr pellet, cm^{-1}): 1580w, 1520m, 1430s, 1340m, 1220w, 1150w, 1100w, 1050vs, 1030vs, 910m, 835s, 775w, 717s, 644w, 514w.

2.3.2. [Cu(mnt)(phen)]$_n$ (2). A procedure similar to the above was used for the synthesis of **2**. Yield: 30.2 mg (79%). $C_{16}H_8CuN_4S_2$ (383.0): Calcd. C, 50.06; H, 2.10; N, 14.59; Cu, 16.55. Found: C, 49.72; H, 2.21; N, 14.37; Cu, 17.25. FT-IR (KBr pellet, cm^{-1}): 2920w, 2200s, 1690w, 1600w, 1580w, 1520m, 1480m, 1430vs, 1340w, 1320w, 1220w, 1150m, 1100w, 854s, 777w, 719vs, 644w, 500w.

3. Results and discussion

3.1. *IR/UV-Vis/Thermal analyses*

In the IR spectra of complex **1**, the C=S and S–C–S stretching bands of dmit show no apparent differences from those in similar complexes, for example, [Zn(dmit)(2,2′-bpy)]$_2$ [4] and [NBu$_4$]$_2$[Cu(dmit)$_2$] [11]. The absorption bands at 1430, 1050(1030), and 835 cm^{-1} can be attributed to $\nu_{C=C}$, $\nu_{C=S}$ and ν_{C-S} of the dmit^{2-} ligand. For **2**, the band at 2200, 1430, and 854 cm^{-1} are, respectively, attributed to $\nu_{C\equiv N}$, $\nu_{C=C}$, and ν_{C-S} of mnt^{2-}. The band at 1580 and 1520 cm^{-1} for the two complexes can be assigned to $\nu_{C=C}$ of the phen ligand. The other bands at 717 cm^{-1} for **1** and 719 cm^{-1} for **2** also originate from phen.

The electronic absorption bands measured in DMF in the range of 190–700 nm occur at 270, 296 (shoulder), 357 and 453 nm for **1**, and at 272, 298 (shoulder), 322 and 366 nm for **2**. For **1** the sharp band at 270 nm is assigned to the π–π* transition of the phen ligand. The shoulder at 296 and broad bands at 357 nm and 453 nm belong to the dmit^{2-} ligand transition [14, 15]. For **2** the sharp band at 272 nm is assigned to the π–π* transition of the phen ligand, overlapping with the mnt^{2-} ligand transition. The shoulder at 298 and broad bands at 322 and 366 nm belong to the mnt^{2-} ligand transition [14]. The ligand-to-ligand charge transfer (LLCT) was not found clearly for either complex. The intensities of LLCT transitions are usually much lower than transitions of the coordinated ligands and often appear at longer wavelength [16]. Therefore, for the two complexes the LLCT transitions bands may be very weak and obscured by broad bands of dithiolate ligands and thus could not be separately elucidated.

To study the thermal stability of **1** and **2**, thermo-gravimetric analysis (TGA) was performed on single crystal samples. The TGA curves indicated that **1** was stable below 202°C and one striking weight loss step occurred from 211 to 288°C (loss 9.77%); **2** was stable below 325°C and one striking weight loss step occurred from 331 to 395°C (loss 7.41%). In addition, both complexes had further weight loss at 422°C (from 422 to 580°C loss 13.22%) for **1** and 500°C (from 500 to 590°C loss 28.11%) for **2**, respectively. According to these results, **2** is more thermally stable than **1**.

3.2. *X-ray molecular structure*

The crystal data and structure refinement parameters for **1** and **2** are listed in table 1. Selected bond lengths and angles are collected in tables 2 and 3. The dimeric structure

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

Cu1–N1	2.039(4)	Cu1–N2	2.043(3)
Cu1–S1	2.261(1)	Cu1–S2	2.269(1)
S1–C13	1.728(4)	S2–C14	1.728(4)
N1–C1	1.326(5)	N1–C5	1.349(5)
N2–C10	1.323(5)	N2–C6	1.364(5)
N1–Cu1–N2	80.93(2)	N1–Cu1–S1	92.44(1)
N1–Cu1–S2	175.11(1)	N2–Cu1–S1	170.93(1)
N2–Cu1–S2	94.19(1)	S1–Cu1–S2	92.44(5)
C13–S1–Cu1	100.39(2)	C14–S2–Cu1	99.77(2)
C1–N1–Cu1	129.4(3)	C5–N1–Cu1	112.6(3)
C10–N2–Cu1	129.8(3)	C6–N2–Cu1	112.5(3)

Table 3. Selected bond lengths (Å) and angles (°) for **2**.

Cu1–N1	2.034(4)	Cu1–S1	2.260(2)
S1–C7	1.739(5)	N2–C8	1.137(8)
N1–C1	1.321(7)	N1–C5	1.366(7)
N1–Cu1–N1A	81.8(3)	N1–Cu1–S1	174.4(1)
S1–Cu1–S1A	91.7(7)	N1–Cu1–S1A	93.3 (1)
C7–S1–Cu1	101.4(2)	C1–N1–Cu1	130.3(4)
C5–N1–Cu1	112.5(4)	N2–C8–C7	178.0(6)

of **1** and the monomeric unit **2** with atom numbering schemes are shown in figures 1 and 2, respectively.

In both **1** and **2**, dithiolate and phen coordinate to Cu(II) as bidentate ligands, and the N_2CuS_2 cores exhibit distorted square planar geometry. The dihedral angle between dithiolate and phen is 7.3° for **1** and 2.4° for **2**, showing that the N_2CuS_2 core is more distorted in **1** than **2**. This distortion induced **1** to form dimers in a head-to-tail arrangement by weak coordination bonds (Cu1–S2A and Cu1A–S2, 3.148 Å) and π–π interactions between dmit^{2-} and phen from different monomers (the distance is about 3.26–3.37 Å). One of the sulfur atoms in each dmit^{2-} ligand of **1** acts as a μ_2-bridge to link two Cu atoms as in similar complexes, for example $[Zn(dmit)(bipy)]_2$, $[Cd(dmit)(bipy)]_2$ and $[Cd(dmit)(phen)]_2$ [4, 17]. In the corresponding complex as a model of blue copper protein, (SP)Cu(mnt) (SP = (−)sparteine (6R, 11S)), the core has a distorted tetrahedral geometry [7]. The bond angles of S1–Cu1–S2 for **1** and S1–Cu1–S1A for **2** are smaller than the corresponding angle for (SP)Cu(mnt) (94.47°). In all of these complexes, the average Cu–N distance is 2.03–2.04 Å and Cu–S (basal plane) bond length is 2.26 Å, in agreement with commonly observed values. The axial Cu–S distance in **1** is ca 3.15 Å longer than the average equatorial Cu–S distance, similar to those in $[Zn(dmit)(bipy)]_2$, $[Cd(dmit)(bipy)]_2$ and $[Cd(dmit)(phen)]_2$ [4, 15]. In addition, the Cu–Cu separation is 3.390 Å, indicating that there is no metal–metal interaction.

In the solid state, the two complexes show very different structural features (figures 3 and 4). In **2**, monomers are further extended into chains in a head-to-tail arrangement by weak Cu–S coordination bonds (Cu1D–S1A, 3.325 Å and Cu1D–S1AB, 3.325 Å) and π–π stacking interactions involving mnt group and proximal phen (the distance between centres is 3.29–3.35 Å). The range and strength of these interactions are similar to the monomeric units in **1**. There are two kinds of chains in **2**, with a dihedral angle

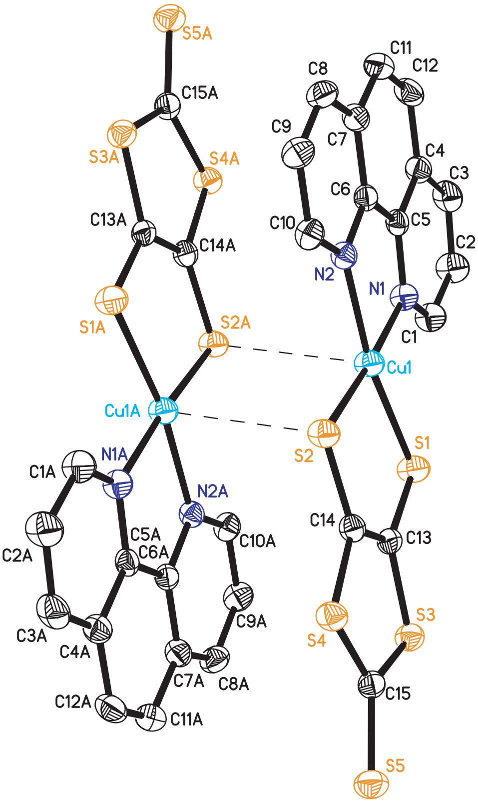


Figure 1. Molecular structure of **1** with the atom-labelling scheme. The hydrogen atoms are omitted for clarity.

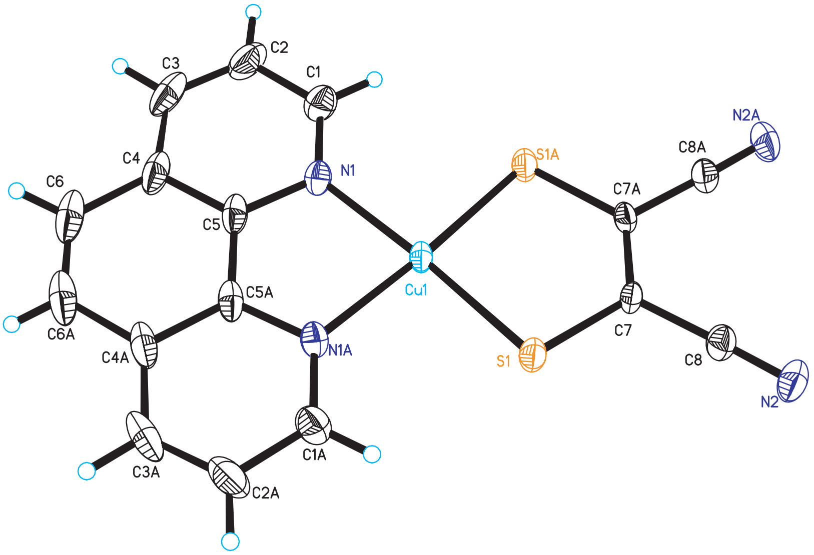


Figure 2. The monomeric structure of **2** with the atom-labelling scheme.

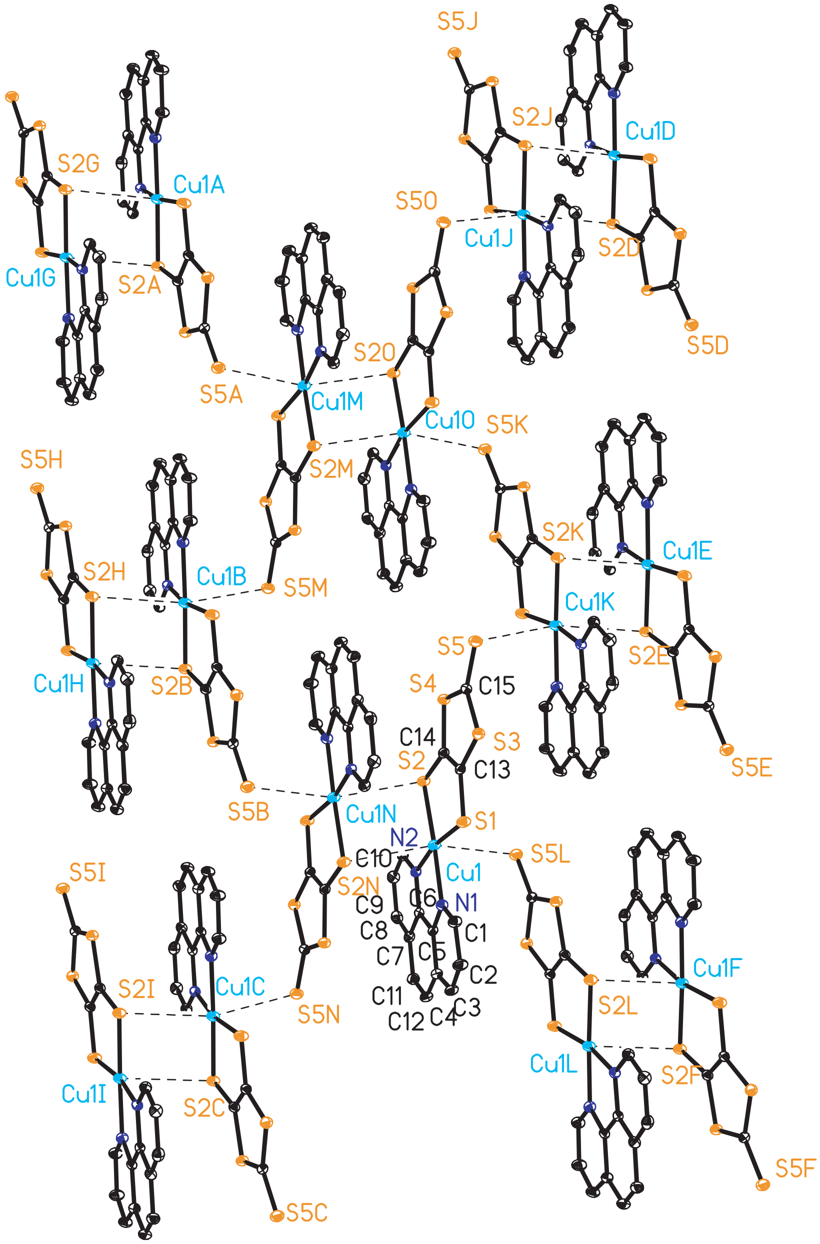


Figure 3. The stacking and the inter-dimer connecting mode in **1**.

between them of 54.9° (figure 5). In **1**, dimers are further extended into two-dimensional supramolecular arrays by weak S5–Cu contacts (Cu1N–S5B, 3.39 Å). This structure is different from **2** and similar dimeric complexes [Zn(dmit)(bipy)]$_2$, [Cd(dmit)(bipy)]$_2$ and [Cd(dmit)(phen)]$_2$.

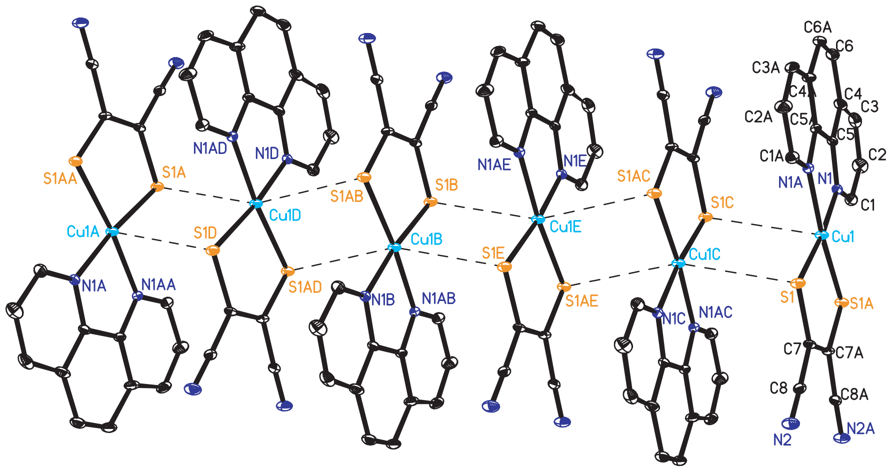


Figure 4. The head-to-tail packing and the inter-monomer connecting mode in **2**.

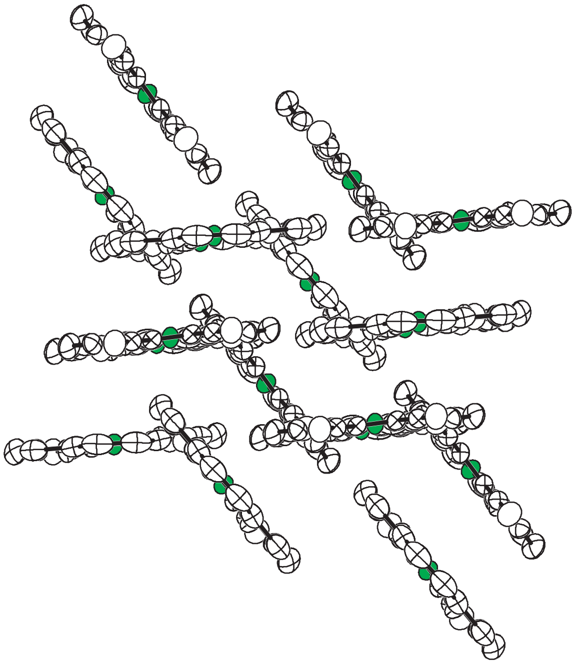


Figure 5. The crystal packing of **2** viewed along the *b*-axis.

3.3. *Cyclic voltammetry*

The cyclic voltammograms of **1** and **2** in DMF are shown in figures 6 and 7. Selected data are listed in table 4. In figure 7 complex **2** shows two clear quasi-reversible processes. The anodic wave II with a cathodic counterpart I and peak III with V

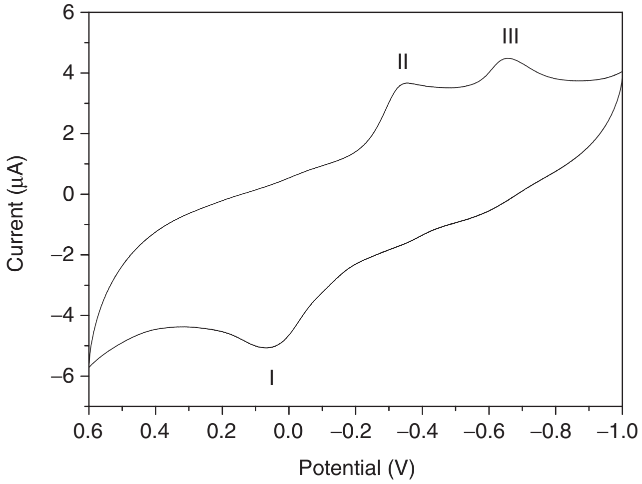


Figure 6. The cyclic voltammogram of **1**.

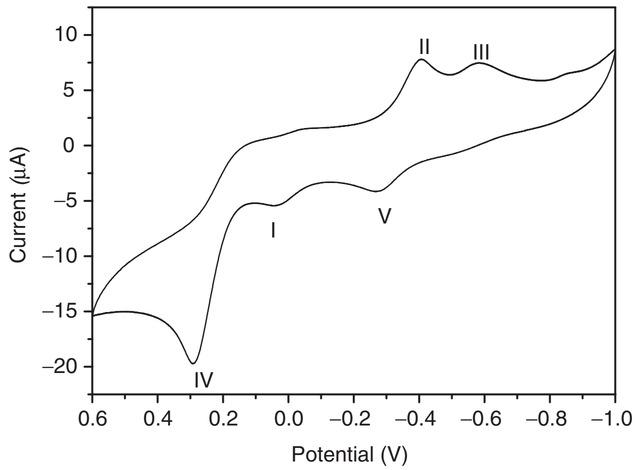


Figure 7. The cyclic voltammogram of **2**.

Table 4. Cyclic voltammetry parameters of **1** and **2**.

Complex	Redox potential (mV)				
1	−654 (I)	−356 (II)		70 (III)	
2	−587 (IV)	−401 (I)	−286 (V)	30 (II)	294 (III)

are assignable to the Cu^{II}/Cu^{I} couple of [Cu(phen)(L)] and $[Cu(phen)(L)]^+$ [18, 19] respectively.

For complex **1** the I–E curve in figure 6 is different from that of **2** in figure 7 and exhibits two anodic peaks at II and III with only one broad cathodic peak I.

Peaks II and III for **1** are also due to the Cu^{II}/Cu^{I} couple of [Cu(phen)(L)] and $[Cu(phen)(L)]^{+}$ [18, 19], respectively. Only one cathodic peak in complex **1** can be explained by the influence of dmit ligand, the potential of the corresponding cathodic counterparts of anodic peaks II and III are too close and merge into one broad cathodic peak. A similar phenomenon can be found in other Cu^{II} complexes containing diimine ligands [18, 20].

Comparing the potential data of the two complexes, **1** oxidizes with a peak at the lowest potential −0.654 V, with **2** having an oxidation peak at −0.587 V, indicating the highly electronegative terminal cyano group stabilizes Cu^{I} [7, 21]; thus the potential of Cu^{II}/Cu^{I} couple of $[Cu(phen)(L)]^{+}$ for **2** is higher than for **1**. These data agree well with those reported [22].

A large cathodic wave IV is observed in figure 7. This is characteristic of redissolution oxidized materials, which deposit on the electrode surface and give highly conducting powders [22].

Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre (CCDC No. 235050 for **1**, CCDC No. 235051 for **2**). That information is available from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

Acknowledgement

We gratefully acknowledge the financial support from the National Nature Science Foundation of China (No. 29833090 and No. 29771025).

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