

含 ONN 席夫碱和 2,2'-联吡啶的铜三元配合物的合成、 晶体结构及电化学性质

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摘要: 合成了一个新颖的含 ONN 席夫碱配体 *N*-水杨醛基-2-氨基乙基苯并咪唑(HL), 并在甲醇体系中合成了它的配合物[Cu(L)(bipy)]ClO₄(bipy 为 2,2'-联吡啶)。利用 X-射线单晶衍射法测定了配合物的晶体结构。配合物[Cu(L)(bipy)]ClO₄ 的晶体属于单斜晶系, *C*2/*c* 空间群, *a*=2.585 5(8) nm, *b*=1.435 5(5) nm, *c*=1.624 2(5) nm, β =124.434(5)°, *Z*=8。在配合物[Cu(L)(bipy)]ClO₄ 中, 每个铜离子的配位数为 5, 分别和配体 L 的 1 个氧原子和 2 个氮原子及 2,2'-联吡啶的 2 个氮原子配位, 形成畸变的三角双锥配位环境。配合物[Cu(L)(bipy)]ClO₄ 中的氢键和 π - π 相互作用将配合物[Cu(L)(bipy)]ClO₄ 连接成二维网络结构。用红外光谱、紫外-可见光谱对配合物[Cu(L)(bipy)]ClO₄ 进行了表征, 并用循环伏安法对配合物进行了电化学性质的研究。

关键词: 铜(II)三元配合物; 晶体结构; 弱相互作用; 电化学性质

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Synthesis, Structure and Electrochemical Properties of Ternary Copper(II) Complex of ONN-donor Schiff Base and 2,2'-Bipyridine

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Abstract: The crystal structure of the complex [Cu(L)(bipy)]ClO₄ (HL=*N*-salicylidene-2-aminoethylbenzimidazole, bipy=2,2'-bipyridine) has been determined by X-ray diffraction method and refined by full-matrix least-squares methods to *R*=0.033 9 and *wR*₂=0.080 4 using 5 079 reflections with *I*>2 σ (*I*). The compound crystallizes in the monoclinic system, space group *C*2/*c*, with *a*=2.585 5(8) nm, *b*=1.435 5(5) nm, *c*=1.624 2(5) nm, β =124.434(5)° and *Z*=8. Each Cu(II) ion adopts distorted N₄O trigonal bipyramidal coordination geometry. The hydrogen-bonding and π - π interactions extend the complex into a quasi two-dimensional networks, and such weak interactions further stabilized the complex. FTIR, UV-Vis and CV were also used to characterize the complex. CCDC: 275659.

Key words: copper(II) ternary complex; crystal structure; weak interactions; electrochemical property

Ternary complexes formed between metal ions and two different types of bioligands, namely heteroaromatic

nitrogen bases and Schiff bases, may be considered as models for substrate metal ion-enzyme interactions and

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other metal ion mediated biochemical interactions^[1]. Among those complexes, copper (II) complexes have been of great interest due to their importance as essentially biologically active models for metalloproteins and for their various geometrical aspects^[2-5]. Both electronic and steric factors play crucial roles in stabilizing the ternary structure, which otherwise, susceptible to conversion into the binary species. Often weak intra- and intermolecular interactions like π - π stacking involving two different ligands or hydrogen bonding stabilize the ternary structure^[6]. Herein, we report the synthesis, crystal structure and electrochemical property of the copper (II) ternary complex $[\text{Cu}(\text{L})(\text{bipy})]\text{ClO}_4$. In the complex, bpy is a *N,N'*-donor 2,2'-bipyridine and L is a anionic ONN-donor Schiff base ($\text{L}=\text{N}$ -salicylidene-2-aminoethylbenzimidazole).

1 Experimental

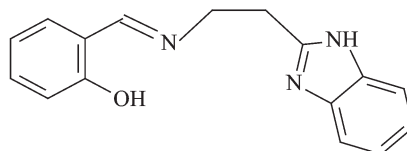
1.1 Materials and methods

All reagents for syntheses and analyses were of analytical grade. Elemental analyses were taken using a Perkin-Elmer 240C analyzer. FTIR spectra (KBr pellet) were obtained on a FTIR 170 SX (Nicolet) spectrometer. ^1H NMR spectra were recorded on a Bruker AC-P500 spectrometer (300 MHz) at 25 °C in CDCl_3 with tetramethylsilane as the internal reference. The electronic absorption spectra UV-Vis spectroscopy were recorded in the 230~900 nm range with a Jasco V-570 spectrophotometer. CV data were collected with LK98 Electrochemical Analyzer coupled to a HP-55 computer.

1.2 Syntheses of compounds

The ligand HL was synthesized by a condensation reaction between 2-(aminoethyl)-benzimidazole dihydrochloride (3.74 g, 16 mmol), previously neutralized with NaOH (1.28 g, 32 mmol), and salicylaldehyde (1.67 mL, 16 mmol) in 50 mL of methanol. The reaction mixture was refluxed for approximately two hours and then a yellow precipitate was obtained. The solid product was washed with MeOH and water and then dried in vacuum to obtain ligand HL with a yield of 96%. m.p. 200~202 °C. Anal. Calcd. for $\text{C}_{16}\text{H}_{16}\text{N}_3\text{O}$ (%): C 72.43, H 5.70, N 15.84; found (%): C 72.59, H 6.02,

N 16.01. FTIR (KBr, cm^{-1}): 2 859w, 1 634s, 1 581s, 1 535s, 1 497s, 1 425s, 1 313m, 1 276s, 1 205m, 1 151m, 1 115m, 1 060m, 1 025m, 968m, 927m, 897m, 749s, 649m, 565w, 471w. ^1H NMR (300 MHz, CDCl_3 ppm): δ : 13.23 (1H, 1H (benzim NH)), 8.35(1H, 1CH=N), 7.23~7.61(4H, CH (benzim)), 6.84~7.23 (4H, CH (ar)), 4.10~4.12(2H, 1CH₂), 3.29~3.34 (2H, 1CH₂).



Scheme 1 Structural diagram of the HL ligand

The single crystals of $[\text{Cu}(\text{L})(\text{bipy})]\text{ClO}_4$ were prepared as follows: HL (26.5 mg, 0.1 mmol) was dissolved in MeOH and 0.14 mL NEt_3 was added. A solution of bpy (15.6 mg, 0.1 mmol) and $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (37.2 mg, 0.1 mmol) in MeOH were then added in turn with stirring at room temperature. The resulting dark green solution was stirred for two hours. Crystals suitable for X-ray structural analysis were obtained by slow evaporation of the solvent at 4 °C. Yield: 70%. Anal. Calcd. for $\text{C}_{26}\text{H}_{22}\text{ClCuN}_5\text{O}_5$ (%): C 53.52, H 3.80, N 12.00; found (%): C 53.50, H 3.58, N 11.90. FTIR (KBr, cm^{-1}): 3 276w, 1 625s, 1 596s, 1 535s, 1 466s, 1 451s, 1 417s, 1 405m, 1 345m, 1 326m, 1 272m, 1 249m, 1 191m, 1 173m, 1 328m, 1 110s, 1 068m, 755s, 622s.

1.3 Crystal structure determination

Diffraction intensities for complex $[\text{Cu}(\text{L})(\text{bipy})]\text{ClO}_4$ was collected on a Bruker Smart 1000 CCD area detector using graphite-monochromatized Mo $K\alpha$ radiation ($\lambda=0.071\,073$ nm) with ω scan mode at 293(2) K. Unit cell dimensions were obtained with least-squares refinements. Semiempirical absorption corrections were applied using SADABS program^[7]. The structures were solved by direct method using the SHELXS-97^[8] and refined by full-matrix least-squares methods on F^2 by SHELXL-97^[9]. Hydrogen atoms were included in calculated positions and refined with fixed thermal parameters riding on their parent atoms. Further crystallographic data and experimental details for structural analyses are summarized in Table 1.

CCDC: 275659.

Table 1 Crystal data and structure refinement summary for $[\text{Cu}(\text{L})(\text{bipy})]\text{ClO}_4$

Empirical formula	$\text{C}_{26}\text{H}_{22}\text{ClCuN}_5\text{O}_5$	Z	8
Formula weight	583.48	μ / mm^{-1}	1.035
Temperature / K	293(2)	$F(000)$	2 392
Crystal system	Monoclinic	Crystal size / mm	0.24×0.22×0.16
Space group	$C2/c$	Range of $\theta / (^\circ)$	2.52~26.37
a / nm	25.855(8)	Range of h, k, l	-32/31, -15/17, -20/20
b / nm	14.355(5)	Reflections collected / unique	14 146 / 5 079
c / nm	16.242(5)	Goodness-of-fit on F^2	0.993
$\beta / (^\circ)$	124.434(5)	$R_1, wR_2 (I > 2\sigma(I))$	0.033 9, 0.080 4
Volume / nm^3	4.972(3)	R_1, wR_2 (all data)	0.063 1, 0.096 3
$D_{\text{calcd}} / (\text{g} \cdot \text{cm}^{-3})$	1.559	Largest diff. Peak and hole / ($\text{e} \cdot \text{nm}^{-3}$)	367 and -306

2 Results and discussion

2.1 Characterization

In the IR spectrum, the complex has strong absorption at 1 451 and 755 cm^{-1} . These are assigned to $\text{C}=\text{N}-\text{C}=\text{C}$ stretching vibration of benzimidazole ring^[10], and C-H vibration of phenyl ring. The sharp band at 1 634 cm^{-1} in the free HL due to the Schiff base $\text{C}=\text{N}$ stretching vibration is shifted to a lower frequency (1 625 cm^{-1}) whereas the band at 1 205 cm^{-1} which is attributed to phenolic C-O stretching vibration of the ligand is shifted to higher frequency (1 275 cm^{-1}) in the complex. These imply direct coordination of the imine nitrogen atom and the phenol groups in the deprotonated form in the HL ligand. Characteristic stretching frequencies for the anions are observed. The perchlorate anion in the complex shows strong symmetric vibrations at 1 110 and 622 cm^{-1} , which are typical ionic perchlorate. These features could be completely confirmed by the single crystal X-ray diffraction study.

The electronic spectrum of the complex was measure in DMF. UV bands at 275 and 280 nm are characteristic of the benzimidazole group and arise from a $\pi-\pi^*$ transition. These are blue-shifted upon coordination, showing clear evidence of $\text{C}=\text{N}$ coordination to copper center^[11]. The band in the region 400~420 nm is assigned to $\pi(\text{benzimi}) \rightarrow \text{Cu}(\text{II})$ LMCT transition^[12]. Trigonal bipyramidal $\text{Cu}(\text{II})$ usually shows a maximum at >800 nm, with a higher energy shoulder^[13]. The fact that the complex consists of a broad band centered at

649 nm, which is attributed to the $\text{Cu}(\text{II})$ $d-d$ transition, indicates significant distortion toward square pyramidal geometry. Therefore, for the complex a change in geometry to a tetragonal site on going from the solid to the solution state has occurred.

2.2 Description of the crystal structures

The crystal structure of $[\text{Cu}(\text{L})(\text{bipy})]\text{ClO}_4$ reveals the presence of ternary copper (II) consisting of a tridentate ONN- donor Schiff base, a bidentate ligand (NN-donor) and a copper (II) center in the discrete monomeric species. The ClO_4^- anion turns out to be disordered and is refined with three oxygen atoms at two different positions. A perspective view of the cation including the atom numbering scheme is shown in Fig. 1. Selected bond distances and angles are given in Table 2. In the cation, each $\text{Cu}(\text{II})$ is coordinated by one

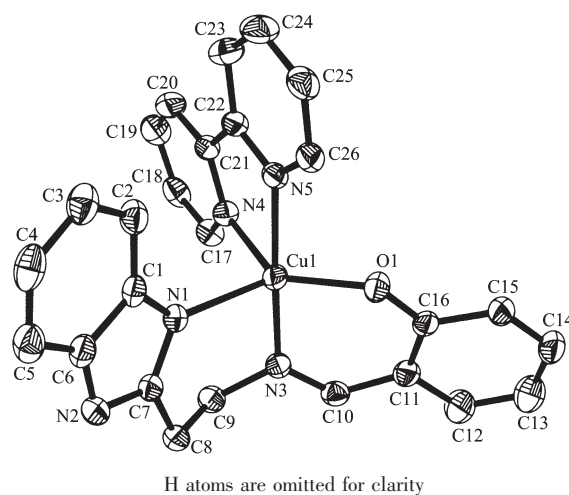


Fig.1 ORTEP view of the cation of $[\text{Cu}(\text{L})(\text{bipy})]\text{ClO}_4$ showing the labeling of atoms with thermal ellipsoids at 30% probability

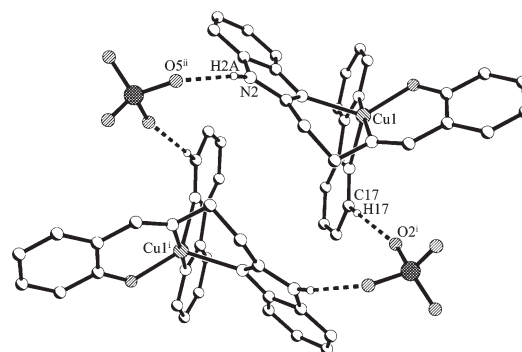
Table 2 Selected bond lengths (nm) and angles (°) for [Cu(L)(bipy)]ClO₄

Cu(1)-O(1)	0.191 8(19)	Cu(1)-N(3)	0.194 8(2)	Cu(1)-N(5)	0.199 8(2)
Cu(1)-N(1)	0.219 0(2)	Cu(1)-N(4)	0.215 9(2)		
O(1)-Cu(1)-N(3)	92.15(8)	O(1)-Cu(1)-N(5)	88.00(8)	N(3)-Cu(1)-N(5)	173.25(9)
O(1)-Cu(1)-N(4)	131.48(8)	N(3)-Cu(1)-N(4)	96.94(9)	N(5)-Cu(1)-N(4)	78.00(9)
O(1)-Cu(1)-N(1)	127.08(8)	N(3)-Cu(1)-N(1)	90.30(8)	N(5)-Cu(1)-N(1)	95.00(8)
N(4)-Cu(1)-N(1)	100.52(8)	C(16)-O(1)-Cu(1)	126.53(17)	C(7)-N(1)-Cu(1)	121.49(17)
C(1)-N(1)-Cu(1)	131.12(17)	(10)-N(3)-Cu(1)	123.85(19)	C(9)-N(3)-Cu(1)	118.11(16)
(17)-N(4)-Cu(1)	128.68(19)	C(21)-N(4)-Cu(1)	112.60(17)	C(26)-N(5)-Cu(1)	117.54(18)
C(22)-N(5)-Cu(1)	122.74(18)				

phenol oxygen atom and four nitrogen atoms, two of which originate from bipy, and the other two from the HL ligand. In pentacoordinated systems, the actual geometry of the complex can be described by a structural index parameter τ , within the structural continuum between square-pyramidal ($\tau=0$) and trigonal-bipyramidal structures ($\tau=1$)^[14]. The τ value for Cu(II) ion of the complex is obtained as $\tau=0.70$, indicating that the coordination environment around the Cu(II) is best described as a distorted trigonal-bipyramid. Thus, the equatorial positions are occupied by N1, N4 and O1 atoms and the axial positions by two nitrogen atoms N3 and N5. The Cu-O bond distance of 0.191 8(19) nm is in the range found for similar Cu(II) complexes^[2]. For the same kind of donor, the axial distances are significantly shorter than the equatorial ones^[13]. In fact, the Cu1-N5 axial distance of 0.199 8(2) nm is shorter than the equatorial Cu1-N4 distance, which is 0.215 9(2) nm. The Cu1-N1 and Cu1-N3 are 0.219 0(2) nm and 0.194 8(2) nm, respectively. Equatorial bond angles deviate largely from the expected value of 120°, the largest deviation being 19.48°, whereas N3-Cu-N5 is 173.25(9)°. The sum of equatorial bond angles at Cu is 359.08°, showing that the metal ion is essentially in the mean plane of the equatorial donors.

The most interesting feature of the crystal structure of the complex is the presence of intermolecular hydrogen bonds and π - π stacking interactions. Two oxygen atoms of the non-coordinated perchlorate anion bridge two adjacent cations by two intermolecular hydrogen bonds of type C-H \cdots O and N-H \cdots O to give a cyclic-dimer structure consisting of two [Cu(L)(bipy)]⁺

cations and two perchlorate anions as shown in Fig.2. The C \cdots O and O \cdots O separations are 0.326 7 and 0.288 1 nm with the H \cdots O distances of 0.236 7 and 0.206 3 nm, respectively, falling into the normal range of hydrogen bond interactions. The bond angles are 163° and 159°, respectively. The adjacent benzimidazole rings of two cyclic-dimers (benzene ring, comprising atoms C1-C6, is designated as ring 1 with centroid Cg1 and corresponding imidazole ring, C1, C6, N2, C7 and N1, as ring 2 with centroid Cg2) involved in the π - π stacking interactions. The perpendicular distance from Cg1 to the plane of symmetry-related ring 2, and from Cg2 to the plane of symmetry-related ring 1 are 0.3548 9 nm and 0.353 26 nm, respectively. The distance between the ring centroids (Cg1 \cdots Cg2) is 0.356 9 nm, indicating only a slightly stacking orientation parallel to each other as shown in Fig.3a. In addition, the two pyridine rings of two adjacent cyclic-dimers (pyridine ring, comprising atoms C17, C18, C19, C20, C21 and N4, is designated as ring 3 with centroid Cg3) also involved in



Symmetry codes: ⁱ $-x, -y+1, -z$; ⁱⁱ $+x, -y+1, -0.5+z$; Dashed lines stand for hydrogen bonds

Fig.2 Hydrogen bonds in [Cu(L)(bipy)]ClO₄

the π - π stacking interactions. The perpendicular distance from Cg3 to the plane of symmetry-related ring is 0.358 6 nm. The distance between the ring centroids is 0.383 3 nm, indicating a slipped stacking orientation parallel to each other as shown in Fig.3b. The π - π stacking interactions of the first type are responsible for

the formation of quasi infinite chains along the a axis as shown in Fig.4a; interactions of the second type link the cyclic-dimer into a quasi one-dimensional structure along the c axis as shown in Fig.4b. Combination of all these weak interactions results in a two-dimensional structure of the crystal.

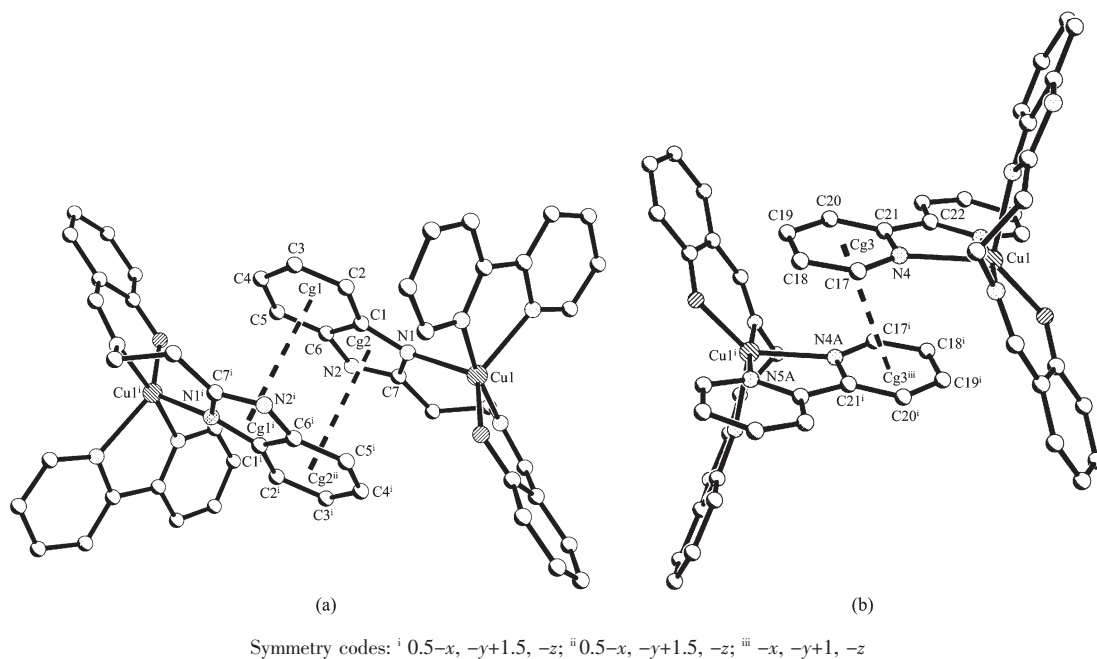


Fig.3 (a) π - π interactions between benzimidazole rings and (b) pyridine rings in $[\text{Cu}(\text{L})(\text{bipy})]\text{ClO}_4$

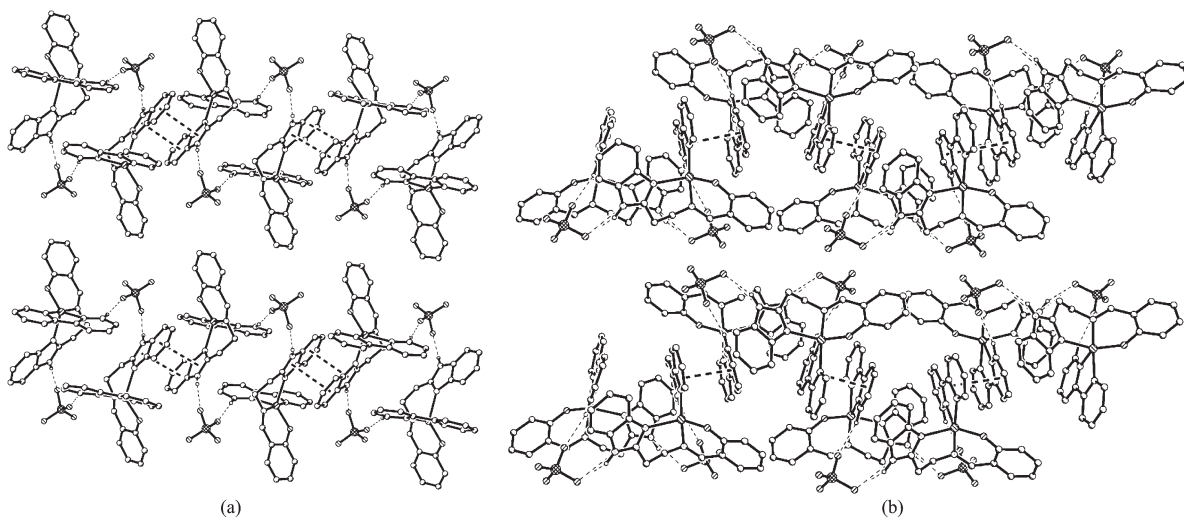


Fig.4 (a) 1-Dimensional structure linked by hydrogen bonds and π - π interactions between benzimidazole rings and (b) pyridine rings in $[\text{Cu}(\text{L})(\text{bipy})]\text{ClO}_4$

2.3 Cyclic voltammogram

In cyclic voltammetry electrochemical measurements (CV) were performed using a three-electrode cell at room temperature. A glass carbon (GC) working (3 mm in diameter) and a Pt wire counter electrode were

employed. The reference electrode is Ag/AgCl (satd). Fig.5 depicts the cyclic voltammogram of the $[\text{Cu}(\text{L})(\text{bipy})]\text{ClO}_4$ complex in DMF solution containing of 0.1 mol \cdot L⁻¹ TBAP at scan rate 100 mV \cdot s⁻¹. Only one pair of redox peaks obtained at $E_{1/2} = -70$ mV can be ascribed

to the $\text{Cu}^{\text{I}}/\text{Cu}^{\text{II}}$. The couple was reversible one-electron redox with $\Delta E=140$ mV. Compared with related complex^[15], the complex shows conspicuously electrochemical reversibility. The observation suggests that an unsaturated nitrogen as the donor atom in the ligand can stabilize more a low oxidation state, such as $\text{Cu}(\text{I})$, than a saturated one, by π -back bonding between the metal and the nitrogen atoms^[16].

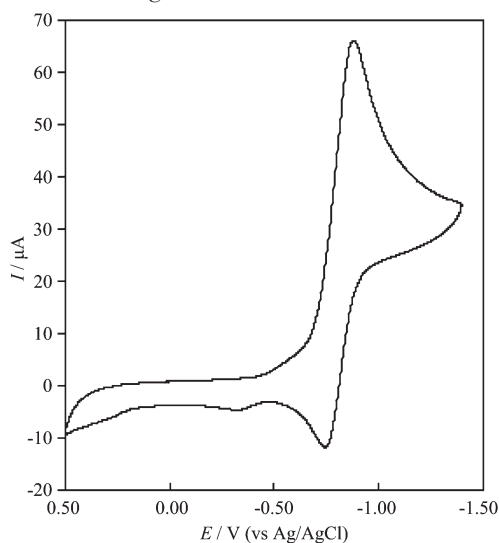


Fig.5 Cyclic voltammogram of $[\text{Cu}(\text{L})(\text{bipy})]\text{ClO}_4$ in DMF solution

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