A thiophenopolyamine Cu(II) complex fixed by atmospheric carbon dioxide: synthesis, structure and properties

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A thiophenopolyamine Cu(II) complex fixed by atmospheric carbon dioxide: synthesis, structure and properties

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A new trinuclear complex, $\{[Cu(L)]_3(\mu_3\text{-}CO_3)\}(ClO_4)_4$ (L = N-(2-thiophenoethyl)-N,N-bis (3-aminopropyl)amine), was synthesized and characterized by single-crystal X-ray analysis. The complex contained three identical mononuclear copper(II) units connected by the μ_3-carbonate formed from atmospheric carbon dioxide. The electronic and magnetic properties were studied by cyclic voltammetry and the measurement of magnetic susceptibility, respectively. The μ_3-bridging model revealed weak ferromagnetic coupling of Cu(II), with the J value of $-11.28\,cm^{-1}$ and the Zeeman splitting g value of 2.06, which were determined by means of magnetic measurements in the 2–300 K range.

1. Introduction

The chemical fixation and activation of carbon dioxide are a hot topic concerning control of atmospheric pollutant caused by excess CO_2 in the atmosphere. A key step in the chemical, photochemical and electrochemical transformations of CO_2 is the formation of a metal-CO_2 complex, since coordination activates this rather inactive molecule toward a number of chemical reactions. Some researchers have reported using the reaction of CO_2 with metal complexes as an attractive C_1 feedstock to prepare useful carbon-containing compounds [1]. Carbonate is an extremely versatile bridging ligand [2], which can generate a large variety of compounds such as dimers [3, 4], trimers [5], tetramers [6], 1D [7] and 2D systems [8] with different polynuclear units. Many studies

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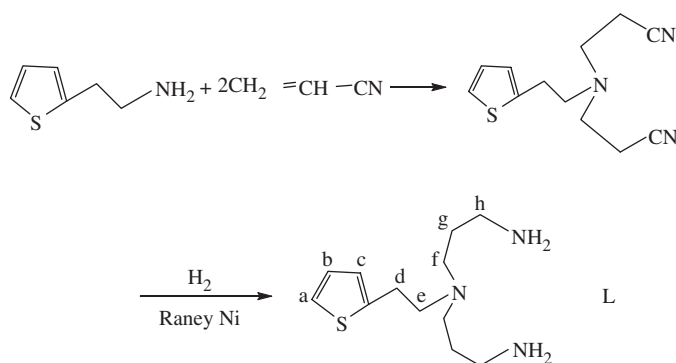
Scheme 1. The synthesis of *N,N*-dipropylamine thiopheneethylamine (L).

have been carried out on the coordination chemistry of CO_2 and its hydration products HCO_3^- and CO_3^{2-} [9, 10]. Although CO_2 absorbed by metal complexes is found, only a few structures of trinuclear complexes with $\mu_3-CO_3^{2-}$ bridged are reported. Recently, Sun reported a tripodal ligand can form head-to-end trigonal huge hole structure containing an imidazole arm [10], but the properties were not studied. The thiophene ring is isoelectronic with imidazole; we have synthesized a thiophene-containing triamine ligand N,N-bis(3-aminopropyl)-2-thiophenoethylamine (L) and its $\mu_3-CO_3^{2-}$ bridged trinuclear copper(II) complexes (scheme 1). The structure, electrochemical and magnetic properties are reported.

2. Experimental

2.1. *Materials and preparation*

Synthesis: Caution! Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only a small amount of compound should be prepared and should be handled with caution.

All reagents and solvents for syntheses and analyses were of analytical grade. Methanol was dried with CaO and distilled prior to use.

2.2. *Physical measurement*

Elemental analyses were performed on a Vario EL III CHNOS elemental analyzer (Elementar, Germany). Infrared spectra (KBr pellet) were recorded on a FT-IR spectrometer (Impact420, Nicolet). ^{1}H NMR spectra were recorded on a Varian Mercury VX-300 spectrometer at 30°C in CDCl$_3$ with TMS as the internal reference. Absorption spectra were recorded on a Shimadzu UV-2450 in the UV-Vis range (190–800 nm). The magnetic properties of {[Cu(L)]$_3$ μ_3-CO$_3$)}(ClO$_4$)$_4$ were measured with a powdered sample on a MPMS-XL7 SQUID magnetometer at an applied field of 1 kG. Cyclic voltammograms were recorded on a CHI 750B electrochemical

Table 1. Crystal data and structure refinement for $[Cu(L)]_3(\mu_3\text{-}CO_3)(ClO_4)_4$.

Empirical formula	$C_{37}H_{69}Cl_4Cu3N_9O_{19}S_3$
Formula weight	1372.61
Crystal system	Trigonal
Space group	$R3c$
Unit cell dimensions ($\mathring{A}$, °)	
a	23.948(3)
b	23.948(3)
c	17.210(5)
α	90
β	90
γ	120
Volume ($\mathring{A}^3$)	8548(3)
Z	6
D_{calcd} (g cm^{-3})	1.602
μ (mm^{-1})	1.482
$F(000)$	4260
Crystal size (mm^3)	$0.22 \times 0.24 \times 0.30$
Temperature (K)	298
Mo Kα radiation ($\mathring{A}$)	0.71073
Theta min-max (Deg)	1.7, 26.0
Data set	-29; 29; -29; 29; -21: 21
Tot., uniq. data, R(int)	24117, 3743, 0.059
Observed data [$I > 2.0\ \sigma(I)$]	3560
N_{ref}, N_{par}	3743, 271
R, wR_2, S	0.0374, 0.0926, 1.07
Max. and av. Shift/error	0.00, 0.00
Flack x	0.031(14)
Min. and max. resd. dens. (e $\mathring{A}^{-3}$)	-0.39, 0.21

analyzer, and the measurements were carried out in DMF solutions (5×10^{-4} mol dm^{-3}) of the complex containing 0.1 mol dm^{-3} tetraethylammonium perchlorate (TEAP) as the supporting electrolyte. A three-electrode cell equipped with a glass carbon working electrode, a platinum wire as the auxiliary electrode and a saturated calomel electrode (SCE) as the reference was used. Scanning rates were in the range $20 \sim 200$ mV s^{-1}. The solution was deaerated for 15 min before measuring. The half-wave potentials were calculated from $(E_{pa} + E_{pc})/2$, and the measured error was 2 mV. Magnetic susceptibility of a crystalline-powdered sample was measured on a SQUID-based sample magnetic meter in the temperature range $2.0 \sim 300$ K, and a diamagnetic correction of -600×10^{-6} cm^3 mol^{-1} was applied to the measured data.

2.3. *Crystal structure determination*

Diffraction intensity data were collected on a SMART-CCD area-detector diffract-ometer at 298 K using graphite monochromatic Mo Kα radiation ($\lambda = 0.71073$ $\mathring{A}$). Data reduction and cell refinement were performed by SMART and SAINT programs [11]. The structure was obtained 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 a riding mode. The summary of the crystallographic data is listed in table 1.

2.4. *Preparation of the ligand*

2.4.1. *N,N*-bis(2-cyanoethyl)-2-thiophenoethylamine (BCETHIOA). A mixture containing 2-thiophenoethylamine (38.2 g, 0.3 mol) and water (200 mL) was added dropwise to a solution of acrylonitrile (32.9 g, 0.62 mol) in an ice bath, then 400 mL water and acrylonitrile (32.9 g, 0.62 mol) were added in the mixture successively. The resulting solution was refluxed for 60 h. The crude *N,N*-bis(2-cyanoethyl)-2-thiophenoethylamine was extracted by dichloromethane, washed with water and dried with anhydrous sodium sulfate. After filtration of sodium sulfate, the solvent was distillated to obtain the product, i.e., BCETHIOA (64.4 g, 0.28 mol), b.p. 180–190°C, in 92% yield. Anal. Calcd for $C_{12}H_{15}N_3S$: C, 61.8; H, 6.5; N, 18.0; S, 13.7%. Found: C, 61.7; H, 6.4; N, 17.8; S, 13.6%. IR (KBr, ν/cm^{-1}): 3446 (NH); 2948, 2924 (Ar, C–H); 2246 (CηN); 1137 (Ar, C–S).

2.4.2. *N,N*-bis(3-aminopropyl)-2-thiophenoethylamine (L). A suspension of 95% ethanol (800 mL) of BCETHIOA (71.5 g, 0.60 mol), NaOH (12.4 g) and Raney-Ni (24 g) were mixed in an autoclave. Hydrogen gas was introduced into the mixture until the pressure is 40 atm. The reduction reaction took place at 50°C. When absorption of hydrogen was complete, the mixture was cooled to room temperature, filtered, and evaporated *in vacuo*. The mixture was purified by extraction with CH_2Cl_2 (5%, 200 mL), drying, filtering, concentrating and fractional distillation to produce *N,N*-bis(3-aminopropyl)-2-thiophenoethylamine (L) (58 g, 0.24 mol), b.p. 184-186°C (10 mmHg) in ca 63% yield. Anal. Calcd for $C_{12}H_{23}N_3S$: C, 59.7; H, 9.6; N, 17.4; S, 13.3%. Found: C, 59.8; H, 9.7; N, 17.6; S, 13.4%. IR (KBr, ν/cm^{-1}): 3365, 3288 (NH); 2930, 2856 (Ar, C–H); 1126 (Ar, C–S); ^{1}H NMR (CDCl$_3$, δ/ppm): 7.11 (t, 1H, CH–S), 6.90 (m, 1H, CH–C–S), 6.80 (s, 1H, CH), 2.95 (t, 2H, C–CH$_2$), 2.70 (p, 6H, CH$_2$–N–(CH$_2$)$_2$), 2.52 (t, 4H, CH$_2$–NH$_2$), 1.59 (m, 4H, CH$_2$), 1.13 (s, 4H, NH$_2$).

2.5. *Preparation of {[CuL]₃(μ₃-CO₃)(ClO₄)₃}(ClO₄) (I)*

L (0.121 g, 0.5 mmol) in 30 mL methanol was added to Cu(ClO$_4$)$_2 \cdot$6H$_2$O (0.185 g, 0.5 mmol) in 10 mL methanol. After stirring at room temperature for 4 d, the resulting blue solution was placed in contact with the atmosphere. Black single crystals suitable for X-ray investigation were obtained by slow evaporation at room temperature over 10 d. Anal. Calcd for $C_{37}H_{69}N_9S_3Cu_3Cl_4O_{19}$: C, 32.5; H, 5.1; N, 9.3%. Found: C, 32.7; H, 5.4; N, 9.5%. IR (KBr, ν/(cm^{-1})): 3427, 3129 (NH); 1093, 621 (ClO$_4^-$); 1458, 832 CO$_3^{2-}$. UV-Vis (CH$_3$CN) λ_{max}/(nm) (ε/(M^{-1}cm^{-1})): 637(824), 290(9110), 272(3363).

3. Results and discussion

3.1. *Preparation of ligand and complexes*

Reaction of 2-thiophenoethylamine with an excess of acrylonitrile leads to the *bis*-adduct, BCETHIOA. The nitrile is easily reduced to the corresponding amine by hydrogenation catalyzed with Raney-Ni in a basic methanol solution. Although sodium

borohydride is often used in such hydrogenation reaction, the difficult purification of the product is inconvenient. The hydrogenation described here is much simpler and the yield of the multiamine is higher.

In the ^{1}H NMR spectrum of L, the doublet at 7.10 ppm, the triplet at 6.80 ppm and the doublet at 6.90 ppm were designated to H(a), H(b) and H(c), the α and β protons of thiophene (labeling of protons is shown in scheme 1). The triplet at 2.95 ppm was H(d) of methylene linked with thiophene. The multiplet e+f may be an overlap of signals of H(e) and H(f) of propylamine because of the similar chemical environment. The other methylene protons H(g) and H(h) of propylamine were a multiplet at 1.59 ppm and triplet at 2.53 ppm, respectively. The integral ratio $1:1:1:2:6:4:4$ of the signals a, b, c, d, (e+f), g and f indicates that *N,N*-bis(3-aminopropyl)-2-thiophe-noethylamine (L) was synthesized.

3.2. *Complex synthesis*

The aqueous solution of the mixture of $Cu(ClO_4)_2 \cdot 6H_2O$ and the ligand L has good affinity for atmospheric CO_2, readily extracting it from the air. In addition, the nonpolar thiophene ring improves the solubility of CO_2. By exposing the mixed solution of $Cu(ClO_4)_2$ and L to the air for 24 h (ligand and copper(II) concentrations 0.01 mol L^{-1}), CO_2 was absorbed forming the triply-bridged carbonate complex **I** in good yield. Similar product could also be obtained by exposing alkaline aqueous solution of $[CuL'](ClO_4)_2$ in the air in Bencini's work [13].

3.3. *Structure description*

The crystal structure of **I** consists of three mononuclear copper(II) units, $[Cu(L)ClO_4]^+$, one isolated perchlorate counter anion and one CO_3^{2-}, which acts as a bridging group connecting the three units. The complex has a C_3 crystallographic axis through C(13) that is perpendicular to the plane containing the carbonate anion. Perspective views of the complex are shown in figures 1 and 2, together with the atom-numbering scheme. Crystallographic data and the details of the data collection are presented in table 1. Typical bond lengths and angles relevant to copper(II) coordination spheres of the complex are listed in table 2. The coordination polyhedron of each copper(II) can be better described as square pyramidal (see figure 2). The configuration formed by the three copper(II) units is an equilateral triangle (see figure 1) with Cu–Cu separation of 4.842 Å. Each copper center is coordinated with three nitrogen atoms of the ligand, one oxygen atom of the perchlorate and one oxygen atom of the carbonate. In the base plane of Cu(II), the distances between Cu(II) and coordinated atoms fall in the range 1.9762.06 Å and Cu(II) departs by 0.12 Å from the mean N$_3$O basal plane. One oxygen of the perchlorate occupies the apical positions in an arrangement with somewhat longer contact (2.498 Å), within the range observed for axial copper–oxygen bonds [14]. The axial Cu–O bonds are almost perpendicular to the respective basal planes. The three planes of the copper ion and coordinated nitrogen atoms from L are vertical to each other and have the same angle of 60.1° with the plane of CO_3^{2-}. All atoms of the terminal thiophene rings are disordered. The three oxygen atoms of free perchlorate located between two cations of the complex form hydrogen bonds (2.439 Å) with hydrogen atoms of amino in each of the ligands from different cations, and the other
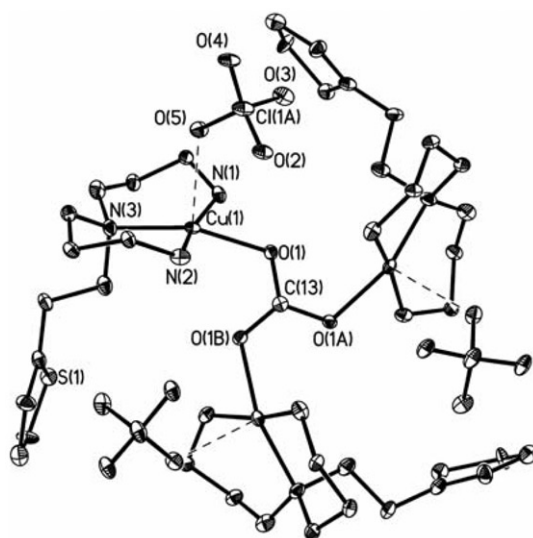
Figure 1. ORTEP view of the molecular structure of the cation of $\{[Cu(L)]_3(\mu_3\text{-}CO_3)\}(ClO_4)_3$.
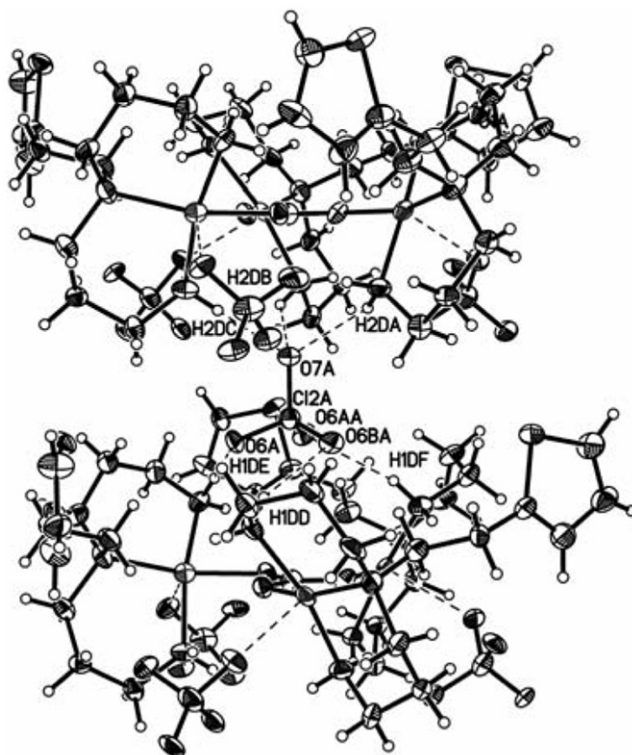

Figure 2. ORTEP view of the molecular structure of $\{[Cu(L)]_6(\mu_3\text{-}CO_3)_2\}^{7+}$.

Table 2. Selected bond lengths (Å) and angles (°) for $[Cu(L)]_3(\mu_3\text{-}CO_3)(ClO_4)_4$.

Cu(1)–O(1)	1.976(3)	Cu(1)–N(1)	1.985(3)
Cu(1)–N(2)	1.979(3)	Cu(1)–N(3)	2.060(4)
O(1)–C(13)	1.261(3)	Cu(1)–O(5)	2.498(3)
O(1)–Cu(1)–O(5)	101.44(11)	O(1)–Cu(1)–N(1)	81.37(16)
O(1)–Cu(1)–N(2)	89.12(16)	Cu(1)–O(1)–Cu(1a)	168.91(13)
O(1)–Cu(1)–N(3)	159.37(14)	Cu(1)–O(1)–C(13)	117.78(17)
O(5)–Cu(1)–N(2)	88.50(13)	O(5)–Cu(1)–N(3)	98.91(14)
O(1b)–Cu(1)–O(5)	140.98(10)	N(1)–Cu(1)–N(2)	167.00(16)
N(1)–Cu(1)–N(3)	97.21(16)	O(1b)–Cu(1)–N(1)	110.14(14)
N(2)–Cu(1)–N(3)	94.80(16)	O(1b)–Cu(1)–N(2)	69.02(14)
O(1b)–Cu(1)–N(3)	113.91(13)		
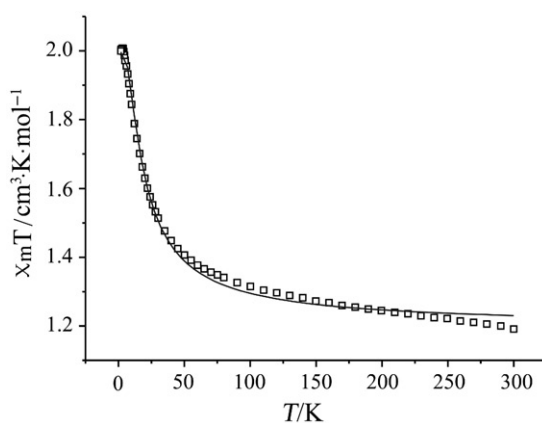
Figure 3. Temperature variation of the magnetic susceptibility of $\{[CuL]_3(\mu_3\text{-}CO_3)\}\cdot(ClO_4)_4$ in the form $\chi_m T$ *vs. T*. Solid lines represent the best fit curves according to the procedure described in the text.

oxygen of perchlorate forms hydrogen bonds (2.305 Å) with three hydrogen atoms of three ligands in the nearest molecules, as shown in figure 2. These intermolecular hydrogen bonds are also found in Escuer's work [14]. The Cl(2)–O(7) in the perchlorate superposes with the C_3 axis. As a consequence of these hydrogen bonds, the trinuclear units form a chain-like arrangement. The chain-like arrangement and $\mu_3\text{-}CO_3^{2-}$ configuration of the complex is very similar to the trinuclear copper(II) $\mu_3\text{-}CO_3^{2-}$ system reported by Escuer. The difference in main bonds and angles between the two complexes are from the different substituted group in the tetraamine of the ligand [14].

3.4. *Magnetic properties*

The temperature dependence of the magnetic susceptibility of $\{[CuL]_3 \mu_3\text{-}CO_3)\}(ClO_4)_4$ measured in the range 1.73−300 K is shown in figure 3 in the $\chi_m T$ *versus T* form (χ_m is the molar susceptibility). The magnetic moment value of 3.116 μ_B at room temperature is very close to the value expected for three uncoupled spins $S = 1/2$ ($\mu_{eff} = 3.0\,\mu_B$). The $\chi_m T$ value increases slowly when the temperature decreases from 100 K to 300 K and increases significantly below 100 K until it reaches a maximum value
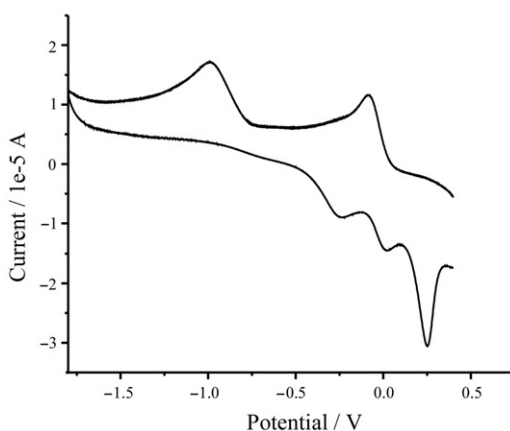
Figure 4. Cyclic voltammogram of **I** in DMF at a scan rate of $0.1\,\mathrm{V\,s^{-1}}$.

of $1.84\ \mathrm{cm^3\,K\,mol^{-1}}$, indicating ferromagnetic coupling between the copper(II) ions. The best fit to this data is obtained using equation (1), which is derived from trinuclear system Hamiltonian operator $H = J(\boldsymbol{S_1 S_2} + \boldsymbol{S_2 S_3} + \boldsymbol{S_1 S_3})$.

$$\chi_{\mathrm{m}} = \frac{N g^2 \mu_{\mathrm{B}}^2}{4kT} \frac{1 + 5e^{-3J/2kT}}{1 + e^{-3J/2kT}} \tag{1}$$

The experiment and calculated temperature dependence of $\chi_{\mathrm{m}} T$ are shown in figure 3. The magnetic parameters of the complex can be estimated as $g = 2.06$ and $J = -11.28\,\mathrm{cm^{-1}}$ with $R = 2.6\%\ 10^{-4}$ (R is an agreement factor defined as $R = (\sum[(\chi_{\mathrm{M}} T)_{\mathrm{calc}} - (\chi_{\mathrm{M}} T)_{\mathrm{obs}}]^2 / \sum (\chi_{\mathrm{M}} T)_{\mathrm{obs}}^2$). A negative value of J also indicates a ferromagnetic interaction. The low J value and rather weak interaction is reasonable since the distances between the copper(II) atoms are quite large (Cu–Cu separation of about 4.842 Å). The ferromagnetic character of these trimeric compounds is consistent with previously reported data [3, 16]. Although the coordination environment of the Cu(II) in the complex described here is the same as the complex reported in reference [14], the magnetic properties of the complexes are different, especially at low temperature, which should be ascribed to the effect of substituted groups.

3.5. *Electrochemistry of the complex*

Electrochemical properties of **I** are studied by means of cyclic voltammetry in DMF. The voltammogram is given in figure 4. When scanning from $-1.8\,\mathrm{V}$ to $0.4\,\mathrm{V}$ at a scan rate of $0.1\,\mathrm{V\,s^{-1}}$, there are three cathodic processes and two anodic processes observed, and the peaks appeared with half-wave potentials ($E_{1/2}$) -0.614 and -0.053 for $\{[\mathrm{CuL}]_3\,\mu_3\text{-}\mathrm{CO_3})\}(\mathrm{ClO_4})_4$, indicating that the complex exhibits reversible Cu(II)Cu(II)Cu(II)/Cu(I)Cu(I)Cu(II) and irreversible Cu(I)Cu(I)Cu(II)/Cu(I)Cu(I)Cu(I) redox processes. The two-couple redox processes can be expressed as follows:

$$\mathrm{Cu(II)Cu(II)Cu(II)} \underset{-2e}{\overset{+2e}{\rightleftharpoons}} \mathrm{Cu(II)Cu(I)Cu(I)} \overset{+e}{\longrightarrow} \mathrm{Cu(I)Cu(I)Cu(I)} \tag{2}$$
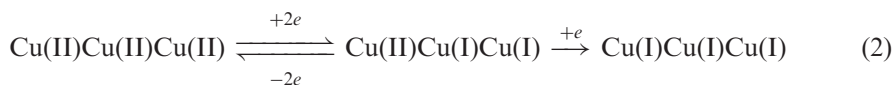
4. Conclusions

A new ligand, *N,N*-bis(3-aminopropyl)-2-thiophenoethylamine, and its trinuclear copper(II) complex were synthesized and characterized. The results show that the catalytic hydrogenation reaction using Raney-Ni as a reductant is a convenient way to reduce the C≡N bond with a high yield. The formation μ_3-CO_3^{2-} bridged complex illustrates that the mixture of the ligand and copper(II) easily absorbs CO_2 from the atmosphere. Comparison with a similar μ_3-CO_3^{2-} system, CO_3^{2-} acts as a bridging group connecting three isolated units in spite of different ligands. The magnetism of the complex shows weak ferromagnetic exchange ($J = -11.28 \, cm^{-1}$). The electrochemical behavior expresses two reduction processes and three oxidation processes ranging from $-1.8 \, V$ to $0.4 \, V$.

Supplementary material

CCDC-620216 contains the supplementary crystallographic data for **I**. These data can be obtained from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk). Copies of this information are available free of charge on request quoting the deposition CCDC number.

Acknowledgements

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