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Thiolato-bridged copper complexes with N,N,S-tridentate ligands[*]

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Thiolato-bridged complexes $[\mathrm{Cu^{II}_2(apaet)Cl_3}]$ and $[\mathrm{Cu^I_3Cu^{II}_3(apampt)_3Cl_6}]$ (Hapaet = 2-[(3-aminopropyl)amino]ethanethiol, Hapampt = 1-[(3-aminopropyl)amino]-2-methylpropane-2-thiol), have been synthesized and characterized by infrared and electronic absorption spectra and temperature dependence of magnetic susceptibilities. X-ray crystallography of the latter complex reveals a localized mixed-valence structure which is supported by the spectroscopic and electrochemical data. Magnetic susceptibility data show that a strong antiferromagnetic interaction is operating between $\mathrm{Cu^{II}}$ ions in both complexes.

Key words: *thiolato-bridged complexes; mixed-valence complexes; Cu; hexanuclear complexes*

1. Introduction

Study on mixed-valent complexes are of interest because of their potential application in the development of functional materials showing efficient long-distance electron transfer in the field of molecular electronics (cf. [1]) and their biological relevance involving multicopper oxidases such as spin-delocalized dinuclear mixed-valent copper cluster found in the '$\mathrm{Cu_A}$' site of cytochrome *c* oxidase and nitrous oxide reductase [2]. Especially thiolato-bridged mixed-valent copper complexes have been focused from the view of model complexes for the latter systems. So far, many attempts to synthesize thiolato-bridged dinuclear $\mathrm{Cu^{II}_2}$ and $\mathrm{Cu^ICu^{II}}$ complexes have been unsuccessful, because thiols usuallly reduce copper(II) to copper(I)

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$$2RS^- + 2Cu^{II} \leftrightarrow RSSR + 2Cu^I$$

Moreover, the electron-rich thiolato groups have a great affinity for various metal ions to form undesirable polymeric species with low solubilities hampering their precise characterization. In this regard, thiolic ligands having nitrogen donor atoms are useful, because formation of discrete thiolato-bridged complexes can be expected to be feasible by virtue of the chelating effect. In fact, dinuclear metal species were isolated for nickel(II) [3–9], cobalt(III) [10], and iron(II) [11] ions. Linear and cyclic trinuclear metal species [12], tetrahedral [13, 14] and adamantane-like [15] tetranuclear species, chain-like polynuclear species [12, 16, 17] were also obtained. For N,N,S tridentate ligands such as 2-[(3-aminopropyl)amino]ethanethiol (Hapaet), linear trinuclear metal species consisting of octahedral-tetrahedral-octahedral coordination environments seems to be most favourable structural pattern and we obtained such species in the cases of Zn^{II} [12], Cd^{II} [18], Mn^{II} [17], Fe^{II} [11], Co^{II} [19], and Ni^{II} [20] including trinuclear heterometal complexes [20] which are formed by one-pot reaction. In this study, we introduced a new thiolic ligand, 1-[(3-aminopropyl)amino]-2-methylpropane-2-thiol (Hapampt) as well as Hapaet, as chelating agents in the hope of attaining to make mixed-valence species by using the thiolic ligands. A preliminary account of this work has been published [21].

2. Experimental

Syntheses were carried out by using standard Schlenk techniques under argon. The thiolic ligand Hapaet was synthesized using a procedure described in the literature [4]. The Hapampt ligand was synthesized as follows. A toluene solution (50 cm^3) of isobutylene sulfide (8.6 g, 0.098 mol) was added dropwise to a toluene solution (200 cm^3) containing 1,3-diaminopropane (74.1 g, 1.00 mol). The solution was refluxed for 2 h. Then, the solvent was removed by distillation and the product was fractionally distilled at reduced pressure. Yield: 10.4 g (65.7%). bp. 79–81°C /5 mmHg. IR (KBr, cm^{-1}): $\nu_{as}(NH_2)$ 3350, $\nu_s(NH_2)$ 3300, $\nu(CH_3)$ 2960, $\nu(CH_2)$ 2860, $\delta(NH_2)$ 1575.

$[Cu_2(apaet)Cl_3]$ (1). To a solution of Hapaet (26 mg, 0.2 mmol) in methanol (2 cm^3) was added a solution of copper(II) chloride dihydrate (34 mg, 0.2 mmol) in methanol (3 cm^3). The reaction mixture was stirred at room temperature for 5 min and filtered. The resulting purple filtrate was allowed to stand several days at 7 °C. Dark purple precipitate deposited was collected by filtration. Yield 22 mg (30%). Found: C, 16.21; H, 3.59; N, 7.22%. Calcd for $C_5H_{13}Cl_3Cu_2N_2S$: C, 16.38; H, 3.57; N, 7.64%. IR (KBr, cm^{-1}): $\nu_{as}(NH_2)$ 3450, $\nu_s(NH_2)$ 3220, $\nu(CH_3)$ 2930, $\nu(CH_2)$ 2880, $\delta(NH_2)$ 1585.

$[Cu_6(apampt)_3Cl_6]\cdot 2H_2O$ ($2\cdot 2H_2O$). To a solution of Hapampt (32 mg, 0.2 mmol) in methanol (5 cm^3) was added a solution of copper(II) chloride dihydrate (34 mg, 0.2 mmol) in methanol (5 cm^3). The solution was stirred at room temperature for 5 min and filtered.

The resulting light brown filtrate was placed at 7 °C for several days to give dark brown crystals. Yield, 27 mg (74% based on the metal source). Found: C, 22.56; H, 4.77; N, 7.41%. Calcd for $C_{21}H_{55}Cl_6Cu_6N_6O_2S_3$ C, 22.64; H, 4.98; N, 7.54%. IR (KBr, cm^{-1}): $\nu_{as}(NH_2)$ 3420, $\nu_s(NH_2)$ 3285, $\nu(CH_3)$ 2950, $\nu(CH_2)$ 2830, $\delta(NH_2)$ 1590.

Measurements. Elemental analyses for carbon, hydrogen, and nitrogen were done using a Perkin-Elmer 2400 Series II CHNS/O Analyzer. Infrared spectra were measured with a JASCO MFT-2000 FT-IR Spectrometer in the 4000–600 cm^{-1} region. The electronic spectra were measured with a Shimadzu UV-vis-NIR Recording Spectrophotometer (Model UV-3100). The temperature dependence of the magnetic susceptibilities was measured with a Quantum Design MPMS-5S SQUID susceptometer operating at a magnetic field of 0.5 T between 4.5 and 300 K. The susceptibilities were corrected for the diamagnetism of the constituent atoms using Pascal's constants [22]. The effective magnetic moments were calculated from the equation $\mu_{eff} = 2.828\sqrt{\chi_A T}$, where χ_A is the atomic magnetic susceptibility. Cyclic voltammetric measurements were carried out on a BAS 100 BW Electrochemical Work Station. A three-electrode cell consisting of a glassy carbon electrode, a platinum-wire counter electrode, and a Ag/AgCl electrode was used.

X-ray crystal structure analysis. Crystals suitable for X-ray diffraction work were obtained as **2**·$2CH_3OH$ from a methanol solution. A black crystal of **2**·$2CH_3OH$ was mounted on a glass fibre with epoxy cement at a room temperature. A preliminary examination was made and data were collected on a Bruker CCD X-ray diffractometer (SMART APEX) using graphite-monochromated Mo K_α radiation. The structure was solved by direct methods and refined by full-matrix least-squares. All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were inserted at their calculated positions and fixed there. All calculations were carried out on a Pentium III Windows NT computer utilizing the SHELXTL software package.

Crystallographic data for **2**·$2CH_3OH$; $C_{23}H_{59}Cl_6Cu_6N_6O_2S_3$ *F.W.* = 1141.88, orthorhombic, space group *Pbca*, a = 18.706(5), b = 18.283(5), c = 23.962(6) Å, V = 8195(4) $Å^3$, Z = 8, D_c = 1.85 $g{\cdot}cm^{-3}$, $\mu(\text{Mo } K_\alpha)$ = 36.34 cm^{-1}, F(000) = 4568, crystal size 0.40 × 0.20 × 0.10 mm^3, 33826 reflections collected, 5936 independent reflections, $R1[I>2\sigma(I)]$ = 0.048, $wR2\ [I>2\sigma(I)]$ = 0.110.

3. Results and discussion

In the previous papers, we reported that reaction of Hapaet ligand with metal ions affords dinuclear nickel(II) complex $[Ni_2(apaet)_2]X_2$ ($X = ClO_4^-, BF_4^-$) [4], linear trinuclear complexes $[M\{M(apaet)_2\}_2]X_2$ (M = Mn [17], Fe [11], Co [19], Cd [18], $X = Cl^-, ClO_4^-$), $[M\{M'(apaet)_2\}_2](ClO_4)_2$ (M = Zn, Cd, Hg; M' = Mn, Fe, Co, Ni) [20], and tetrahedral tetranuclear palladium(II) complex $[Pd_4(apaet)_4]Cl_4$ [14]. In the present case, the reaction of Hapaet with copper(II) gave a different species. Elemental analysis of the isolated complex shows a stoichiometry Cu : apaet$^-$ = 2:1, which is consistent with the formulae for a copper(II) species [Cu_2(apaet)Cl_3] (**1**). On the other hand, the reaction of the methylated thiol, Hapampt, with copper(II) afforded a mixed-valent species, [Cu_6(apampt)$_3Cl_6$]·$2H_2O$ (**2**·$2H_2O$). In the infrared spectrum of **1**, the absorption bands due to apaet$^-$ ligand appear as a set of distinctive bands in a similar wavenumber region to that of the free thiol, Hapaet, with lacking the ν(SH) band (Fig. 1). The infrared spectrum of **2**·$2H_2O$ is essentially the same as that of **1** except for the bands due to the methyl groups.

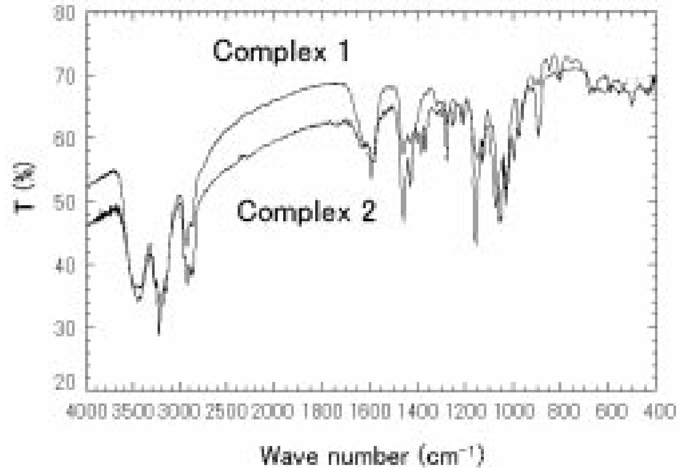

Fig. 1. Infrared spectra of [Cu_2(apaet)Cl_3] (**1**) and [Cu_6(apampt)$_3Cl_6$]·$2H_2O$ (**2**·$2H_2O$)

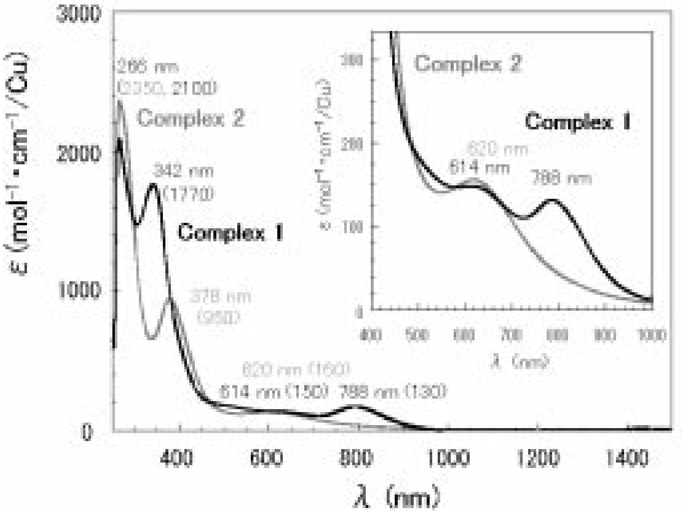

Fig. 2. Electronic absorption spectra of [Cu_2(apaet)Cl_3] (**1**) and [Cu_6(apampt)$_3Cl_6$]·$2H_2O$ (**2**·$2H_2O$) in DMF

The electronic absorption spectra in DMF are shown in Fig. 2. The bands at the visible region (**1**: 614 and 788 nm, **2**·$2H_2O$: 620 nm) may be assigned to d–d transitions judging from the intensities of the absorption bands. The band at the near-ultraviolet region (**1**: 342 nm, **2**·$2H_2O$: 378 nm) should correspond to the $\sigma(S) \rightarrow d(Cu)$ LMCT [23]. The absorption at the ultraviolet region (266 nm) may be assigned to the $\sigma(Cl) \rightarrow d(Cu)$ LMCT band [24]. We could not observe any IT band in the present complexes and thus the mixed-valence state of **2**·$2H_2O$ seems to be fully localized.

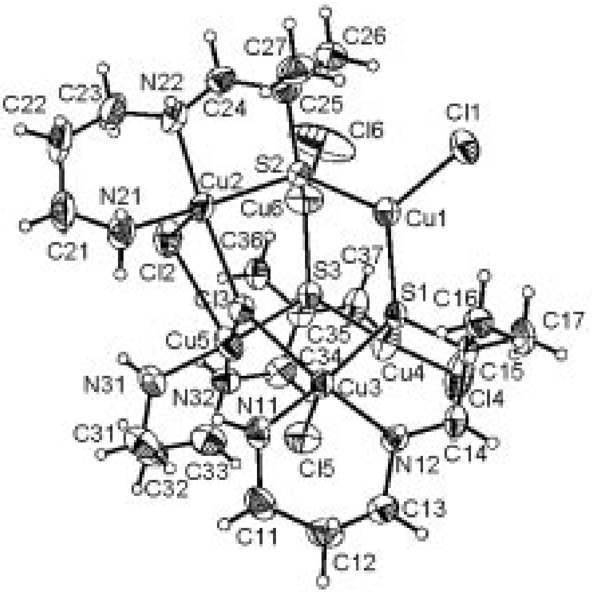

Fig. 3. ORTEP drawing of the structure of $[Cu_6(apampt)_3Cl_6]\cdot 2CH_3OH$ (**2**·$2CH_3OH$) showing the 50% probability thermal ellipsoids and atom labelling scheme. Methanol molecules are omitted for clarity

The X-ray crystal structural analysis of **2**·$2CH_3OH$ reveals a unique hexanuclear structure that is distinctly different from those of any previously structurally characterized thiolato complexes with N,N,S-tridentate ligands (Fig. 3) [4–20]. Selected bonding parameters are listed in the table. The hexanuclear core is shown in Fig. 4. Based on the charge consideration and the different coordination environments around the copper atoms, we can assign the Cu1, Cu4, and Cu6 atoms to copper(I) and the Cu2, Cu3, and Cu5 atoms to copper(II), respectively. The Cu^I–Cu^I, Cu^{II}–Cu^{II}, and Cu^I–Cu^{II} distances are 3.521(2)–3.777(2), 3.850(1)–4.625(1), and 3.375(1)–5.420(2) Å, respectively. The Cu^I atoms form a chair-like six-membered [–Cu1–S1–Cu4–S3 –Cu6–S2–] ring with thiolato-sulfur atoms of $apampt^-$, whereas the Cu^{II} atoms form two adjacent planar four-membered rings [–Cu2–Cl3–Cu5–Cl2–] and [–Cu3–Cl5 –Cu5–Cl3–] with chloride ions. The coordination geometries of the Cu^I atoms are trigonal with two thiolato-sulfur atoms of $apampt^-$ and chloride ion. The Cu^I–S bond distances [2.225(2)–2.259(2) Å] are within the normal range found in Cu^I complexes

[25]. The Cu^{I}–Cl distances [2.216(3)–2.238(2) Å] are in the normal range of the Cu^{I}–Cl distances [25]. On the other hand, there are two kinds of coordination geometries for the Cu^{II} atoms. The Cu2 and Cu3 atoms take an elongated square-pyramidal geometry with two amino-nitrogen atoms and thiolato-sulfur atom of $apampt^{-}$ (N21, N22, S2 for Cu2; N11, N12, S1 for Cu3) and chloride ion (Cl3) in the equatorial plane and a chloride ion (Cl2 for Cu2; Cl5 for Cu3) at the apex, while the Cu5 atom has a distorted octahedral geometry with two amino-nitrogen atoms and thiolato-sulfur atom of $apampt^{-}$ (N31, N32, S3) and three chloride ions (Cl2, Cl3, Cl5). The Cu^{II}–S distances [2.225(2)–2.273(2) Å] are comparable to the values found in thiolato-bridged $Cu^{I}Cu^{II}$ mixed-valent complexes [26, 27], although these distances are similar to those of the Cu^{I}–S bonds. The Cu^{II}–Cl distances (2.370(2)–2.607(2) Å for the square-pyramidal Cu atoms; 2.696(2)–2.839(2) Å for the octahedral Cu atom) are in the normal range for the Cu^{II}–Cl distances [25].

Table. Selected bond distances (Å) and angles (°) with their estimated standard deviations in parentheses $\left[Cu^{I}_{3}Cu^{II}_{3}(apampt)_{3}Cl_{6}\right]\cdot 2CH_{3}OH\ (\mathbf{2}\cdot 2CH_{3}OH)$

Cul–Cu2	3.958(1)	Cu4–Cu6	3.777(2)	Cu3–C13	2.396(2)
Cul–Cu3	3.925(1)	Cu5–Cu6	3.730(2)	Cu3–C15	2.557(2)
Cul–Cu4	3.722(1)	Cul–S1	2.226(2)	Cu4–S1	2259(2)
Cul–Cu5	5.229(2)	Cul–S2	2.225(2)	Cu4–S3	2.237(2)
Cul–Cu6	3.521(2)	Cul–Cll	2226(2)	Cu4–C14	2.238(2)
Cu2–Cu3	4.625(1)	Cu2–S2	2.273(2)	Cu5–S3	2.253(2)
Cu2–Cu4	5.420(2)	Cu2–N21	2.005(6)	Cu5–N31	1.979(5)
Cu2–Cu5	3.850(1)	Cu2–N22	2.019(6)	Cu5–N32	2.051(5)
Cu2–Cu6	3.506(2)	Cu2–C12	2.607(2)	Cu5–C12	2.762(2)
Cu3–Cu4	3.375(1)	Cu2–C13	2.370(2)	Cu5–C13	2.696(2)
Cu3–Cu5	3.872(2)	Cu3–S1	2.271(2)	Cu5–C15	2.839(2)
Cu3–Cu6	5.396(2)	Cu3–N11	1.990(5)	Cu6–S2	2.230(2)
Cu4–Cu5	3.547(2)	Cu3–N12	2.022(5)	Cu6–S3	2.232(2)
				Cu6–Cl6	2.216(3)
S1–Cul–S2	114.89(7)	SI–Cu3–C13	89.77(7)	S3–Cu5–Cli	92.98(6)
S1–Cul–Cll	124.60(8)	Sl–Cu3–C15	98.77(7)	S3–Cu5–C15	89.99(7)
S2–Cul–Cll	120.14(8)	N11–Cu3–N12	90.4(2)	N31–Cu5–N32	92.4(2)
S2–Cu2–N21	163.1(2)	N11–Cu3–C13	89.5(2)	N31–Cu5–C12	86.3(2)
S2–Cu2–N22	87.6(2)	N11–Cu3–C15	97.1(2)	N31–Cu5–C13	86.5(2)
S2–Cu2–C12	99.94(7)	N12–Cu3–C13	170.5(2)	N31–Cu5–C15	94.7(2)
S2–Cu2–C13	89.58(7)	N12–Cu3–C15	99.8(2)	N32–Cu5–C12	110.6(2)
N21–Cu2–N22	90.6(2)	C13–Cu3–C15	89.68(7)	N32–Cu5–Cl3	169.9(2)
N21–Cu2–Cl2	97.0(2)	S1–Cu4–S3	109.48(7)	N32–Cu5–C15	91.9(2)
N21–Cu2–C13	90.0(2)	S1–Cu4–C14	123.83(8)	Cl2–Cu5–C13	79.38(6)
N22–Cu2–Cl2	98.8(2)	S3–Cu4–C14	122.43(8)	C12–Cu5–C15	157.49(7)
N22–Cu2–Cl3	1723(2)	S3–Cu5–N31	175.1(2)	Cli–Cu5–C15	78.24(6)1
S1–Cu3–N11	164.1(2)	S3–Cu5–N32	89.0(2)	S2–Cu6–C16	127.6(1)
S1–Cu3–N12	87.7(2)	S3–Cu5–Cl2	88.73(7)	S3–Cu6–C16	119.5(1)
				S2–Cu6–S3	111.51(7)

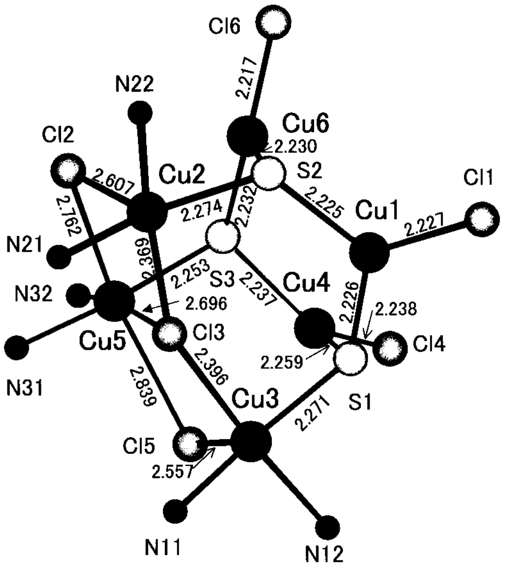

Fig. 4. Core structure of $[Cu_6(apampt)_3Cl_6]\cdot 2CH_3OH$ ($\mathbf{2}\cdot 2CH_3OH$)

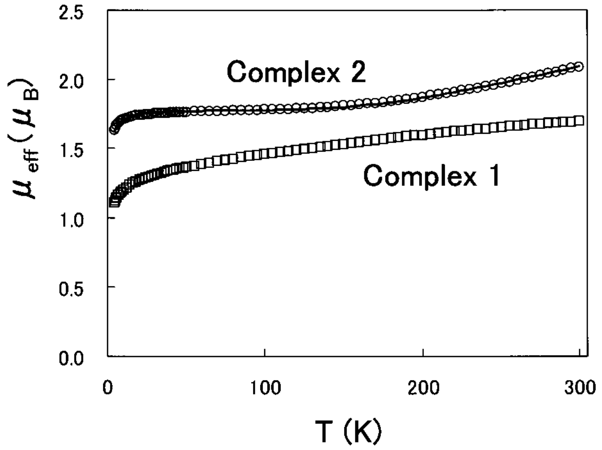

Fig. 5. Temperature dependence of the magnetic moments of $[Cu_2(apaet)Cl_3]$ (**1**) and $[Cu_6(apampt)_3Cl_6]\cdot 2H_2O$ ($\mathbf{2}\cdot 2H_2O$)

The magnetic moments of **1** and $\mathbf{2}\cdot 2H_2O$ are 1.70 μ_B per $[Cu_2(aaet)Cl_3]$ unit and 2.10 μ_B per $[Cu_6(apampt)_3Cl_6]\cdot 2H_2O$, which are lower than the spin-only values, 2.45 and 3.00μ_B, respectively. Temperature dependence of magnetic moments is displayed for **1** and $\mathbf{2}\cdot 2H_2O$ in Fig. 5. The magnetic moments are both decreased with lowering the temperature. The temperature dependence of **1** could not be interpreted by the Bleaney–Bowers equation based on the dinuclear copper(II) structure. Therefore, the structure of **1** may be considered to be polymeric one as one of the possible structures

[28]. On the other hand, the temperature-dependent profile of **2**·2H$_2$O is fully explained by the van Vleck equation based on the Heisenberg model $H = -2JS_{\mathrm{Cu2}}S_{\mathrm{Cu3}} -2J'(S_{\mathrm{Cu2}}S_{\mathrm{Cu5}}+S_{\mathrm{Cu3}}S_{\mathrm{Cu5}})$ (see Fig. 4). The parameters obtained by the simulation are as follows: $J = -602$ cm^{-1}, $J' = -2.5$ cm^{-1}, $g = 2.06$, $\theta = -0.91$ K. The present results suggest that a strong antiferromagnetic interaction is mainly operating between the Cu2 and Cu3 atoms. In relation to this, it is to be noted that the bond distances of Cu2–Cl3 [2.370(2) Å] and Cu3–Cl3 [2.396(2) Å] are significantly shorter that those of Cu2–Cl2, Cu5–Cl2, Cu5–Cl3, Cu5–Cl5, and Cu3–Cl5 [2.557(2)–2.839(2) Å] and the Cu2–Cl3–Cu3 angle [152.07(9)°] is large, which is a favourable feature for the strong antiferromagnetic interaction via the bridging Cl atom [29].

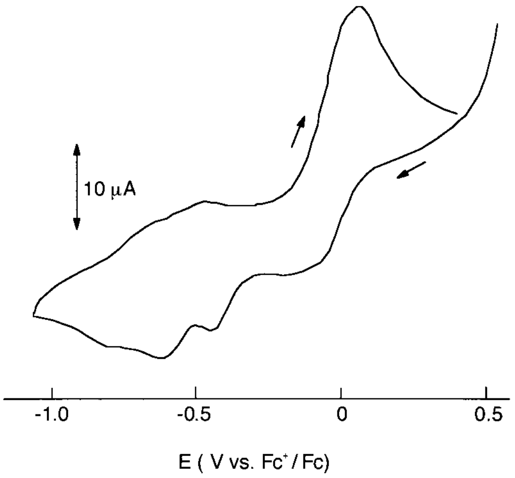

Fig. 6. Cyclic voltammogram of [Cu$_6$(apampt)$_3$Cl$_6$]·2H$_2$O (**2**·2H$_2$O) in DMF 0.5 × 10^{-3} M; electrolyte: 0.1 M tetra-*n*-butylammonium perchlorate

In order to examine the mixed-valence state, the cyclic voltammetric measurement was performed for **2**·2H$_2$O (Fig. 6). In the +0.5 to –1.0 V versus Fc$^+$/Fc region, three reduction waves are observed at around –0.1, –0.45, and –0.62 V. The first wave seems to be coupled with an anodic wave at +0.06 V. This redox wave may be due to Cu(II)/Cu(I) couple of the Cu$^{\mathrm{I}}$S$_2$Cl moiety. The second and third reduction waves have not clear coupled-oxidation waves. These waves may correspond to reduction of Cu$^{\mathrm{II}}$→Cu$^{\mathrm{I}}$ of the Cu$^{\mathrm{II}}$N$_2$SCl$_2$ and Cu$^{\mathrm{II}}$N$_2$SCl$_3$ moieties.

4. Conclusions

N,N,S-donor tridentate thiols, 2-[(3-aminopropyl)amino]ethanethiol (Hapaet) and 1-[(3-aminopropyl)amino]-2-methylpropane-2-thiol (Hapampt) were synthesized and proved to be useful ligands for the synthesis of thiolato-bridged copper(II) and copper(I, II) mixed-valent complexes. Spectroscopic and electrochemical data as well as structural feature support a localized mixed-valence state of the thiolato-bridged copper complex with apampt$^-$. Steric hindrance of the methyl groups of apampt$^-$ may contribute to the stabilization of the mixed-valent state by protecting against the oxidation.

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