Inorganica Chimica Acta, 186 (1991) 165–169

Spectroscopic and electrical properties of $[Cu_4(dmit)_3]^{2-}$ and $[Cu_4(dsis)_3]^{2-}$ cluster anion complexes and their oxidized species (dmit = 4,5-dimercapto-1,3-dithiole-2-thionate; dsis = 4,5-di(hydroseleno)-1,3-diselenole-2-selonate)

Akito Yokozawa and **Gen-etsu Matsubayashi***

Department of Applied Chemistry, Faculty of Engineering, Osaka University, Yamadaoka, Suita, Osaka 565 (Japan)

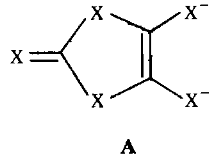
(Received March 18, 1991)

Abstract

$[Cu_4(dmit)_3]^{2-}$ and $[Cu_4(dsis)_3]^{2-}$ (dmit = 4,5-dimercapto-1,3-dithiole-2-thionate(2 −); dsis = 4,5-di(hydroseleno)-1,3-diselenole-2-selonate(2 −)) cluster anion complexes, in which the anions consist of tetrahedron skeletons of copper atoms chelated and bridged by dmit-sulfur and dsis-selenium atoms, were prepared. Molecular interactions among the anion moieties through S–S and Se–Se contacts in the solid state were deduced from electronic reflectance spectra. They were oxidized by $[FeCp_2]^+$ and $[FeCp^*_2]^+$ cations (Cp and Cp* = the cyclopentadienyl and pentamethylcyclopentadienyl anions, respectively) to afford complexes containing partially oxidized cluster anion moieties. The ligand-centered oxidation was confirmed by X-ray photoelectron and ESR spectra. They behave as semiconductors with electrical conductivities of $1 \times (10^{-3}–10^{-7})$ S cm^{-1} measured for the compacted pellets.

Introduction

Many planar metal complexes with the 4,5-dimercapto-1,3-dithiole-2-thionate(2 −) ligand (dmit: **A**, X = S), $[M(dmit)_2]^{n-}$ (M = Ni(II), Pd(II), Pt(II) and Au(III); $n < 1$) exhibit good electrical conductivities [1], some of which become superconductors at low temperatures [2–4]. Two- or three-dimensional, close intermolecular contacts of the sulfur atoms produce conduction pathways in the crystals. Metal complexes with the 4,5-di(hydroseleno)-1,3-diselenole-2-selonate(2 −) ligand (dsis: **A**, X = Se) are also expected to become excellent molecular assemblies having more effective molecular interactions through atomic contacts of selenium which has spatially more extended orbitals than sulfur. They may become good electrical conductors with two- or three-dimensional conduction pathways, if they are partially oxidized.



(X = S and Se)

A

Very few works, however, on dsis–metal complexes have been studied [1,5–10]. Although non-planar, bulky dmit- and dsis–metal complexes are also expected to behave as new conductors having multidimensional molecular interactions through S–S and Se–Se contacts in the solid states, few non-planar dmit–metal complexes have been studied [11–13].

This paper reports the preparations of $[Cu_4(dmit)_3]^{2-}$ and $[Cu_4(dsis)_3]^{2-}$ cluster anion complexes as well as their oxidized complexes and their electrical properties and discusses the electronic states based on IR, electronic absorption, powder reflectance, ESR and X-ray photoelectron spectra. The X-ray structure analysis of [*N*-methylpyridinium]$_2[Cu_4(dmit)_3]$ has already appeared [14].

Experimental

Materials

4,5-Bis(benzoylthio)-1,3-dithiole-2-thione [15] and 4,5-bis(benzoylseleno)-1,3-diselenole-2-selone [5] were prepared as described previously. $[Cu(MeCN)_4][ClO_4]$ was prepared by the modified procedure of the literature method [16]. $[FeCp_2][PF_6]$ (Cp = the cyclopentadienyl anion) and $[FeCp^*_2][BF_4]$ (Cp* = the pentamethylcyclopentadienyl anion) were

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*Author to whom correspondence should be addressed.

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prepared by reactions of ferrocene and decamethylferrocene with a concentrated aqueous nitric acid solution, followed by addition of aqueous solutions of $[NH_4][PF_6]$ and of $[NH_4][BF_4]$, respectively.

Preparations of $[Cu_4(dmit)_3]^{2-}$ and $[Cu_4(dsis)_3]^{2-}$ cluster anion complexes

All the procedures for preparations of the following complexes were performed under nitrogen atmosphere.

4,5-Bis(benzoylthio)-1,3-dithiole-2-thione (170 mg, 420 μmol) was dissolved in a methanol (10 cm^3) solution containing sodium metal (22 mg, 960 μmol) affording Na_2dmit in the solution. A methanol (3 cm^3) solution of $[NBu^n{}_4]Br$ (90 mg, 280 μmol) was added to it, followed by addition of an acetonitrile (6 cm^3) solution of $[Cu(MeCN)_4][ClO_4]$ (170 mg, 520 μmol) with stirring. Immediately a brown solid precipitated, which was collected by filtration, washed with diethyl ether and water, and dried *in vacuo*. They were recrystallized from acetone to afford brown microcrystals of $[NBu^n{}_4]_2[Cu_4(dmit)_3]$ (**1**) (82% yield). *Anal.* Calc. for $C_{41}H_{72}Cu_4N_2S_{15}$: C, 37.08; H, 5.46; N, 2.11. Found: C, 36.38; H, 5.25; N, 2.13%. A similar reaction using *N*-methylpyridinium iodide [mpy]I instead of $[NBu^n{}_4]Br$ afforded a brown solid of $[mpy]_2[Cu_4(dmit)_3]$ (**2**) (74% yield). *Anal.* Calc. for $C_{21}H_{16}Cu_4N_2S_{15}$: C, 24.45; H, 1.56; N, 2.72. Found: C, 24.64; H, 1.58; N, 2.74%.

4,5-Bis(benzoylseleno)-1,3-diselenole-2-selone (100 mg, 160 μmol) was dissolved in a methanol (10 cm^3) solution containing sodium metal (9.8 mg, 430 μmol). A methanol solution of $[NBu^n{}_4]Br$ (56 mg, 170 μmol) and an acetonitrile solution of $[Cu(MeCN)_4][ClO_4]$ (69 mg, 210 μmol) was added to it to afford a brown solid of $[NBu^n{}_4]_2[Cu_4(dsis)_3]$ (**3**), which was collected by filtration, washed with diethyl ether and water, and dried *in vacuo* (86% yield). *Anal.* Calc. for $C_{41}H_{72}Cu_4N_2Se_{15}$: C, 24.24; H, 3.57; N, 1.38. Found: C, 24.62; H, 3.50; N, 1.46%.

Preparations of oxidized complexes of the $[Cu_4(dmit)_3]^{2-}$ and $[Cu_4(dsis)_3]^{2-}$ anions

To an acetonitrile (5 cm^3) solution of complex **1** (17 mg, 13 μmol) was added with stirring an acetonitrile (5 cm^3) solution of $[FeCp_2][PF_6]$ (11 mg, 33 μmol). A black solid of $[NBu^n{}_4]_{0.2}[Cu_4(dmit)_3]$ (**4**) precipitated immediately, which was collected by filtration, washed with acetonitrile, and dried *in vacuo* (75% yield). *Anal.* Calc. for $C_{12.2}H_{7.2}Cu_4N_{0.2}S_{15}$: C, 16.43; H, 0.81; N, 0.31. Found: C, 16.01; H, 0.74; N, 0.68%.

Complex **3** (17 mg, 8.4 μmol) was dissolved in acetonitrile (40 cm^3), and to the solution was added an acetonitrile (2 cm^3) solution of $[FeCp_2][PF_6]$ (17 mg, 51 μmol). A black solid of $[NBu^n{}_4]_{0.16}[Cu_4(dsis)_3]$ (**5**) precipitated immediately, which was collected by filtration, washed with acetonitrile, and dried *in vacuo* (55% yield). *Anal.* Calc. for $C_{11.6}H_{5.8}Cu_4N_{0.16}Se_{15}$: C, 8.76; H, 0.37. Found: C, 8.96; H, 0.36%.

An acetone (2 cm^3) solution of $[FeCp^*{}_2][BF_4]$ (28 mg, 68 μmol) was added with stirring to an acetone (5 cm^3) solution of complex **1** (26 mg, 20 μmol) to yield immediately a black solid of $[FeCp^*{}_2]_{1.2}[Cu_4(dmit)_3]$ (**6**) (84% yield). *Anal.* Calc. for $C_{33}H_{36}Fe_{1.2}S_{15}$: C, 31.10; H, 2.94. Found: C, 31.37; H, 3.00%. A similar reaction of complex **3** (10 mg, 4.9 μmol) with $[FeCp^*{}_2][BF_4]$ (11 mg, 27 μmol) in acetonitrile (40 cm^3) gave a black solid of $[FeCp^*{}_2]_{0.5}[Cu_4(dsis)_3]$ (**7**) (52% yield). *Anal.* Calc. for $C_{19}H_{15}Cu_4Fe_{0.5}Se_{15}$: C, 13.35; H, 0.88. Found: C, 12.96; H, 1.12%.

Physical measurements

Electrical conductivities were measured for compacted pellets in the range from −30 to 30 °C by the conventional two-probe method [17]. IR [17], electronic absorption [17], ESR [18] and X-ray photoelectron spectra [19] were recorded as described previously. Cyclic voltammograms were measured for complexes dissolved in *N,N*-dimethylformamide containing $[NBu^n{}_4][ClO_4]$ as a supporting electrolyte, using a conventional cell consisting of two platinum plates as working and counter elecrodes and a saturated calomel electrode (SCE) as reference. ^{13}C NMR spectra were recorded on a JEOL JNM-GSX-450 spectrometer. Chemical shifts were measured relative to tetramethylsilane as internal standard.

Results and discussion

Properties of $[Cu_4(dmit)_3]^{2-}$ and $[Cu_4(dsis)_3]^{2-}$ cluster anion complexes

As was reported in the previous paper [14], the $[Cu_4(dmit)_3]^{2-}$ anion has a distorted tetrahedron geometry of copper atoms which are coordinated by dmit-sulfur atoms (Fig. 1). A similar Cu_4S_6 cluster structure with dithiolate–chelate ligands was reported only for the $[Cu_4\{o\text{-}(SCH_2)_2C_6H_4\}_3]^{2-}$ anion complex [20]. Cu(1), Cu(2) and Cu(3) atoms are chelated by the dmit ligands and bridged by a sulfur atom of another dmit ligand to assume a trigonal planar array of sulfur atoms around the metal atom. On the other hand, the Cu(4) atom also having a trigonal planar array of sulfur atoms is coordinated by the dmit-sulfur atoms only through the bridging mode.

The chelating mode of the dmit ligand in the solid state indicates the non-equivalence of the corresponding atoms of each half of the ligand caused

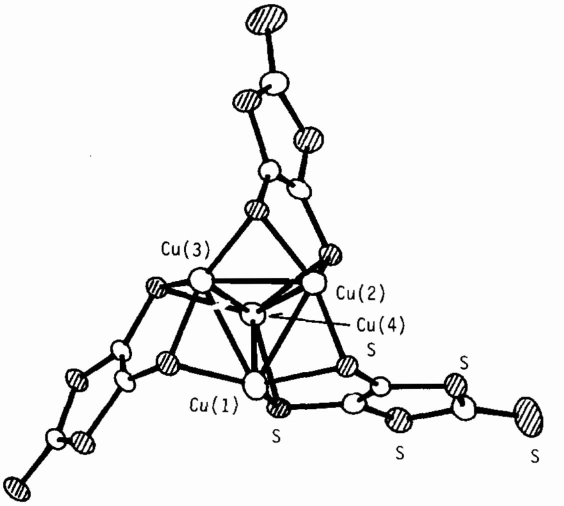

Fig. 1. Molecular geometry of the anion moiety of $[mpy]_2[Cu_4(dmit)_3]$ (**2**) [14].

by the two kinds of sulfur atoms bridging with the copper atoms. This is also evident in solution because the ^{13}C NMR spectrum of $[NBu^n_4]_2[Cu_4(dmit)_3]$ in dimethyl sulfoxide-d_6 shows three signals at δ 136.0 (C=C), 138.9 (C=C) and 209.3 (C=S) due to the dmit unit. $[NBu^n_4]_2[Cu_4(dsis)_3]$ (**3**) is also likely to assume a similar structure constructed with the Cu_4-tetrahedron chelated with three dsis ligands.

The electronic absorption spectrum of complex **2** in acetonitrile and its powder reflectance spectrum are illustrated in Fig. 2. An intense absorption band at 458 nm ($\epsilon = 2.4 \times 10^4$ dm^3 cm^{-1} mol^{-1}) is ascribed to the π–π^* transition of the dmit ligand. The π–π^* band of the $[Au(dmit)_2]^-$ complex is also observed at a similar wavelength (468 nm in acetonitrile) [1], while the bands for Na_2dmit (514 nm in methanol), $[Zn(dmit)_2]^{2-}$ (530 nm in acetonitrile) and $[Cu(dmit)_2]^{2-}$ complexes (540 nm in acetonitrile) [21] occur at a somewhat longer wavelength. In the $[Au(dmit)_2]^-$ and $[Cu_4(dmit)_3]^{2-}$ ions, +1.5 and +1.3 charges of the metal ions, respectively, formally participate in one dmit ligand, while it is a +1.0 charge in the other three ions. Since positive charges can stabilize preferably the ground state of the dmit ligand, the former two complexes seem to result in π–π^* transitions with higher energies. $[NBu^n_4]_2[Cu_4(dsis)_3]$ also exhibits an absorption spectrum similar to that of the $[Cu_4(dmit)_3]^{2-}$ complex. The intense band due to the π–π^* transition occurs at a longer wavelength (483 nm, $\epsilon = 2.5 \times 10^4$ dm^3 cm^{-1} mol^{-1} in acetonitrile) than the dmit analog. The same tendency was also observed for the spectra of $[M(dmit\ or\ dsis)_2]^{2-}$ (M = Au, $n = 1$ [1]; M = Zn [8] and Cu, $n = 2$ [9]) complexes.

The powder reflectance spectrum of complex **2** shows another broad band around 580 nm besides the above-mentioned π–π^* transition band. This broad band seems to arise from the molecular interactions among the anion moieties through sulfur–sulfur contacts in the solid state, as the dimerized anion moieties with further two-dimensional molecular interactions were clarified in the crystal structure of complex **2** [14]. Complex **1** shows the same absorption spectrum in acetonitrile as complex **2**, while the powder reflectance band due to the molecular S–S interaction appears as a shoulder at 540 nm. The selenium analog **3** also exhibits a broad re-

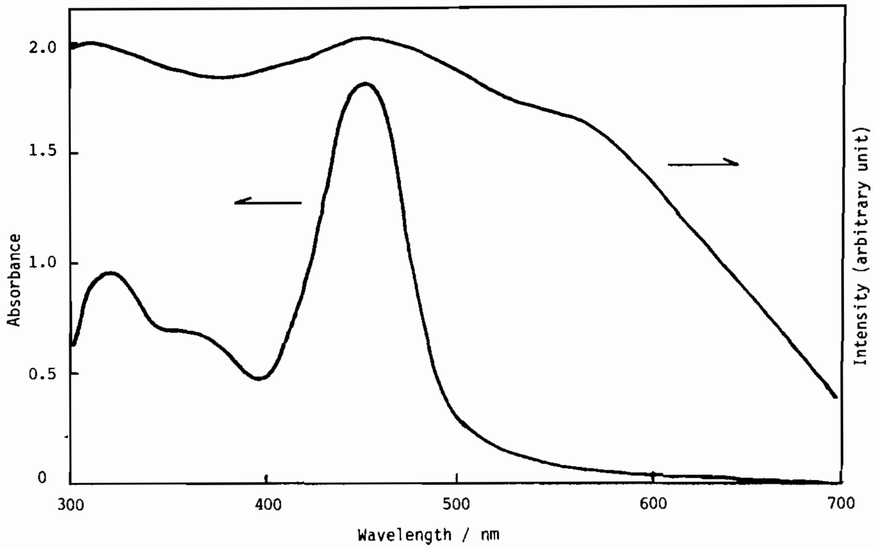

Fig. 2. The electronic absorption spectrum of complex **2** (8.7×10^{-5} mol dm^{-3}) in acetonitrile and its powder reflectance spectrum.

flectance band around 600 nm which is ascribed to the interanionic molecular interaction through selenium–selenium contacts.

Oxidized complexes of the $[Cu_4(dmit)_3]^{2-}$ and $[Cu_4(dsis)_3]^{2-}$ anions

Figure 3 illustrates the cyclic voltammograms of complexes **1** and **3** measured in *N,N*-dimethylformamide. Both the complexes are oxidized at low potentials. Although the first oxidation processes for both the complexes are pseudo-reversible, the second oxidations occur as irreversible processes. The dsis complex is oxidized at a somewhat lower potential than the corresponding dmit analog, which is the same tendency observed for $[M(dmit\ or\ dsis)_2]^{n-}$ complexes (M = Au, $n = 1$ [1]; M = Cu, $n = 2$ [9]; M = Ni, $n = 2$ [9]).

The $[Cu_4(dmit)_3]^{2-}$ and $[Cu_4(dsis)_3]^{2-}$ anion complexes are oxidized by $[FeCp_2]^+$ and $[FeCp^*_2]^+$ cations to form partially oxidized species **4**–**7**. Oxidation by the $[FeCp_2]^+$ cation affords complexes containing the $[NBu^n_4]^+$ cation.

Table 1 lists the binding energies of Cu $2p_{3/2}$ electrons determined from X-ray photoelectron spectra and $\nu(C=C)$ stretching frequencies in the IR spectra of the cluster complexes. The values of the binding energies of the partially oxidized complexes **4**–**7** are almost the same as those of complexes **1** and **3**, which indicates that the oxidation essentially occurs at the dmit and dsis ligand centers. In accordance with this, appreciable broad, approximately isotropic signals were observed in the powder ESR spectra for complexes **4**–**7** at $g = 2.03$–2.07 (peak-to-peak linewidth 12–35 mT at room temperature). These findings indicate the presence of paramagnetic species with dmit- and dsis-centered oxidation, as observed for oxidized metal complexes: $[Au(dmit)_2]^{n-}$ and $[Au(dsis)_2]^{n-}$ ($n = 0 - 0.22$) [1]; $[Rh(dmit)_2]^{n-}$ ($n = 0.4$–1.5) [22]; $[M(dmit)_2]^{n-}$ (M = Ni, Pd, or Pt; $n = 0.6$ or 1) [23]; $[Pt(dmit)(L\text{-}L)]^{n-}$ (L-L = 2,2′-bipyrimidine or *N*-ethyl-2-methylpyridine-2-carbaldimine; $n = 0$ or 0.53) [24]. The $\nu(C=C)$ frequencies of the oxidized complexes occur in the region 1380–1220 cm^{-1}, which are lower than those of the unoxidized complexes **1**–**3**. This is also consistent with the above-mentioned ligand-centered oxidation [12, 23].

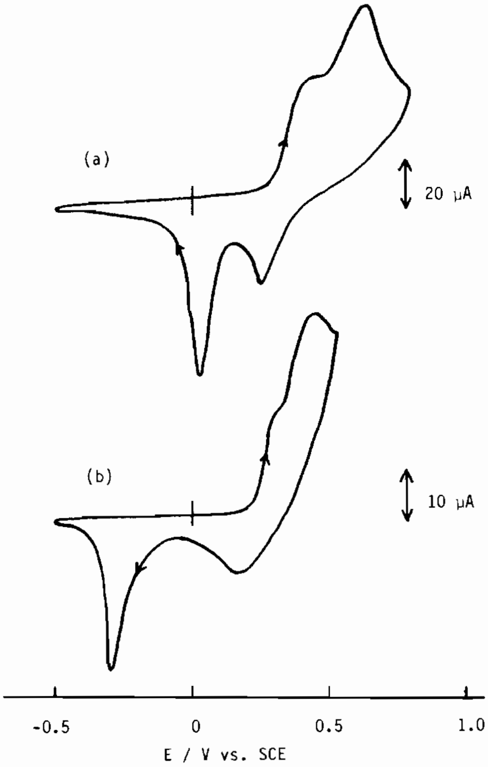

Fig. 3. Cyclic voltammograms of complexes **1** (5.1×10^{-4} mol dm^{-3}) (a) and **3** (3.0×10^{-4} mol dm^{-3}) (b) in *N,N*-dimethylformamide at room temperature; 0.1 mol dm^{-3} $[NBu^n_4][ClO_4]$, scan rate, 0.1 V s^{-1}.

TABLE 1. Binding energies of Cu $2p_{3/2}$ electrons and $\nu(C=C)$ stretching frequencies of the ligands of the Cu_4-cluster complexes

Complex	E_b (eV)	$\nu(C=C)$ (cm^{-1})
1	932.9	1410
3	932.8	1420
4	933.0	1380 1220(br)
5	932.9	1380(br)
6	932.9	1410 1220
7	932.9	1380(br)

br: broad.

TABLE 2. Electrical conductivities (σ) and activation energies (E_a) of the Cu_4-cluster complexes[a]

Complex	$\sigma_{25\,°C}$ (S cm^{-1})	E_a (eV)
1	1.4×10^{-8}	
3	6.0×10^{-8}	
4	1.6×10^{-3}	0.23
5	2.0×10^{-7}	
6	2.2×10^{-6}	0.38
7	1.9×10^{-5}	0.32

[a] Measured for compacted pellets.

Table 2 summarizes electrical conductivities of the dmit and dsis complexes and their activation energies measured for compacted pellets. Complexes **1** and **3** have low conductivities, while the other complexes behave as semiconductors in the temperature range from −30 to 30 °C. They are partially oxidized in the ligands, affording sulfur–sulfur and selenium–selenium contacts in the solid state, which lead to electrical conduction pathways exhibiting considerable conductivities. These molecular interactions were assumed from the broad band tailed to long wavelengths observed in the powder reflectance spectra of the oxidized complexes.

Several non-planar bulky complexes, such as $[V(dmit)_3]^-$ [11, 12] and $[V(dmit)_3]^{0.5-}$ complexes [13], were reported to exhibit electrical conductivities. Thus, dmit– and dsis–metal cluster complexes, although they are bulky, may also become electrical conductors having multi-dimensional conduction pathways constructed with S–S and Se–Se contacts.

Acknowledgement

This work was supported by a Grant-in-Aid for Scientific Research on Priority Areas No. 02230220 from the Ministry of Education, Science and Culture, Japanese Government.

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