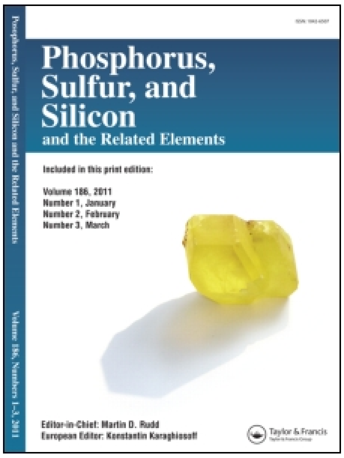

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Gen-Etsu Matsubayashi[a]
[a] Institute of Chemistry, College of General Education, Osaka University, Toyonaka, Osaka, Japan

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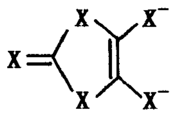
STRUCTURES AND PROPERTIES OF $[CU_4(C_3X_5)_3]^{2-}$ (X = S AND SE) CLUSTER ANION COMPLEXES

GEN-ETSU MATSUBAYASHI
Institute of Chemistry, College of General Education, Osaka University, Toyonaka, Osaka 560, Japan

Abstract $[Cu_4(C_3X_5)_3]^{2-}$ (X = S and Se) [$C_3S_5^{2-}$= 4,5-dimercapto-1,3-dithiole-2-thionate(2-) and $C_3Se_5^{2-}$ = 4,5-di(hydroseleno)-1,3-diselenole-2-selonate(2-)] cluster anion complexes were prepared. Molecular interactions among the anion moieties through S-S and Se-Se contacts in the solid state were deduced from X-ray structure analysis and electronic reflectance spectra. They reacted with $[FeCp_2]^+$ and $[FeCp^*_2]^+$ cations (Cp and Cp* = the cyclopentadienyl and decamethylcyclopentadienyl anions, respectively) to give partially oxidized species with ligand-centered oxidation. They behave as semiconductors with electrical conductivities of $1x(10^{-3}-10^{-7})$ S cm^{-1} measured for the compacted pellets.

INTRODUCTION


(X = S, Se)
(A)

Many planar $[M(C_3S_5)_2]^{n-}$ [M = Ni, Pd, Pt,and Au; n<1; $C_3S_5^{2-}$ = **A** (X = S)] complexes exhibit high electrical conductivities,[1] some of which exhibit superconductivity at low temperatures.[2-4] Two-dimensional molecular interactions through S-S contacts form conduction pathways in the crystals. Metal complexes with the $C_3Se_5^{2-}$ ligand may also become excellent conductors having effective molecular interactions through Se-Se contacts owing to spatially more extended orbitals of selenium. However, very few works on conducting C_3Se_5-metal complexes have been studied.[1,5,6] Nonplanar C_3X_5-metal complexes (X = S and Se) are also expected to behave as new conductors which have multi-dimensional, intermolecular S-S and Se-Se contacts in the solid state. Some conducting, nonplanar C_3S_5-metal complexes were reported.[7-9] Here, we report the preparations of $[Cu_4(C_3X_5)_2]^{2-}$ (X = S and Se) cluster anion complexes as well as their oxidized complexes and their electrical properties. Electronic states of the complexes are discussed based on electronic absorption, powder reflectance, ESR, and X-ray photoelectron spectra.

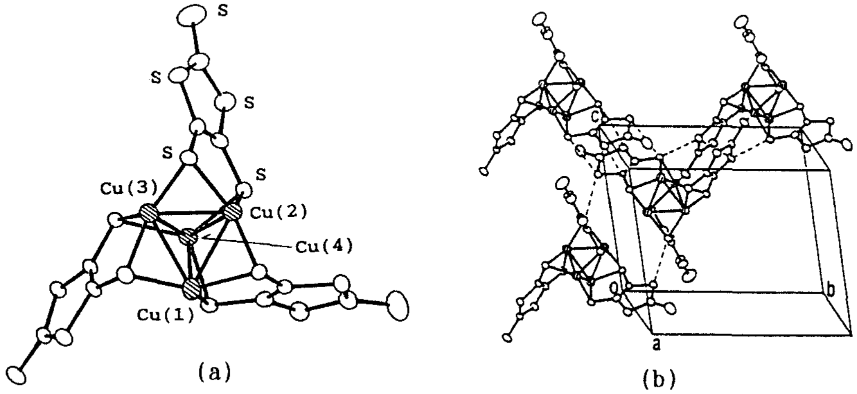
EXPERIMENTAL

Reactions of $[Cu(MeCN)_4][ClO_4]$ with $Na_2C_3X_5$ (X = S and Se)[10,11] in acetonitrile/methanol in the presence of $NBu^n{}_4Br$ afforded $[NBu^n{}_4]_2[Cu_4(C_3X_5)_3]$. Oxidation of these complexes by reactions with $[FeCp_2][PF_6]$ (Cp = the cyclopentadienyl anion) in acetonitrile gave $[NBu^n{}_4]_{0.2}[Cu_4(C_3S_5)_3]$ and $[NBu^n{}_4]_{0.16}[Cu_4(C_3Se_5)_3]$. The oxidation reactions using $[FeCp^*{}_2][BF_4]$ (Cp* = the decamethylcyclopentadienyl anion) yielded $[FeCp^*{}_2]_{1.2}[Cu_4(C_3S_5)_3]$ and $[FeCp^*{}_2]_{0.5}[Cu_4(C_3Se_5)_2]$. The molecular and crystal structures of $[Mepy]_2[Cu_4(C_3S_5)_3]$ (Mepy = N-methylpyridinium) were clarified by X-ray single-crystal structure analysis.[12]

The reaction of $AgClO_4$ with $Na_2C_3S_5$ in acetonitrile/methanol gave $[Ag_4(C_3S_5)_3]^{2-}$ cluster anion complexes.[13]

RESULTS AND DISCUSSION

The $[Cu_4(C_3S_5)_3]^{2-}$ anion has a distorted tetrahedron geometry of



(a)

(b)

FIGURE 1 (a) Molecular structure of the anion of $[Mepy]_2$-$[Cu_4(C_3S_5)_3]$ and (b) packing diagram of the anion moieties.[12]

copper atoms coordinated by C_3S_5-sulfur atoms, as illustrated in Fig. 1-a.[12] This Cu_4S_6 geometry having the dithiolato-chelate ligands (Cu-Cu, 2.608-3.150 Å) is close to that of the $[Cu_4\{\underline{o}$-$(SCH_2)_2C_6H_4\}_3]^{2-}$ anion complex.[14] In the present complex, Cu(1), Cu(2), and Cu(3) atoms are chelated by a C_3S_5-ligand and bridged by a sulfur atom of another ligand, assuming a trigonal planar array of sulfur atoms around the copper atom (Cu-S, 2.211-2.368 Å). The Cu(4) atom, although it has also a trigonal planar array of sulfur atoms, is coordinated by sulfur atoms only through the bridging mode. The anions form a dimer unit having the intermolecular Cu(4)-S interaction (2.495 Å) and some nonbonded S-S contacts (<3.7 Å) in the solid state. The dimeric units interact with each other through several S-S contacts to form a two-dimensional molecular interaction sheet parallel to the $\underline{bc}$ plane, the N-methylpyridinium cations being arranged between the sheets (see Fig. 1-b). The C_3Se_5-analog is also likely to assume the Cu_4Se_6 core geometry similar to that of the Cu_4S_6 core. Furthermore, the anion moieties seem to interact with each other through Se-Se contacts, as deduced from the electronic powder reflectance spectrum described below.

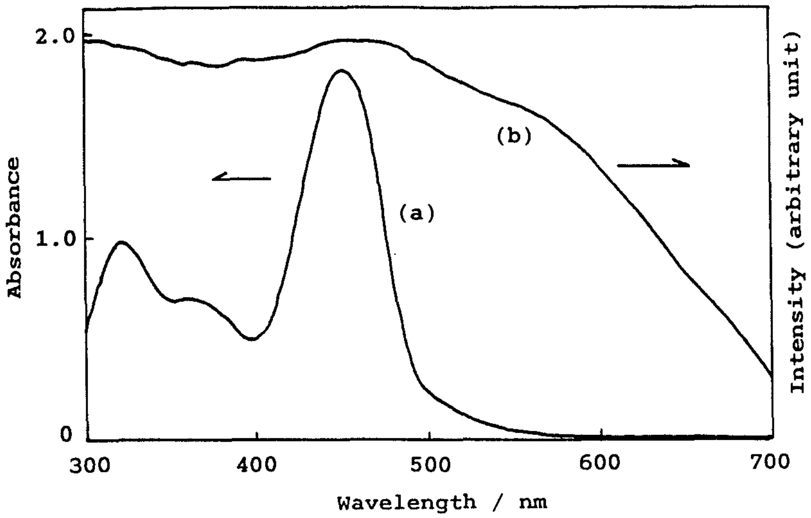


FIGURE 2 (a) Electronic absorption (8.7×10^{-5} mol dm^{-3}) and (b) reflectance spectra of $[Mepy]_2[Cu_4(C_3S_5)_3]$.

Figure 2 shows the electronic absorption spectrum of $[Mepy]_2[Cu_4(C_3S_5)_3]$ in acetonitrile and its powder reflectance spectrum. An intense absorption band at 458 nm is ascribed to π-π^* transition of the C_3S_5-ligand, as observed for other C_3S_5-metal complexes.[1,15] The reflectance spectrum exhibits another broad band around 580 nm besides the π-π^* transition band. This broad band seems to arise from the molecular interactions among the anion moieties through S-S contacts in the solid state, as described in the crystal structure. In $[NBu^n{}_4]_2[Cu_4(C_3S_5)_3]$ this intermolecular band is observed at 540 nm. The selenium analog also exhibits a broad reflectance band around 600 nm presumably due to Se-Se contacts besides the π-π^* transition band observed at 483 nm.

The $[Cu_4(C_3X_5)_3]^{2-}$ (X = S and Se) anions are oxidized at low potentials; first oxidation peak potentials are 0.45 (X = S) and 0.35 V vs. SCE (X = Se).[5] Thus, they can be oxidized by $[FeCp_2]^+$ and $[FeCp^*{}_2]^+$ cations to form the partially oxidized complexes.

TABLE I Binding energies of Cu $2p_{3/2}$ electrons $(E_b)^*$, electrical conductivities (σ) and activation energies $(E_a)^{**}$ of the $[Cu_4(C_3X_5)_3]$ (X = S and Se) cluster complexes.

Complex	E_b / eV	$\sigma_{25°C}$ / S cm^{-1}	E_a/ eV
$[NBu^n{}_4]_2[Cu_4(C_3S_5)_3]$	932.9	$1.4x10^{-8}$	
$[NBu^n{}_4]_2[Cu_4(C_3Se_5)_3]$	932.8	$6.8x10^{-8}$	
$[NBu^n{}_4]_{0.2}[Cu_4(C_3S_5)_3]$	933.0	$1.6x10^{-3}$	0.23
$[NBu^n{}_4]_{0.16}[Cu_4(C_3Se_5)_3]$	932.9	$2.0x10^{-7}$	
$[FeCp^*{}_2]_{1.2}[Cu_4(C_3S_5)_3]$	932.9	$2.2x10^{-6}$	0.38
$[FeCp^*{}_2]_{0.5}[Cu_4(C_3Se_5)_3]$	932.9	$1.9x10^{-5}$	0.32

* Determined from X-ray photoelectron spectra. ** Measured for compacted pellets.

Table I shows binding energies of copper $2p_{3/2}$ electrons of the $[Cu_4(C_3X_5)_3]$ (X = S and Se) complexes determined from X-ray photoelectron spectra. The binding energies of the partially oxidized species are almost the same as those of the $[Cu_4(C_3X_5)_3]^{2-}$ (X = S and Se) complexes. These findings indicate that for the partially oxidized complexes the oxidation occurs essentially at the C_3X_5-centers. The presence of the paramagnetic species due to the C_3X_5-centered oxidation is confirmed from the appreciable, broad ESR signals at g = 2.03-2.07 (peak-to-peak linewidths 12-35 mT at room temperature) observed for these partially oxidized complexes, which are close to the signals of other oxidized C_3S_5-metal complexes.[1,16,17]

Electrical conductivities of the complexes measured for compacted pellets and their activation energies for the electrical conduction are also listed in Table I. Oxidized complexes behave as semiconductors in the temperature range from -30 to 30°C. In these complexes, the ligand-centered oxidation accelerates the molecular interactions through S-S and Se-Se contacts to form effective conduction pathways in the solid state. This is also estimated from the broad bands tailed to long wavelengths observed in the electronic reflectance spectra of these oxidized complexes.

Cluster metal complexes with the sulfur- and selenium-rich ligands, $C_3X_5^{2-}$ (X = S and Se), may become new electrical conductors with multi-dimensional conduction pathways, as well as bulky $[V(C_3S_5)_3]^{n-}$ (n = 1 and 0.5) complexes.[7-9]

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