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Preparation, Spectroscopic Characterization, and Molecular Structure of Copper(I) Aliphatic Thiolate Complexes

Kiyoshi Fujisawa,* Sadako Imai, Nobumasa Kitajima, and Yoshihiko Moro-oka*

Research Laboratory of Resources Utilization, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226, Japan

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Copper(I)−thiolate clusters are of significant interest because of their biological relevance to the cysteine-rich copper(I) proteins such as metallothioneins,[1] copper-regulatory proteins (ACE1[2] and AMT1[3]), and phytochelatins.[4] Accordingly, many examples of polymeric monothiolate copper(I) clusters have been synthesized and characterized by X-ray crystallography[5] (Cu_4S_4,[6] Cu_4S_6,[7] Cu_5S_6,[8] Cu_5S_7,[9] Cu_8S_8,[10] $Cu_{12}S_{12}$[11]).

Mononuclear copper(I)−thiolate and −thioether complexes are also important because recently the highly conserved motif XMTCXXC (where X stands for any amino acid) could be found in ATX1,[12] HAH1,[13] P-type ATPase (CCC2;[14] CopA and CopB[15]), and copper-transporting ATPase (Menkes' disease[16] and Wilson's disease[17]). In the case of ATX1, the copper(I) ion is speculated to be coordinated in a mononuclear fashion (not cluster) with this motif.[18] However, mononuclear copper(I) complexes with monothiolate ligands are rare. Only three arene thiolate complexes ($Cu(SAr)_2$ and $Cu(SAr)_3$) have been reported so far.[19,20] In addition, because an arene thiol has characteristic absorption bands in the UV region, these very intense bands must obscure the assignments of MLCT (metal to ligand charge transfer) bands, luminescence, and Cu−S stretching frequencies in UV resonance Raman spectroscopy. We report herein the first characterization of the mononuclear two-coordinate aliphatic thiolate copper(I) complex $[NEt_4][Cu(SAd)_2]$ (**1**) (AdS^-: adamantane thiolate anion) and the aliphatic thiolate copper(I) cluster $[NEt_4][Cu_5(SAd)_6]$ (**2**). They were characterized by X-ray crystallography as well as by spectroscopic methods including UV, luminescence, FT-far-IR, and FT-Raman spectroscopy in order to elucidate coordination numbers and modes of these copper-binding proteins.

The two-coordinate complex ($[NEt_4][Cu(SAd)_2]$ (**1**)) and the cluster ($[NEt_4][Cu_5(SAd)_6]$ (**2**)) were synthesized by the direct addition of the sodium salt of the thiol (NaSAd) to a solution of $Cu(MeCN)_4PF_6$.[21] Variations in reaction conditions yielded the same products in diminished yields but gave no evidence of the formation of higher oligomers of other compositions.

The linear coordination structure of **1** and the cluster structure of **2** were revealed by X-ray crystallographic determinations (Figure 1).[22] To the best of our knowledge, no mononuclear aliphatic two-coordinate monothiolate copper(I) complex has been reported so far: **1** is the first example of such a complex. The anion of **1** has a linear coordination structure (S−Cu−S angle; 180.0° for **1**) with crystallographic C_2 symmetry. The Cu−S distance of 2.147(1) Å is substantially shorter than the average

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(21) Experimental procedures and spectroscopic characterization for all new compounds are provided in the Supporting Information.

(22) X-ray structure analyses: Data were obtained with Mo Kα radiation and structures were solved and refined by standard methods. **1** (298 K): white, orthorhombic (*Pbca*), $a = 10.681(2)$ Å, $b = 25.524(3)$ Å, $c = 10.516(1)$ Å, $V = 2867(1)$ Å^3, $Z = 4$, 1019 observed data ($I > 5\sigma(I)$, $3 \le 2\theta \le 45°$), R (R_w) = 6.95 (6.76) with GOF = 6.04. **2** (298 K): yellow, orthorhombic ($Pca2_1$), $a = 13.004(2)$ Å, $b = 22.181(9)$ Å, $c = 23.679(3)$ Å, $V = 6830(6)$ Å^3, $Z = 4$, 4128 observed data ($I > 3\sigma(I)$, $3 \le 2\theta \le 50°$), R (R_w) = 4.81 (4.07) with GOF = 2.15. Details are available in the Supporting Information.

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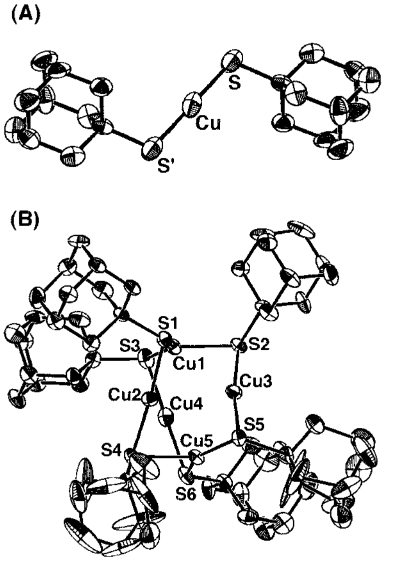

Figure 1. ORTEP views of the X-ray crystal structures of the anions of (A) $[NEt_4][Cu(SAd)_2]$ (**1**) and (B) $[NEt_4][Cu_5(SAd)_6]$ (**2**), showing selected atoms.

Cu−S distances in three-coordinate arene thiolate complexes ($[NEt_4][Cu(SPh)_3]$ (2.250(9) Å)[20b] and $[PPh_4][Cu(SPh)_3]$ (2.295(35)Å)[20c]). They are similar to the average Cu−S distances for the two-coordinate copper sites of **2** (2.175 Å) and $[NEt_4][Cu_5(SBu^t)_6]$ (**3**) (2.164 Å).[8] The core structure of **2** was in accord with that of **3**. In compound **2**, the Cu_5S_6 core of the cage may be described as a trigonal bipyramid of metal atoms (Cu1 and Cu5, trigonal planar coordination (Cu_{trig}); Cu2, Cu3, and Cu4, linear digonal coordination (Cu_{dig})). The notable geometric property is found in the Cu_{dig}−S bond length (2.175 Å), which is significantly shorter than the Cu_{trig}−S bond length (2.291 Å). The observed change in the Cu−S distances as a function of coordination number should influence the physicochemical properties of these complexes.

In the absorption spectra, the higher energy absorption band at 253 nm for **1**, which is not observed in the spectra of the free thiolate or $Cu(MeCN)_4PF_6$, is assigned as $M(Cu_{dig})LCT$ transitions. The absorption spectrum of $[NEt_4][Ag(SAd)_2]$ supports these assignments, since the $M(Ag_{dig})LCT$ band was shifted to higher energy at 231 nm.[23] On the other hand, the cluster **2** exhibits absorption bands at 273 and 300 nm (sh). The former band is assigned to an $M(Cu_{dig})LCT$ transition, and the latter is also assignable to an $M(Cu_{trig})LCT$ transition. These results show that the changes in the coordination environment have remarkable effects on the energy of the MLCT transitions. The observed decrease in energy for the MLCT transition in going from two- to three-coordination is most likely caused by an increase in the ligand field splitting associated with the copper(I) ion.[24]

The copper(I) metallothionein from *Neurospora crassa* exhibits a corrected emission maximum at 565 nm upon excitation at 310 nm.[25] This large Stokes shift has been ascribed to the facts that only triplet luminescence is taking place and that the absorption between 280 and 350 nm takes place in overlapping MLCT and copper(I) $^1[d^9s^1]$ excited states.[26] Complexes **1** and **2** emit luminescence (excitation: 320 nm, 140 K) which is observed at 600 and 618 nm, respectively (see the Supporting Information). Since the mononuclear copper(I) compound **1** in the solid sate is also emissive, cluster formation is not a criterion for luminescence.[1a] The emissions are most likely associated with spin-forbidden transitions, which are not easily detected in the absorption spectrum because of low extinction coefficients. Since the ground state is a singlet, the emitting state is probably a triplet. This triplet state is also suggested by the oxygen quenching experiments of **2** in solution (data not shown).

Vibrational spectroscopy is also useful in elucidating the structure and geometry of copper(I) thiolate compounds.[27] The Cu−S stretching modes are observed in the far-infrared regions and in the low-energy Raman shift regions, 50−500 cm^{-1}.[9b,28] Group theory predicts that ν_s and ν_{as} are Raman active for trigonal planar geometry (D_{3h}), while only ν_{as} is IR active ($\nu_{as} > \nu_s$).[29] In contrast, in linear two-coordinate geometry, only ν_s is Raman active and ν_{as} is IR active ($\nu_s < \nu_{as}$). The Cu−S stretching frequencies are assigned on the basis of comparisons of the vibrational spectra of complexes **1** and **2** with those of the related Ag thiolate complexes.[23] For the linear two-coordinate complex **1**, 333 cm^{-1} (ν_{as}, IR) and 299 cm^{-1} (ν_s, Raman) were assigned to ν(Cu-S) vibrations. These ν(Cu−S) frequencies of **1** are consistent with those of the two-coordinate copper sites of **2** (326 cm^{-1} (ν_{as}, IR) and 297 cm^{-1} (ν_{as}, Raman)). On the other hand, the ν(Cu−S) frequencies in the three-coordinate copper sites of **2** were observed around 278 cm^{-1}. In order to confirm these assignments, we prepared the ^{34}S-labeled thiolate complex $[Cu(^{34}SAd)_2]^-$ and cluster $[Cu_5(^{34}SAd)_6]^-$. The observed isotropic frequency shifts for Cu−S and Cu−^{34}S are in good agreement with the expected shifts for diatomic harmonic oscillators, suggesting that these bands for **1** and **2** are assignable to ν(Cu−S) vibrations (see the Supporting Information). Moreover, these assignments were confirmed by UV resonance Raman spectroscopy (299 cm^{-1} for **1**).[30] These results indicated that it may be used to differentiate the coordination numbers and geometries by use of the ν(Cu−S) frequencies.

Further research will focus on preparing new compounds, especially mononuclear aliphatic three-coordinate copper(I) complexes, as benchmarks for future spectroscopic studies (e.g., X-ray absorption) and on elucidation of coordination environments of copper(I) proteins.

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Supporting Information Available: Text presenting experimental procedures and spectroscopic characterization for all new compounds and experimental details of the X-ray structure determinations of **1** and **2**, diagrams showing the atomic numbering for **1** and **2** (Figures S1 and S2), tables listing crystallographic data, positional and isotropic thermal parameters, anisotropic thermal parameters, and bond lengths and angles for **1** and **2** (Tables S1−S5), and luminescence, far-IR, and Raman spectra of **1** and **2** (Figures S3−S7) (29 pages). X-ray crystallographic files, in CIF format, for **1** and **2** are available on the Internet only. Ordering and access information is given on any current masthead page.

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