A S-Bridged $Co^{III}Cu^{II}Co^{III}$ Trinuclear Complex with an Unusual Copper(II) Ion Bound by Four Aliphatic Thiolato Donors

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Treatment of $\Delta\Delta$-[Ni^{II}{Co^{III}(aet)$_2$(*R*,*R*-chxn)}$_2$](ClO_4)$_4$ (Haet = 2-aminoethanethiol, *R*,*R*-chxn = 1*R*,2*R*-cyclohexanediamine) with $Cu(ClO_4)_2$ in water gave $\Delta\Delta$-[Cu^{II}{Co^{III}(aet)$_2$(*R*,*R*-chxn)}$_2$](ClO_4)$_4$ (**1**), in which a central copper(II) ion is surrounded by four aliphatic thiolato donors in a twisted square-planar geometry. Complex **1** was converted to $\Delta\Delta$-[$Cu^{I}Cl${Co^{III}(aet)$_2$(*R*,*R*-chxn)}$_2$](ClO_4)$_2$ (**2**) by treatment with NaCl in water, while **2** was reverted back to **1** by treatment with $NaClO_4$.

Coordination species of copper bearing thiolate ligands have attracted considerable attention for many years.[1] This is not only because of their importance in copper-containing metalloenzymes but also because of their intriguing structural versatility arising from the redox-active nature of both copper and thiolate. To date, a variety of copper species with thiolate ligands, involving mononuclear Cu^{I} and Cu^{II},[2] polynuclear Cu^{I} and Cu^{II},[3] and mixed-valent $Cu^{I}Cu^{II}$,[4] have been reported. Of these complexes, Cu^{II}–thiolate species are difficult to isolate because of the intramolecular redox reaction between Cu^{II} and thiolate to form Cu^{I}–thiolate and/or Cu^{I}/Cu^{II}–disulfide species.[5] For example, we have shown that the reactions of *fac*(*S*)-[M(aet)$_3$] (M = Rh^{III} and Ir^{III}) with $Cu(NO_3)_2$ result in the formation of $Cu^{I}_4M_4$ octanuclear complexes having thiolate-type aet and disulfide-type cysta ligands, [Cu_4{M(aet)$_3$}$_2$(M_2(aet)$_4$(cysta))]$^{6+}$ (Haet = 2-aminoethanethiol, H_2cysta = cystamine).[6] Thus, the isolation of Cu^{II}–thiolate species has been a synthetic challenge in metal thiolate chemistry. Here we report that a Cu^{II}–thiolate species, $\Delta\Delta$-[Cu^{II}{Co(aet)$_2$(*R*,*R*-chxn)}$_2$]$^{4+}$ (*R*,*R*-chxn = 1*R*,2*R*-cyclohexanediamine), in which a Cu^{II} ion is coordinated by four thiolato groups from two [Co(aet)$_2$(*R*,*R*-chxn)]$^+$ units, is obtained by the reaction of $\Delta\Delta$-[Ni{Co(aet)$_2$(*R*,*R*-chxn)}$_2$]$^{4+}$ with $Cu(ClO_4)_2$. The reversible conversion of this Cu^{II}–thiolate species to the corresponding Cu^{I}–thiolate species is also reported.

Treatment of a red-brown solution of $\Delta\Delta$-[Ni{Co(aet)$_2$(*R*,*R*-chxn)}$_2$](ClO_4)$_4$[7] with $Cu(ClO_4)_2\cdot 6H_2O$ in a 1:1 ratio in water gave a dark green solution, from which a dark green complex **1** was obtained by adding aqueous $NaClO_4$.[8] X-ray fluorescence spectrometry indicated that **1** contains Co and Cu as a metal component, and its elemental analytical data were in good agreement with a formula for a 2:1 adduct of [Co(aet)$_2$(*R*,*R*-chxn)]$^+$ and Cu^{2+}. The EPR spectrum of a solid sample of **1** at 77 K displayed a simple isotropic signal with $g = 2.03$,[9] supporting the presence of Cu^{2+}. The structure of **1** was determined by single-crystal X-ray analysis, which revealed the presence of discrete complex cations and perchlorate anions, besides water molecules.[10] The 1:4 ratio of cations and anions implies that the complex cation of **1** is in a tetracationic form. As shown in Figure 1, the complex cation of **1** contains two Δ-[Co(aet)$_2$(*R*,*R*-chxn)]$^+$ units that are linked by a Cu atom to form a linear S-bridged trinuclear structure in $\Delta\Delta$-[Cu{Co(aet)$_2$(*R*,*R*-chxn)}$_2$]$^{4+}$. The bond distances and angles of the Δ-[Co(aet)$_2$(*R*,*R*-chxn)]$^+$ units in **1** (av Co–S = 2.259(3), Co–N = 1.993(8) Å) are similar to those in the parental $\Delta\Delta$-[Ni{Co(aet)$_2$(*R*,*R*-chxn)}$_2$]$^{4+}$ (av Co–S = 2.235(5), Co–N = 1.986(14) Å).[7] The central Cu atom bound by four thiolato atoms (av Cu–S = 2.302(3) Å) is assignable to have a +II oxidation state based on the total charge balance of the complex cation. In common, a copper ion with aliphatic thiolato donors tends to adopt a +I oxidation state,[5b] and **1** is the second example of a crystallographically characterized Cu^{II} species with four aliphatic thiolato donors.[11] In addition, the $Cu^{II}S_4$ coordination sphere in **1** is highly distorted from square-planar to tetrahedral geometry with a dihedral angle of 49.7°, which is not so common for Cu^{II} species with four S donors.[11,12]

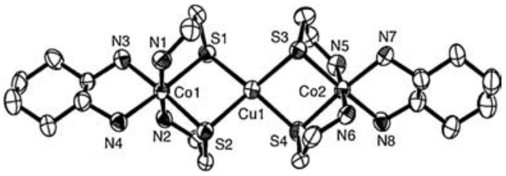

Figure 1. Perspective view of one of the two independent complex cations in **1**. H atoms are omitted for clarity.

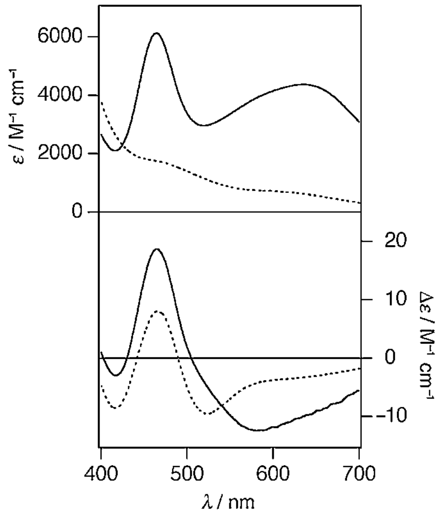

Figure 2. Absorption and CD spectra of **1** (—) and **2** (- - -) in water.

The electronic absorption spectrum of **1** in water is characterized by two intense visible bands at 642 and 464 nm assignable to S-to-Cu^{II} charge-transfer transitions (Figure 2).[13] In the corresponding region, **1** exhibits a negative and a positive CD bands, compatible with its chiral structure. The cyclic voltammogram (CV) of **1** in 0.1 M aqueous $NaClO_4$ displays a reduction at

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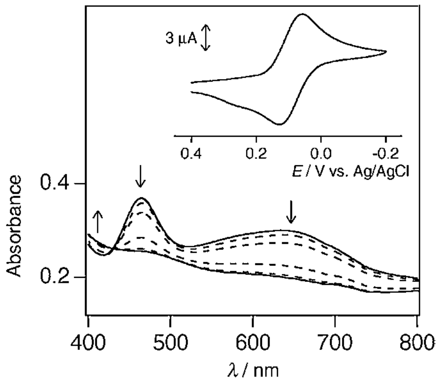

Figure 3. Sequential absorption spectra obtained during a spectropotentiostatic experiment for **1** in 0.1 M aqueous $NaClO_4$ at applied potentials from +0.4 to −0.2 V. The inset shows a cyclic voltammogram of **1** at a grassy-carbon electrode in 0.1 M aqueous $NaClO_4$ with a scan rate of $0.1\ V\,s^{-1}$.

+0.06 V (vs. Ag/AgCl), which is coupled with an oxidation at +0.13 V (Figure 3). This redox couple is assigned to a +I/+II redox process of the central Cu atom, taking account of the fact that no redox wave was observed for $\Delta\Delta$-[Ni{Co(aet)$_2$(R,R-chxn)}$_2$](ClO$_4$)$_4$ in this potential range.[14] In the potential step spectroelectrochemistry, the visible absorption bands for **1** decreased with an isosbestic point at 430 nm on decreasing the potential from +0.40 V to −0.20 V (Figure 3). The increase of the potential to +0.40 V recovered the original absorption spectrum. These results imply that the central Cu^{II} in **1** is reversibly converted to Cu^{I}, retaining the S-bridged trinuclear structure.

When excess NaCl was added to an aqueous solution of **1**, a dark brown powder **2** was precipitated.[15] The presence of Cu atom in **2**, as well as Co atom, was confirmed by X-ray fluorescence spectrometry. In contrast to **1**, **2** is EPR silent in the solid state, suggestive of the +I oxidation state for Cu in **2**. The absorption spectrum of **2** shows broad, less intense bands in the visible region, although its CD spectral pattern is similar to that of **1** in this region (Figure 2). This absorption spectral feature is essentially the same as that of a reduced form of **1** found in the spectroelectrochemistry (Figure 3). Based on these results, together with the elemental analysis and the ESI mass spectroscopy, it is assigned that **2** is a S-bridged $Co^{III}Cu^{I}Co^{III}$ trinuclear complex, [CuCl{Co(aet)$_2$(R,R-chxn)}$_2$](ClO$_4$)$_2$, in which a Cl^- ion coordinates to the Cu^{I} center.[16] Here, it should be noted that treatment of a dark brown solution of **2** with excess $NaClO_4$ in water gave a dark green solution, the absorption spectrum of which is the same as that of **1**. This implies that the removal of a Cl^- ion from the coordination sphere of Cu^{I} by treating with ClO_4^- led to the autoxidation to form **1**. Thus, the presence of a chloride ion in the coordination sphere is essential for the stabilization of the +I oxidation state of Cu in this trinuclear structure.[17]

In conclusion, we showed that a rare +II oxidation state of Cu bearing four aliphatic thiolato donors is created in the S-bridged $Co^{III}Cu^{II}Co^{III}$ complex **1**, which was derived from $\Delta\Delta$-[Ni{Co(aet)$_2$(R,R-chxn)}$_2$]$^{4+}$ through the metal replacement reaction. The moderate electron-donating property of thiolato groups bound to a Co^{III} center, which is analogous to thioether groups, together with steric factors that exclude the formation of an ideal tetrahedral geometry favorable for Cu^{I} in this trinuclear structure, seems to be responsible for this result. Notably, the +II oxidation state of Cu in this trinuclear structure was found to be interconvertible to the +I oxidation state by the addition/removal of a Cl^- ion, accompanied by the drastic change of absorption spectra in the visible region.

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8 Calcd for $\mathbf{1}\cdot 3H_2O$: C, 20.60; H, 5.01; N, 9.61%. Found: C, 20.65; H, 4.83; N, 9.58%. Yield: 56%.

9 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

10 Crystal data for $\mathbf{1}\cdot 3.25H_2O$: fw 1170.69, Monoclinic, $P2_1$, $a = 16.818(5)$, $b = 15.623(4)$, $c = 18.630(6)$ Å, $\beta = 107.926(10)°$, $V = 4657(2)$ Å^3, $Z = 4$, $D_{calcd} = 1.670\ g\,cm^{-3}$, 42649 reflections measured, 20054 independent. $R_1 = 0.0744$ ($I > 2\sigma(I)$), $wR_2 = 0.2135$ (all data). CCDC: 745597. Crsytal **1** contains two independent, yet nearly the same complex cations in the unit cell.

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14 The CV for $\Delta\Delta$-[Ni{Co(aet)$_2$(R,R-chxn)}$_2$](ClO$_4$)$_4$ showed only irreversible reduction waves in the potential range between −0.6 and −1.0 V.

15 Calcd for $\mathbf{2}\cdot 3H_2O$: C, 23.96; H, 5.83; N, 11.17%. Found: C, 23.88; H, 6.07; N, 11.13%. Yield: 29%.

16 The ESI mass spectrum of **2** showed signals corresponding to [CuCl{Co(aet)$_2$(R,R-chxn)}]$^+$ ($m/z = 423$) and {[CuCl{Co(aet)$_2$(R,R-chxn)}$_2$]ClO$_4$}$^+$ ($m/z = 847$), suggestive of the coordination of a Cl^- ion to the Cu^{I} center.

17 The cyclic voltammogram of **2** resembled that of **1**, giving a reduction wave at +0.09 and a coupled oxidation wave at +0.17 V. Another oxidation wave was also observed at +0.26 V, which corresponds to a minor oxidation wave at ca. 0.25 V for **1**.[9]

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