Synthesis of a New Mixed-valence Decanuclear Cu(I)-Cu(II) Cluster with a Hexamethylene Dithiocarbamate Ligand

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Abstract

A new mixed-valence decanuclear Cu(I)-Cu(II) cluster, $[Cu^I_6Cu^{II}_4Br_6(Hm\text{-}dtc)_8]\cdot 2CHCl_3$ (1) (Hm–dtc⁻ = hexamethylene–dithiocarbamate) with a dithiocarbamate derivative has been synthesized and structurally characterized. Complex **1** consists of four mononuclear Cu(II) dithiocarbamate units and bridging Cu(I)-Br moieties. This decanuclear cluster forms an infinite one-dimensional assembly by weak Cu•••S contacts between the mononuclear Cu(II) dithiocarbamate units. This complex shows large absorptions broadened to NIR region, which might be induced by the delocalization of the d-electron of copper(II) ions.

Keywords: mixed-valence copper cluster, hexamethylene-dithiocarbamate ligand, 1-D assembly, absorption spectra

1. Introduction

Polynuclear metal complexes represent one of the most attractive areas in the field of materials science, because their characteristic assembled structures and electronic states, which have the feature of the organic–inorganic hybrid materials, have new chemical and/or physical properties such as catalytic activity,[1-4] gas adsorption,[5-7] and conductive,[8-10] magnetic,[11-13] and nonlinear optical properties.[14-15] There is much interest in their design and synthesis; in particular, the establishment of a rational synthetic method for mixed–valence polynuclear metal complexes such as mixed–valence coordination polymers and mixed–valence metal clusters is important in developing the chemistry of functional materials, because these complexes have potential applications as new opto–electronic materials based on carrier–transport properties, valence fluctuations and intervalence charge–transfer transitions.[16-18]

Dithiocarbamate (dtc) derivatives are good candidates for ligands in mixed–valence polynuclear metal complexes. This is because ligands that contain dithiocarboxyl groups have the ability not only to bridge metal ions by

sulfur atoms, which have large atomic orbitals, in the ligands but also to stabilize Cu complexes in a wide range of oxidation states such as Cu(I), Cu(II), and Cu(III).[19-32] To date, several mixed–valence metal clusters and coordination polymers have been synthesized from dithiocarbamate derivatives.[23-29] We demonstrated that 1D mixed–valence Cu(I)–Cu(II) coordination polymers containing a dithiocarbamate ligand and Br or I anions, [$Cu^I_2Cu^{II}$ X_2(Hm–dtc)$_2$(CH$_3$CN)$_2$]$_n$ (Hm–dtc$^-$ = hexamethylene–dithiocarbamate; X = Br$^-$ or I$^-$), exhibited semiconducting properties at relatively small activation energies (E_a = 0.56 eV, X = Br$^-$; E_a = 0.48 eV, X = I$^-$),[23] and that they could be employed as sensitizing materials for dye–sensitized solar cells (DSSCs).[24] In addition, we have presented a new mixed–valence systems consisting of a cluster unit in which Cu(I), Cu(II), and Cu(III) ions coexist; the formula of these systems is [$Cu^I_6Cu^{II}Cu^{III}$Br$_7$ (Hm–dtc)$_4$]•3CHCl$_3$.[25] This complex shows a unique intervalence charge transfer band in the UV–vis–NIR region in the solid state, which is induced by the assembly of mixed–valence octanuclear Cu(I)/Cu(II) /Cu(III) units. In this paper, we report the synthesis, X-ray crystal structure, and magnetic properties of a new mixed-valence decanuclear Cu(I)-Cu(II) cluster, [$Cu^I_6Cu^{II}_4$Br$_6$(Hm-dtc)$_8$]•2CHCl$_3$ (1).

2. Experimental details

2.1. Materials

A mononuclear metal complex, Cu(Hm-dtc)$_2$ was prepared by a procedure similar to that in the literature.[31] The reagents were purchased from Tokyo Kasei Kogyo Co., Ltd., and Aldrich Chemical Co., Inc. All the chemicals were used without further purification.

2.2. Synthesis

Complex 1 was prepared cleanly as a single phase black crystalline product via room temperature by a reaction of a H$_2$O/acetone solution of CuBr$_2$ with a CHCl$_3$ solution of Cu(Hm–dtc)$_2$ as the ratio of 2 to 3. A solution of CuBr$_2$ (0.045 g, 0.20 mmol) dissolved by a minimal amount of distilled water (two drops) was diluted

with 20 ml of acetone, and this solution was then added to a 20 ml CHCl$_3$ solution of Cu(Hm–dtc)$_2$ (0.123 g, 0.30 mmol). The reaction mixture was stirred for 5 min and then filtrated. Crystals of complex 1 suitable for X–ray analysis were obtained from the filtrate after several days. Anal. Calcd for [$Cu^I_6Cu^{II}_4$Br$_6$(Hm-dtc)$_8$]•2CHCl$_3$ (C$_{58}$H$_{98}$Br$_6$Cl$_6$Cu$_{10}$N$_8$S$_{16}$): C, 25.35; H, 3.59; N, 4.08. Found: C, 25.27; H, 3.64; N, 4.07.

2.3. X-ray Structure determination

Single crystal X-ray data collection was performed on a Rigaku Mercury70 diffractometer with graphite monochromated Mo-Kα (0.71069 Å) radiation. The data were collected at a temperature of -152 ± 1 °C to a maximum 2θ value of 55.0°. A total of 1080 oscillation images were collected. The structure was solved by a direct method (SIR2008) and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. All calculations were performed using the CrystalStructure 4.0 crystallographic software package.[33]

2.4. Crystal Data of Complex 1

Formula C$_{29}$H$_{49}$Br$_3$Cl$_3$Cu$_5$N$_4$S$_8$, Formula weight 1374.01, Triclinic P-1 (#2), a = 12.550(9) Å, b = 13.879(10) Å, c = 15.329(11) Å, α = 108.381(5)°, β = 99.291(6)°, γ = 109.987(5)°, V = 2270(3) Å^3, Z = 2, D_{calc} = 2.010 g/cm^3, F(000) = 1360.00, μ(Mo-Kα) = 55.256 cm^{-1}, T = -152 ± 1 °C, R_1 (I > 2.00 $\sigma(I)$) = 0.0810, R (All reflections) = 0.1244, wR_2 (All reflections) = 0.2466. CCDC: 862807.

3. Results and Discussion

Single–crystal X–ray analysis reveals the formation of a mixed–valence Cu(I)-Cu(II) cluster of formula [$Cu^I_6Cu^{II}_4$Br$_6$ (Hm-dtc)$_8$]•2CHCl$_3$ (1). The structures of the decanuclear cluster are shown in Fig. 1 and Fig. 2. The asymmetric unit of the cluster 1 in Fig. 1 consists of six crystallographically independent copper ions, four Hm-dtc$^-$ ligands and three bromide anions, where hydrogen atoms and the CHCl$_3$ crystal solvents are omitted for clarity. Fig. 2 is the view of the
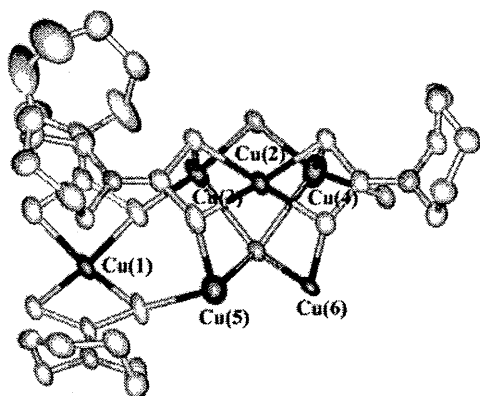
Fig. 1. Asymmetric unit of decanuclear Cu(I)–Cu(II) cluster **1**: Cu, red–brown; Br, orange; S, yellow; C, white; and N, blue. Hydrogen atoms and crystal solvents are omitted for clarity.
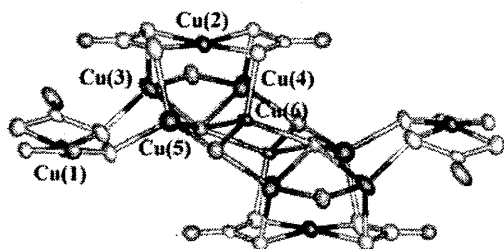

Fig. 2. Crystal structure of decanuclear Cu(I)–Cu(II) cluster **1**, where hexamethylene groups, hydrogen atoms and the $CHCl_3$ crystal solvents are omitted for clarity.

decanuclear copper cluster **1**, where hexamethylene groups, hydrogen atoms and the $CHCl_3$ crystal solvents are omitted for clarity. Four mononuclear Cu(Hm–dtc)$_2$ units are connected by eight Cu ions and six Br anions in the figure. However, we concluded that the copper ions of Cu(5), Cu(6), Cu(5*) and Cu(6*) were positionally-disordered copper ions, because obtained R_1 value of the least-squares refinement decreased with the treatment of the disordered copper ions. When the occupancies of the Cu(5), Cu(6), Cu(5*) and Cu(6*) ions were 1.0, the obtained R_1 ($I >$ 2.00 $\sigma(I)$) value was 0.1097. On the other hand, the R_1 values decreased to 0.0810 when the occupancies of the four copper ions were 0.5. The result of the elemental analysis also suggested that this complex was decanuclear copper cluster including

disordered copper ions. The obtained values in the elemental analysis were C = 25.27, H = 3.64 and N = 4.07, which were closer to the values of decanuclear copper cluster (C = 25.35, H = 3.59 and N = 4.08) than those of dodecanuclear copper cluster (C = 24.23, H = 3.44 and N = 3.90). The Cu ions of the mononuclear units, Cu(1) and Cu(2), have distorted square–planar coordination geometries in which the Hm–dtc$^-$ ligands coordinate with the Cu ions in four–membered chelate rings. The other Cu ions connecting the mononuclear units, Cu(3), Cu(4), Cu(5) and Cu(6), have tetrahedral S$_2$Br$_2$ or S$_1$Br$_3$ coordination geometries. Usually, the oxidation states of Cu complexes with dithiocarbamate ligands can be determined by the Cu–S distances. In the mononuclear Cu(1)(Hm–dtc)$_2$ and Cu(2)(Hm–dtc)$_2$ units, the average Cu–S distances are 2.313(5) Å and 2.307(4) Å, respectively, which are similar to the typical Cu(II)–S distances for Cu(II)–dithiocarbamate complexes such as Cu^{II}(Et$_2$dtc)$_2$ (2.312 Å av.), Cu^{II}(EtPr–dtc)$_2$ (2.284 Å av.), Cu^{II}(n–Bu$_2$dtc)$_2$ (2.308 Å av.) and Cu^{II}(Bz$_2$dtc)$_2$ (2.293 Å av.),[30-31] and larger than those of the typical Cu(III)–S distances for Cu(III)–dithiocarbamate
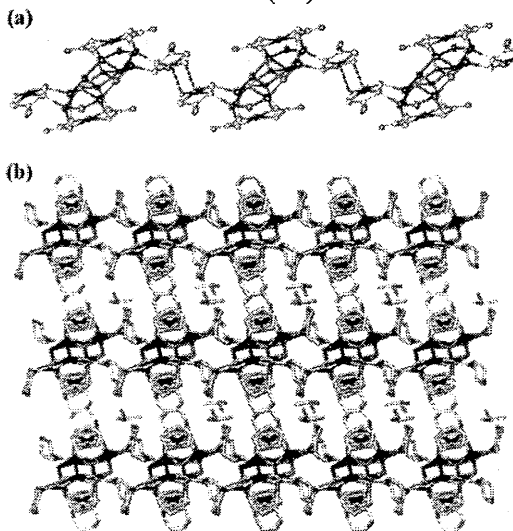
(a)

(b)

Fig. 3. (a) Infinite chain structures formed by assembly of decanuclear cluster units of **1**. Hexamethylene groups of Hm-dtc ligands are omitted for clarity. (b) Packing diagram of **1** viewed along diagonal of a-axis and c-axis. Hydrogen atoms are omitted for clarity.
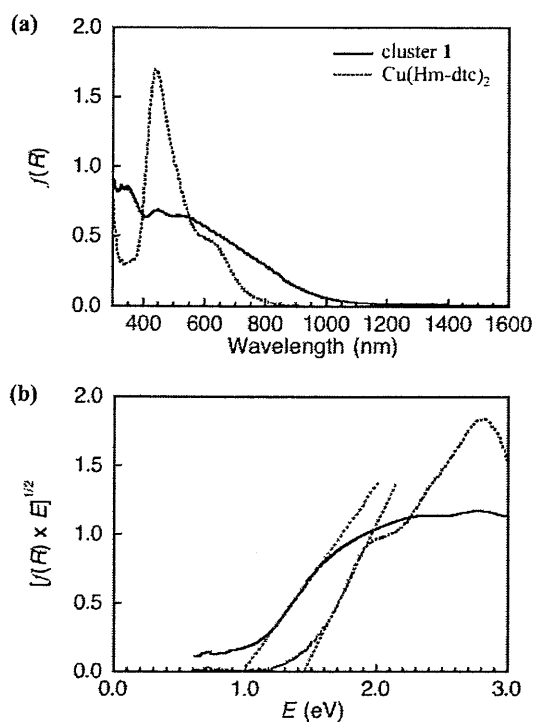
Fig. 4. (a) Diffuse-reflectance UV-vis-NIR absorbance spectrum of complex 1 (0.01 mmol) mixed with MgO (80 mg). (b) Kubelka-Munk plot for the band gap evaluation of complex 1.

complexes such as $[Cu(Me_2dtc)_2](ClO_4)$ (2.234 Å av.) and $[Cu(Et_2dtc)_2](FeCl_4)$ (2.208 Å av.).[32] Based on its charge neutrality, it is concluded that this complex is in the mixed–valence state with formula $[Cu^I_6Cu^{II}_4Br_6(Hm\text{-}dtc)_8]\cdot 2CHCl_3$, in which the square–planar Cu(1) and Cu(2) with the of the mononuclear Cu(Hm–dtc)$_2$ units are divalent, and the Cu(3), Cu(4), Cu(5) and Cu(6) with distorted tetrahedral coordination geometries are monovalent, and the Cu(5) and Cu(6) are positionally–disordered copper ions.

The decanuclear clusters align with head–to–tail linkage on the basis of the formation of weak coordination bonds between these clusters, constructing an infinite 1D assemblage in the crystal, as shown in Fig. 3(a). In this 1D assemblage, two Cu(Hm-dtc)$_2$ units are joined to each other and form a dimer unit with weak Cu–S bonds; the Cu(1)–S(4**) separation is 2.748(3) Å, which is longer than the intramolecular Cu(1)–S and Cu(2)–S distances in the mononuclear units. Fig.

3(b) is a packing diagram viewed along the 1D assemblages, which are fully isolated from each other because of the hexamethylene groups of the dithiocarbamate ligands and the CHCl$_3$ crystal solvents.

Figure 4(a) shows the diffuse–reflection spectra of the decanuclear cluster 1 and mononuclear complex Cu(Hm-dtc)$_2$ converted from diffusion-reflectance spectroscopy (R) using the Kubelka-Munk function: $f(R) = (1\text{-}R)^2/2R$. Complex 1 and Cu(Hm-dtc)$_2$ exhibit strong absorptions in the UV to NIR region attributed to the ligand to metal charge transfer (LMCT) and the d-d transition of the Cu(II) ions. Especially the absorption of complex 1 extend to the NIR region because of the delocalization of the d-orbitals caused by the strong intercluster or intracluster interactions. To determine the band gap (E_g) of complex 1 and Cu(Hm-dtc)$_2$ the Kubella-Munk plot,[7] $(f(R)\cdot E)^{1/2}$ versus E was employed (Figure 4(b)). The E_g corresponds to the intersection point between the base line along the energy axis and a line extrapolated from the linear potion of the threshold. Thus, E_g of complex 1 and Cu(Hm-dtc)$_2$ were determined to be 0.98 eV and 1.44 eV, respectively.

4. Conclusions

We found a simple synthetic method to create a new mixed-valence Cu(I)-Cu(II) decanuclear cluster, $[Cu^I_6Cu^{II}_4Br_6(Hm\text{-}dtc)_8]$ $\cdot 2CHCl_3$, from a mononuclear Cu(II) complex, Cu(Hm-dtc)$_2$, and copper(II) bromide, CuBr$_2$. This mixed-valence Cu(I)-Cu(II) cluster has been structurally and optically characterized.

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