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Magnetic and Conducting Properties of New Halide-Bridged Mixed-Valence $Cu^{I}-Cu^{II}$ 1D Coordination Polymers Including a Hexamethylene Dithiocarbamate Ligand

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New mixed-valence $Cu^{I}-Cu^{II}$ coordination polymers with one-dimensional, infinite-chain structures, $[Cu^{I}_2Cu^{II}X_2(Hm\text{-}dtc)_2(CH_3CN)_2]_n$ [Hm-dtc$^-$ = hexamethylene dithiocarbamate; X = Br^- (**1**), I^- (**2**)], have been prepared and structurally characterized by X-ray diffraction. These complexes consist of a mononuclear copper(II) unit $Cu^{II}(Hm\text{-}dtc)_2$ and dinuclear copper(I) units $Cu^{I}_2(CH_3CN)_2X_2$. Magnetic studies have revealed that these complexes have a relatively strong antiferromagnetic interaction [$J = -26.9$ cm^{-1} (**1**) and $J = -22.2$ cm^{-1} (**2**)] between the unpaired electrons of the Cu^{II} ions through the dinuclear copper(I) halide unit of $Cu^{I}_2X_2$ in the chain. The electrical properties of **1** and **2** are investigated using an impedance spectroscopy technique, and it is revealed that these complexes exhibit intriguing semiconducting properties with small activation energies [$E_a = 0.562$ eV (**1**) and $E_a = 0.479$ eV (**2**)].

Crystal engineering of coordination polymers is one of the most attractive subjects in the field of materials science because of their versatile chemical and physical properties such as magnetic and conductive, dielectric, gas-absorbing, and catalytic properties.[1−3] A designed synthesis of electroconductive materials, in particular, has been a great challenge in the field of coordination polymers, both for fundamental interests as a d−π system[4] and for applications in new optoelectronic devices such as electroluminescent devices, thin-film transistors, and solar cells. However, only a few studies on the carrier transport properties of electroconductive coordination polymers[5] have been conducted because of synthetic challenges.

Coordination polymers, including dithiocarbamate ligands, are one of the important candidates for conducting materials because of the strong metal−metal interaction through the sulfur-rich dithiocarbamate ligands with expanded highest occupied molecular orbitals (HOMOs). From this viewpoint, we have attempted to investigate the magnetic and conducting properties of new halide-bridged mixed-valence $Cu^{I}-Cu^{II}$ coordination polymers with infinite-chain structures, including a dithiocarbamate ligand, $[Cu^{I}_2Cu^{II}X_2(Hm\text{-}dtc)_2(CH_3CN)_2]_n$ [Hm-dtc$^-$ = hexamethylene dithiocarbamate; X = Br^- (**1**), I^- (**2**)], where, in order to study the conducting properties, impedance measurements have been performed for the mixed-valence coordination polymers.

Complex **1** was synthesized by the reaction of a $CHCl_3$ solution of $Cu^{II}(Hm\text{-}dtc)_2$ with an acetone/acetonitrile solution of $Cu^{I}Br\cdot S(CH_3)_2$. The reaction mixture was filtered, and black single crystals with block shapes suitable for X-ray diffraction were obtained from the filtrate in a couple of days. Complex **2** was synthesized by using a similar procedure with CuI as the copper halide source instead of $Cu^{I}Br\cdot S(CH_3)_2$.

A single-crystal X-ray analysis for complex **1** reveals the formation of a coordination polymer, $[Cu_3Br_2(Hm\text{-}dtc)_2(CH_3CN)_2]_n$, having a one-dimensional (1D) infinite-chain structure, as shown in Figure 1a. Mononuclear copper units $Cu(Hm\text{-}dtc)_2$ were connected by bromide-bridged copper dinuclear units including acetonitrile, $Cu_2Br_2(CH_3CN)_2$, to

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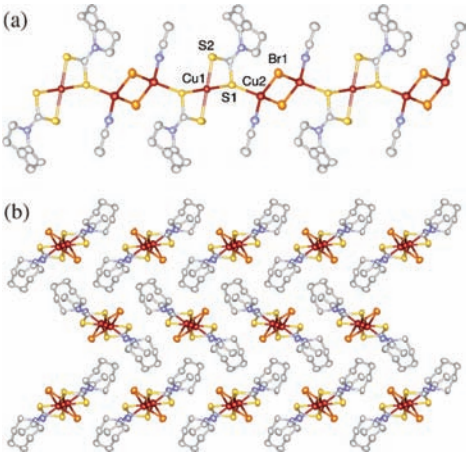

Figure 1. (a) Infinite-chain structure of a mixed-valence 1D coordination polymer of **1**. (b) Packing diagram of **1** as viewed parallel to the *a* axis. Color code: Cu, red-brown; Br, orange; I, purple; S, yellow; C, white; N, blue. H atoms are omitted for clarity.

construct the 1D infinite chain. The Cu ion of the mononuclear unit had a square-planar coordination geometry in which Hm-dtc$^-$ ligands coordinated with a Cu ion with four-membered chelate rings. In the mononuclear unit, the average Cu$-$S distance was 2.3040 Å, which was similar to the typical Cu$^{II}-$S distances for copper(II) dithiocarbamate complexes such as Cu^{II}(Et$_2$dtc)$_2$ [2.312 Å (ave)], Cu^{II}(EtPr-dtc)$_2$ [2.284 Å (ave)], Cu^{II}(*n*-Bu$_2$dtc)$_2$ [2.308 Å (ave)], and Cu^{II}(Bz$_2$dtc)$_2$ [2.293 Å (ave)].[6,7] The Cu2 ion in the dinuclear unit Cu$_2$Br$_2$(CH$_3$CN)$_2$ had a distorted tetrahedral coordination geometry bound by two bridging Br anions, one S atom of Cu(Hm-dtc)$_2$, and one N atom of acetonitrile. Considering the charge neutrality, it was concluded that this complex was in a mixed-valence state with a formula of [Cu$^I_2$Cu^{II}Br$_2$(Hm-dtc)$_2$(CH$_3$CN)$_2$]$_n$, in which the square-planar Cu1 was divalent and the tetrahedral Cu2 was monovalent. Figure 1b shows the packing diagram of the 1D chains for **1** as viewed parallel to the *a* axis. The nearest-neighbor S$\cdots$S and S$\cdots$Br separations between the 1D chains were 3.8837(11) and 7.0504(9) Å, and the interchain nearest Cu$^{II}\cdots$Cu^{II} separation was 8.28(7) Å. The 1D chain structure of **2**, [Cu$^I_2$Cu^{II}I$_2$(Hm-dtc)$_2$(CH$_3$CN)$_2$]$_n$, was quite similar to that of **1**, as shown in Figure S2 in the Supporting Information. The coordination geometries of Cu1 and Cu2 were also similar to those of **1**.

To study the interaction between the paramagnetic Cu^{II} centers of the mononuclear Cu^{II}(Hm-dtc)$_2$ units through the diamagnetic dinuclear Cu$^I_2$X$_2$ units, the magnetic susceptibilities were measured from 2.0 to 300 K with SQUID at 10 kOe using polycrystalline samples of **1** and **2**. The effective magnetic moments at 300 K were 1.61 μ_B for **1** and 1.62 μ_B for **2**, which were in agreement with the expected value (1.73 μ_B) for the Cu^{II} ions ($S = {}^1/_2$) in a mononuclear Cu^{II}(Hm-dtc)$_2$ unit. Figure 2 shows the plots of the molar magnetic susceptibilities χ_M against temperature for **1** (red) and **2** (blue). The χ_M values increased with decreasing temperature, reaching a maximum of 0.00310 emu$\cdot$mol^{-1} at 50 K (**1**) and 0.00380 emu$\cdot$mol^{-1} at 40 K (**2**), and then the values rapidly decreased, which indicated the existence of relatively strong antiferromagnetic interactions between Cu^{II} ions in the 1D infinite chains. The experimental data were fitted for **1** and **2** using the Bonner$-$Fisher equation for an infinite-spin linear chain.[1a] The best-fit parameters of the exchange interaction (J) were found to be -26.9 cm^{-1} ($R = 5.77 \times 10^{-7}$; **1**) and -22.2 cm^{-1} ($R = 2.90 \times 10^{-7}$; **2**), where the R factor was defined as $\sum(\chi_M{}^{obs} - \chi_M{}^{calc})^2/\sum(\chi_M{}^{obs})^2$. Results of the analysis indicated that the complexes had a relatively large exchange interaction between Cu^{II} ions through diamagnetic Cu$^I_2$X$_2$ units, where the intrachain Cu$^{II}\cdots$Cu^{II} separations were 10.5(2) Å for **1** and 10.5078(19) Å for **2**. Usually, bridging Br anions or bridging ligands, including S atoms, induce a strong antiferromagnetic interaction between Cu^{II} ions[9] because the energy difference of the magnetic orbital of the Cu^{II} ion and the σ orbitals of the Br anions or HOMOs of the bridging ligands was small. The large antiferromagnetic interaction for these complexes might be realized by the approaching energy levels of the magnetic orbital of the Cu^{II} ion, and the HOMOs of the Hm-dtc$^-$ ligand, the Cu^I ion, and the halogen ions of B$^-$ or I$^-$.

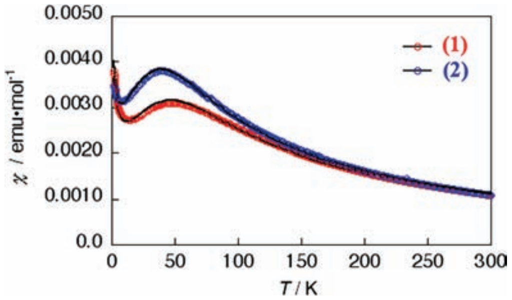

Figure 2. Temperature dependence of molar magnetic susceptibility χ_M for **1** (red) and **2** (blue). The solid lines are fit results for the χ_M data of **1** and **2** obtained by using the Bonner$-$Fisher equation.

The conducting properties of the mixed-valence 1D coordination polymers **1** and **2** were investigated using complex impedance spectroscopy, which was a powerful technique for studying the carrier transport and dielectric properties of bulk samples and electric devices. These impedance measurements were performed on powder-pressed pellet samples sandwiched by brass electrodes (diameter: 13 mm); the thicknesses of the pellet samples of **1** and **2** were 0.141 and 0.135 mm, respectively. The frequency dependence of the electric properties was often represented in terms of the complex impedance (Z^*), complex permittivity (ε^*), and electric modulus (M^*). These parameters were related to each other as follows:[8] $Z^* = Z' - jZ''$, $\varepsilon^* = \varepsilon' - j\varepsilon''$, and $M^* = M' + jM'' = 1/\varepsilon^* = j\omega C_0 Z^*$, where $\omega = 2\pi f_r$ (f_r = resonance frequency), $j = (-1)^{1/2}$, and C_0 is the vacuum capacitance of the circuit elements. The plots of Z' versus Z'' (Nyquist diagram) at different temperatures are shown in Figure 1a for **1** and in Figure 1b for **2**. In these plots, parts of the semicircular arcs were obtained, and the diameters of the semicircular arcs for both complexes decreased with an increase

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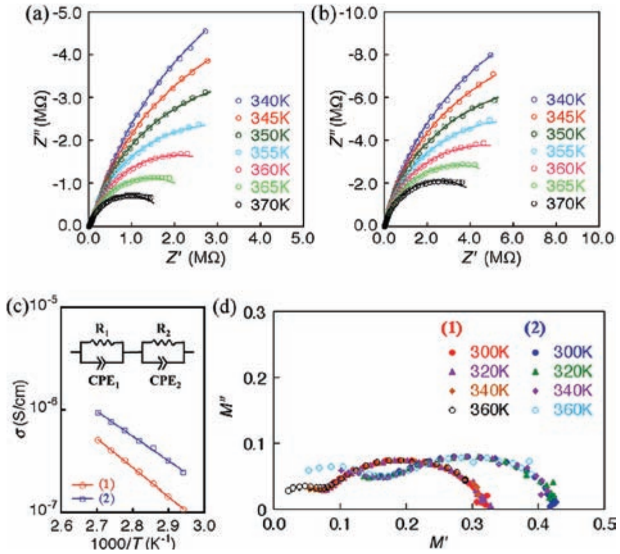

Figure 3. Complex impedance $Z'-Z''$ plots of **1** (a) and **2** (b) at selected temperatures. The solid lines are fit results with an equivalent circuit in the inset of part c. (c) Variation of σ_{dc} (due to bulk) of **1** (red) and **2** (blue) with inverse temperature and the equivalent circuit model for **1** and **2** (inset). (d) Complex modulus plots of **1** and **2** at selected temperatures.

in the temperature, indicating a semiconducting behavior. *ZView* software[9] was used for fitting the experimental data in the frequency range of 200 Hz to 1 MHz. The results obtained from the least-squares fitting with the equivalent circuit model in Figure 3c (inset) are listed in Tables S1 and S5 in the Supporting Information. The equivalent circuit consisted of two resistances (R_1 and R_2) and two constant phase elements (CPE_1 and CPE_2). The bulk direct-current (dc) conductivity was calculated from R_1, which was estimated by recalculation with the averaged CPE-α values in Tables S1 and S5 in the Supporting Information, and the activation energies E_a of **1** and **2** were estimated from the variation of σ_{dc} as a function of the temperature (Figure 3c) using the relation[8] $\sigma_{dc} = \sigma_0 \exp(-E_a/kT)$, where k is Boltzmann's constant. The values of the estimated activation energies, $E_a = 0.562$ eV (**1**) and $E_a = 0.479$ eV (**2**), were relatively small in the case of coordination polymers.

Figure 3d shows the complex electric modulus spectra of complexes **1** and **2** at different temperatures, in which two depressed semicircular arcs derived from the bulk resistivity in the high-frequency region (right arcs) and the contact resistivity at the electrode interface in the higher frequency region (left arcs) are clearly observed. The diameters of the right arcs for both complexes did not change with changing temperatures, which implied that the capacitance in the bulk samples did not depend on the temperature, indicating that the conductivity relaxation process dominated the impedance behavior in this system.

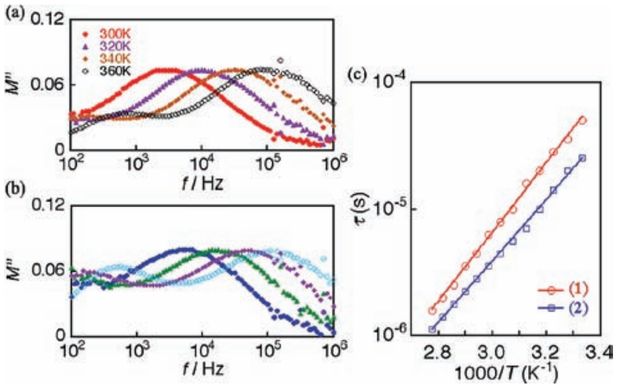

Figure 4. (a) Imaginary parts of the electric modulus M'' as a function of the frequencies for **1** (a) and **2** (b) at selected temperatures. (c) Arrhenius plots of **1** (red) and **2** (blue) of the relaxation times against inverse temperatures.

Parts a and b of Figure 4 show variations of the imaginary components of electrical modulus M'' for **1** and **2** with frequency at different temperatures. Both complexes showed a quite similar temperature dependence; that is, M''_{max} shifted toward the higher frequency side with an increase in the temperature, indicating a correlation between the motions of mobile charge. The peak frequency of the plots helped to evaluate the relaxation time (τ) using the relation $\omega_{max}\tau = 1$. The variation of τ as a function of the inverse of the absolute temperature appeared to be linear and followed the relation[8c] $\tau^{-1} = \tau_0^{-1} \exp(-E_a/kT)$. The estimated activation energies from the relaxation process of **1** and **2** were 0.542 and 0.482 eV, respectively, which were in good agreement with the values estimated from the conductivities of the bulk samples.

In summary, we synthesized new halide-bridged mixed-valence $\mathrm{Cu^I}-\mathrm{Cu^{II}}$ coordination polymers with 1D infinite-chain structures. These complexes show a relatively strong antiferromagnetic interaction and semiconducting behaviors, which might be realized by the approaching energy levels of the magnetic orbital of the $\mathrm{Cu^{II}}$ ion and the HOMOs of the dithiocarbamate ligand, the $\mathrm{Cu^I}$ ion, and the bridging Br or I anions.

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Supporting Information Available: Crystallographic data in CIF format, synthesis, XPS, TG-DTA, impedance results, UV−vis−near-IR, and crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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