Molecular Alloy with Diluted Magnetic Moments—Molecular Kondo System

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S *Supporting Information*

ABSTRACT: $[Ni_{1-x}Cu_x(tmdt)_2]$ (tmdt = trimethylenetetrathiafulvalenedithiolate) was prepared for realizing molecular Kondo systems. Magnetic moments ($S = \frac{1}{2}$) are considered to exist at the central $\{CuS_4\}$ parts of $Cu(tmdt)_2$ molecules. The χT-versus-T curve of the system with $x \approx 0.15$ showed a broad peak at ~10 K. The decrease in the χT value below 10 K is consistent with a singlet ground state, as expected for a Kondo system. However, in the system with $x \approx 0.27$, the χT value decreased when the temperature was lowered to 2 K, indicating antiferromagnetic interactions between magnetic moments through π–d interactions. Although the susceptibility anomaly suggested that the π–d interactions become important at $T < 20$ K, the observed resistivity (ρ_{obs}) showed no resistivity minimum characteristic of a Kondo system down to 4.2 K. However, the differential resistivity $\Delta\rho(T) = \rho_{obs} - \rho_L(T)$ showed a logarithmic resistivity increase at 8−20 K with decreasing temperature, where $\rho_L(T)$ is a fitted function of ρ_{obs} obtained at $T > 50$ K that is considered to represent approximately the temperature dependence of the resistivity without spin scattering of the conduction electrons.

The development of new molecular conductors exhibiting electromagnetic properties that have not yet been realized in molecular systems is very essential for future studies of the chemistry of molecular conductors. For example, even the rather familiar properties of inorganic materials, such as metallicity and superconductivity, contributed greatly to the field of molecular conductors when they were first observed in molecular systems.[1] It is well-known that various magnetic organic conductors, such as paramagnetic organic superconductors, ferromagnetic organic metals, antiferromagnetic organic superconductors, and field-induced organic superconductors were developed more than 10 years ago.[2−4] However, except in systems such as the field-induced organic superconductors,[3a,4] no significant π–d coupling has been observed in the hitherto-developed magnetic organic conductors because the magnetic anions in these conductors are located separately from the organic conduction layers. One of the most prominent phenomena arising from the interaction between localized magnetic moments and conduction electrons is the Kondo effect observed in inorganic alloys with diluted magnetic moments.[5] Therefore, the development of a molecular metal exhibiting the Kondo effect would provide useful information for elucidating the interaction between

magnetic moments and π-conduction electrons in molecular conductors. In this paper, we report the preparation and electromagnetic properties of a single-component molecular metal with diluted magnetic moments.

Since the discovery of the single-component molecular metal $[Ni(tmdt)_2]$ (tmdt = trimethylenetetrathiafulvalenedithiolate) in 2001,[6] various single-component molecular metals have been developed.[7] Among them, a series of isostructural $[M(tmdt)_2]$ (M = Ni, Cu, Pd, Au, Pt) systems was most extensively studied. An important feature of $[M(tmdt)_2]$ is that its electronic band structure near the Fermi level, which is mainly determined by three molecular orbitals designated as *sym-Lπ*, *asym-Lπ(d)*, and *pdσ(−)* (Figure 1),[8] can easily be changed by exchanging the
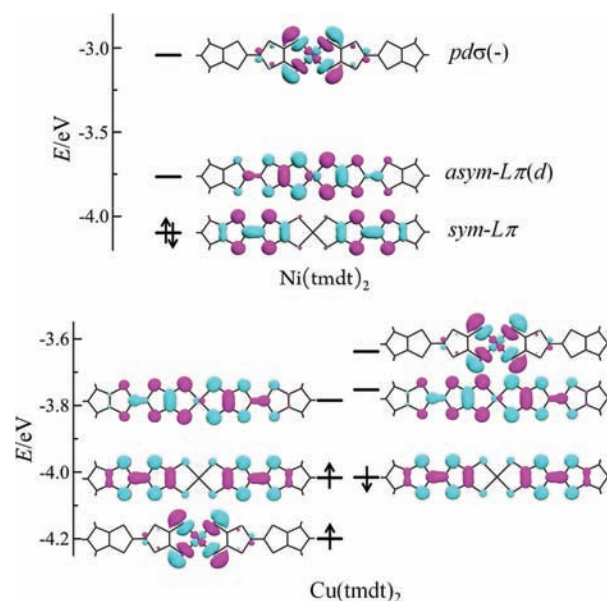

Figure 1. Non-spin-polarized MOs of $Ni(tmdt)_2$ and spin-polarized MOs of $Cu(tmdt)_2$ that play crucial roles in the construction of the electronic band structure of $[M(tmdt)_2]$ (M = Ni, Cu) near the Fermi level.[9]

central M atom. In $M(tmdt)_2$ (M = Ni, Pd, Pt) with even numbers of total electrons, the energy of *pdσ(−)* is much higher than those of *sym-Lπ* and *asym-Lπ(d)*, and *sym-Lπ* and *asym-Lπ(d)* form stable 3D metal bands (in this paper, $[M(tmdt)_2]$ and $M(tmdt)_2$ represent the crystal of a single-

component molecular conductor and its constituent molecule, respectively). In $Au(tmdt)_2$ with an odd number of total electrons, *asym-Lπ(d)* becomes a singly occupied molecular orbital (SOMO), and $[Au(tmdt)_2]$ becomes a magnetic conductor that transits from a paramagnetic metal to an antiferromagnetic metal at 110 K.[10] In $Cu(tmdt)_2$, the energy of $pd\sigma(-)$ is strongly reduced, and $pd\sigma(-)$ becomes a SOMO. Because the $pd\sigma(-)$ MO has an amplitude only at the central $\{MS_4\}$ part of the molecule (see Figure 1), it behaves as a *magnetic orbital*, like the d orbitals of transition-metal atoms such as Fe, Co, and Ni. $[Cu(tmdt)_2]$ becomes an unprecedented molecular conductor in which an antiferromagnetic chain and π-conduction electrons coexist, though the system consists of single molecules.[11] The 1D Heisenberg behavior proves the existence of one localized spin ($S = \frac{1}{2}$) on the central $\{CuS_4\}$ part of each $Cu(tmdt)_2$ molecule.[11] Because the crystal structures of $[Ni(tmdt)_2]$ and $[Cu(tmdt)_2]$ are almost identical to each other, it was expected that a molecular metal with diluted magnetic moments, $[Ni_{1-x}Cu_x(tmdt)_2]$, could be prepared by alloying $[Ni(tmdt)_2]$ and $[Cu(tmdt)_2]$. Unlike hitherto-reported magnetic organic conductors,[2a,3a] the magnetic moments in $[Ni_{1-x}Cu_x(tmdt)_2]$ should be embedded in the sea of π-conduction electrons. Consequently, a large π–d coupling, which was barely realized in traditional molecular conductors, should be realized.

$M(tmdt)_2$ (M=Ni, Cu, Au, ...)
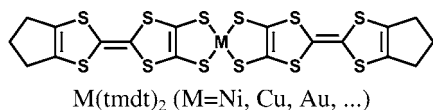
$(Me_4N)_2[Ni(tmdt)_2]$ and $(Me_4N)_2[Cu(tmdt)_2]$ were prepared under a strictly inert atmosphere according to the literature.[3a,12] The crystals of $[Ni_{1-x}Cu_x(tmdt)_2]$ were prepared electrochemically from a CH_3CN solution containing suitable amounts of $(Me_4N)_2[Ni(tmdt)_2]$ and $(Me_4N)_2[Cu(tmdt)_2]$ along with $(^nBu_4N)PF_6$ as the electrolyte. After a current of 0.4 μA was applied for 4 weeks, small black crystals were obtained (Figure 2a).

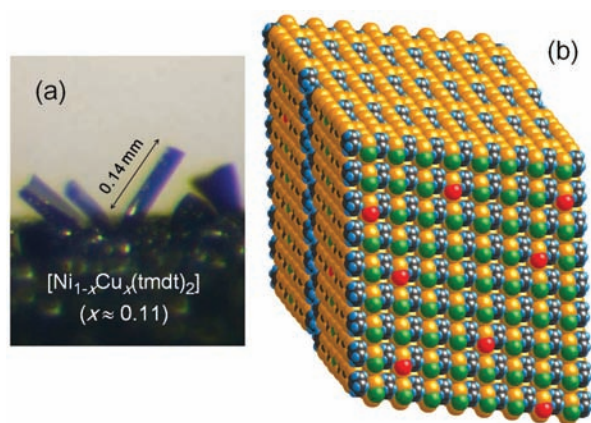**Figure 2.** (a) Crystals of $[Ni_{1-x}Cu_x(tmdt)_2]$ ($x \approx 0.11$) grown on a Pt electrode. (b) Molecular packing and schematic drawing of the possible distribution of Cu atoms [or magnetic moments ($S = \frac{1}{2}$)] in the crystal. Yellow, green, and red spheres represent S, Ni, and Cu atoms, respectively.

The x values were determined by electron probe microanalysis (EPMA). The measurements were performed on 3–6 points of each microcrystal. The obtained x values were distributed around the average value within an accuracy of $\pm3\%$. The average x values were larger than the mixing ratio of $(Me_4N)_2[Ni(tmdt)_2]$ and $(Me_4N)_2[Cu(tmdt)_2]$) in the CH_3CN solutions from which the crystals were grown.

X-ray diffraction (XRD) experiments were performed on a crystal of $[Ni_{1-x}Cu_x(tmdt)_2]$ having a maximum dimension of 0.14 mm using a Rigaku Saturn 724R CCD system.[13] The x value was determined to be ~0.11 by EPMA. Because the molecular dimensions of $Ni(tmdt)_2$ and $Cu(tmdt)_2$ are almost identical to each other, it was highly possible that the $Ni(tmdt)_2$ and $Cu(tmdt)_2$ molecules would be randomly distributed in the crystal. In fact, no XRD patterns such as diffuse streaks and diffuse sheets suggesting a nonhomogenous distribution of $Cu(tmdt)_2$ were observed. Because the unit cell volume is 556 Å,[3] the average density of Cu atoma is ~1 Cu atom/5000 Å^3 (Figure 2b). Thus, $[Ni_{1-x}Cu_x(tmdt)_2]$ is regarded as a molecular conductor with sufficiently diluted magnetic moments.

The magnetic susceptibilities of $[Ni_{1-x}Cu_x(tmdt)_2]$ were measured for polycrystalline samples with average x values of 0.098, 0.13, 0.18, and 0.27 over the temperature range 2−300 K using a Quantum Design MPMS-7XL superconducting quantum interference device magnetometer. As shown in Figure 3a, the temperature dependence of the susceptibilities corrected for Pascal's diamagnetic terms showed a constant paramagnetic susceptibility (χ) of 2.5×10^{-4} emu/mol at $T > 50$ K. This χ value approximately equals the susceptibility of $[Ni(tmdt)_2]$ at 295 K ($\sim3 \times 10^{-4}$ emu/mol).[6] Below 40 K, the susceptibility increased as the temperature decreased and showed a distinct x dependence below 20 K. Interestingly, the large increase in the susceptibility was observed in a narrow range of x around $x \approx 0.15$, whereas the samples with x values of 0.098 and 0.27 showed an inconspicuous increase in susceptibility at low temperatures. Except for the sample with $x \approx 0.27$, the dependence of the susceptibility on temperature below 6 K became fairly weak. The gradual increase in the susceptibilities of the samples with x values of 0.09−0.18 below 6 K is considered to be mainly due to paramagnetic impurities (Figure 3a). In other words, it appears that the intrinsic susceptibility of $[Ni_{1-x}Cu_x(tmdt)_2]$ tends to be constant at low temperatures (<6 K). The χT values of the samples with x values of 0.13 and 0.18 increased below ~30 K and showed broad peaks at ~10 K (Figure 3a). The sample with $x \approx 0.098$ also showed an inconspicuous broad hump in the same temperature region. Furthermore, the susceptibility increase observed below 30 K was rapidly suppressed with an increase in magnetic field. As shown in Figure 3b, the broad peak in the χT-versus-T curve became almost nonexistent above 3 T. These magnetic behaviors indicated $[Ni_{1-x}Cu_x(tmdt)_2]$ ($x = 0.098−0.18$) to be a molecular Kondo system.[5,14] Though the slope of the χT-versus-T curve of $[Ni_{1-x}Cu_x(tmdt)_2]$ ($x \approx 0.098, 0.13, 0.18$) changed at low temperatures, the susceptibility of the sample with $x \approx 0.27$ showed no distinct anomaly down to 2 K. The χT value of $[Ni_{1-x}Cu_x(tmdt)_2]$ ($x \approx 0.27$) decreased with decreasing temperature, suggesting antiferromagnetic interactions between the magnetic moments. It would be natural that with increasing x the magnetic moments should begin to interact antiferromagnetically with each other through the interaction between the π-conduction electrons and the $pd\sigma(-)$ orbital of $Cu(tmdt)_2$ [hereafter, this interaction will simply be called the π–d interaction, by analogy to the s−d interaction in inorganic conductors, because the conduction electron is the π
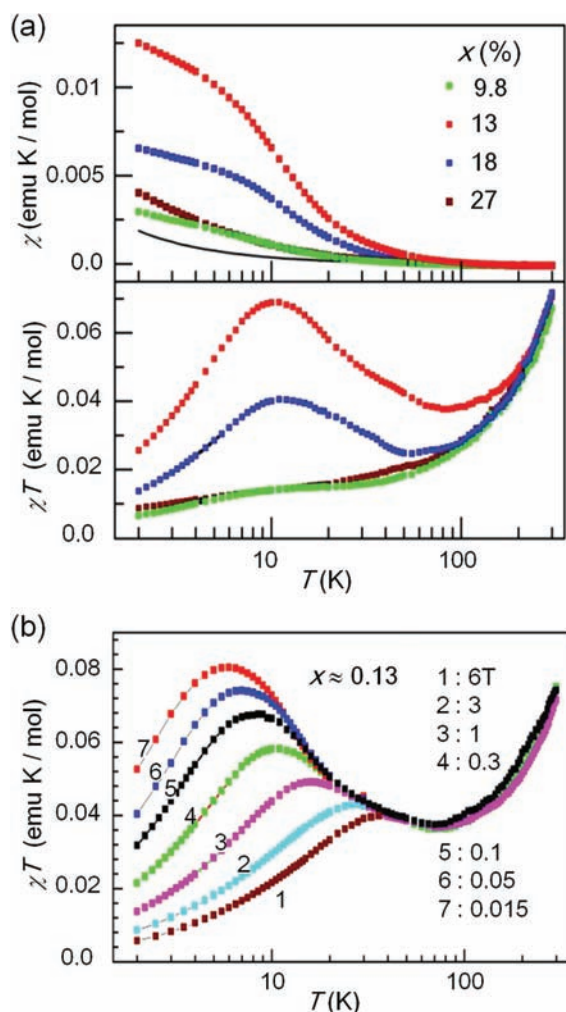
Figure 3. (a) Temperature dependence of (top) the magnetic susceptibility χ and (bottom) χT for $[Ni_{1-x}Cu_x(tmdt)_2]$ ($x \approx 0.098$, 0.13, 0.18, 0.27). The black line, which shows the calculated susceptibility due to 1% paramagnetic impurities ($S = \frac{1}{2}$), suggests that the susceptibility increase for the samples with $x = 0.098-0.18$ below ~6 K is mainly due to paramagnetic impurities. (b) Magnetic field (B) dependence of the χT-versus-T curve of the sample with $x \approx 0.13$ for $B = 0.015-6$ T.

electron and the $pd\sigma(-)$ orbital with the unpaired spin is a d-like orbital (see Figure 1)].

To observe the resistivity minimum characteristic of a Kondo system, we tried to prepare single crystals of $[Ni_{1-x}Cu_x(tmdt)_2]$. Although sufficiently large single crystals were hardly obtained, we succeeded in preparing single crystals of $[Ni_{1-x}Cu_x(tmdt)_2]$ ($x \approx 0.11$) with maximum sizes of ~0.14 mm. Using these crystals, we performed four-probe single-crystal resistivity measurements over the temperature range 4.2–300 K. As shown in Figure 4, the resistivity decreased with decreasing temperature. The room-temperature conductivity was 150 S cm^{-1}. Although the temperature dependence of the resistivity became weak at low temperature, the expected resistivity minimum was not observed. Because the resistivity of $[Ni_{1-x}Cu_x(tmdt)_2]$ is much larger than that of usual inorganic metals, we hypothesized that the temperature dependence of the resistivity of $[Ni_{1-x}Cu_x(tmdt)_2]$ due to electron scattering by phonons covered the temperature dependence of the resistivity by magnetic scattering. Therefore, we tried to
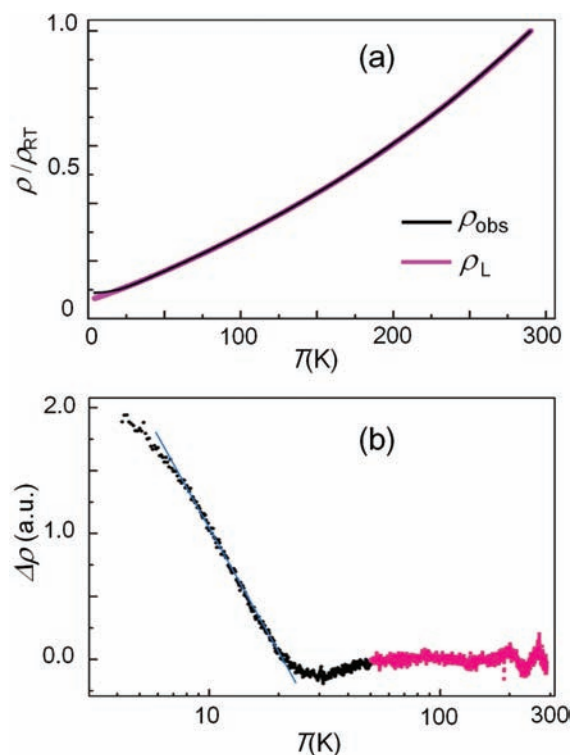

Figure 4. (a) Resistivity of $[Ni_{1-x}Cu_x(tmdt)_2]$ ($x \approx 0.11$). ρ_{RT} is 6.5×10^{-3} Ω cm. The red line is the fitted curve of the resistivity (ρ_L) calculated from the data at $T > 50$ K: $\rho_L(T)$ (Ω cm) = 4.2×10^{-4} + $(1.1 \times 10^{-5})T + (5.4 \times 10^{-8})T^2 - (2.5 \times 10^{-10})T^3 + (9.5 \times 10^{-13})T^4 - (1.1 \times 10^{-15})T^5$. (b) Temperature dependence of the resistivity difference $\Delta\rho = \rho_{obs} - \rho_L(T)$.

subtract the resistivity due to phonon scattering from the observed resistivity (ρ_{obs}). Because the susceptibility behavior suggests that the $\pi-d$ interaction in $[Ni_{1-x}Cu_x(tmdt)_2]$ should be unimportant at $T > 50$ K, the temperature dependence of the resistivity above 50 K was considered to represent the resistivity without any contribution from the spin scattering of the π-conduction electrons. The temperature dependence of ρ_{obs} (in Ω cm) above 50 K was fitted by the following function: $\rho_L(T) = \rho_0 + a_1T + a_2T^2 + a_3T^3 + a_4T^4 + a_5T^5$ (Figure 4a). Next, $\rho_L(T)$ was extrapolated down to 4.2 K, and the quantity $\Delta\rho = \rho_{obs} - \rho_L(T)$ was calculated as a rough estimate of the temperature dependence of the resistivity due to the $\pi-d$ interaction. As shown in Figure 4b, $\Delta\rho$ was approximately zero between 20 and 50 K, indicating that the observed resistivity can be expressed only by $\rho_L(T)$ down to 20 K. $\Delta\rho$ then increased as the temperature was lowered, where, as mentioned above, χ also increased as T decreased (Figure 3a). At 8–20 K, $\Delta\rho$ shows log T dependence. However, the T dependence of $\Delta\rho$ becomes sluggish below 6 K, consistent with the susceptibility behavior at low temperature.

In conclusion, we have prepared the molecular Kondo system $[Ni_{1-x}Cu_x(tmdt)_2]$. The χT-versus-T curve of the sample with $x \approx 0.098-0.18$ showed a broad peak at ~10 K. The decrease in χT below 10 K is consistent with the singlet ground state expected for a Kondo system. However, for $x \approx 0.27$, the χT value decreased as the temperature was lowered to 2 K, indicating antiferromagnetic interactions between the magnetic moments through $\pi-d$ interactions. The observed resistivity did not show a resistivity minimum. However, the resistivity difference $\Delta\rho = \rho_{obs} - \rho_L(T)$ exhibited a logarithmic

increase below 20 K, where $\rho_L(T)$ was obtained by the fitting of the observed resistivity data at $T > 50$ K where spin scattering of the π-conduction electron is considered to be negligible. The present work will contribute to elucidating the interaction between magnetic moments and π-conduction electrons in molecular conductors and promote the development of new types of magnetic molecular conductors having large coupling between magnetic moments and π-conduction electrons.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Preparation, electromagnetic properties, and additional structural data (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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■ ACKNOWLEDGMENTS

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(13) XRD spots were indexed using the Twinsolve module of CrystalClear (Rigaku Corporation Inc.). Crystallographic data for $[Ni_{1-x}Cu_x(tmdt)_2]$ ($x \approx 0.11$): triclinic, space group $P\bar{1}$; $a = 6.419(2)$ Å, $b = 7.457(2)$, $c = 12.041(3)$, $\alpha = 90.54(2)°$, $\beta = 96.94(2)°$, $\gamma = 103.55(2)°$; $V = 557.2(2)$ Å^3 at 293 K; $Z = 1$. The final R factor was 0.099.

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