

Synthesis and Physical Properties of New Organic Conductor with Triangular Lattice

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Abstract

Recently, materials with a triangular lattice have attracted much attention due to their interesting physical properties, such as a quantum spin liquid. It has been reported that organic conductors κ -(ET)₂Cu₂(CN)₃ (**1**) and κ -(ET)₂Ag₂(CN)₃ (**2**) show quantum spin liquid behavior, where ET is bis(ethylenedithio)tetrathiafulvalene. These two salts are the only ones known as κ -type ET salt organic conductors with a nearly regular triangular lattice. Therefore, in order to develop new materials with a regular triangular lattice, we synthesized κ -(ET)₂Cu_{2x}Ag_{2(1-x)}(CN)₃ (**3**) by mixing Cu⁺ and Ag⁺ ions. We analyzed the element distribution and composition ratio in the crystal by scanning electron microscope (SEM) and energy dispersive x-ray spectroscopy (EDX). The Cu⁺ and Ag⁺ ions were distributed uniformly in the crystals. The x was found to be $x = 0.82 \pm 0.01$ for batch #1, and $x = 0.81 \pm 0.06$ for batch #2. The mixed crystal showed semiconducting behavior with activation energy (E_a/k_B) of 711 K. This material is considered a Mott insulator.

Key words: Organic conductor, triangular lattice, x-ray diffraction, SEM/EDX, electrical resistivity

1. Introduction

Recently, materials with a triangular lattice have attracted much attention due to their interesting character, such as a spin liquid. In 2003, the first quantum spin liquid was discovered in an organic Mott insulator κ -(ET)₂Cu₂(CN)₃ (**1**) having a triangular lattice⁽¹⁾, where ET is bis(ethylenedithio)tetrathiafulvalene. This material has a layered crystal structure and κ -type molecular arrangement as shown Fig.1. ET forms a dimer that has one hole, and therefore, one spin $S = 1/2$. Spins on dimers form triangular lattices and interact anti-ferromagnetically, which causes spin frustration and quantum spin liquid behavior. Recently, by substituting Cu for Ag, κ -(ET)₂Ag₂(CN)₃ (**2**) was synthesized.^(2,3) It also has a triangular lattice and shows quantum spin liquid behavior. However, there is no report of a

mixed crystal. Here, we report the synthesis and transport properties of the mixed crystal κ -(ET)₂Cu_{2x}Ag_{2(1-x)}(CN)₃ (**3**).

2. Materials and Methods

2-1 Preparation of single crystals of κ -(ET)₂Cu_{2x}Ag_{2(1-x)}(CN)₃ (**3**)

Electrocrystallization was performed at the temperature of 293 or 303 K. Typically, ET (7.6 mg, 0.02 mmol) was placed in the anodic compartment, and tetrabutylammonium (TBA)·Ag(CN)₂ (32.3 mg, 0.08 mmol) and CuCN (7.4 mg, 0.08 mmol) were placed in the cathodic compartment. Reagents in both compartments were dissolved in a mixture of 1,1,2-trichloroethane (15 ml) and acetonitrile (3 ml) under a N₂ atmosphere. A constant current (1 or 0.2 μ A) was passed between the two platinum electrodes over about two weeks or three months.

2-2 Single-crystal X-ray crystallography

Single-crystal X-ray diffraction data of **3** were collected on the diffractometer (XtaLAB Rigaku Oxford diffraction at 298 K) using graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å).

2-3 SEM/EDX analysis

The ratio of Cu and Ag in **3** was determined by scanning

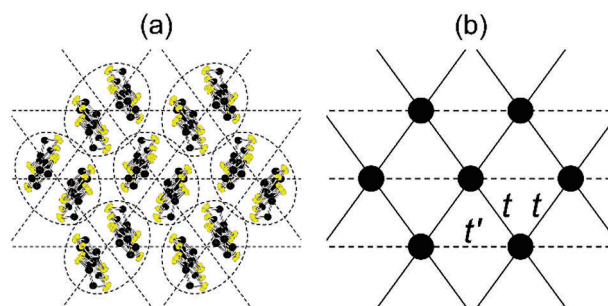


Fig. 1. (a) κ -type molecular arrangement in ET layer. (b) ET dimer represented by the black circle forms a triangular lattice with interdimer transfer interactions, t and t' .

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electron microscope (SEM) equipped with energy dispersive X-ray spectroscopy (EDX).

2-4 Conductivity measurement

The direct current conductivity of **3** was measured using a standard four-probe technique with gold wires ($\phi = 15 \mu\text{m}$) attached to a single crystal with carbon paste.

3. Results and Discussion

3-1 Crystal structure

Hexagonal or rhomboid plate-shaped single crystals of **3** were grown on the anodic electrode in batch #1 and #2. X-ray diffraction measurement was performed on a crystal (#2-c1) from batch #2. It was found that **3** is isostructural to $\kappa\text{-(ET)}_2\text{Cu}_2(\text{CN})_3$ (**1**) and $\kappa\text{-(ET)}_2\text{Ag}_2(\text{CN})_3$ (**2**).

Table 1 shows the lattice constants of the mixed crystal (#2-c1), **1** and **2**.⁽³⁾ The deviations of the in-plan lattice constants b and c from those of **1** and **2** are less than 1% in the mixed crystal. Since the structure of the mixed crystal is very similar to those of **1** and **2**, it is a candidate for a quantum spin liquid with a nearly regular triangular lattice.

3-2 Elemental analysis

Fig. 2 shows the EDX mapping of Ag and Cu for the crystal (#1-c1) from batch #1 and the crystal (#2-c1) from batch #2.

Table 1. Lattice constants of a mixed crystal, **1**, and **2**

	$\kappa\text{-(ET)}_2\text{Cu}_{1.5}\text{Ag}_{0.5}(\text{CN})_3$	1 (Cu)	2 (Ag)
space group	$P2_1/c$	$P2_1/c$	$P2_1/c$
a (Å)	16.1621 (2)	16.080	15.055
b (Å)	8.63480 (10)	8.5837	8.7030
c (Å)	13.4614 (2)	13.3946	13.412
β (°)	114.061 (2)	113.3490	91.307
V (Å ³)	1715.40 (5)	1697.4	1756.8
T (K)	298	300	300

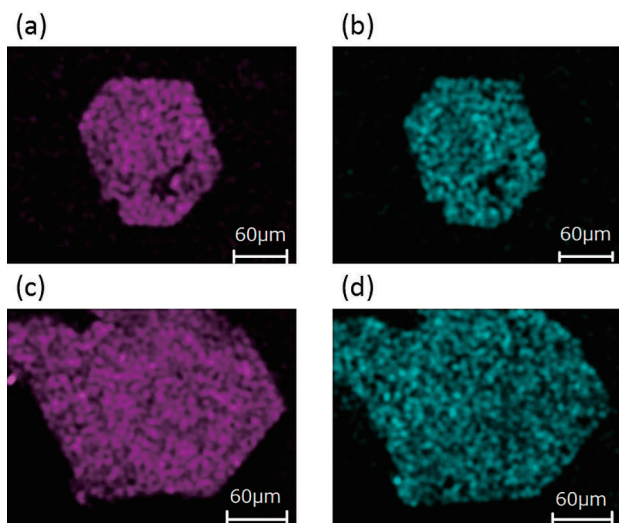


Fig. 2. EDX mapping of (a) Ag and (b) Cu for #1-c1, (c) Ag and (d) Cu for #2-c1. Each scale bar is 60 μm long.

Cu and Ag are distributed homogeneously in the crystal. The ratios of Cu and Ag ($\text{Cu} : \text{Ag} = x : (1-x)$) were determined by quantitative EDX analysis ($x = 0.81$ for #1-c1 and $x = 0.75$ for #2-c1). It is consistent with X-ray diffraction analysis of #2-c1. EDX mapping was performed on several crystals from #1 and #2. Batch #1 has little sample dependence ($x = 0.82 \pm 0.01$) while #2 has certain sample dependence ($x = 0.81 \pm 0.06$).

Though equal amounts of Cu and Ag were used, the concentration of Cu was higher than that of Ag in the crystals.

3-3 Electrical conductivity of $\kappa\text{-(ET)}_2\text{Cu}_{2x}\text{Ag}_{2(1-x)}(\text{CN})_3$ (**3**)

Fig. 3 (a) displays the temperature dependence of resistivity of the mixed crystal (#2-c4, $x = 0.87$). The intralayer resistivity was $0.06 \Omega\text{cm}$ at room temperature. The compound shows semiconducting behavior. The activation energy (E_a) was obtained from the slope of Arrhenius Plot (Fig.3(b)) using the relation, $\ln \rho \propto \exp(E_a/k_B T)$, where k_B denotes Boltzmann's constant. The activation energy (E_a/k_B) of **3** ($x = 0.87$) was 711 K, which is in between **1** (420–500 K)⁽⁴⁾ and **2** (1000 K). Thus, we conclude that **3** is a Mott insulator as is the case of mother compounds **1** and **2**.

Conclusion

In summary, we succeeded in synthesizing new organic conductors $\kappa\text{-(ET)}_2\text{Cu}_{2x}\text{Ag}_{2(1-x)}(\text{CN})_3$ with a triangular lattice by mixing Cu and Ag. In the crystal, both Cu and Ag distributed homogeneously. The temperature dependence of the resistivity shows semiconducting behavior with an activation energy of 711 K. The mixed crystal is considered a Mott insulator.

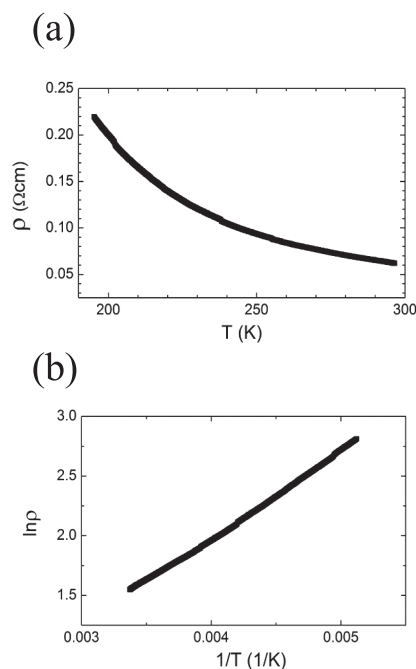


Fig. 3. The temperature dependence of resistivity of $\kappa\text{-(ET)}_2\text{Cu}_{2x}\text{Ag}_{2(1-x)}(\text{CN})_3$ ($x = 0.87$) (a) and the Arrhenius Plot (b).

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三角格子を持つ新しい有機伝導体の合成と物性

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要旨

近年, 三角格子を持つ物質はスピン液体などの興味深い性質を持つことで注目されている。κ-(ET)₂Cu₂(CN)₃とκ-(ET)₂Ag₂(CN)₃は三角格子を持つモット絶縁体であり, スピン液体の振る舞いを示すことが報告されている。しかし, ほぼ正三角形の構造を持つκ型ET塩有機伝導体はこの二つしか知られていない。

そこで, 今回我々は新しい正三角形の構造を持つ物質を開発するために, 銅イオンと銀イオンを混ぜて, 有機伝導体の混晶試料κ-(ET)₂Cu_{2x}Ag_{2(1-x)}(CN)₃を合成した。2種類のバッチ (#1, #2) について結晶構造と物性を調べた。X線構造解析によって, この混晶は同形構造を持つことが分かった。SEM/EDX分析により, 結晶内の元素分布や組成比を調べた結果, 銅イオンと銀イオンはともに結晶内に一様に分布し, その比は上記の化学式において, #1では $x = 0.82 \pm 0.01$, #2では $x = 0.81 \pm 0.06$ であることが分かった。また, #2の結晶について面内の電気抵抗を測定した結果, 半導体的な挙動を示し, その活性化エネルギー (E_a/k_B) は711 Kであった。これは二つの母物質の活性化エネルギーの値の間であることから, 得られた混晶はモット絶縁体であると考えられる。

重要語句: 有機伝導体, 三角格子, X線構造解析, SEM/EDX, 電気抵抗

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