

SYNTHESIS, STRUCTURE AND PROPERTIES OF A LINEAR COPPER(I) COORDINATION POLYMER WITH TETRAKIS(ETHYLTHIO)TETRATHIAFULVALENE

XINMIN GAN, MEGUMU MUNAKATA,* TAKAYOSHI KURODA-SOWA,
MASAHIKO MAEKAWA and MIKIKO YAMAMOTO

Department of Chemistry, Faculty of Science and Technology, Kinki University,
Kowakae, 3-4-1, Higashi-Osaka, Osaka 577, Japan

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Abstract—A new linear coordination polymer composed of copper(I) cations and tetrakis(ethylthio)tetrathiafulvalene (TTC₂-TTF) molecules has been synthesized by the reaction of copper(I) perchlorate and TTC₂-TTF in acetone under argon. The compound, [Cu(TTC₂-TTF)]ClO₄, was characterized by spectroscopic and X-ray crystallographic methods. It is a 1:1 metal-ligand complex in which each of the copper(I) ions is tetrahedrally coordinated by four sulphur atoms from the bridging TTC₂-TTF molecules to form coordination polymeric chains which are separated from each other by the perchlorate anions in the crystal. The complex was doped with iodine to afford {[Cu(TTC₂-TTF)]ClO₄}I, which exhibits a conductivity of $6 \times 10^{-4} \text{ S cm}^{-1}$ at 25 °C for a compacted pellet.

Tetrathiafulvalene (TTF) and some of its derivatives can be easily oxidized to the stable radical cations and they are one of the major components of numerous materials termed "synthetic metals" which exhibit electroconductivity over a wide range, from semiconductor to superconductor.¹⁻⁴ In recent years this type of compound has attracted great interest. Most of the synthetic metals are composed of organic radical ions. Although some of them contain metal atoms in the anion part, these metal ions are not coordinated to the organic molecules.³ In an effort to develop a new type of low-dimensional conductive compound, we are currently studying the metallotetrathiafulvalene polymers, in which TTF or its derivatives directly coordinate to the metal ions. Tetrakis(ethylthio)tetrathiafulvalene (TTC₂-TTF), which has a central tetrathio-TTF (C₆S₄) π system and a side ethylthio chain system, is a single-component organic semiconductor with low conductivity ($\sigma_{\text{RT}} \approx 10^{-10} \text{ S cm}^{-1}$)⁵ and its physical properties have been widely investigated,^{6,7} while its chemical properties have

received much less attention.⁸ We have previously synthesized the complexes of TTC₂-TTF with copper(I) halides^{9,10} and we found that these 2:1 metal-ligand complexes have one- or two-dimensional polymeric structure in which the halide ions behave as bridge to link the metal ions. As a part of our systematic study of the metallotetrathiafulvalene polymers we hoped to obtain a coordination polymer without halide as the bridging group, where the metal ions are linked only by tetrathiafulvalene molecules in the compound. In this paper we report the synthesis and structural characterization of a linear coordination polymer composed of copper(I) ions and bridging tetrakis(ethylthio)tetrathiafulvalene molecules, [Cu(TTC₂-TTF)]ClO₄, and the properties of its iodine-doped compound.

EXPERIMENTAL

General

The preparation of the complex was performed under argon using the usual Schlenk techniques. The reagent TTC₂-TTF (m.p. 70 °C) was prepared

* Author to whom correspondence should be addressed.

according to the literature.¹¹ Copper(II) perchlorate (Wako) was used as purchased. Acetone was dried and distilled by a standard method before use. IR spectra and electronic spectra as KBr discs were recorded with a Jasco 8000 FT-IR spectrometer and Hitachi 150-20 spectrophotometer, respectively. Electrical resistivity was measured by a conventional two-probe method at 25°C with compacted pellets.

Preparation of [Cu(TTC₂-TTF)]ClO₄ and its iodine-doped compound

Copper(II) perchlorate hexahydrate (9.3 mg, 0.025 mmol) and copper plates (3 × 3 × 1 mm, five pieces) were stirred in acetone (10 cm³) for 30 min under an ethylene atmosphere, and the resultant colourless copper(I) solution was added to a TTC₂-TTF (22.2 mg, 0.05 mmol) solution in acetone (10 cm³). Then, under an argon atmosphere, the mixture was filtered and the orange filtrate was sealed in four 7-mm diameter glass tubes. After standing for 7 days at 25°C, orange crystals of [Cu(TTC₂-TTF)]ClO₄ (**1**) were obtained, yield 70%. Found: C, 27.5; H, 3.2. Calc. for C₁₄H₂₀ClCuO₄S₈: C, 27.7; H, 3.3%. IR (cm⁻¹): 2959 (w), 2922 (w), 2864 (w), 2822 (w), 1446 (s), 1419 (s), 1371 (s), 1273 (s), 1142 (s), 1086 (vs), 966 (m), 900 (m), 758 (s), 625 (s). Electronic spectrum (λ_{max}, nm): 421 (s).

Finely powdered [Cu(TTC₂-TTF)]ClO₄ [**1**]; 20 mg, 0.033 mmol] was placed in the arm of an h-shaped glass tube which contained iodine (20 mg, 0.079 mmol) in the other arm. The h-shaped tube was sealed under argon and was allowed to stand at ambient temperature. After 5 days, a black solid (24 mg) with the composition {[Cu(TTC₂-TTF)]ClO₄}I (**2**) was obtained. Found: C, 22.7; H, 2.8. Calc. for C₁₄H₂₀ClCuIO₄S₈: C, 22.9; H, 2.7%. IR (cm⁻¹): 2957 (w), 2924 (w), 2862 (w), 2824 (w), 1446 (s), 1402 (s), 1377 (s), 1332 (s), 1273 (s), 1143 (s), 1109 (s), 1087 (vs), 966 (m), 897 (s), 756 (m), 626 (s). Electronic spectrum (λ_{max}, nm): 423 (s), 857 (br).

X-ray structure determination

A suitable orange crystal of **1** for X-ray diffraction study was mounted on a Rigaku AFC-5R diffractometer with graphite-monochromated Mo-K_α radiation. The conditions for data collection and crystal data are listed in Table 1. A total of 1723 independent reflections with $I \geq 3\sigma(I)$ was used in the structure determination and refinement. The structure was solved by a direct method (MITHRIL)¹² and refined by full-matrix least squares with anisotropic thermal parameters. Isotropic

Table 1. Crystal data and measurement conditions for complex **1**

Molecular formula	C ₁₄ H ₂₀ ClCuO ₄ S ₈
Formula weight	607.78
Crystal dimension (mm)	0.1 × 0.2 × 0.5
Crystal system	Monoclinic
Space group	C2/c
<i>a</i> (Å)	20.085(2)
<i>b</i> (Å)	8.128(7)
<i>c</i> (Å)	14.602(2)
β (°)	90.969(9)
<i>V</i> (Å ³)	2383(2)
<i>Z</i>	4
<i>D_c</i> (g cm ⁻³)	1.694
λ (Mo-K _α) (Å)	0.71069
μ (Mo-K _α) (cm ⁻¹)	17.24
Scan type	ω-2θ
Scan rate (° min ⁻¹)	8.0
Scan width (°)	(0.90 + 0.30 tan θ)
2θ _{max} (°)	55.0
No. of reflections measured	3020
No. of reflections observed [$I \geq 3\sigma(I)$]	1723
<i>R</i>	0.045
<i>R_w</i>	0.055

hydrogen atoms were located by Fourier difference synthesis, using the program system TEXSAN.¹³ Reliability factors are defined as $R = \Sigma ||F_0| - |F_c|| / \Sigma |F_0|$ and $R_w = [\Sigma w(|F_0| - |F_c|)^2 / \Sigma w F_0^2]^{1/2}$, where $w = 4F_0^2 / \Sigma \sigma^2(F_0^2)$. Atomic scattering factors and anomalous dispersion terms were taken from ref. 14. The final *R* and *R_w* values were 0.045 and 0.055, respectively. The atomic coordinates, full set of bond lengths and angles, thermal parameters, and *F_c* and *F₀* tables have been deposited with the Editor as supplementary material.

RESULTS AND DISCUSSION

*Crystal structure of [Cu(TTC₂-TTF)]ClO₄ (**1**)*

The structure of [Cu(TTC₂-TTF)]⁺ in **1** is illustrated in Fig. 1. Figure 2 shows the packing arrangement in the crystal. Selected bond lengths and angles are given in Table 2.

In compound **1**, each of the copper atoms is coordinated in a distorted tetrahedral geometry to four sulphur atoms from the ligand, with bond angles around copper ranging from 93.1(1) to 122.2(1)°. The average Cu—S bond length is 2.311(2) Å, which is shorter than the Cu—S bond length in the complexes of TTC₂-TTF with copper(I) halides [X = Cl, 2.405(2); X = Br, 2.349(1); X = I, 2.369(2) Å].^{9,10} The molecular structure of TTC₂-

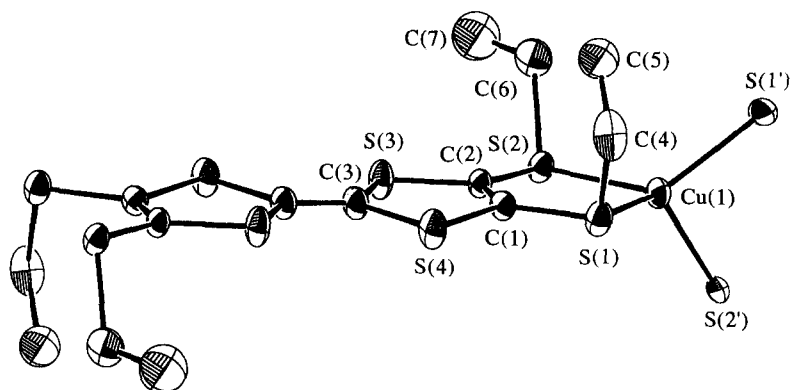


Fig. 1. The structure and atomic numbering schemes of $[\text{Cu}(\text{TTC}_2\text{-TTF})]^+$ in **1**.

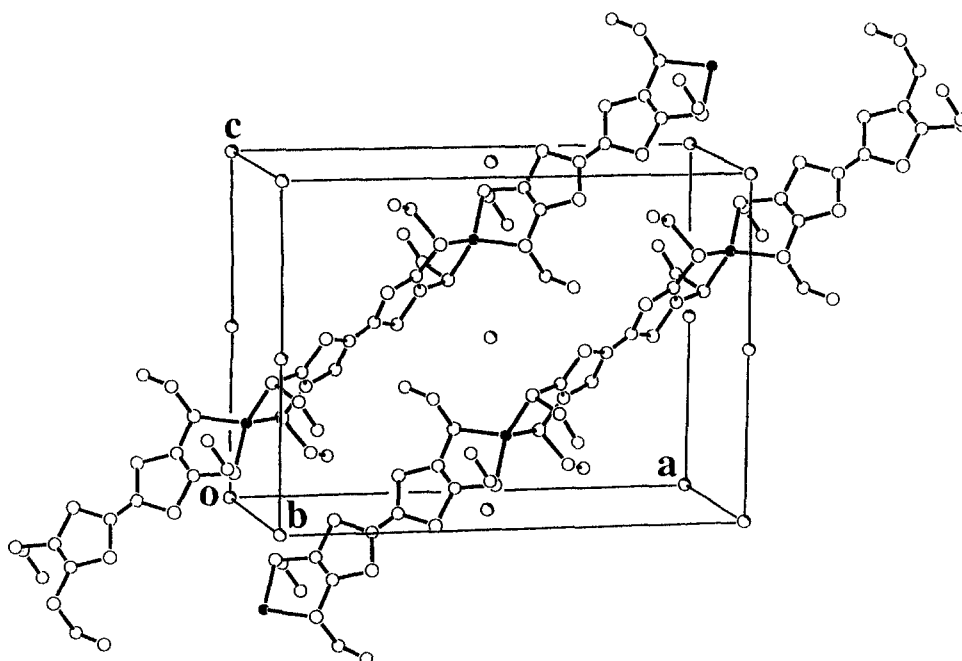


Fig. 2. The polymeric chain arrangement in the crystal (the perchlorate ions are represented by the partially hatched balls for clarity).

TTF in the present complex is a chair-like form, while the free TTC₂-TTF molecule has a boat-like form.¹⁵ The four ethyl groups of TTC₂-TTF in **1** elongate nearly perpendicular to the central C₆S₈ group. Two ethyl groups at one end take the same orientation, while the other two ethyl groups are orientated in the opposite direction. This conformation is different from that of the free TTC₂-TTF molecule¹⁵ and from that in the halide complexes.^{9,10} It is known that the central C=C bond length is the charge-sensitive parameters for a TTF-type molecule and the C=C bond distance is expected to increase with decreasing electron density in the highest occupied (bonding) molecular

orbital.¹⁶⁻¹⁸ In **1**, the central C=C bond length of TTC₂-TTF is 1.337 Å. According to the correlation between the bond length and the degree of charge transfer of TTF-type donors,¹⁸ the degree of charge transfer of TTC₂-TTF in **1** is close to zero.

It is noted that TTC₂-TTF molecules behave as bridging groups in **1** and the metal ions are linked by TTC₂-TTF molecules to form coordination polymeric chains (Fig. 2). In the crystal these polymeric chains are separated from each other by the perchlorate ions. The shortest S...S distance between the neighbouring chains is 4.0 Å, which is longer than the sum of the van der Waals radii (3.6 Å) of two sulphur atoms.¹⁹ Therefore, the S...S

Table 2. Selected bond lengths (Å) and angles (°) of complex **1**

Cu(1)—S(1)	2.284(1)	S(3)—C(3)	1.757(5)
Cu(1)—S(2)	2.338(2)	S(4)—C(1)	1.749(4)
S(1)—C(1)	1.760(5)	S(4)—C(3)	1.751(5)
S(1)—C(4)	1.850(7)	C(1)—C(2)	1.323(6)
S(2)—C(2)	1.750(4)	C(3)—C(3')	1.337(9)
S(2)—C(6)	1.888(7)	C(4)—C(5)	1.46(1)
S(3)—C(2)	1.757(5)	C(6)—C(7)	1.39(1)
S(1)—Cu(1)—S(1')	122.2(1)	S(3)—C(3)—S(4)	114.2(2)
S(1)—Cu(1)—S(2)	93.1(1)	C(5)—C(4)—S(1)	115.8(5)
S(1)—Cu(1)—S(2')	122.0(1)	C(7)—C(6)—S(2)	111.9(6)
S(2)—Cu(1)—S(2')	105.7(1)	C(1)—S(1)—Cu(1)	98.4(2)
C(2)—C(1)—S(1)	125.7(3)	C(1)—S(1)—C(4)	100.2(3)
C(2)—C(1)—S(4)	118.3(4)	C(4)—S(1)—Cu(1)	109.6(2)
S(1)—C(1)—S(4)	115.9(3)	C(2)—S(2)—Cu(1)	97.7(2)
C(1)—C(2)—S(2)	125.1(3)	C(2)—S(2)—C(6)	101.1(2)
C(1)—C(2)—S(3)	116.8(3)	C(6)—S(2)—Cu(1)	107.2(2)
S(2)—C(2)—S(3)	117.9(3)	C(2)—S(3)—C(3)	95.3(2)
C(3')—C(3)—S(3)	122.7(6)	C(1)—S(4)—C(3)	95.0(2)
C(3')—C(3)—S(4)	123.1(5)		

Table 3. The electroconductive properties of iodine-doped copper(I) coordination polymers with TTC₂-TTF

Compound	Colour	$\sigma_{25^\circ\text{C}}$ (S cm ⁻¹)	Reference
{[Cu(TTC ₂ -TTF)]ClO ₄ }I	black	6×10^{-4}	This work
[(CuCl) ₂ (TTC ₂ -TTF)]I	black	6×10^{-7}	9
[(CuBr) ₂ (TTC ₂ -TTF)]I	black	3×10^{-7}	9
[(CuI) ₂ (TTC ₂ -TTF)]I _{1.5}	black	2×10^{-3}	10

interaction between the polymeric chains is very weak in the present complex.

Spectroscopic and electrical properties of **1** and **2**

Important information about the oxidation state of TTC₂-TTF in **1** and **2** was obtained from their IR spectra. It is well known^{20–22} that the central C=C stretch of TTF undergoes a large frequency shift on oxidation, for example, from 1512 cm⁻¹ in neutral TTF²⁰ to 1413 cm⁻¹ in (TTF)Br.²¹ Similarly, the central C=C stretching frequency of TTC₂-TTF is also sensitive to its oxidation state. In the IR spectra of free TTC₂-TTF and **1**, the central C=C stretching band of TTC₂-TTF occurs at 1448 and 1446 cm⁻¹, respectively, which indicates the presence of neutral TTC₂-TTF in **1**. The IR spectrum of the iodine-doped compound **2** reveals two sharp bands at 1446 and 1332 cm⁻¹, which arise from neutral TTC₂-TTF and TTC₂-TTF⁺ radical cation, respectively. In the electronic spectra, **1** and **2** show strong absorption bands at 421 and 423 nm,

respectively. These bands may be ascribed to local excitation of the TTC₂-TTF molecule, since the free TTC₂-TTF ligand also exhibits an absorption band at 419 nm. The other broad absorption band around 857 nm in the spectrum of **2** may arise from a TTC₂-TTF/TTC₂-TTF⁺ charge-transfer transition.²²

One of the common features of the conducting complex is that the constituent molecules are in a mixed-valence (or partial-oxidation) state.^{23,24} Although **1** is an insulator ($\sigma_{25^\circ\text{C}} < 10^{-12}$ S cm⁻¹), **2** behaves as a semiconductor: $\sigma_{25^\circ\text{C}} = 6 \times 10^{-4}$ S cm⁻¹. This may be due to the TTC₂-TTF⁺/TTC₂-TTF⁺ and/or TTC₂-TTF/TTC₂-TTF⁺ interaction in the crystal.²² The electroconductive properties of iodine-doped copper(I) coordination polymer with TTC₂-TTF are summarized in Table 3.

In conclusion, the sulphur-rich ligand TTC₂-TTF reacts with copper(I) perchlorate to form a 1:1 metal–ligand complex. All the copper atoms in the complex are coordinated to the sulphur atoms from the bridging organic ligand to form coordination

linear chains. The iodine-doped product behaves as a semiconductor.

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