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Copper(I) Iodide Coordination Polymer with Tetrakis(ethylthio)tetrathiafulvalene (TTC_2-TTF) and the Iodine-Doped Compound

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The title complex was synthesized by the reaction of copper(I) iodide and tetrakis(ethylthio)-tetrathiafulvalene (TTC_2-TTF) in acetonitrile under argon atmosphere. The new compound, $[(CuI)_2TTC_2\text{-}TTF]$, crystallizes in the monoclinic system, space group $P2_1/m$ with unit-cell dimensions a=9.843(2), b=12.946 (2), c=10.079(1) Å, β=99.91(1)°, V=1265.2(4) $Å^3$, and Z=2. It is a neutral 2 : 1 (metal/ligand) complex in which each metal ion is tetrahedrally coordinated by two bridging iodide ions and two sulfur atoms from TTC_2-TTF to form coordination polymeric chains. The average Cu–I and Cu–S bond lengths are 2.601 and 2.369 Å, respectively. The complex was doped with iodine to afford $[(CuI)_2TTC_2\text{-}TTF]I_{1.5}$ which exhibits a conductivity of 2×10^{-3} $S\,cm^{-1}$ at 25 °C for a compacted pellet.

Tetrathiafulvalene (TTF) and its derivatives are constituent of a class of substances known as "organic metals" or "synthetic metals" which exhibit conductivity in wide electrical conductive range, from semiconductor to superconductor, and have attracted great interest.[1—3] Most of this kind of compounds are composed of organic radical ions. Although some of them contain metal atoms in an anion part, these metal ions are not coordinated to the organic molecules.[3] Recent work in our laboratory has focused on metallotetrathiafulvalenes polymers, in which TTF or its derivatives directly coordinate to the metal ions.[4] Tetrakis(ethylthio)tetrathiafulvalene (TTC_2-TTF), which has a central tetrathio-TTF (C_6S_4) π system and a side ethylthio chain system, is a single-component organic semiconductor[5] and its physical properties have been widely investigated.[6,7] While the chemical compound of TTC_2-TTF was reported little, the only compound of TTC_2-TTF reported so far is the charge-transfer complex $[TTC_2\text{-}TTF]\cdot[TCNQ]$.[8] In this paper we report the synthesis and structural characterization of copper(I) iodide coordination polymer with TTC_2-TTF, $[(CuI)_2TTC_2\text{-}TTF]$, the first metal complex of TTC_2-TTF, and the properties of its iodine-doped compound.

Experimental

General. The preparation of the complex was performed under argon atmosphere using usual Schlenk techniques. The reagent TTC_2-TTF (mp 70 °C) was prepared according to the literature.[9] Copper(I) iodide (Wako) was used as purchased. Acetonitrile 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 pellet.

Preparation of $[(CuI)_2TTC_2\text{-}TTF]$ and Its Iodine-Doped Compound. A solution of copper(I) iodide (19.5 mg, 0.1 mmol) in acetonitrile (5 cm^3) was added to a TTC_2-TTF (22.2 mg, 0.05 mmol) solution in acetonitrile (5 cm^3) under Ar. After being stirred for 10 min at 70 °C the resultant orange solution was filtered and the filtrate was sealed in two 10 mm diameter glass tubes, which were allowed to stand in a Dewar vessel filled with 70 °C water. After one week orange crystals of $[(CuI)_2TTC_2\text{-}TTF]$ (**1**) were obtained, yield 60%. Found: C, 20.45; H, 2.35%. Calcd for $C_{14}H_{20}Cu_2I_2S_8$: C, 20.36; H, 2.44%. IR (cm^{-1}) 2978(s), 2961(s), 2924(s), 2864(s), 1446(s), 1410(s), 1373(s), 1273(s), 1055(m), 966(m), 897(s), 756(s), 491(w). Electronic spectrum (λ_{max}, nm) 422(s).

Finely powdered complex **1** (20 mg, 0.024 mmol) was placed in a hand of an h-shape glass tube which contained iodine (20 mg, 0.079 mmol) in another hand. The h-shape tube was sealed under Ar and was allowed to stand at ambient temperature. After 3 d black solid (24 mg) with the composition $[(CuI)_2TTC_2\text{-}TTF]I_{1.5}$ (**2**) was obtained. Found: C, 16.32; H, 1.98%. Calcd for $C_{14}H_{20}Cu_2I_{3.5}S_8$: C, 16.55; H, 1.89%. IR (cm^{-1}) 2955(w), 2924(w), 2864(w), 2820(w), 1446(m), 1404(s), 1375(s), 1331(s), 1273(s), 1055(m), 966(m), 897(s), 756(s), 493(m). Electronic spectrum (λ_{max}, nm) 424(s), 767(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 $K\alpha$ radiation. The conditions for data collection and crystal data are listed in Table 1. A total of 1991 independent reflections with $I\geq3\sigma(I)$ was used in the structure determination and refinement. The structure was solved by a direct method (MITHRIL)[10] and refined by full-matrix least squares with anisotropic thermal parameters. Isotropic hydrogen atoms were located by Fourier difference synthesis, using the program system TEXSAN.[11] Reliability factors are defined as $R=\sum||F_o|-|F_c||/\sum|F_o||$ and $R_w=[\sum w(|F_o|-|F_c|)^2/\sum wF_o^2]^{1/2}$, where $w=4F_o^2/\sum\sigma^2(F_o^2)$. Atomic scattering factors and anomalous dispersion terms were taken from Ref. 12. The final R and R_w values were 0.034 and 0.039, respectively. The full set of bond lengths and angles, thermal parameters, and F_c and F_o tables have been deposited as Document No. 67068 at the Office of the Editor of Bull. Chem. Soc. Jpn. as supplementary materials.

Results and Discussion

Crystal Structure of 1. The molecular structure of **1** is illustrated in Fig. 1. Figure 2 shows the packing

Table 1. Crystal Data and Measurement Conditions for Complex (**1**)

Molecular formula	$C_{14}H_{20}Cu_2I_2S_8$
Formula weight	825.75
Crystal dimension/mm	0.20×0.20×0.10
Crystal system	Monoclinic
Space group	$P2_1/m$
a/Å	9.843(2)
b/Å	12.946(2)
c/Å	10.079(1)
β/°	99.91(1)
V/Å^3	1265.2(4)
Z	2
D_c/g cm^{-3}	2.167
λ/(Mo $K\alpha$)/Å	0.71069
μ(Mo $K\alpha$)/cm^{-1}	47.40
Scan type	ω–2θ
Scan rate/°min^{-1}	4.0
Scan width/°	$(0.84+0.30\tan\theta)$
$2\theta_{\max}$/°	55.0
No. of reflections measured	3201
No. of reflections observed $[I\geq3\sigma(I)]$	1991
R	0.034
R_w	0.039

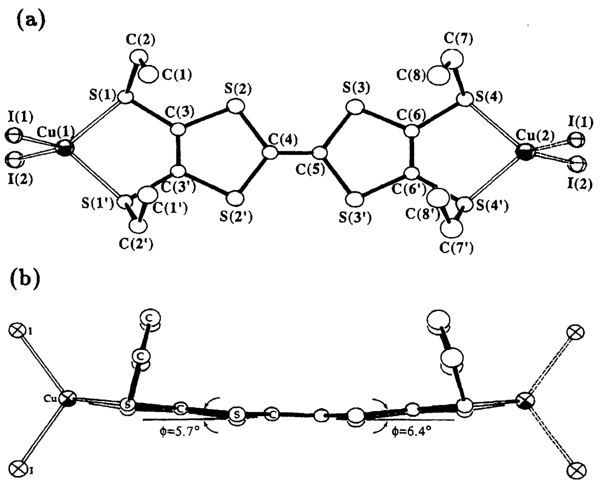

Fig. 1. Molecular structure and atomic numbering schemes of **1** (top view(a) and side view(b)).

Table 2. Atomic Coordinates of Non-H Atoms and Equivalent Isotropic Thermal Parameters

Atom	x	y	z	B_{eq}/Å^2
I(1)	0.11293(6)	1/4	0.37638(6)	2.97(2)
I(2)	−0.23951(7)	1/4	0.04044(6)	3.63(3)
Cu(1)	−0.1500(1)	1/4	0.3019(1)	3.36(5)
Cu(2)	0.0297(1)	1/4	0.1201(1)	3.61(5)
S(1)	−0.2787(1)	0.1206(1)	0.3917(1)	2.47(5)
S(2)	−0.4979(2)	0.1361(1)	0.5630(2)	3.12(6)
S(3)	−0.7115(2)	0.1360(1)	0.7750(2)	3.12(6)
S(4)	−0.8801(2)	0.1202(1)	0.9945(1)	2.94(6)
C(1)	−0.1022(7)	0.1099(6)	0.6415(7)	4.1(3)
C(2)	−0.1850(6)	0.0421(5)	0.5286(6)	3.2(3)
C(3)	−0.3791(5)	0.1985(4)	0.4797(5)	2.2(2)
C(4)	−0.5531(8)	1/4	0.6315(8)	2.5(3)
C(5)	−0.6451(8)	1/4	0.7182(8)	2.3(3)
C(6)	−0.7937(6)	0.1982(4)	0.8930(5)	2.3(2)
C(7)	−0.7410(9)	0.0414(6)	1.0831(8)	5.2(4)
C(8)	−0.619(1)	0.0988(8)	1.1533(9)	6.4(5)

Table 3. Selected Bond Lengths (Å) and Angles (°) of Complex (**1**)

Cu(1)–I(1)	2.568(1)	C(3)–C(3′)	1.33(1)
Cu(1)–I(2)	2.631(1)	C(4)–S(2)	1.754(5)
Cu(1)–S(1)	2.371(2)	C(4)–C(5)	1.36(1)
Cu(2)–I(1)	2.572(1)	C(5)–S(3)	1.749(4)
Cu(2)–I(2)	2.633(2)	C(6)–S(3)	1.746(5)
Cu(2)–S(4)	2.367(2)	C(6)–C(6′)	1.34(1)
C(1)–C(2)	1.490(9)	C(6)–S(4)	1.758(5)
C(2)–S(1)	1.831(6)	C(7)–S(4)	1.815(8)
C(3)–S(1)	1.756(5)	C(7)–C(8)	1.48(1)
C(3)–S(2)	1.749(5)		
I(1)–Cu(1)–I(2)	116.07(5)	I(1)–Cu(2)–I(2)	115.87(5)
I(1)–Cu(1)–S(1)	117.79(5)	I(1)–Cu(2)–S(4)	116.95(5)
I(2)–Cu(1)–S(1)	105.87(5)	I(2)–Cu(2)–S(4)	106.71(5)
S(1)–Cu(1)–S(1′)	89.90(8)	S(4)–Cu(2)–S(4′)	90.43(8)

arrangement in the crystal. Atomic coordinates of nonhydrogen atoms and equivalent isotropic thermal parameters are listed in Table 2, and selected bond lengths and angles are summarized in Table 3, respectively.

In compound **1** each copper atom is tetrahedrally coordinated by two bridging iodide ions and two sulfur atoms from the ligand with the average Cu–I bond length of 2.601 Å and Cu–S bond length of 2.369 Å. The TTC_2-TTF molecular structure in the present complex is a boat-like form (Fig. 1(b)). The four ethyl groups elongate nearly perpendicular to the central C_6S_8 group. The central skeleton is appreciably nonplanar, and the tilt angles are 5.7° and 6.4°. This conformation is rather analogous to that of neutral TTC_2-TTF molecule.[13] It is known that the central C=C bond length and the C–S bond length of the heterocycle of TTF is the charge-sensitive parameters for TTF molecule.[14] In **1** the central C=C bond length and the average C–S bond length of TTC_2-TTF are 1.36 and 1.75 Å, respectively. According to the correlation between the bond length and the degree of charge transfer of TTF type dornors,[14] the degree of charge transfer of TTC_2-TTF in **1** is closed to zero.

It is noted that TTC_2-TTF molecules and iodide ions behave as bridging groups in the complex and the metal ions are linked by TTC_2-TTF molecules and iodide ions to form coordination polymeric chains. In crystal phase it is observed that to decrease the repulsion between the ethyl groups in neighboring chains all the ethyl groups in a polymeric chain take same orientation while the ethyl groups in its two neighboring chains orientate to the opposite direction so that these polymeric chains can pack more close to each other. The shortest S···S distance between the neighboring polymeric chains is S(1)···S(3) (3.717 Å) and S(2)···S(2) (3.743 Å) (Fig. 2). These values are close to the van der Waals radius sum

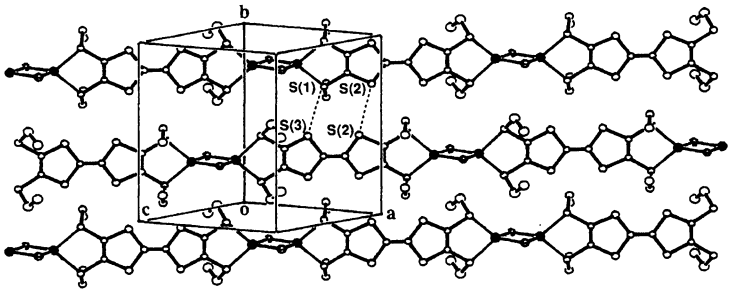

Fig. 2. The polymeric chain arrangement in the crystal.

(3.60 Å) of two sulfur atoms.[15] Therefore the S···S interaction between the linear chains is not strong in the present complex.

Spectroscopic and Electrical Properties of 1 and 2. Important information about the oxidation state of TTC$_2$-TTF in **1** and **2** was obtained from their IR spectra. It is well known[16—18] that the central C=C stretch of TTF undergoes large frequency shift on oxidation, for example, from 1512 cm^{-1} in neutral TTF[16] to 1413 cm^{-1} in (TTF)Br.[17] Similarly the central C=C stretching frequency of TTC$_2$-TTF is also sensitive to its oxidation state. In the IR spectrum of free TTC$_2$-TTF and **1** the central C=C stretching band of TTC$_2$-TTF occurs at 1448 and 1446 cm^{-1}, respectively, which indicates the presence of neutral TTC$_2$-TTF in **1**. While the IR spectrum of the iodine-doped compound **2** reveals two sharp bands at 1446 and 1331 cm^{-1}, which are arisen from the neutral TTC$_2$-TTF and TTC$_2$-TTF$^{+\bullet}$ radical cation, respectively. In the electronic spectra **1** and **2** show a strong absorption band at 422 and 424 nm, respectively. These bands may be ascribed to local excitation of TTC$_2$-TTF molecule, since the free TTC$_2$-TTF ligand also exhibits the absorption band at 419 nm. While the another broad absorption band around 767 nm in the spectrum of **2** may be arisen from TTC$_2$-TTF/TTC$_2$-TTF$^{+\bullet}$ charge-transfer transition.[18]

One of the common features of the conducting complex is that the constituent molecules are in a mixed-valence (or partial-oxidation) state.[19,20] Although **1** is an insulator ($\sigma_{25^\circ\mathrm{C}}<10^{-12}$ S cm^{-1}) **2** behaves as a semiconductor: $\sigma_{25^\circ\mathrm{C}}=2\times10^{-3}$ S cm^{-1}. This may be due to the (TTC$_2$-TTF)$^{+\bullet}$/(TTC$_2$-TTF)$^{+\bullet}$ and/or (TTC$_2$-TTF)/(TTC$_2$-TTF)$^{+\bullet}$ interaction in the crystal.[18]

In conclusion, the sulfur-rich ligand TTC$_2$-TTF can react with copper(I) iodide to form a neutral 2 : 1 (metal/ligand) complex. It is the first metal complex of TTC$_2$-TTF. All the copper atoms in the complex are coordinated by the bridging iodide and the organic ligand to form coordination linear chains. The iodine-doped product behaves as a semiconductor.

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