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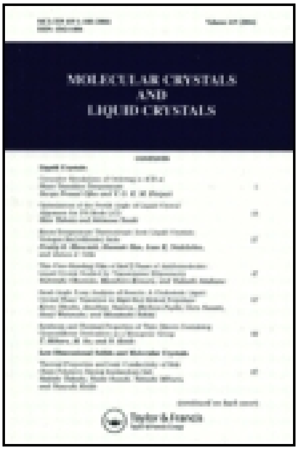

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$TTC_1TTF^\dagger$ Cation Coordinated to Copper(I): Crystal Structure and Properties of $[(TTC_1TTF)CuBr_2]_2$

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TTC_1TTF^+ CATION COORDINATED TO COPPER(I): CRYSTAL STRUCTURE AND PROPERTIES OF $[(TTC_1TTF)CuBr_2]_2$

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Abstract One-electron oxidation of tetrakis(methylthio)tetrathiafulvalene (TTC_1TTF) by $CuBr_2$ yields a black copper(I) coordination compound, $[(TTC_1TTF)CuBr_2]_2$ (**1**), whose structure has been determined by means of X-ray crystallography. **1** has a dimer structure consisting of a Cu_2Br_2 rhomboid with terminal Br^- and TTC_1TTF^+ which coordinate to Cu(I) through one of four SMe groups. TTC_1TTF^+ form columnar stacks with the shortest S•••S contact of 3.44 Å. Since most of TTC_1TTF^+ cation radicals in crystal form spin-pairs, a weak ESR signal observed at g = 2.008 is attributed to TTC_1TTF^+ radicals remain as free from pair formation located at crystal surface. Crystal Data: triclinic ($P\bar{1}$), a = 10.053(1) Å, b = 10.618(1) Å, c = 9.722(2) Å, α = 90.85(1)°, β = 91.04(1)°, γ = 110.487(9)°, V = 971.7(3) Å^3, Z = 1, R = 0.036, R_w = 0.036.

INTRODUCTION

Tetrakis(methylthio)tetrathiafulvalene (TTC_1TTF) is known as a good electron-donor and easily oxidized to a cation and even to a dication. $TTC_1TTF{\bullet}HCBD$[1] (HCBD = hexacyanobutadiene) and $TTC_1TTF{\bullet}I_{2.47}$[2] have been reported as charge transfer (CT) complexes and in ionic compounds of $(TTC_1TTF)_2[Mo_6Cl_8(NCS)_6]$[3] and $(TTC_1TTF)(AuCl_4)_2$,[4] TTC_1TTF has +1 and +2 charge, respectively. Besides electron-donor character, TTC_1TTF has coordination ability to metal ions through its terminal SMe groups. We have already reported syntheses and crystal structures of a series of copper(I) coordination compounds of neutral TTC_1TTF, $[(Cu_2(\mu\text{-}X)_2(TTC_1TTF)]$ (X = Cl, Br, I),[5] and revealed that TTC_1TTF acts as a bridging ligand to form 1-dimensional[4] or 2-dimensional polymer structures. Although these coordination compounds are insulators, they become conductors by I_2 doping. It is suggested that if oxidized TTC_1TTF can be used as a bridging ligand, we may have new conducting compounds. Along this direction, we could obtain black crystals of conducting $[(TTC_1TTF)CuBr_2]_2$ (**1**) with coordinated TTC_1TTF^+. To the best of our knowledge, this is the first example of a copper(I) coordination compound with TTC_1TTF^+ cation radical. We report here synthesis, crystal structure and physicochemical properties of **1**.

EXPERIMENTAL

Synthesis of $[(TTC_1TTF)CuBr_2]_2$ (1)

All manipulations were carried out under argon or ethylene atmosphere by using the standard Schlenk technique. A solution of cupric bromide (3.35 mg, 0.015 mmol) in acetonitrile (5.0 mL) was poured into a warm solution (60 °C) of TTC_1TTF (5.83 mg, 0.015 mmol) in acetonitrile (5.0 mL). A resultant brown solution was kept at 60 °C for 1.5 h and sealed in a glass tube. After standing for a week at room temperature black columnar crystals were obtained. Analytical data for **1**: Found: C 19.90, H 1.86 %; Calcd for $C_{20}H_{24}Br_4Cu_2S_{16}$: C 19.62, H 1.98 %.

X-ray Crystallography

Diffraction data for **1** was collected at ambient temperature using the ω–2θ scan technique on a Rigaku AFC5R four-circle diffractometer equipped with graphite monochromated Mo-Kα radiation (λ 0.71069 Å). The data were corrected for Lorentz and polarization effects. Crystallographic data are summarized in Table I. The structure

TABLE I Crystallographic data for $[(TTC_1TTF)CuBr_2]_2$ (1).

Empirical formula	$C_{20}H_{24}Br_4Cu_2S_{16}$
Formula weight	1224.2
Crystal system	triclinic
Space group (no.)	$P\bar{1}$(2)
a (Å)	10.053(1)
b (Å)	10.618(1)
c (Å)	9.722(2)
α (deg)	90.85(1)
β (deg)	91.04(1)
γ (deg)	110.487(9)
V (Å^3)	971.7(3)
Z	1
d_{calc}(g cm^{-3})	2.092
μ (cm^{-1})	60.17
λ(Å)	0.71069
R,[a] R_w[b]	0.036, 0.036

[a] $R = \Sigma(||F_o|-|F_c||)/\Sigma|F_o|$.

[b] $R_w = \{\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2\}^{1/2}$ with $w = 4F_o^2/\Sigma\sigma^2(F_o)^2$.

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TABLE II Selected bond lengths and angles for [(TTC$_1$TTF)CuBr$_2$]$_2$ (**1**).

Bond Lengths (Å)			
Cu(1)-Br(1)	2.495(1)	C(1)-C(2)	1.346(8)
Cu(1)-Br(1')	2.587(1)	C(3)-C(4)	1.363(9)
Cu(1)-Br(2)	2.379(1)	C(5)-C(6)	1.379(9)
Cu(1)-S(2)	2.381(2)		
Bond Angle(deg)			
Cu(1)-Br(1)-Cu(1')	74.35(4)	Br(1)-Cu(1)-Br(1')	105.65(4)
Br(1)-Cu(1)-Br(2)	121.29(5)	Br(1)-Cu(1)-S(2)	101.79(6)
Br(1)-Cu(1)-Br(2)	110.92(5)	Br(1)-Cu(1)-S(2)	93.32(6)
Br(2)-Cu(1)-S(2)	119.69(6)		

was solved by direct methods. The non-hydrogen atoms were refined anisotropically by full-matrix least-squares calculations. Hydrogen atoms were included but not refined. The calculation was performed on a VAX computer by using the program system TEXSAN.[6] Selected bond lengths and angles are listed in Table II.

Measurements of Physicochemical Properties

Electronic spectra were obtained using a HITACHI 150-20 spectrophotometer. ESR measurements were performed on JEOL JES TE-200 spectrometer with ES-PRIT 425 Data System. Magnetic susceptibility was measured by Quantum Design MPMS$_5$ system. X-ray photoelectron spectrum was measured on Shimadzu ESCA-850 system.

RESULTS AND DISCUSSION

Structure of [(TTC$_1$TTF)CuBr$_2$]$_2$] (1)

1 has a dimer structure with a center of symmetry composed of a Cu$_2$Br$_2$ rhomboid, two terminal Br atoms and two TTC$_1$TTF (Figure 1). The copper atom is coordinated by two bridging Br atoms, one terminal Br atom and one of four sulfur atoms of the TTC$_1$TTF. The SBrCu(μ-Br)$_2$CuSBr framework has been already reported in [Cu[2-(3,3-dimethyl-2-thiabutyl)-pyridinium}Br$_2$]$_2$.[7] Bond angles around the copper atom are ranging from 93.3° to 121.3°, showing a distorted tetrahedral geometry. The bridging Cu-Br bond length of 2.54 Å in average is shorter than that of the pyridinium compound (2.597 Å)[7] whereas the terminal Cu-Br bond length (2.379(1) Å) and the Cu-S bond length (2.381(2) Å) are a little longer than those of the pyridinium compound (2.363 Å and 2.276 Å, respectively).[7] As can be seen from the crystal packing view shown in Figure 2, all of the TTC$_1$TTF are parallel to each other. TTC$_1$TTF of adjacent molecules form columnar stacks in *c*-axis direction. There are two types of the nearest S•••S contact

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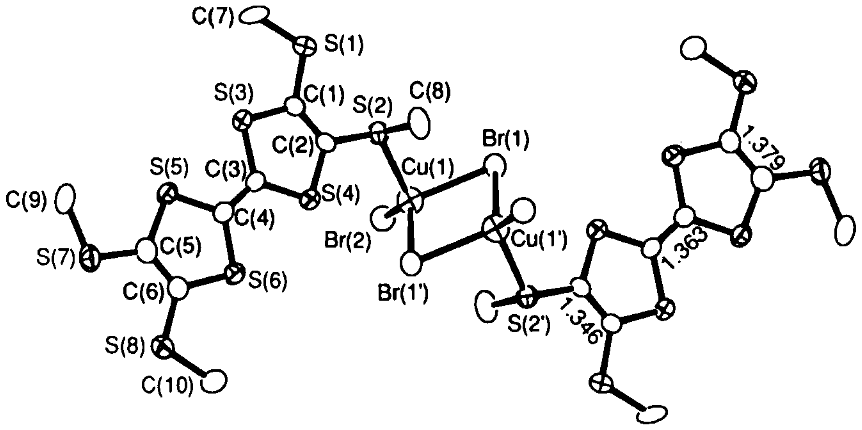

FIGURE 1 Molecular structure of [(TTC$_1$TTF)CuBr$_2$]$_2$ (**1**).

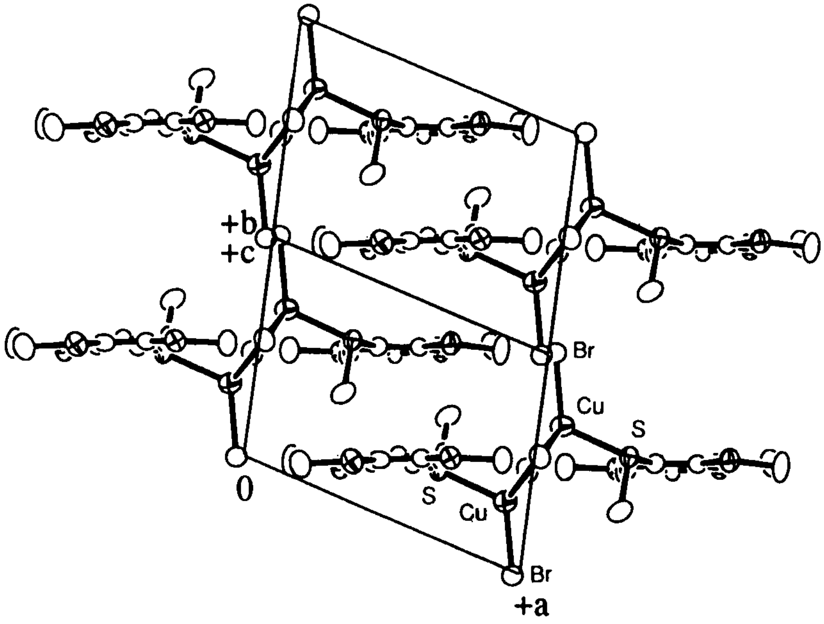

FIGURE 2 Crystal packing view of **1**.

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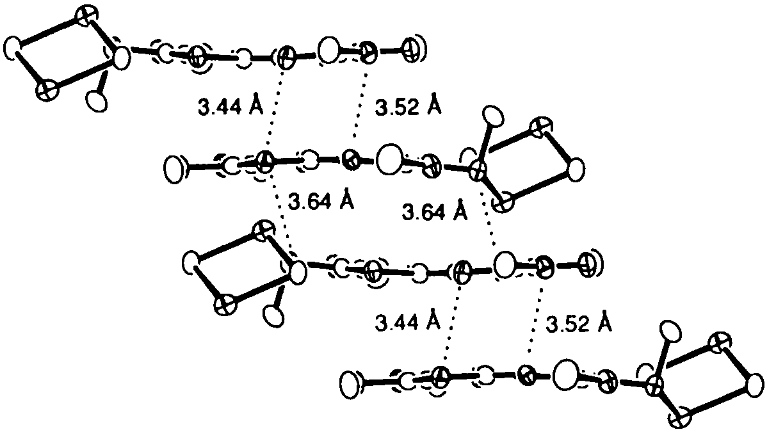

FIGURE 3 π–π Stacking of TTC_1TTF and S•••S contacts in **1**.

between TTC_1TTF planes, 3.44 Å and 3.64 Å, respectively (Figure 3). These stacks are connected through bridging Cu_2Br_2 rhomboids, resulting in 3-dimensional network structure.

Copper Valence and Structure of TTC_1TTF^+

Although the starting material was $CuBr_2$, the copper valence state in **1** was determined to be +1 by ESCA, which means TTC_1TTF has +1 charge. This indicates that the one-electron oxidation of TTC_1TTF by copper(II) ion results in a formation of TTC_1TTF cation and copper(I) ion. As shown in Figure 1, the C=C bond lengths of TTC_1TTF are 1.346(8) Å, 1.363(9) Å, and 1.379(9) Å corresponding to the inner, the middle, and the outer C=C bond, respectively. It is well-known that the central C=C bond lengths in TTF and its derivatives are well correlated to their molecular charge.[1] For example, the central C=C bond lengths of TTC_1TTF with +1 charge in $(TTC_1TTF)_2[Mo_6Cl_8(NCS)_6]$[3] and $(TTC_1TTF)[CuCl_2]$[4] are 1.380 Å and 1.382 Å, respectively, which are clearly elongated from that of the neutral one (1.348 Å)[1]. In compound **1**, however, not the middle but the outer C=C bond length is most affected by one-electron oxidation. Since TTC_1TTF in **1** is asymmetric, namely SMe groups in one end are coordinated to a copper ion while those of the other end are not, unpaired electron in each TTC_1TTF resides mainly on the outer five-membered ring, resulting in the elongation of the outer C=C bond length more than the middle one.

Physicochemical Properties

Electronic absorption spectrum of **1** using CsI disk shows two broad bands in visible region (λ_{max} = 440 and 880 nm). Although the former band was also observed for the

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pyridinium salts (420 nm) with similar framework and tentatively assigned to a sulfur-copper type CT transition,[7] the latter is characteristic for **1**. A possible assignment for this band is a π–π* transition of stacked TTC_1TTF^+ cations.

An X-band ESR spectrum of micro-crystalline samples of **1** observed at room temperature consists of a broad (ΔH = 2.8 mT) asymmetric line at g = 2.008. On the basis of a comparison of g-values reported for TTF^+ radicals in solid state,[8] the observed signal is reasonably assigned to TTC_1TTF^+ radicals broadened by anisotropy. However, the spin density estimated from comparison with DPPH (diphenylpicrylhydrazyl) standard was less than 1 %, indicating most of TTC_1TTF^+ radicals form spin-paired dimers. Such dimer formations often occur in TTF^+ radical salts.[9] Since magnetic susceptibility measured by SQUID does not show temperature dependence except for Curie-like behavior at low temperature, the observed ESR signal is not due to thermally activated spins but intrinsic radical species with low concentration. This implies the spin-pair formation occurs through S•••S contacts between adjacent TTC_1TTF^+ radicals, not through a Cu_2Br_2 rhomboid. As radicals located at the crystal surface could not form spin-pair, their ESR signals can be observed.

The electrical conductivity of the compacted disk of **1** was measured by conventional four-probe method at temperature range of 250-330 K. Conductivity at 330 K is $10^{-4.5}$ Scm^{-1} and it decreases as decreasing temperature. The activation energy (E_g) estimated from the σ-1/T plot is 0.16 eV for temperature above 298 K and 0.07 eV for that below 298 K.

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