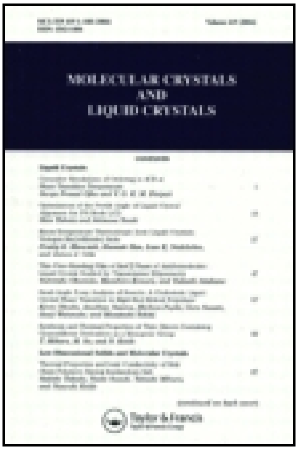

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Syntheses, Characterization and X-Ray Crystal Structures of Tetrakis(Ethylthio)Tetrathiafulvalenium Hexachlorodicopper(II) and Hexabromodicopper(II)

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SYNTHESES, CHARACTERIZATION AND X-RAY CRYSTAL STRUCTURES OF TETRAKIS(ETHYLTHIO)TETRATHIAFULVALENIUM HEXACHLORODICOPPER(II) AND HEXABROMODICOPPER(II)

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Abstract Oxidation of tetrakis(ethylthio)tetrathiafulvalene (TTC$_2$-TTF) with $CuCl_2$ and $CuBr_2$ in acetonitrile yielded the organic radical cation salts, (TTC$_2$-TTF)$_2$[Cu_2Cl_6] **1** and (TTC$_2$-TTF)$_2$[Cu_2Br_6] **2**, whose structures have been determined by X-ray structure analysis. Both **1** and **2** crystallize in the triclinic system, space group $P\bar{1}$, with one molecule per unit cell. **1**: a = 12.065(4), b = 12.644(3), c = 8.988(2) Å, α = 103.54(2), β = 90.24(2), γ = 112.42(2)°. **2**: a = 12.330(3), b = 12.647(2), c = 8.956(2) Å, α = 101.72(2), β = 94.66(2), γ = 111.69(1)°. Both structures consist of two segregated stacks of TTC$_2$-TTF$^+$ donors and $Cu_2X_6^{2-}$ acceptors associated via short S•••X contacts. Consistent with the structural results, the two compounds exhibit low electrical conductivities with $\sigma_{25\,^\circ C}$ being 4 x 10^{-8} and 8 x 10^{-8} S cm^{-1} for **1** and **2**, respectively.

INTRODUCTION

The use of sulfur-containing molecules as precursors for synthesis of conductive or superconductive materials is of continuing interest. Coupled with suitable electron acceptors, Tetrathiafulvalene (TTF) and its derivatives can give rise to conductive molecular stacks through S•••S molecular interactions.[1-5] The electrical properties of these donor-acceptor complexes can be varied over a wide range by changing the nature of the acceptor species.[3] Numerous charge-transfer complexes arising from the organic donors derived from TTF and the inorganic acceptors such as copper halide anions, have been characterized and some of them are found to exhibit high conductivity or superconductivity.[6-8] Tetrakis(ethylthio)tetrathiafulvalene (TTC$_2$-TTF) contains a central tetrathio-TTF (C_6S_8) π system and the side ethyl chain, and its physical properties have been extensively studied.[9,10] It forms an organic charge-transfer compound with TCNQ (tetracyanoquinodimethane) in which the donor and acceptor molecules are alternately stacked in the crystal.[11] However, the corresponding complex of TTC$_2$-TTF with an inorganic acceptor is not known. We have previously reported a number of polymeric co-ordination copper(I) complexes with neutral TTC$_2$-TTF.[12] This paper reports the structures and properties of the TTC$_2$-TTF$^+$ radical cation salts with copper(II) halide anions.

EXPERIMENTAL

General Procedures and Techniques

The preparation of the complexes was performed under an argon atmosphere using usual Schlenk techniques. The reagent TTC$_2$-TTF (m.p. 70 °C) was prepared according to the literature.[13] Copper(II) chloride and copper(II) bromide (Wako, Japan) were used as purchased. Acetonitrile was dried and distilled by a standard method before use. IR spectra were recorded as KBr disks on a JASCO 8000 FT-IR spectrometer. Electric resistivities were measured by a conventional two-probe method at 25 °C with compacted pellets.

Preparation of the Complexes

$(TTC_2\text{-}TTF)_2[Cu_2Cl_6]$ **1.** A solution of copper(II) chloride (26.8 mg, 0.2 mmol) in acetonitrile (10.0 cm^3) was slowly added to a TTC$_2$-TTF (44.4 mg, 0.1 mmol) solution in the same solvent (5.0 cm^3). The mixture was stirred and filtered, and the deep-red filtrate was sealed in five 7 mm diameter glass tubes. After standing for two weeks at room temperature black crystals of **1** were isolated, yield 40%. (Found: C, 27.64; H, 3.12. Calc. for $C_{28}H_{40}Cl_6Cu_2S_{16}$: C, 27.35; H, 3.28%). IR spectrum (cm^{-1}): 2978(w), 2951(w), 2920(w), 2862(w), 1452(w), 1427(w), 1383(s), 1323(vs), 1255(s), 1240(s), 1051(w), 962(w), 480(m), 462(m).

$(TTC_2\text{-}TTF)_2[Cu_2Br_6]$ **2.** A solution of copper(II) bromide (44.6 mg, 0.2 mmol) in acetonitrile (5.0 cm^3) was slowly added to a TTC$_2$-TTF (44.4 mg, 0.1 mmol) solution in the same solvent (5.0 cm^3). The black microcrystalline precipitate was redissolved by warming the reaction mixture on a water bath at 70 °C. The solution was filtered and the deep-red filtrate was transferred to a glass tube. After standing in a Dewar vessel at 50 °C for one week black crystals of **2** were obtained, yield 60%. (Found: C, 22.23; H, 2.47. Calc. for $C_{28}H_{40}Br_6Cu_2S_{16}$: C, 22.48; H, 2.69%). IR spectrum (cm^{-1}): 2972(w), 2953(w), 2922(w), 2860(w), 1441(w), 1419(w), 1398(s), 1331(vs), 1259(s), 1234(s), 1031(m), 976(w), 493(m), 474(m).

X-ray Structure Determination

Black single crystals of **1** and **2** were mounted with paraffin on a thin glass fiber for X-ray structure analysis. Diffraction data were collected on a Rigaku AFC-5R four-circle diffractometer with graphite-monochromated Mo-K_α radiation. The structure was solved by a direct method (MITHRIL)[14] and refined by full-matrix least-squares minimization of $\Sigma w(|F_o| - |F_c|)^2$. Anisotropic temperature factors were refined for all non-hydrogen atoms. Isotropic hydrogen atoms were located by Fourier difference synthesis. The data were corrected for Lorentz and polarization effects. All calculations

TABLE I Crystal and final structure refinement data

	1	**2**
Formula	$C_{28}H_{40}Cl_6Cu_2S_{16}$	$C_{28}H_{40}Br_6Cu_2S_{16}$
Formula weight	1229.40	1496.10
Crystal dimensions (mm)	0.29 x 0.23 x 0.20	0.35 x 0.25 x 0.40
Crystal system	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a/Å	12.065(4)	12.330(3)
b/Å	12.644(3)	12.647(2)
c/Å	8.988(2)	8.956(2)
α/°	103.54(2)	101.72(2)
β/°	90.24(2)	94.66(2)
γ/°	112.42(2)	111.69(1)
V/Å^3	1225.6(6)	1251.8(5)
Z	1	1
D_c/g cm^{-3}	1.666	1.984
μ(Mo-K_α)/Å	18.80	62.62
Scan type	ω - 2θ	ω - 2θ
Scan rate/° min^{-1}	8.0	8.0
Scan width/°	(0.89 + 0.30 tan θ)	(1.05 + 0.30 tan θ)
$2\theta_{max}$/°	55.0	55.0
No. reflections measured	5904	6001
No. observations [I>3σ(I)]	3367	3693
R	0.040	0.040
R_w	0.045	0.043

were performed using a TEXSAN crystallographic software package[15] on a micro VAX computer. Atomic scattering factors and anomalous dispersion terms were taken from ref. 16. Reliability factors are defined as $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o^2]^{1/2}$, where $w = 4F_o^2/\sigma^2(F_o^2)$.

A summary of crystallographic data is given in Table I. The selected bond lengths and bond angles are listed in Table II. The full lists of the atomic coordinates, anisotropic thermal parameters, bond lengths and angles, and observed and calculated structure factors are available from the authors on request.

TABLE II Selected bond lengths (Å) and bond angles (°) for **1** and **2**

	1(X=Cl)	**2**(X=Br)		**1**(X=Cl)	**2**(X=Br)
Cu-X(1)	2.319(2)	2.455(1)	S(4)-C(11)	1.742(4)	1.739(5)
Cu-X(1')	2.287(2)	2.429(1)	S(5)-C(13)	1.816(6)	1.811(7)
Cu-X(2)	2.180(2)	2.333(1)	S(5)-C(14)	1.738(4)	1.743(5)
Cu-X(3)	2.174(2)	2.317(1)	S(6)-C(8)	1.723(4)	1.732(5)
S(1)-C(2)	1.803(5)	1.799(6)	S(6)-C(14)	1.758(4)	1.746(5)
S(1)-C(3)	1.738(4)	1.741(5)	S(7)-C(6)	1.729(4)	1.736(5)
S(2)-C(3)	1.738(4)	1.731(5)	S(7)-C(7)	1.718(4)	1.725(5)
S(2)-C(7)	1.720(4)	1.720(5)	S(8)-C(5)	1.820(5)	1.808(6)
S(3)-C(8)	1.720(4)	1.721(5)	S(8)-C(6)	1.729(4)	1.740(5)
S(3)-C(11)	1.762(4)	1.755(5)	C(7)-C(8)	1.395(5)	1.378(6)
S(4)-C(10)	1.811(6)	1.820(6)			
X(1)-Cu-X(1')	86.44(5)	87.48(3)	X(1')-Cu-X(3)	99.26(9)	98.71(4)
X(1)-Cu-X(2)	96.79(8)	99.40(4)	X(2)-Cu-X(3)	102.5(1)	99.89(4)
X(1)-Cu-X(3)	140.60(7)	140.42(4)	Cu-X-Cu'	93.56(5)	92.52(3)
X(1')-Cu-X(2)	140.61(8)	140.75(4)			

RESULTS AND DISCUSSION

Crystal Structures

The reaction of TTC_2-TTF with an excess of CuX_2 (X = Cl or Br) giving the radical cation salts $(TTC_2\text{-}TTF)_2[Cu_2X_6]$, suggests that the following redox reaction occurs.

$$4\,CuX_2 + 2\,TTC_2\text{-}TTF^0 \longrightarrow 2\,CuX + 2\,TTC_2\text{-}TTF^+ + Cu_2X_6^{2-}$$

As Cu^{I} ion is more effectively solvated by acetonitrile than the corresponding Cu^{II} ion,[17] the radical cation TTC$_2$-TTF$^+$ crystallized out together with the unreduced copper(II) halide anions [Cu$_2$X$_6$]$^{2-}$.

The compounds **1** and **2** are isomorphous with an isostructural (TTC$_2$-TTF)$_2$[Cu$_2$X$_6$] unit. Figure 1 illustrates an ORTEP view of **1** together with atom numbering scheme, while Figure 2 shows a packing arrangement in the crystal. The structure consists of two segregated stacks of TTC$_2$-TTF$^+$ donors and Cu$_2$X$_6$$^{2-}$ acceptors. The donors face to each other to assume a dimeric structure, with close intradimeric S•••S contacts of 3.430(2) [S(2)•••S(6)] and 3.456(2) Å [S(3)•••S(7)] in **1** and 3.519(2) [S(2)•••S(6)] and 3.465(2) Å [S(3)•••S(7)] in **2**. These values are appreciably shorter than the usual van der Waals separations (3.60 Å).[18] It is interesting to note that no substantially close S•••S contacts are found between the adjacent dimers. We assume that the extended terminal ethyl groups of TTC$_2$-TTF and the anion columns prevent such intermolecular interactions. The [Cu$_2$X$_6$]$^{2-}$ anion in both **1** and **2** involves a dimeric, edge-shared bitetrahedron in which the Cu-X bond lengths for the bridging ligands are significantly longer than those of the corresponding terminal ligands in both cases, Table II. Coupled with these dimers are pairs of radical cation TTC$_2$-TTF$^+$, and the association between them occurs via short contacts of the central TTF sulfur atoms and the bridging halide ions. At least two such short S•••X contacts are identified in

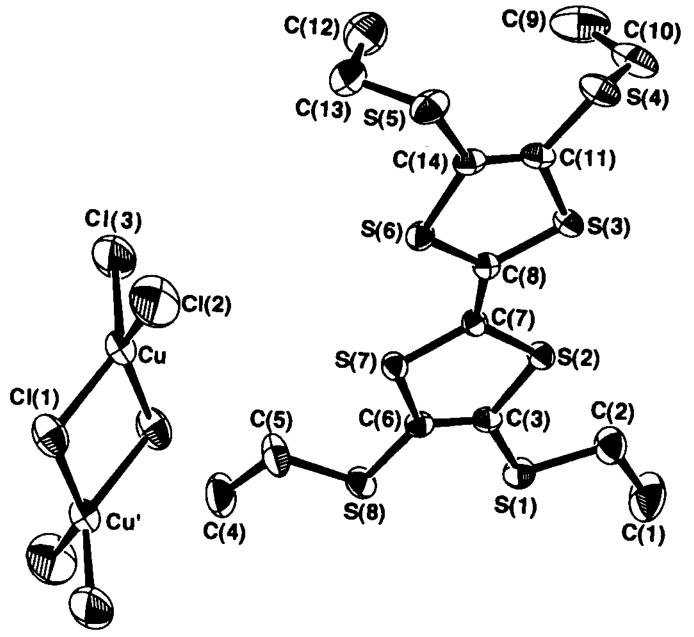

FIGURE 1 ORTEP view of (TTC$_2$-TTF)$_2$[Cu$_2$Cl$_6$] with atom numbering scheme

each structure, namely S(7)•••Cl(1) 3.521(2) Å and S(3)•••Cl(1) 3.545(2) Å for **1**, and S(6)•••Br(1) 3.665(2) Å and S(2)•••Br(1) 3.759(2) Å for **2**. These interactions are van der Waals in nature. Thus each $[Cu_2X_6]^{2-}$ anion acts as a linking group between two pairs of TTC_2-TTF^+ dimers, which generates a one-dimensional chain arrangement of the organic cations and inorganic anions along the *a* axis.

The central C=C bond distance for the TTC_2-TTF^+ entity is 1.395(5) Å in **1** and 1.378(6) Å in **2**. This distance is the charge-sensitive parameter for all the TTF-type molecules, which is expected to increase with decreasing of electron density in the highest occupied (bonding) molecular orbitals.[19] In a series of TTC_1-TTF^0, TTC_1-TTF^+ and TTC_1-TTF^{2+} complexes this C=C bond distance has been reported as 1.336(7)-1.352(16), 1.382(4) and 1.426(19) Å, respectively.[20-22] As TTC_1-TTF and TTC_2-TTF have the same tetrathio-TTF π system, it leaves little doubt that the C=C bond distances of 1.395(5) and 1.378(6) Å observed in this work correspond to the TTC_2-TTF^+ radical cation.

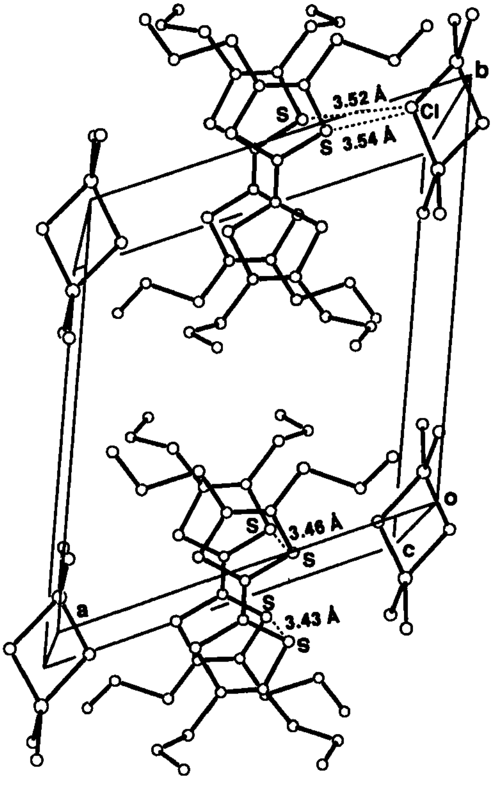

FIGURE 2 Unit cell packing diagram of **1**. The dashed lines show the close S•••S contacts and S•••Cl contacts

Spectroscopic and Electrical Properties

The infrared resonance spectroscopy can also be utilized to probe the oxidation state of TTC_2-TTF in **1** and **2**. It is well known[19,23,24] that the central C=C stretch of TTF undergoes large frequency shift on oxidation, for example, from 1512 cm^{-1} for a totally symmetric normal modes in neutral TTF[23] to 1413 cm^{-1} for a monovalent TTF^+ moiety in (TTF)Br.[24] The IR spectrum of the free TTC_2-TTF molecule shows the central C=C stretching band at 1448 cm^{-1}. Upon oxidation with copper(II) halide this frequency shifts to 1323 and 1331 cm^{-1} for **1** and **2**, respectively. These data are qualitatively in accord with the magnitude and direction of the bond order changes from the central C=C.[23,24]

One of the common features of the sulfur-based conducting charge-transfer complexes is the presence of short S•••S intermolecular contacts, which provides the electron-conduction pathways within the layers of donor molecules.[4] As mentioned previously, both complexes **1** and **2** involve short S•••S contacts in each of the TTC_2-TTF dimers, while between these dimers no significantly close S•••S contacts are found. Both **1** and **2** behave as semiconductors at room temperature with conductivities $\sigma_{25\,°C}$ being 4×10^{-8} and 8×10^{-8} S cm^{-1} for **1** and **2**, respectively. The observed high resistivity is presumably due to the poor interdimeric interactions in the structure.

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