Coordination Assembly of TTF Derivatives through CuI Bridges

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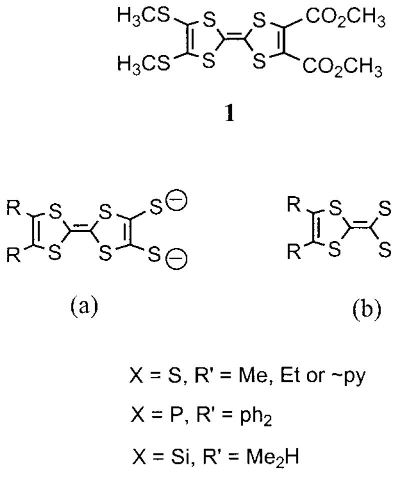
Keywords: Tetrathiafulvalene / Copper(I) complexes / Crystal structures / Molecular assembly

The sulfur-rich ligand $C_{12}H_{12}O_4S_6$ (**1**) and complexes $[(C_{12}H_{12}O_4S_6)CuI]_2$ (**2**) and $[(C_7H_6O_4S_3)CuI]_\infty$ (**3**) have been synthesized and characterized crystallographically. Molecules of compound **1**, a tetrathiafulvalene (TTF) derivative, have a boat-shaped configuration and are packed discretely within the crystal. Compound **1** coordinates to a rhomboid CuI center forming a dimeric TTF derivative **2**. In complex **2** the boat-shaped configuration of **1** is flattened. Molecules of **2** are packed regularly and compactly in the crystal and are arranged side by side with short S···S contacts, which assemble the molecules into a 1D ribbon structure. This provides evidence that metal coordination or assembly is a useful stratagem for changing the molecular configuration and packing that further influence the intermolecular interactions. Complex **3** has a step-like polymeric structure formed by copper-iodine bridges and copper-sulfur bridges (coordinated thiocarbonyl).

Introduction

Although tetrathiafulvalene (TTF) and its derivatives have been intensively investigated for several decades, these unique functional molecules continue to attract great attention. So far, much research on the design and preparation of dimeric and oligomeric TTFs has been reported by organic chemists. The reported dimeric TTFs can be roughly divided into two types: one is linked through conjugated π systems and the other through nonconjugated σ chains.[1–4] Recently, a new kind of dimeric TTF has been reported, in which two TTF units are connected by metal coordination. Great efforts in synthesis and characterization have revealed the wide application of TTF derivatives with additional groups having coordinating properties. The incorporation of TTF units into dithiolate ligands is one of the successful examples (see a in Scheme 1) and a series of metal coordinated bis-TTF complexes was reported by Kobayashi et al.[5–9] The metal coordination extends and enhances the π conjugation of the sulfur-rich system, and hence provides the complexes with novel conductive and magnetic properties. Furthermore, the coordination of TTF derivatives to metal ions is expected to give new bis-TTF or polymolecular systems with improved inter- or intra- molecular interactions. The synthesis of a number of metal complexes of TTF derivatives with coordinating groups of alkylthiole,[10–13] phenylphosphite,[14,15] pyridine[16–18] or alkylsilyl[19] (see b in Scheme 1) has provided insight into the role of metal ions in molecular assembly.



Scheme 1.

The synthesis and coordination properties of TTF derivatives attracted our interest.[20–22] Here, structures of dimethyl 2-[4,5-bis(methylthio)-1,3-dithiol-2-ylidene]-1,3-dithiole-4,5-dicarboxylate (**1**) and its derivatives are studied. Detailed discussions about the roles of metal coordination in the molecular assembly are presented.

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DOI: 10.1002/ejic.200401002

Results and Discussion

Synthesis and Characterization

Some methods for synthesizing the asymmetric compound **1** have been reported.[23,24] However, the detailed procedures have only recently been reported by Hudhomme et al. and McCullough et al.[25,26] Followed these latter methods, the compound was synthesized successfully in our laboratory. The details can be found in the experimental section. Single crystals of **1** were obtained and its molecular structure was reported for the first time (see next section).

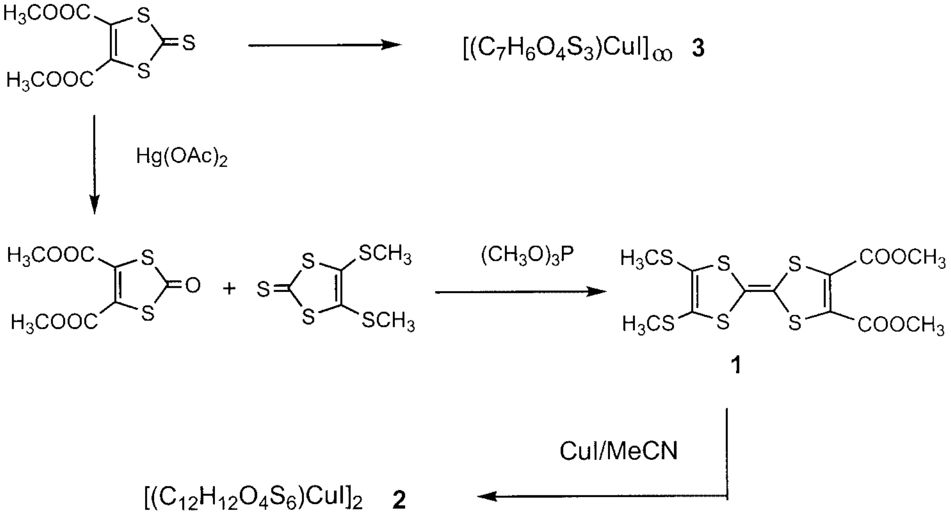
Scheme 2 exhibits the synthetic routes for compounds **1**, **2** and **3**. Compound **2** (D-σ-D type) was synthesized by refluxing a mixture of **1** and CuI in acetonitrile under argon. The inorganic-organic hybrid compound **2** was stable under ambient conditions. The cyclic voltammetry of **2** was studied in acetonitrile containing 0.1 mol dm^{-3} Et_4NClO_4. Two reversible redox peaks were detected and the results are listed in Table 1 together with the data of the free ligand **1**. The potential shift of **1** for the methylthio group coordinated with the Cu^I ion was not observed, which was different from the electrochemical behavior of the dithiolate complexes.[27] This might be a result of the complex dissociating to free ligand **1** and solvated CuI in a dilute solution of acetonitrile at a concentration of ca. 10^{-3} mol dm^{-3}. This indicates that the coordination of the methylthiol group to copper(I) is not as strong as that of thiolate. It should be also pointed out that the oxidation of Cu^I was not observed from cyclic voltammetry. In the IR spectra of **2**, the stretching band of C=C was observed at 1431 cm^{-1} with a slightly red shift compared to that of **1** at 1439 cm^{-1}. It is well known that the central C=C stretching of TTF undergoes a large down-shift in frequency on oxidation (normally more than 50–100 cm^{-1}).[28,29] Therefore, the ligand in the CuI complex is in neutral state, which is in agreement with the molecular composition deduced from microanalysis. A slightly blue shift was observed for the C=O stretching bands of the carboxyl group. The complex **3** was synthesized by a similar method to that of **2** in acetonitrile, the reaction proceeded readily at room temperature due to the strong tendency of the C=S group to coordinate to Cu^I ions. The C=S vibrational mode of complex **3** appears at 1065 cm^{-1} which is shifted to a lower frequency in comparison with that of the free ligand at 1088 cm^{-1}.

Table 1. Data from cyclic voltammetry of compound **1** and **2** in acetonitrile (V, vs. SCE).

	$E_{1/2}(1)$	$E_{pa}(1)$	$E_{pc}(1)$	$E_{1/2}(2)$	$E_{pa}(2)$	$E_{pc}(2)$
1	0.596	0.638	0.554	0.854	0.896	0.811
2	0.594	0.641	0.548	0.842	0.892	0.792

Description of Structures

$C_{12}H_{12}O_4S_6$ (1): The ORTEP view of **1** and atom labeling scheme are shown in Figure 1. Atom pair O(3)/O(3′) is presented with occupancies of 0.60 and 0.40, respectively, due to the C=O bond disorders over two orientations. The distances of the C=C double bonds are 1.344(4), 1.337(4) and 1.341(4) Å for C(1)–C(2), C(3)–C(4) and C(5)–C(6), respectively (Table 2). The central C=C bond is slightly shorter than the others. The TTF moiety takes on a boat-shaped configuration formed by three planes defined as plane 1: S(3), S(4) C(3), C(4), S(5), S(6) (central plane), plane 2: S(1), S(2) C(1), C(2), S(3), S(4) and plane 3: S(5), S(6), C(5), C(6), C(9), C(11). Their mean deviations are 0.0107, 0.0395 and 0.0389 Å, respectively. The planes 1 and 2 share a common line along S(3)–S(4) with a dihedral angle of 19.15(3)° and the planes 1 and 3 share a common line along S(5)–S(6) with a dihedral angle of 11.39(7)° (Figure 2, top). The contributions of the TTF fragment to the boat shaped configuration, are the envelope configurations, on C(3) or C(4), of both of the five-membered dithiol rings. In the crystal structure, four molecules are contained in a unit cell with different orientations, being a direct consequence of the symmetrical operation of a $P2_1/c$ (no.14) space group.



Scheme 2.

Table 2. Selected bond lengths [Å] and angles [°] and the important interaction distances for **1**–**3**.

1		**2**		**3**	
S(1)–C(1)	1.745(3)	Cu(1)–I(1)	2.5676(10)	Cu(1)–I(1)	2.6223(7)
S(2)–C(2)	1.741(3)	Cu(1)–S(1)	2.3497(16)	Cu(1)–S(1)	2.2806(11)
C(1)–C(2)	1.344(4)	Cu(1)–S(2)	2.3604(16)	S(1)–C(1)	1.653(4)
C(3)–C(4)	1.337(4)	Cu(1)–I(1^{ii})	2.6030(12)	Cu(1)–I(1^{iv})	2.6650(7)
C(5)–C(6)	1.341(4)	S(1)–C(3)	1.763(5)	Cu(1)–I(1^{v})	2.6450(7)
		S(2)–C(4)	1.760(5)		
S(1)–C(1)–C(2)	122.6(2)	C(5)–C(6)	1.343(6)	Cu(1)–S(1)–C(1)	108.48(13)
S(2)–C(2)–C(1)	123.9(2)			S(1)–Cu(1)–I(1)	120.04(4)
		S(1)–Cu(1)–S(2)	91.36(5)	I(1^{iv})–Cu(1)–I(1^{v})	110.54(2)
O(2)···O(4^{i})	3.031(2)	I(1)–Cu(1)–I(1^{ii})	118.42(3)		
		Cu(1)–I(1)–Cu(1^{ii})	61.58(3)	Cu(1)···Cu(1^{iv})	3.0053(8)
		S(1)–C(3)–C(4)	125.6(4)	Cu(1)···Cu(1^{v})	3.0053(8)
		S(2)–C(4)–C(3)	125.1(4)	S(1)···S(3^{vi})	3.591(3)
				S(1)···I(1)	3.707
		Cu(1)···Cu(1^{ii})	2.6469(15)		
		S(2)···S(6^{iii})	3.586(2)		
		S(4)···S(6^{iii})	3.599(2)		

^{i} $x, 1 + y, z$; ^{ii} $1 - x, 1 - y, -z$; ^{iii} $1 - x, 1 - y, 1 - z$; ^{iv} $x - 1/2, -y + 1/2, 1 - z$; ^{v} $x + 1/2, -y + 1/2, 1 - z$; ^{vi} $x - 1/2, 3/2 - y, 1 - z$

The shortest S···S distance between two molecules is 4.072 Å, significantly longer than the van der Waals radius sum (3.7 Å). Thus, the S···S interaction within this crystal is negligible.

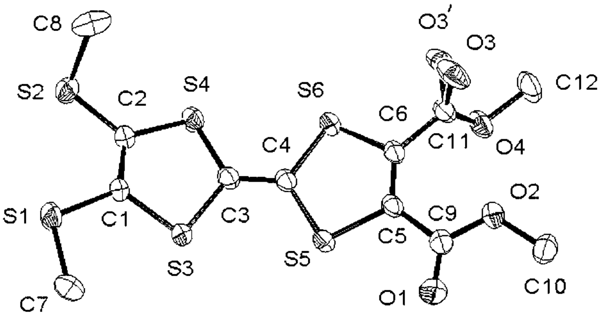


Figure 1. An ORTEP view of **1** showing the atom labeling scheme. Non-H atoms are shown as 50% probability displacement ellipsoids. H-atoms have been omitted for clarity.

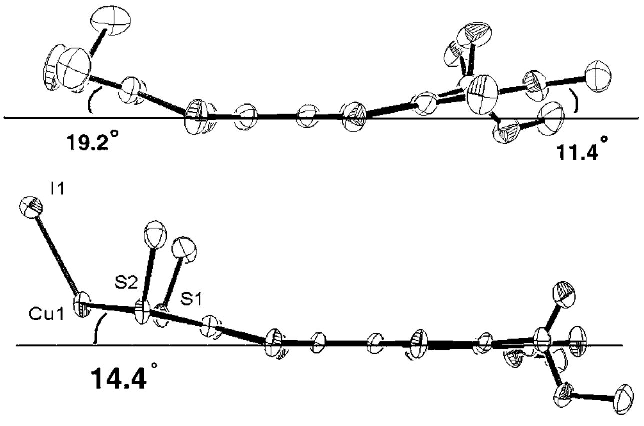


Figure 2. Side views of **1** (top) and **1**·CuI (**2**) (bottom) showing the change in the dihedral angles of the ligand.

[$(C_{12}H_{12}O_4S_6)CuI]_2$ (2): An ORTEP view of complex **2** with atom labeling is shown in Figure 3. The methylthiol groups of ligand **1** are coordinated to the coppers of rhomboid Cu_2I_2 to produce a dimeric structure. The geometry around the copper atom is a distorted tetrahedron with an I–Cu–I angle of 118.42(3)° and S–Cu–S angle of 91.36(5)°. The Cu–I and Cu–S distances are in agreement with those of the corresponding compounds.[3,12]

Some changes are found by comparing the structures of complex **2** and the ligand **1**. When the coordination bonds are formed, the S(1)–C(1) and S(2)–C(2) distances of **1** [1.745(3) and 1.741(3) Å] are elongated to 1.763(5) and 1.760(5) Å, respectively. Correspondingly the angles of S(1)–C(1)–C(2) and S(2)–C(2)–C(1) [122.6(2) and 123.9(2)°] are enlarged to 125.6(4) and 125.1(4)°, respectively (Table 2). The boat configuration of **1** is flattened in complex **2**. The dihedral angle changes from 19.15(3)° to 14.44(5)° at the methylthio-side and on the carboxyl ester side plane 3 is completely coplanar with plane 1 (b in Figure 2). The mean deviation of the new plane, C(3)–C(6), S(3)–S(6), C(9), C(11), is 0.0269 Å. These changes enhance the delocalization of the conjugated π electrons of the TTF derivative.

The boat-shaped configuration might be one of the important reasons for the discrete packing of **1** (no S···S contacts). However, the molecular packing of **2** is very regular and compact. The bis-TTF compound approximately resembles a planar ruler and twelve sulfur atoms lie on the sides. The molecules are further arranged side by side and S···S contacts are shown between S(2), S(6^{iii}) (3.586(2) Å, iii: $1 - x, 1 - y, 1 - z$) and S(4), S(6^{iii}) [3.599(2) Å], which assembles the molecules into a 1D ribbon structure along the [001] direction (Figure 4). Sulfur atoms from two neighboring molecules are alternately contacted as an occluded slide fastener. Between these ribbons, only weak C–H···O and C–H···I interactions are found.

A similar compound was reported by Delhaès,[30] who studied the crystal structure and properties of the radical salt, but unfortunately the chemical composition of those radical salts were not characterized. However, the crystal structure of the neutral complex can be compared with that

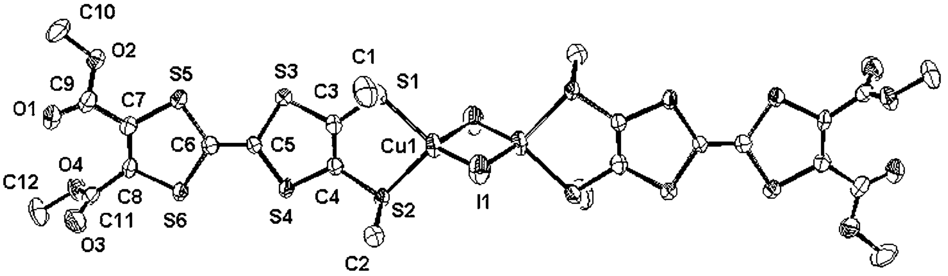


Figure 3. An ORTEP view of **2** showing the atom labeling scheme. Non-H atoms are shown as 50% probability displacement ellipsoids. H-atoms have been omitted for clarity.

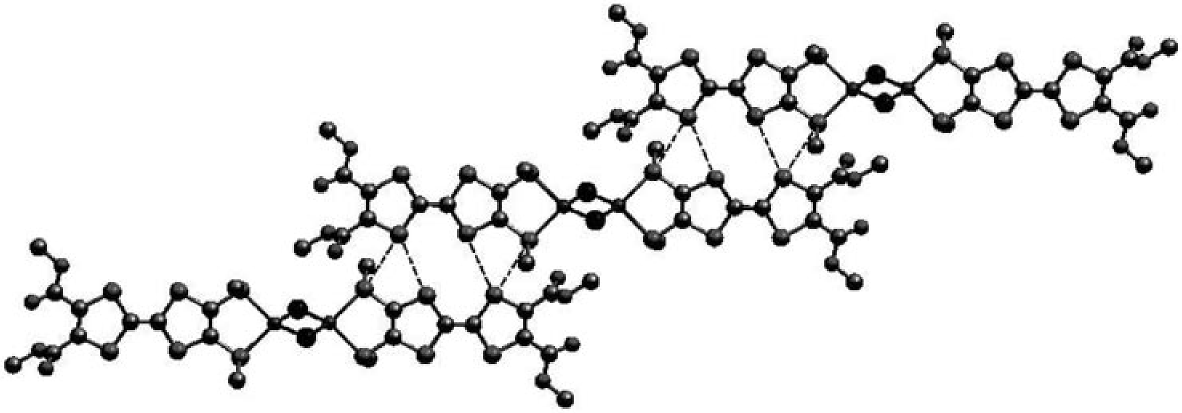


Figure 4. Part of an intermolecular contacts assembled ribbon. Dashed lines are used to represent short S···S contacts.

of **2**. Although the difference between these two molecules is only at the terminal substituted groups, ethylenedithiol group instead of di(methyl carboxylate) of **2**, the crystal systems and molecular packing of them are completely different from each other.

[($C_7H_6O_4S_3$)CuI]$_\infty$ (3): Figure 5 gives the ORTEP view of the unit of complex **3** with selected atom labeling. The geometry around the copper atom is a distorted tetrahedron with three iodide ions and a thiocarbonyl sulfur atom from the ligand. Through iodine bridges, the $C_7H_6O_4S_3CuI$ units form a step-like polymeric structure (or chain) propagated in the direction of the *a* axis (Figure 6). The Cu(1)–I(1) distance, 2.6223(7) Å, for **3** is somewhat shorter than those for [($C_5H_4S_5$)CuI][31] and [($C_5H_6S_5$)CuI],[32] sulfur-rich complexes with ligands of 4,5-bisalkylthiol-1,3-dithiole-2-thione. The Cu–S (thiocarbonyl sulfur) distance of 2.2806(11) Å and the S(1)=C(1) distance of 1.653(4) Å are within the expected values for these kinds of CuI complexes.[13,14]

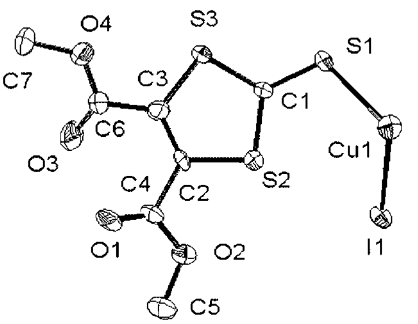


Figure 5. An ORTEP view of **3** showing the atom labeling scheme. Non-H atoms are shown as 50% probability displacement ellipsoids. H-atoms have been omitted for clarity.

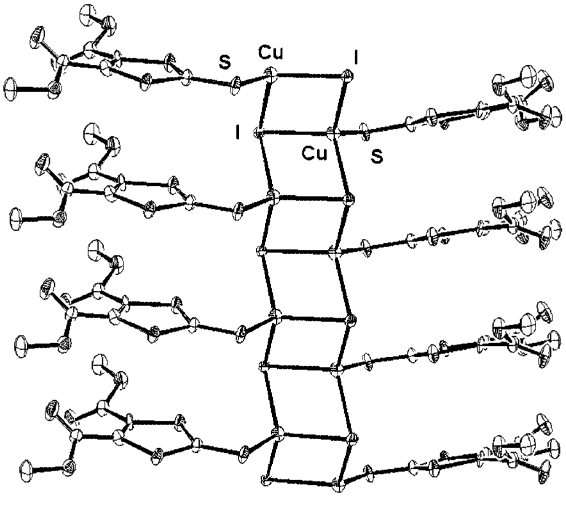


Figure 6. The $C_7H_6O_4S_3CuI$ units of **3** form a step-like chain structure propagated in the direction of the *a* axis.

Unlike [($C_5H_6S_5$)CuI], no significant S···S contacts exist between the ligands within the chains, however short interchains, S···S contacts, occur between S(1) and S(3^{vi}), 3.591(3) Å (vi: $x - 1/2$, $3/2 - y$, $1 - z$). With these contacts,

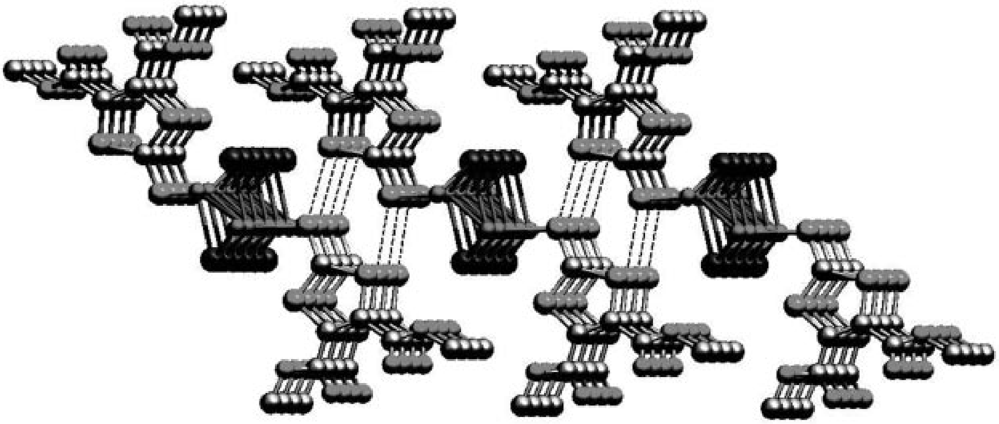


Figure 7. The representation shows the short S···S contacts (dashed lines) between the 1D chains, viewed along the direction of the chains.

a novel two-dimensional network is formed. Figure 7 shows the molecular packing and the intermolecular S···S contacts, when looking along the *a* axis.

Conclusions

Although the copper halogen frameworks are dramatically changed due to the coordination of different halogen ions and other ligands, only two types of CuI coordination centers, rhomboid and step-like structures, have been reported for sulfur-rich compounds (TTF derivatives).[3,31,32] The thiocarbonyl sulfur coordination usually produces step-like structures, whereas the chelate coordination of *ortho*-bis(alkylthiol) groups prefer a rhomboid structure. The Cu–S (thiocarbonyl) coordination bond is stronger than the Cu–S (methylthio) bond. In the case where both groups exist, the thiocarbonyl group predominantly coordinates to Cu^I, giving a step-like polymeric structure.[32] Both the change in the substituted groups, and also metal coordination are useful stratagems for rearranging the molecular packing, which further influences the intermolecular interactions of the TTF derivatives. Besides the molecular packing, the configuration of the TTF moiety is also affected by these stratagems. The room temperature conductivity (σ_{RT}) of I_2 doped **2** (1.0×10^{-3} S cm^{-1}) is one order of magnitude greater than that of the I_2 doped ligand **1** (2.0×10^{-4} S cm^{-1}), under the same conditions. The results also illustrate the effects of metal coordination on the molecular arrangement and the intermolecular interactions in crystals.

Experimental Section

General Remarks: The reagents, 4,5-bis(methylthio)-1,3-dithiole-2-thione ($C_5H_6S_5$), dimethyl 2-thioxo-1,3-dithiole-4,5-dicarboxylate ($C_7H_6O_4S_3$) and dimethyl 2-oxo-1,3-dithiole-4,5-dicarboxylate ($C_7H_6O_5S_2$), were prepared according to the literature.[33–35] Acetonitrile was dried by a standard method and distilled before use. Elemental analyses of C, H and N were performed with an MOD 1106 elemental analyzer. The IR spectra were recorded as KBr discs on a Nicolet Magma 550 FT-IR spectrometer. ^1H NMR spectra were recorded with an INOVA-400 spectrophotometer. Cyclic voltammetry (CV) was performed with a model CHI600 electrochemistry workstation, with a cell containing a Pt plate as the working electrode, a Pt wire as the counter electrode and saturated calomel electrode (SCE) as a reference electrode. The electrical conductivity was measured with a conventional two-probe method at room temperature with compressed discs.

Synthesis of Compounds

$C_{12}H_{12}O_4S_6$ (1): The compound was synthesized by a coupling reaction from 4,5-bis(methylthio)-1,3-dithiole-2-thione ($C_5H_6S_5$) and dimethyl 2-oxo-1,3-dithiole-4,5-dicarboxylate ($C_7H_6O_5S$), using a similar method to that reported.[25,26] A mixture of the reactants (1 mmol, respectively) was refluxed for 2 h in trimethyl phosphite (10 mL) and toluene (10 mL) under argon. The dark purple solution was then evaporated and the residue was purified by chromatography on a silica gel column (CH_2Cl_2). $C_{12}H_{12}O_4S_6$ (412.58) dark-red crystals, (yield: 145 mg, 35%). ^1H NMR: $\delta = 3.43$ (s, CH_3S–), 3.85 (s, CH_3O–) ppm. IR: 1726 (s, C=O), 1708 (s, C=O), 1272 (s, COOC), 1438 (m, C=C) cm^{-1}; m.p. 86–87 °C; calcd. C 34.93, H 2.93; found C 34.85, H 3.06%.

$[(C_{12}H_{12}O_4S_6)CuI]_2$ (2): Ligand **1** (41.2 mg, 0.1 mmol) in acetonitrile (5.0 mL) was added to an acetonitrile solution (5.0 mL) of CuI (19.3 mg, 0.1 mmol). The mixture was stirred for 2 h while refluxing under argon. The red filtrate was evaporated slowly under ambient conditions. Orange crystals suitable for X-ray crystal determination were obtained after two days, which were filtered and washed with acetonitrile, and finally dried in vacuo (yield: 48 mg, 40%). IR: 1743 (s, C=O), 1725 (s, C=O), 1251 (s, COOC), 1431 (m, C=C) cm^{-1}. $C_{24}H_{24}O_8S_{12}Cu_2I_2$ (1206.07): calcd. C 23.90, H 2.01; found C 23.67, H 2.26%.

$[(C_7H_6O_4S_3)CuI]_\infty$ (3): A solution of the ligand $C_7H_6O_4S_3$ (25 mg, 0.1 mmol) in acetonitrile (5.0 mL) was added to an acetonitrile solution (5.0 mL) of CuI (19.1 mg, 0.1 mmol). The mixture was stirred for 30 min at room temperature under argon. The red filtrate was evaporated slowly under ambient conditions. Red crystals suitable for X-ray crystal determination were obtained after several days, which were filtered and washed with acetonitrile, and finally dried in vacuo (yield: 27 mg, 60%). IR: 1759 (s, C=O), 1728 (s, C=O), 1258 (s, COOC), 1065 (m, C=S) cm^{-1}. $C_7H_6O_4S_3CuI$ (440.75): calcd. C 19.10, H 1.38; found C 19.05, H 1.36%.

X-ray Crystallographic Study: All measurements were carried out with a Rigaku Mercury CCD diffractometer at 193 K with graphite-monochromated Mo-K_α ($\lambda = 0.71073$ Å) radiation. X-ray crystallographic data for compounds **1**–**3** were collected and processed

Table 3. Crystallographic data for compounds **1**–**3**.

Compound	**1**	**2**	**3**
Empirical formula	$C_{12}H_{12}O_4S_6$	$C_{24}H_{24}O_8S_{12}Cu_2I_2$	$C_7H_6O_4S_3CuI$
Formula mass	412.58	1206.07	440.75
Color, habit	dark-red, platelet	orange, prism	red, platelet
Crystal system	monoclinic	triclinic	orthorhombic
Crystal size [mm]	0.60 × 0.21 × 0.09	0.15 × 0.10 × 0.10	0.40 × 0.40 × 0.15
Space group	$P2_1/c$ (no. 14)	$P\bar{1}$ (no. 2)	$P\ 2_1\ 2_1\ 2_1$ (no. 19)
a [Å]	14.371(2)	7.981(3)	4.0923(6)
b [Å]	4.2903(4)	8.394(4)	9.2312(11)
c [Å]	27.876(3)	15.107(6)	31.897(5)
α [°]	90	86.77(1)	90
β [°]	94.023(5)	77.646(11)	90
γ [°]	90	81.566(12)	90
Z	4	1	4
T [K]	193	193	193
V [Å^3]	1714.4(3)	977.7(7)	1205.0(3)
$D_{calcd.}$ [mg m^{-3}]	1.598	2.048	2.429
μ [mm^{-1}]	0.809	3.350	4.887
F(000)	848.00	588.00	840.00
Reflections collected	13688	6842	8755
Unique reflections	3212	3567	2640
Observations [$I > 2\sigma(I)$]	3100	3146	2624
Variables	213	222	148
R_1 [$I > 2\sigma(I)$]	0.0433	0.0416	0.0268
wR_2	0.0850	0.0826	0.0604
Goodness of fit indicator	1.168	1.117	1.146

$R_1 = \Sigma||F_o| - |F_c||/\Sigma |F_o$ and $wR_2 = [\Sigma(w(F_o^2 - F_c^2)^2)/\Sigma w(F_o^2)^2]^{1/2}$

using CrystalClear (Rigaku).[36] The structures were solved by direct methods using SHELXS-97[37] and the refinements against all reflections of the compounds were performed using SHELXL-97.[38] The non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined using the theoretical riding model. A summary of the experimental details and selected results for compounds **1**–**3** is given in Table 3. The selected bond lengths and angles are listed in Table 2.

CCDC No. 256152–256154 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Measurements of Conductivity: To confirm the effect of coordination assembly, compounds **1** and **2**, as precursors, were doped by iodine using the gaseous diffusion method at 50 °C. The dark-red color of compound **2** turned gradually into black after a week. The conductivity (σ_{RT}) of the I_2 doped compound **2** was 1.0×10^{-3} S cm^{-1} which was measured by a conventional two-probe method for compacted pellets at room temperature. The conductivity of the I_2 doped ligand **1** was 2.0×10^{-4} S cm^{-1}, doped and measured under the same experimental conditions.

Acknowledgments

This work was supported by the National Natural Science Foundation (20071024, 20371033), P. R. China. The authors are also grateful to the Key Laboratory of Organic Synthesis of Jiangsu Province, Suzhou University, for financial support.

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Received: December 05, 2004