An Air-induced Synthesis of a Salt [$AuCl_2$(DDDT)](MET-TTF) (DDDT = 5,6-Dihydro-1,4-dithiin-2,3-dithiolate, MET-TTF = Bis(methylthio)ethylenedithiotetrathiafulvalene)

Wei Yang[a,b], Zhi-Gang Ren[b], Guo-Qing Bian[b], Qin-Yu Zhu[b], and Jie Dai[b]

[a] Department of Basic Course, Suzhou Polytechnical Institute of Agriculture, Suzhou 215008,
People's Republic of China
[b] College of Chemistry, Chemical Engineering and Materials Science,
Soochow University, Suzhou 215123, Jiangsu, People's Republic of China

Reprint requests to Prof. J. Dai. E-mail: daijie@suda.edu.cn,
or to Dr. G.-Q. Bian. E-mail: biangq@suda.edu.cn

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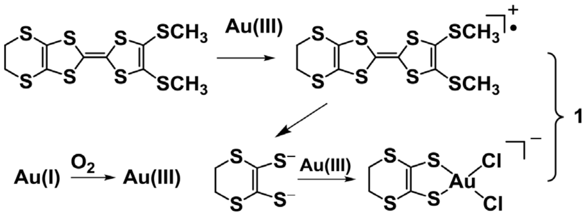
Reaction of $Au(PPh_3)Cl$ with MET-TTF in the presence of air resulted in a new charge-transfer salt [$AuCl_2$(DDDT)](MET-TTF) (**1**, DDDT = 5,6-dihydro-1,4-dithiin-2,3-dithiolate, MET-TTF = bis(methylthio)ethylenedithiotetrathiafulvalene). During the air-induced reaction, the Au(I) is oxidized to Au(III), while two C–S bonds in MET-TTF were cleaved simultaneously. In the crystal the radical cations in **1** are assembled into a 1D structure by intermolecular S···S, S···C, and C···C contacts.

Key words: Tetrathiafulvalene, Charge Transfer, Gold Complex, Crystal Structure

Introduction

Metal-dithiolene complexes form very attractive categories of molecular metals and superconductors. They can have various oxidation states and can range from electron acceptors to donors [1 – 4]. Notwithstanding that the research history can be traced to the first observation of metallic behavior in crystalline metal-dithiolene complexes in 1981 [5, 6], the preparation of single-component molecular conductors based on metal-dithiolene and -tetrathiafulvalene (TTF) complexes has been realized only very recently [7, 8]. On the other hand, di- and polynuclear gold dithiolene complexes have attracted much attention due to their rich luminescence properties [9]. We are interested in the synthesis of new dithiolene and TTF compounds [10 – 13] and have reported binuclear metal complexes with TTF fused dithiolate ligands [12]. In this paper, we describe the synthesis and crystal structure of a new mixed-ligand dithiolene complex containing a TTF radical cation, $[AuCl_2(DDDT)]^-(MET\text{-}TTF)^{\bullet+}$ (**1**, DDDT = 5,6-dihydro-1,4-dithiin-2,3-dithiolate, MET-TTF = bis(methylthio)ethylenedithiotetrathiafulvalene) [14]. We found that the synthetic reaction is an unusual air-induced oxidation process, where Au(I) is oxidized into Au(III), and two C-S bonds in MET-TTF were cleaved. The intermolecular contacts in the crystal are also discussed.



Scheme 1.

Results and Discussion

Synthesis of 1

Refluxing of $Au(PPh_3)Cl$ and MET-TTF (molar ratio 1 : 1) in CH_2Cl_2 for 0.5 h produced an orange solution. To prevent the rapid evaporation of CH_2Cl_2, the solution was sealed in a vessel filled with air. Therein the crystals of **1** formed after one day, while the solution sealed under argon remained unchanged after several days. Thus, it is obvious that the air is important for the synthesis of **1**. As shown in Scheme 1, the oxidation state of Au raises from +1 to +3, which implies oxidation by the oxygen in air. At the same time, MET-TTF is also oxidized to the MET-TTF$^{\bullet+}$ radical cation since TTF derivatives are readily oxidized by high-valent coinage metals. It is further partly degradated to give the DDDT^{2-} dianion *via* the cleavage of two C–S bonds. Such decomposition might be driven by the catalysis at Au(III) centers. Thereby the [$AuCl_2$(DDDT)]$^-$ anion is formed which together with the MET-TTF$^{\bullet+}$ radical cation provides the charge-transfer salt **1**. However, the oxidation and catalysis reactions are more complicated, since the yield of **1** is quite low (10 %). Attempts to achieve higher yields by increasing the sealing time up to 1 week or sealing with extra air were not successful.

*IR and ESR spectra of **1***

In the IR spectrum of **1**, strong bands at 1303 and 1336 cm^{-1} may be assigned to the stretching of the central C=C bond of the TTF unit, which confirms the one-electron oxidation to give the radical cation MET-TTF$^{\bullet+}$, as compared to 1385 cm^{-1} for the neutral MET-TTF. The medium band at 1396 cm^{-1} correlates with the C=C stretching in the DDDT unit.

The solid-state ESR spectrum of **1** was measured at 110 K (Fig. 1). A sharp signal was observed with g = 2.0083, which confirms the radical state of the MET-TTF$^{\bullet+}$ cation. The square planar Au(III) ion in the anion [$AuCl_2$(DDDT)]$^-$ has a d^8 configuration, with no unpaired electrons.

*Crystal and molecular structure of **1***

The crystal structure of **1** has been determined by single-crystal X-ray diffraction. Compound **1** crystallizes in the monoclinic space group *C*2/*c*, and each asymmetric unit consists of one MET-TTF$^{\bullet+}$ radical cation and one [$AuCl_2$(DDDT)]$^-$ anion with a dihedral angle between the planes of the cation and the anion of about 88°, as shown in Fig. 2. In the [$AuCl_2$(DDDT)]$^-$ anion, the gold center is in a square-planar coordination of two Cl$^-$ ions and one DDDT^{2-} dianion, which is consistent with a d^8 electron configuration for Au(III) [15]. The C(1)–C(2) bond length is 1.341(16) Å, which is typical for a C=C double bond length for DDDT^{2-} complexes (1.32 – 1.37 Å) [15 – 21] such as [$Au(DDDT)_2$] (1.35(4) Å) [15] and (TTF)[$Au(DDDT)_2$] (1.370 Å) [16]. The S–Au–S angle of 90.70(11)° and the average Au–S bond length of

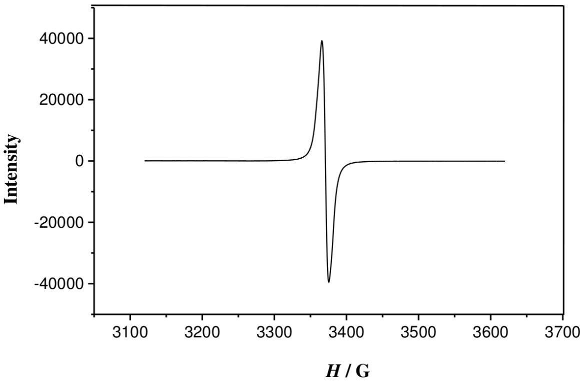


Fig. 1. ESR spectrum of **1** (recorded on an EMX-10/12 spectrometer at 110 K).

Table 1. Selected short contacts (Å) in compound **1**.

S(7)···S(10)^{i}	3.518(4)	C(7)···S(10)^{i}	3.457(4)
C(9)···C(9)^{i}	3.223(4)	S(5)···S(5)^{ii}	3.383(5)
S(12)···S(4)^{iii}	3.501(5)	S(4)···S(12)^{iv}	3.501(5)

Symmetry codes: ^{i} $1-x$, $-y$, $1-z$; ^{ii} $1-x$, y, $0.5-z$; ^{iii} $-0.5+x$, $0.5+y$, z; ^{iv} $0.5+x$, $-0.5+y$, z.

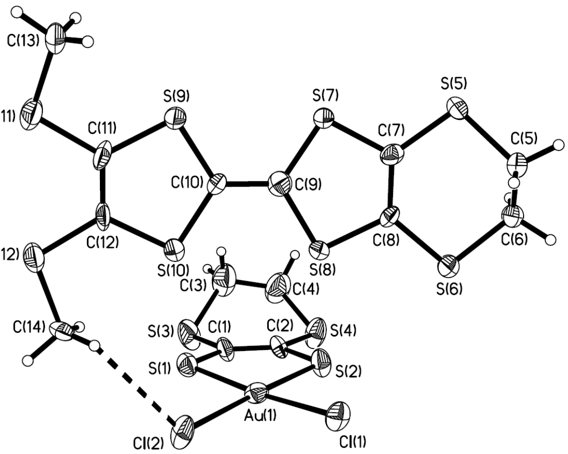


Fig. 2. Perspective view of **1** with crystallographic numbering scheme adopted (displacement ellipsoids at the 30 % probability level). A short contact C(14)–H(14)···Cl(2) is indicated as broken line. A similar contact exists between C(13)–H(13) and Cl(1)^{v} of a neighboring molecule (symmetry code (v): $-0.5+x$, $-0.5+y$, z). Selected bond lengths (Å) and angles (deg): Au(1)–Cl(1) 2.380(3), Au(1)–Cl(2) 2.372(3), Au(1)–S(1) 2.274(3), Au(1)–S(2) 2.262(3), C(1)–C(2) 1.341(16), C(9)–C(10) 1.381(15), C(1)–S(1) 1.754(13), C(1)–S(3) 1.745(12), C(2)–S(2) 1.763(12), C(2)–S(4) 1.746(11), C(9)–S(7) 1.726(12), C(9)–S(8) 1.730(12), C(10)–S(9) 1.723(10), C(10)–S(10) 1.726(11); Cl(1)–Au(1)–Cl(2) 93.44(11), Cl(1)–Au(1)–S(2) 87.05(11), Cl(2)–Au(1)–S(1) 89.01(11), S(1)–Au(1)–S(2) 90.70(11), C(10)–C(9)–S(7) 122.5(9), C(10)–C(9)–S(8) 121.1(9), S(7)–C(9)–S(8) 116.2(7), C(9)–C(10)–S(9) 122.2(9), C(9)–C(10)–S(10) 122.1(8), S(9)–C(10)–S(10) 115.6(6); H(14)···Cl(2) 2.84, C(14)···Cl(2) 3.473(13), C(14)–H(14)···Cl(2) 123.2; H(13)···Cl(1A) 2.87, C(13)···Cl(1A) 3.645(16), C(13)–H(13)···Cl(1A) 136.6.

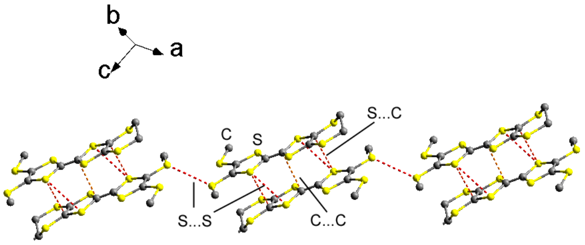


Fig. 3. The 1D structure of **1** showing S···S, S···C and C···C contacts within the radical dimer and the inter-dimer S···S contacts.

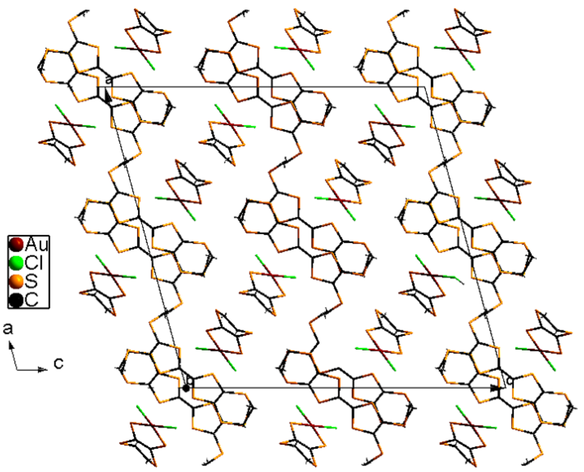


Fig. 4. The molecular packing of **1** showing the arrangement of the cations and anions.

2.268(3) Å are comparable to those in [Au(DDDT)$_2$] (89.2(3)° and 2.30(2) Å) and (TTF)[Au(DDDT)$_2$] (89.78° and 2.307 Å). The TTF moiety of the MET-TTF radical cation is nearly planar with a maximum deviation of 0.077(3) Å, which is different from the boat-shaped structure usually found in neutral derivatives of TTF. Since the central C=C distance of the TTF unit is the charge-sensitive parameter for the electronic state of the TTF derivatives, 1.33 – 1.35 Å for TTF^0, 1.38 – 1.40 Å for TTF$^{\bullet+}$, and 1.42 – 1.43 Å for TTF^{2+}, respectively [22], the C(9)–C(10) distance (1.381(15) Å) confirms that the MET-TTF unit in **1** is a radical cation.

As shown in Fig. 3, two parallel MET-TTF$^{\bullet+}$ radical cations are stacked *via* two S(7)···S(10)$^{\mathrm{i}}$ contacts (3.518(4) Å), two C(7)···S(10)$^{\mathrm{i}}$ contacts (3.457(4) Å), and one C(9)···C(9)$^{\mathrm{i}}$ contact (3.223(4) Å; Table 1), the distances of the atoms in the pairs being shorter than the sum of the van der Waals radii (for symmetry codes see Table 1). Thus pairs of anions might be viewed as dimers, and these kinds of dimers are usually found in TTF radical compounds. By another S(5)···S(5)$^{\mathrm{ii}}$ contact (3.383(5) Å) the dimers interact with two neighboring dimers along the crystallographic *b* direction, and expands the array structure to a 1D structure, as shown in Fig. 3. Fig. 4 shows the molecular packing of **1** as viewed down the crystallographic *b* axis.

Conclusion

In summary, a charge-transfer salt [$AuCl_2$(DDDT)]$^-$MET-TTF$^{\bullet+}$ (**1**) has been synthesized by the reaction of Au(PPh_3)Cl and MET-TTF. This is a unique reaction involving air-induced Au(I)/Au(III) oxidation and MET-TTF cleavage. The radical cations are assembled into a 1D structure containing radical pairs formed *via* S···S, S···C and C···C contacts.

Experimental Section

*Synthesis of [$AuCl_2$(DDDT)](MET-TTF) (**1**)*

A CH_2Cl_2 solution (5 mL) containing MET-TTF (12.0 mg, 0.03 mmol) [6] and Au(PPh_3)Cl (16.0 mg, 0.03 mmol) was stirred at 30 °C for 0.5 h and then filtered. The orange filtrate was sealed with air in a glass tube (diameter = 8 mm, length = 40 cm). Dark-blue crystals of **1** were formed within 2 d. The crystals were washed with Et_2O and dried in air. Yield: 2.4 mg (10 % based on MET-TTF). – Anal. for $C_{14}H_{14}AuCl_2S_{12}$: calcd. C 20.14, H 1.69. found: C 19.65, H 1.82 %. – IR (KBr, cm^{-1}): ν = 1396(m), 1336(vs), 1303(s), 476(m), 459(m).

X-Ray structure determination

Crystal data for **1**: $C_{14}H_{14}AuCl_2S_{12}$, M_r = 834.84, dark-blue crystal, 0.40 × 0.15 × 0.10 mm^3, T = 193 K, monoclinic, space group $C2/c$, a = 27.105(5), b = 807530(18), c = 24.735(5) Å, β = 105.10(3)°, V = 5038.7(18) Å^3, Z = 8, D_calcd = 2.20 g·cm^{-3}, F(000) = 3224 e, μ = 7.0 mm^{-1}, 27119 reflections collected, 5736 unique (R_int = 0.0690), 264 refined parameters, $R1$ = 0.0782, $wR2$ = 0.1952 based on 5255 observed reflections with $I \geq 2.0\ \sigma(I)$, $R1$ = 0.0886, $wR2$ = 0.1997 and S = 1.380 for all unique reflections, residual electron density 0.33 / –1.55 e Å^{-3}.

Data collections were performed on a Rigaku Mercury CCD diffractomer with graphite-monochromatized MoK_α radiation (λ = 0.71073 Å). The crystal structure was solved by Direct Methods (SHELXS-97 [23]) and refined on F^2 by full-matrix least-squares techniques with SHELXL-97 [23]. All non-hydrogen atoms were refined anisotropically, while all H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms with U_iso(H) = 1.2 U_eq.

CCDC 757933 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.

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