Silver(I) Coordination Polymer of 2,5-Bis-(4′,5′-bis(methylthio)-1′,3′-dithiol-2′-ylidene)-1,3,4,6-tetrathiapentalene (TTM-TTP) and Its Highly Conductive Iodine Derivative

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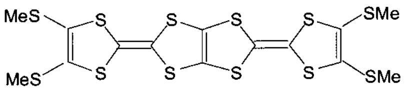
Introduction

Tetrathiafulvalene (TTF) and its analogues are excellent electron donors and have long received much attention. They can be easily oxidized to stable radical cations and are also one of the major components in a number of electroconductive materials known as so-called "organic metals" whose conductivity can be varied over a wide range from semiconductor to superconductor.[1−4] Many TTF derivatives are inclined to react with organic or inorganic acceptors to afford charge-transfer complexes[5] or charge-transfer salts[6] in which partial or complete charge-transfer takes place. However, it is noted that although some charge transfer salts for TTF and its derivatives contain metal atoms in an anion part, only a few examples of the coordination of metal atoms to TTF derivatives were observed.[7−10]

Recently, bis- and tris-tetrathiafulvalene (TTF) systems have received considerable attention because most organic metals and organic superconductors involve TTF and its derivatives.[11] The insertion of a tetrathiapentalene (TTP) unit into the central C$=$C bond of the TTF skeleton has been regarded as one of the most important strategies of molecular design, mainly owing to both decreasing on-site Coulombic repulsion in the dicationic states by extension of π-conjugation and leading to 2-D organic metals stable down to low temperature.[12] In this context, the crystal structures and physical properties of some organic conductors[12b,c,13−15] and a superconductor[16] based on various TTP derivatives have been reported. Despite these achievements, no example of a metal coordination polymer with TTP derivatives was observed. On the other hand, the coordination of metal ions to TTP derivatives is expected to be a versatile route for the preparation of a wide variety of conductive TTP complexes that exhibit different electrical properties, because a coordination polymeric network can be achieved through the coordination of metal ions and S$\cdots$S contacts. As a result, we report here on the synthesis, characterization and physical properties of a 1-D silver(I) coordination polymer of 2,5-bis(4′,5′-bis(methylthio)-1′,3′-dithiol-2′-ylidene)-1,3,4,6-tetrathiapentalene (TTM-TTP) with S$\cdots$S contacts.



TTM-TTP

Experimental Section

General Considerations. 2,5-Bis(4′,5′-bis(methylthio)-1′,3′-dithiol-2′-ylidene)-1,3,4,6-tetrathiapentalene (TTM-TTP) was synthesized according to the literature.[12b] Electrical conductivity was measured by a conventional two-probe method at room temperature with a compressed pellet. The iodine-doped sample was prepared via vapor diffusion method.

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Table 1. Selected Bond Lengths (Å) and Angles (deg) for **1**

Bond Distances			
Ag1−S1	2.7547(5)	Ag1−S2	2.6122(5)
Ag1−S11	2.6606(5)	Ag1−S12	2.7976(5)
Ag1−O1	2.600(1)	C3−C4	1.349(2)
C5−C6	1.345(2)	C7−C8	1.340(2)
C9−C10	1.345(2)	C11−C12	1.349(2)
C4−S2	1.756(2)	C4−S4	1.759(2)
C3−S1	1.744(2)	C3−S3	1.756(2)
C5−S3	1.755(2)	C5−S4	1.750(2)
C6−S5	1.769(2)	C6−S6	1.764(2)
Bond Angles			
S1−Ag1−S2	77.55(2)	S1−Ag1−S11	165.28(2)
S1−Ag1−S12	98.53(2)	S2−Ag1−S11	104.11(2)
S2−Ag1−S12	161.78(2)	S11−Ag1−S12	75.24(2)

Preparation of [Ag(TTM-TTP)(CF_3SO_3)] (1) and [Ag(TTM-TTP)(CF_3SO_3)](I_3)$_{0.29}$ (2). $AgCF_3SO_3$(38.5 mg, 0.15 mmol) was dissolved in 1 mL of acetonitrile at room temperature, while TTM-TTP (5.64 mg, 0.01 mmol) was dissolved in 4 mL of benzene at 65 °C. Then, the solution of $AgCF_3SO_3$ was mixed with the solution of TTM-TTP, and the mixture was stirred at 65 °C for 30 min and filtered. The filtrate was introduced into a glass tube and layered with hexane as a diffusion solvent. The glass tube was sealed under Ar and stands at 50 °C in the dark. After standing for two weeks, orange needle crystals of [Ag(TTM-TTP)(CF_3SO_3)] (**1**) suitable for X-ray analysis were isolated. Anal. Calcd for $C_{15}H_{12}AgS_{13}F_3O_3$: C, 21.92; H, 1.47. Found: C, 21.61; H, 1.47. IR(KBr, cm^{-1}): 2914(w), 1622(m), 1419(m), 1350(m), 1288(vs), 1228(m), 1163(s), 1022(s), 968(m), 891(m), 765(m), 634(s), 572(m), 518(m), 447(m), 426(m).

The orange crystals of complex **1** were ground, and the obtained powder sample (17.6 mg, 0.021 mmol) was introduced into one arm of an h-shaped glass tube which contained iodine (20.7 mg, 0.081 mmol) in another arm. The glass tube was sealed under Ar and was left standing at room temperature. After 3−4 weeks, black solid (20 mg) with the composition [Ag(TTM-TTP)(CF_3SO_3)](I_3)$_{0.29}$ (**2**) was obtained. Anal. Calcd for $C_{15}H_{12}AgS_{13}F_3O_3I_{0.88}$: C, 19.41; H, 1.30. Found: C, 19.35; H, 1.20. IR(KBr, cm^{-1}): 2927(vw), 1638(w), 1390(s), 1340(s), 1307(m), 1267(s), 1175(w), 1145(m), 1030(m), 887(w), 771(w), 635(m), 467(m), 416(w).

X-ray Structure Determination. An orange needle crystal of complex **1** was mounted on a glass fiber. All measurements were made on a Quantum CCD area detector coupled with a Rigaku AFC8 diffractometer with graphite monochromated Mo Kα radiation. The data were collected at a temperature of −123 °C to a maximum 2θ value of 55.1°. The linear absorption coefficent, μ, for Mo−Kα radiation is 18.32 Å. A symmetry-related absorption correction was applied. The data were corrected for Lorentz and polarization effects. The structure was solved by direct method and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. All calculations were performed using the TEXSAN crystallographic package. Crystal data for **1**: $C_{15}H_{12}AgS_{13}F_3O_3$, formula = 821.90; orange needle; monoclinic; space group $P2_1/n$ (No.14); $a = 24.186(1)$, $b = 12.189(1)$, $c = 8.963(1)$ Å; $\beta = 92.344(2)$°; $V = 2640.1(5)$ Å^3; $Z = 4$; $D_{calcd} = 2.068$ g/cm^3; μ(Mo Kα) = 18.32 cm^{-1}; $T = 152(2)$ K, $R = 0.021$, $R_w = 0.049$. Selected bond distances and angles are summarized in Table 1.

Results and Discussion

Properties. The electric conductivities of the free TTM-TTP, complex **1**, and its iodine-doped compound **2** were measured by the conventional two-probe technique at room temperature. The free TTM-TTP is an insulator ($\sigma_{25°C} < 10^{-12}$ S cm^{-1}); complex **1** and the iodine-doped compound **2** show different conductivities with $\sigma_{25°C}$ of 7.1×10^{-6} and 0.85 S cm^{-1}, respectively. This may be due to ligand−ligand interactions of TTM-TTP$^{+\bullet}$/TTM-TTP or TTM-TTP$^{+\bullet}$/TTM-TTP$^{+\bullet}$ to afford electric conduction pathways.[10a] An intense well-resolved ESR resonance was observed with g values of 2.007 and 2.004, which can be ascribed to TTM-TTP$^{+\bullet}$ cation radicals,[17] for complex **1** and the iodine-doped compound **2**, respectively. The spin density for the TTM-TTP cation radicals was measured with the DPPH (diphenylpicrylhydrazyl) as a standard, being 15.8% for **1** and 87.0% for **2**, respectively. It is noted that the high conductivity of **2** is attributable to its high spin density.

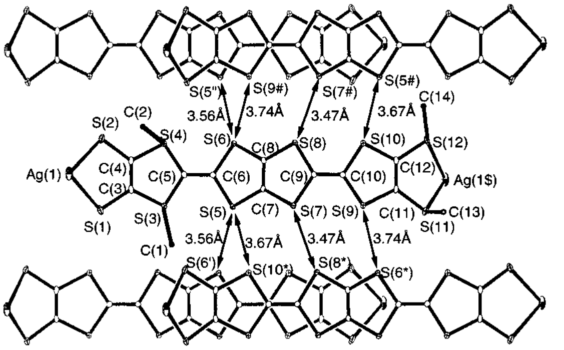

Figure 1. Top view of complex **1** with side-by-side S···S contacts.

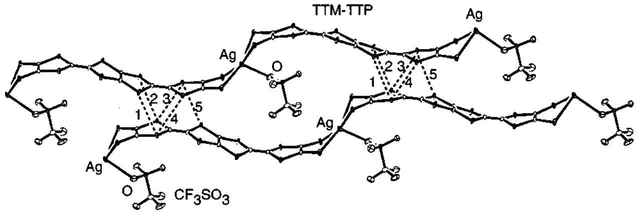

Figure 2. Side view of complex **1** with face-to-face S···S contacts (1, 3.68 Å; 2, 3.71 Å; 3, 3.55 Å; 4, 3.68 Å; 5, 3.66 Å).

Crystal Structure and Features of [Ag(TTM-TTP)(CF_3SO_3)]. The crystallographic studies revealed that complex **1** consists of 1-D chains in which the silver(I) ion is a distorted square pyramidal coordination sphere (Figure 1). Each silver(I) ion interacts with four sulfur atoms, on the basal plane of the square pyramid, from two different TTM-TTP molecules, and the fifth coordination site is occupied by one oxygen atom of the $CF_3SO_3^-$ group. The silver(I) ion is displaced about 0.38 Å above the plane defined by the S1, S2, S11, and S12 atoms. One TTM-TTP molecule asymmetrically bridges two silver(I) atoms to give rise to a 1-D waving chain, and the coordinated $CF_3SO_3^-$ groups sit on the same side of the chain (Figure 2). The TTM-TTP molecules are stacked in a face-to-face manner, and the overlap mode of these molecules is the so-called ring-over-bond type (Figure 1). As shown in Figure 1, there are several side-by-side intermolecular S···S contacts less than the sum of the van der Waals radii (3.70 Å) along the transverse direction, the shortest S···S contact being 3.47 Å. Such short S···S distances are also observed in the face-to-face stacks where the shortest S···S contact is 3.55 Å (Figure 2).

Examples of metal complexes of TTF and its analogues are rare, especially for silver(I). To our knowledge, only two silver(I) coordination polymers with TTF derivatives were observed and characterized, that is, [Ag(TMT-TTF)(CF_3SO_3)][8c] and [Ag(CM-TTF)(CF_3SO_3)].[9b] Compared with [Ag(TMT-TTF)(CF_3SO_3)], complex **1** comprises only one type of chain instead of two independent polymeric chains interwoven with each other as in [Ag(TMT-TTF)(CF_3SO_3)]. In addition, the coordination of silver(I) in [Ag(TMT-TTF)(CF_3SO_3)] involves a distorted triangular prism geometry, and however, silver(I) in complex **1** exhibits a square pyramidal sphere which is similar to that of

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Table 2. Conductivities of Some Metal Complexes with TTF and Its Derivatives

complex	$\sigma_{25°C}$(un-doped) S cm^{-1}	$\sigma_{25°C}$(I_2-doped) S cm^{-1}	ref
$(CuI)_2TTC_2$-TTF	$<10^{-12}$	2×10^{-3}	7a
$(CuCl)_2TTC_2$-TTF	$<10^{-12}$	6×10^{-7}	7b
$(CuBr)_2TTC_2$-TTF	$<10^{-12}$	3×10^{-7}	7b
[Cu(TTC_2-TTF)]ClO_4	$<10^{-12}$	6×10^{-4}	7c
[Cu(TTC_2-TTF)]BF_4	$<10^{-12}$	2×10^{-5}	9a
[Cu(TTC_3-TTF)]ClO_4	$<10^{-12}$	4×10^{-5}	9a
[$Cu_2(\mu\text{-}Cl)_2(\mu-$TTM-TTF)]	$<10^{-12}$	2.5×10^{-4}	8a
[$Cu_2(\mu\text{-}Br)_2(\mu$-TTM-TTF)]	$<10^{-12}$	7.9×10^{-3}	8a
[$Cu_2(\mu\text{-}I)_2(\mu$-TTM-TTF)]	$<10^{-12}$	2.0×10^{-2}	8a
[Cu(CM-TTF)][ClO_4]THF	$<10^{-12}$	10^{-7}	9b
[Ag(CM-TTF)(CF_3SO_3)]	$<10^{-12}$	$<10^{-12}$	9b
[Ag(TTM-TTF)(CF_3SO_3)]	$<10^{-12}$	2.8×10^{-4}	8c
[$Rh_2(O_2CCH_3)_4$(TTF)]	$<10^{-12}$	2.0×10^{-7}	10a
[$CuBr_2$(TTMTTF)]	3.2×10^{-5}		8b
[Ag(TTM-TTP)(CF_3SO_3)]	7.1×10^{-6}	0.85	this work

silver(I) in [Ag(CM-TTF)(CF_3SO_3)]. The free TMT-TTF molecule adopts a nonplanar boat conformation[18] which is maintained in the silver(I) complex [Ag(TMT-TTF)(CF_3SO_3)].[8c] Interestingly, the molecular conformation of TTM-TTP in **1** exhibits a chairlike form compared with that of the free TTM-TTP molecule which is almost planar.[12b] In complex **1**, the TTM-TTP molecule bends at each dithiole sulfur, and the dihedral angles between two adjacent C_2S_4 planes are 17.2, 17.8, 16.5, and 19.4°, respectively (Figure 2). The similar bend (9, 19, 19, and 11°) was also observed in the molecule D of complex α-$(TTM\text{-}TTP)_2I_3$.[19] On the other hand, the shortest S···S distance in [Ag(TMT-TTF)(CF_3SO_3)] between two chains is 4.00 Å which precludes any strong S···S contacts,[8c] and the adjacent chains in [Ag(CM-TTF)(CF_3SO_3)] hold together through S···S contacts of 3.686 Å to form a 2-D network.[9b] However, the crystal of **1** involves the shorter side-by-side S···S contacts along the transverse direction and the shorter face-to-face S···S contacts in the stacking columns to give rise to a 3-D network. To the best of our knowledge, most of the metal complexes with TTF and its derivatives are insulators except [$CuBr_2$(TTM-TTF)];[8b] the highly conductive behavior of complex **1** and its iodine-doped compound **2** can be ascribed to the extensive shorter S···S contacts and the ladderlike arrangement of sulfur atoms in TTM-TTP molecules. The conductive properties of some metal complexes with TTF and its derivatives are summarized in Table 2.

As is well known, incomplete charge transfer is one of the most important features in the conducting complexes,[17,20] while the degree of charge transfer for the CT complexes with TTF and its derivatives can be estimated according to the change of some bond distances with respect to those of the neutral TTF and TTF analogues.[5c,18] Despite the relatively higher spin density of 15.8% which indicates partial charge transfer in **1**, it is noted that no significant structural information on the degree of charge transfer was obtained. This can be rationalized in terms of the HOMO of TTM-TTP molecule spreading more on the larger molecule than that of the TTF series.[19] It is noteworthy that we have observed two kinds of crystals in the experiment, one with orange color (complex **1**) and the other with dark orange color. Interestingly, the dark orange crystals exhibit a strikingly similar IR absorption characteristic when compared to that of the iodine-doped compound **2** between 1307 and 1638 cm^{-1} in which a strong broad absorption band at 1390 cm^{-1} takes the place of the band of 1419 cm^{-1} in **1**. This phenomenon implies that the dark orange crystals might possess a similar charge-transfer degree to that of the iodine-doped compound **2**. However, our attempt to collect the dark orange crystals failed because its yield is very low, and no crystal suitable for X-ray analysis can be obtained. The further study on this phenomenon is in progress so as to obtain a detailed understanding of the relationship between structures and properties.

Conclusion

Complex **1** consists of 1-D waving chains which are stacked in a ring-over-bond mode. In this complex, there exist many shorter side-by-side and face-to-face S···S contacts, among which the shortest side-by-side intermolecular S···S contact along the transverse direction is 3.47 Å and the shortest face-to-face S···S contact is 3.55 Å. Thus, complex **1** can be regarded as a 3-D supramolecular network constructed via coordination bonds and S···S contacts. At room temperature, the free TTM-TTP behaves as an insulator; however, the silver(I) complex **1** and its iodine-doped compound **2** demonstrate different conductivities with $\sigma_{25°C}$ of 7.1×10^{-6} and 0.85 S cm^{-1}. To the best of our knowledge, the latter is the most conductive silver(I) coordination polymer of TTF derivatives.

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Supporting Information Available: An X-ray crystallographic file in CIF format for the structure determination of [Ag(TTM-TTP)(CF_3SO_3)]. This material is available free of charge via the Internet at http://pubs.acs.org.

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