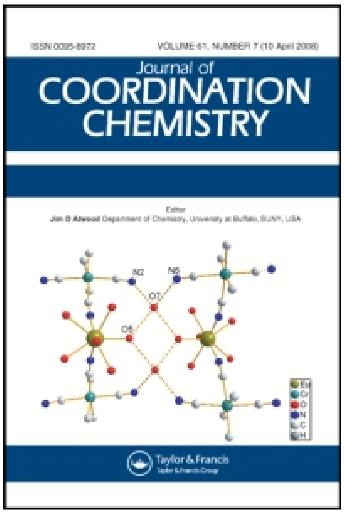

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A silver(I) coordination derivative of 2,3-dimethylthio-6-pyridyl tetrathiafulvalene, synthesis, crystal structure and electrochemical properties

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A silver(I) coordination derivative of 2,3-dimethylthio-6-pyridyl tetrathiafulvalene, synthesis, crystal structure and electrochemical properties

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A silver coordination compound $[Ag(I)(DMT–TTF\text{-}py)_2CH_3CN]\ ClO_4 \cdot CH_2Cl_2$ has been synthesized by reaction of DMT–TTF-py with $AgClO_4$. Structure analysis shows that the cations self-assemble to dimeric units through $Ag \cdots Ag$ interactions. Each silver(I) has a T-shaped AgN_3 coordination geometry. In the dimeric units, there are short $C \cdots S$ and $C \cdots C$ contacts between the two DMT–TTF-py molecules. The dimeric units are further assembled to a zigzag packing structure. The cyclic voltametric behavior of the ligand shows two-step reversible redox waves, which are shifted to lower values due to coordination to silver.

Keywords: Tetrathiafulvalene; Silver complex; Crystal structure; Electrochemistry

1. Introduction

As precursors of charge-transfer or radical materials [1], tetrathiafulvalene (TTF) derivatives can be oxidized to the corresponding radical cation and dication species sequentially. A challenge in TTF chemistry is to prepare new compounds with multifunctional subunits, in order to develop properties such as supramolecular responses and chemical on–off switches [2]. As a typical system, TTF-spacer-A compounds in which the subunits A were pyridine or bipyridine have attracted attention [3]. In these cases, the TTF moiety and the functional group are linked by a σ- or π-spacer. Very recently, Zhang reported a new TTF-py compound that has pyridine directly attached to the TTF moiety without a spacer [4]. Complexes of this ligand would lead to increased coupling between the organic π electrons and the metal d electrons.

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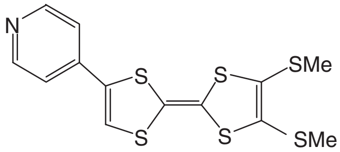

Figure 1. DMT–TTF-Py ligand.

Here we report a new compound in which TTF is directly linked to the pyridine group. Figure 1 gives the structure of the ligand, 2,3-dimethylthio-6-pyridyl-tetrathiafulvalene, DMT–TTF-py. The synthesis and crystal structure of the silver complex are reported. The compound shows reversible two-step redox reactions.

2. Experimental

2.1. *Instruments*

Elemental analyses (C, H and N) were performed using an EA 1110 elemental analyzer. IR spectra were recorded as KBr pellets on a Nicolet Magna 550 FT-IR spectrometer. Cyclic voltammetry (CV) experiments were performed on a CHI600 electrochemistry workstation in a three-electrode system, a single-compartment cell equipped with a platinum working electrode, a platinum wire counter electrode, and a saturated calomel electrode (SCE) as reference.

2.2. *Preparation of DMT–TTF-py*

The compound was synthesized by a coupling reaction from precursors of 4,5-dimethylthio-1,3-dithiole-2-one (0.8334 g, 4.3 mmol) and 4-(4′-pyridyl)-1,3-dithiole-2-one (0.8975 g, 4.3 mmol). This method is based on the strategy described by Becker and Khodorkovsky with some improvements [5]. The mixture was refluxed in triethyl phosphite (12 mL) for 4 h under an argon atmosphere at 135°C. After removal of the solvent, column chromatography of the crude product on silica gel with CH_2Cl_2–MeOH in 100 : 3 v/v afforded DMT–TTF-py as a red solid, which was washed with water. The pure red compound was dried *in vacuo* (yield: 27.2%). Anal. Calcd for $C_{13}H_{11}NS_6$: C, 41.80; H, 2.95; N, 3.75%. Found: C, 41.65; H, 2.97; N, 3.56%.

2.3. *Synthesis of the title complex*

To a solution of DMT–TTF-py (7.5 mg, 0.02 mmol) in dichloromethane (2 mL) was added a solution of $AgClO_4$ (4.1 mg, 0.01 mmol) in acetonitrile (2 mL). (Caution! Silver perchlorate is potentially explosive and should be handled carefully in very small quantities). The mixture was stirred for 30 min at room temperature, and the salmon pink of the ligand turned red. The solution was filtered and the filtrate was kept at room temperature. Dark-red single crystals were obtained from the filtrate by slow evaporation of the solvent. Yield: 35.9%. IR (KBr, cm^{-1}): 1605, 1559, 1489, 1420, 1389, 1088 and 771 cm^{-1}. Anal. Calcd for $C_{29}H_{27}N_3S_{12}O_4Cl_3Ag$: C, 34.42; H, 2.74; N, 4.42. Found: C, 34.59; H, 2.71; N, 4.33.

Table 1. Crystal data and technical details of structure refinement.

Formula	$C_{29}H_{27}AgCl_3N_3O_4S_{12}$
Formula weight	1080.48
Temperature (K)	193(2)
Wavelength (Å)	0.71073
Crystal size (mm^3)	0.30 × 0.25 × 0.10
Crystal system	Monoclinic
Space group	$P2_1/c$
a (Å)	13.643(5)
b (Å)	26.346(7)
c (Å)	12.135(4)
β (°)	109.678(9)
V ($Å^3$)	4107(2)
Z	4
$F(000)$	2176
No. of reflections	34,760
No. of unique	7501
No. of reflections $[I > 2\sigma(I)]$	5961
Goodness-of-fit (S)	1.163
R_1	0.0938
wR_2	0.1604

2.4. *Structure determination and refinement*

A single crystal with dimension $0.30 \times 0.25 \times 0.10\,mm^3$ was mounted on a Rigaku Mercury CCD area detector with graphite monochromated Mo-Kα radiation. ($\lambda = 0.071073$ nm) by using an ω scan mode at 193 (2) K. Out of the total 34,760 reflections collected in the $3.03 \leq \theta \leq 25.35°$ range, 7501 were independent with $R_{int} = 0.0798$, of which 5961 were observed ($I > 2\sigma(I)$) and used in the succeeding refinement. Corrections for Lp factors and empirical absorption adjustment were applied and all non-hydrogen atoms were refined with anisotropic thermal parameters. The final refinement including hydrogen atoms converged to R $(gt) = 0.0938$, $wR = 0.1720$. $w = 1/[\sigma^2(F_o^2) + (0.0363P)^2 + 30.1625P]$, where $P = (F_o^2 + 2F_c^2)/3)$. The relative large R factors attribute to the serious disorder of the ClO_4^- ion. Crystal data and technical details of structure refinement for the title compound are listed in table 1, and selected bond lengths and angles in table 2.

3. Results and discussion

3.1. *Discussion of the synthesis*

This synthetic method is based on the strategy described in the literature [5], in which the ligand was synthesized by a coupling reaction from precursors, 4-(4′-pyridyl)-1,3-dithiole-2-thione and 4,5-dimethylthio-1,3-dithiole-2-thione, yield: 15%. The modification of the synthetic route we made was that two organic-ones were used instead of two thiones for the coupling reaction, which improved the yield. The synthetic procedure of a similar ligand (TTF-py) recently reported [4] is completely different from that we used. The ligand was synthesized from the lithium salt of TTF via an organic tin medial product, and then treated by $Pd(PPh_3)_4$ and 4-iodopyridine.

Table 2. Selected bond lengths (Å) and angles (°).

Bond	Dist.	Bond	Dist.	Bond	Dist.
Ag(1)–N(1)	2.137(6)	S(4)–C(9)	1.769(8)	C(2)–C(3)	1.382(11)
S(1)–C(8)	1.760(8)	S(5)–C(10)	1.736(9)	C(3)–C(4)	1.393(11)
S(1)–C(6)	1.778(8)	S(5)–C(12)	1.801(10)	C(3)–C(6)	1.482(11)
S(2)–C(7)	1.722(8)	S(6)–C(11)	1.761(8)	C(4)–C(5)	1.386(11)
S(2)–C(8)	1.750(8)	S(6)–C(13)	1.801(11)	C(6)–C(7)	1.323(11)
S(3)–C(9)	1.756(8)	N(1)–C(1)	1.336(10)	C(8)–C(9)	1.338(11)
S(3)–C(10)	1.782(9)	N(1)–C(5)	1.339(10)	C(10)–C(11)	1.341(12)
S(4)–C(11)	1.757(9)	N(3)–C(28)	1.107(11)	C(28)–C(29)	1.443(14)
S(4)–C(9)	1.769(8)	C(1)–C(2)	1.396(11)		
Angle	(°)	Angle	(°)	Angle	(°)
N(2)–Ag(1)–N(1)	171.1(3)	C(2)–C(3)–C(6)	122.4(7)	C(8)–C(9)–S(3)	125.5(6)
C(7)–S(2)–C(8)	94.8(4)	C(4)–C(3)–C(6)	119.6(7)	C(8)–C(9)–S(4)	122.0(6)
C(9)–S(3)–C(10)	94.3(4)	C(5)–C(4)–C(3)	118.7(7)	S(3)–C(9)–S(4)	112.4(4)
C(11)–S(4)–C(9)	94.1(4)	N(1)–C(5)–C(4)	124.3(8)	C(11)–C(10)–S(5)	125.6(7)
C(10)–S(5)–C(12)	102.7(5)	C(7)–C(6)–C(3)	126.0(7)	C(11)–C(10)–S(3)	115.8(7)
C(1)–N(1)–C(5)	116.4(7)	C(7)–C(6)–S(1)	116.0(6)	S(5)–C(10)–S(3)	118.1(5)
C(1)–N(1)–Ag(1)	123.9(6)	C(3)–C(6)–S(1)	118.0(6)	C(10)–C(11)–S(4)	117.5(7)
C(5)–N(1)–Ag(1)	119.6(5)	C(6)–C(7)–S(2)	119.7(6)	C(10)–C(11)–S(6)	126.1(7)
N(1)–C(1)–C(2)	123.6(8)	C(9)–C(8)–S(2)	121.5(6)	S(4)–C(11)–S(6)	116.3(5)
C(3)–C(2)–C(1)	119.2(8)	C(9)–C(8)–S(1)	123.6(6)	N(3)–C(28)–C(29)	179.1(11)
C(2)–C(3)–C(4)	117.9(7)	S(2)–C(8)–S(1)	114.8(4)		

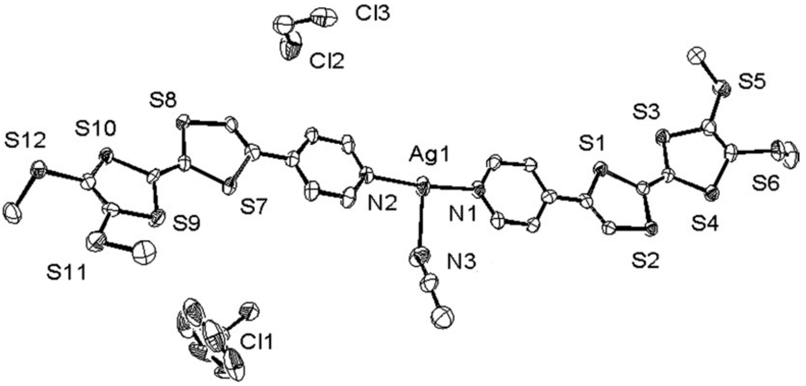

Figure 2. ORTEP drawing of [Ag(I)(DMT–TTF-py)$_2$CH$_3$CN] ClO$_4\cdot$CH$_2$Cl$_2$ with the atom labeling scheme (50% probability thermal ellipsoids). The oxygen atoms of perchlorate are disordered around C11.

3.2. *Crystal structure description*

The crystal structure of the title complex has been determined by X-ray crystal diffraction and its structure is shown in figure 2. The complex crystallizes in monoclinic space group $P2_1/c$. The fundamental unit contains a [Ag(I)(DMT–TTF-py)$_2$CH$_3$CN]$^+$ cation, a ClO_4^- anion and one uncoordinated dichloromethane. The ligand is coordinated to silver(I) in a near linear geometry with a N(2)–Ag(1)–N(1) angle of 171.1(3)°. Another nitrogen atom from acetonitrile is also weakly coordinated to silver(I) giving the silver(I) a T-shaped AgN$_3$ coordination geometry. Bond lengths of Ag(1)–N(1), Ag(1)–N(2) and Ag(1)–N(3) are 2.137(6), 2.128(6),

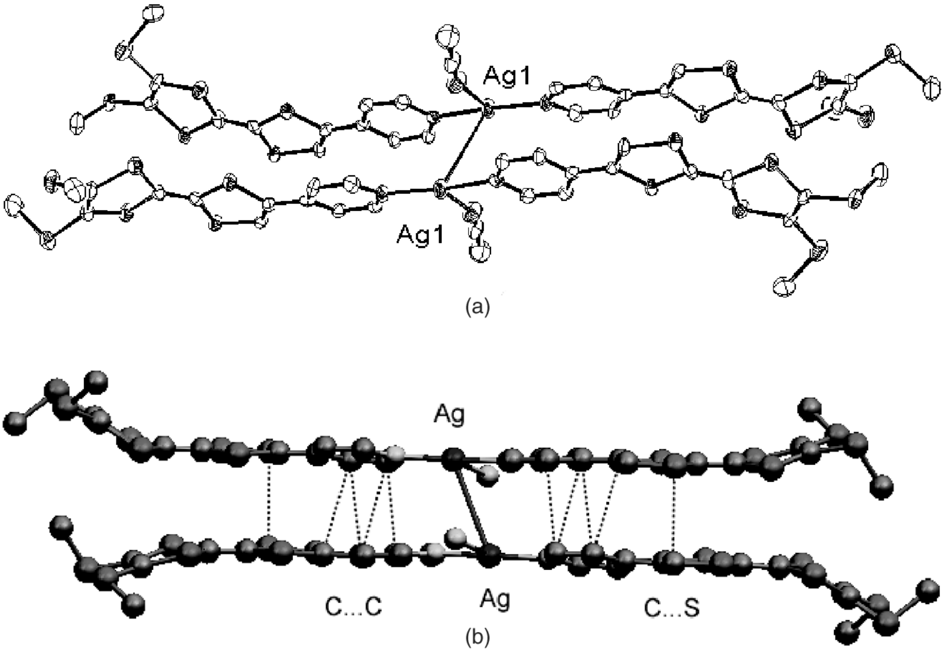

Figure 3. Self-assembled dimeric unit of $[Ag_2(DMT–TTF\text{-}Py)_4(CH_3CN)_2]^{2+}$, showing the weak Ag···Ag bond (a) and short C···S and C···C interactions between the two DMT–TTF-py molecules (b).

and 2.269(6) Å, respectively. The central C=C distance of the TTF moiety, C(8)–C(9) 1.338(11) Å, is close to that found in the neutral TTF compound (1.331 Å) [6].

The complex cations, $[Ag(I)(DMT–TTF\text{-}py)_2CH_3CN]^+$, self-assemble to dimeric units of $[Ag_2(DMT–TTF\text{-}py)_4(CH_3CN)_2]^{2+}$ through Ag···Ag interactions (figure 3). Each dimeric unit is centrosymmetric with a crystallographic centre of symmetry at the mid-point of Ag···Ag bond. The Ag···Ag distance within the dimeric unit is 3.517(1) Å, longer than typical Ag–Ag bonds [7], but shorter than weak Ag···Ag contacts [8]. In the dimeric unit, in addition to Ag···Ag contact, there are short C···S contacts, 3.420(9) Å, and C···C contacts (3.269–3.345 Å) between the two DMT–TTF-py molecules (figure 3b). Outside the T-shaped AgN_3 coordination sphere, two additional weak Ag···S contacts, 3.368(3) and 3.412(3) Å, connect silver atoms to the neighboring dimeric units. Besides the Ag···S contacts, short C···C, 3.373(12) Å, and S···S contacts, 3.596(3) Å, between neighboring dimeric units exist. Figure 4 shows the zigzag packing structure of the title compound. Details of the intermolecular interactions for the title compound are listed in table 3.

3.3. *Cyclic voltammetry of the title complex*

The redox behavior of ligand and complex were investigated by cyclic voltammograms (figure 5) and the results are shown in table 4. All electrochemical measurements were carried out in a mixed solvent ($CH_2Cl_2 : CH_3CN$, 1 : 1 in volume) to insure the ligand and the complex have appropriate solubility. Both the ligand and complex exhibit two

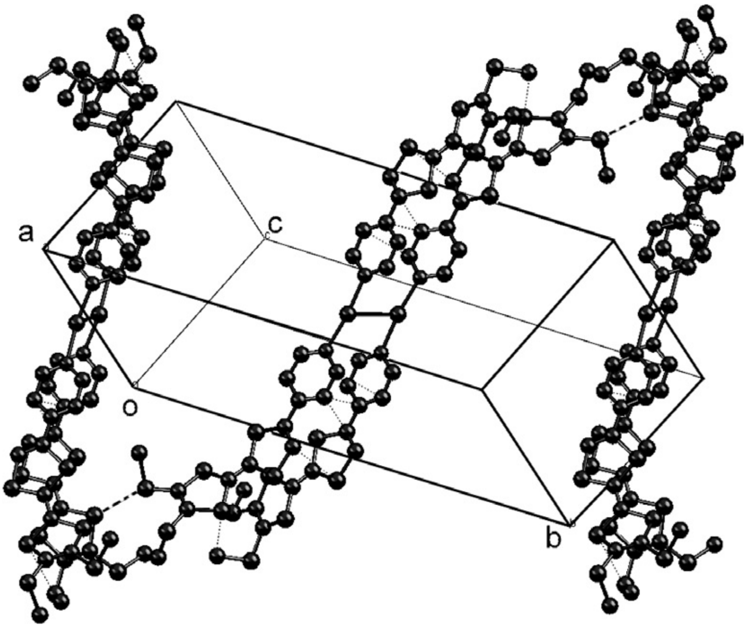

Figure 4. The zigzag arrangement of the title compound, showing the crystal cell.

Table 3. Significant intermolecular contacts (Å) for 1.

Contact	Dist.	Contact	Dist.	Contact	Dist.
Ag(1) ··· S(2^{ii})	3.368(3)	Ag(1) ··· S(12^{ii})	3.412(3)	C(4) ··· C(16^{i})	3.333(14)
C(4) ··· C(19^{i})	3.346(12)	C(5) ··· C(16^{i})	3.331(12)	C(5) ··· C(17^{i})	3.269(13)
C(7) ··· S(8^{i})	3.420(9)	S(2^{ii}) ··· S(10^{iii})	3.567(3)	S(2^{ii}) ··· S(12^{iii})	3.520(3)
S(5) ··· S(9^{iv})	3.596(3)	C(7) ··· C(5^{ii})	3.373(12)	C(4) ··· C(4^{ii})	3.345(13)
C(18) ··· C(24^{iii})	3.166(13)	C(18) ··· C(23^{iii})	3.367(12)		

i: $-x+1$, $-y+1$, $-z+1$; ii: $-x+1$, $-y+1$, $-z+2$; iii: $-x$, $-y+1$, $-z$; iv: $-x+1$, $y+1/2$, $-z+3/2$.

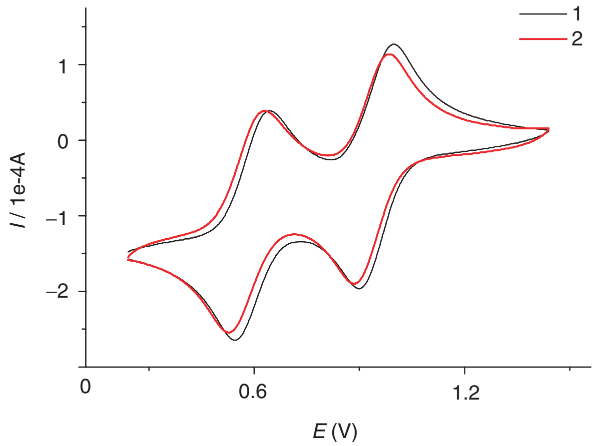

Figure 5. Cyclic voltammogram of ligand (line 1) and complex (line 2) (CH_2Cl_2/CH_3CN in 1 : 1 volumes, Bu_4NClO_4, 0.1 mol L^{-1}, 100 m Vs^{-1}).

Table 4. Electrochemistry data (V).

	$E_{ox}^{(1)}$	$E_{re}^{(1)}$	$E_{1/2}^{(1)}$	$\Delta E^{(1)}$	$E_{ox}^{(2)}$	$E_{re}^{(2)}$	$E_{1/2}^{(2)}$	$\Delta E^{(2)}$	$\Delta E_{1/2}$
Ligand	0.5385	0.4552	0.4969	0.0833	0.8311	0.7493	0.7902	0.0818	0.2933
Complex	0.5239	0.4389	0.4814	0.0850	0.8196	0.7379	0.7788	0.0817	0.2974

reversible single-electron redox waves, corresponding to the TTF/$TTF^{\bullet +}$ and $TTF^{\bullet +}$/TTF^{2+} couples, respectively [1]. The potentials of the silver complex shift to lower values relative to those of the DMT–TTF-py ligand, impling that the d^{10} Ag^+ acts as an electron-rich center. When the Ag–N coordination bond is formed, the filled *d* electrons of silver ion donate back to the π orbital of the ligand. In this case, both the $E_{1/2}(1)$ and $E_{1/2}(2)$ are shifted, different from other ion sensitive crown-TTF derivatives [2]. The $E_{1/2}(2)$ is usually unchanged for the crown-TTF system, due to dissociation of the guest ion from the TTF hosts when the TTF is one electron oxidized. Therefore, the silver complex of DMT–TTF-py is very stable in solution even in the +1 oxidized state of the ligand.

In conclusion, this work demonstrates the influences of Ag(I) metal coordination on the TTF derivative, which shows that the complex cations assemble to dimeric units through Ag $\cdots$ Ag interactions and the redox potentials are changed.

Supplementary material

Details of crystal data in CIF format, (CCDC 621018), are available via request free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44 1223 336033).

Acknowledgments

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