

# Synthesis and Crystal Structures of Silver Thianthrene Complexes with Weakly Coordinating Anions

Rachmat Triandi Tjahjanto and Johannes Beck

Institute of Inorganic Chemistry, Bonn University, Gerhard-Domagk-Str. 1, 53121 Bonn, Germany

Reprint requests to Prof. Dr. J. Beck. Fax: +49 (228) 73 5660. E-mail: j.beck@uni-bonn.de

*Z. Naturforsch.* **2007**, 62b, 1291–1297; received May 8, 2007

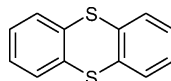
Two novel silver complexes with thianthrene (TA) as a ligand have been synthesized in the poorly coordinating solvent liquid sulfur dioxide, using silver salts with weakly coordinating anions  $[\text{BF}_4]^-$  and  $[\text{SbF}_6]^-$ . Both colorless compounds contain discrete molecular entities and  $\text{SO}_2$  molecules included in the crystal structure. Selection of crystals and the diffraction data collection were performed at low temperatures (123 K). The tris( $\mu$ -thianthrene- $\kappa^2\text{S}$ )disilver(I) bis(hexafluoroantimonate) sulfur dioxide solvate  $[\text{Ag}_2(\text{TA})_3][\text{SbF}_6]_2 \cdot 5 \text{SO}_2$  (**1**) (monoclinic,  $P2_1/c$ ,  $a = 21.644(3)$ ,  $b = 12.4216(4)$ ,  $c = 21.934(3)$  Å,  $\beta = 115.04(1)^\circ$ ,  $Z = 4$ ) is made up of complexes bearing three TA units acting as bridging ligands with both S atoms towards two  $\text{Ag}^+$  ions with  $d(\text{Ag}^+ - \text{Ag}^+) = 2.911$  Å giving the  $[\text{Ag}_2(\text{TA})_3]^{2+}$  unit approximately  $D_{3h}$  molecular symmetry. The bis( $\mu$ -thianthrene- $\kappa^2\text{S}$ )disilver(I) bis(tetrafluoroborate) sulfur dioxide solvate  $[\text{Ag}_2(\text{TA})_2][\text{BF}_4]_2 \cdot 3 \text{SO}_2$  (**2**) (monoclinic,  $C2/c$ ,  $a = 21.0045(6)$ ,  $b = 7.4553(2)$ ,  $c = 22.6024(6)$  Å,  $\beta = 109.65(0)^\circ$ ,  $Z = 4$ ) is made up of  $[\text{Ag}_2(\text{TA})_2]^{2+}$  units with two bridging TA units coordinating two  $\text{Ag}^+$  ions with  $d(\text{Ag}^+ - \text{Ag}^+) = 2.925$  Å giving the complexes approximately  $D_{2h}$  molecular symmetry. Weak, secondary bonds between  $\text{Ag}^+$  and the F atoms of the anions, such as  $\text{Ag} \cdots \text{F} - \text{SbF}_5 = 2.862(4)$  Å in **1** or  $\text{Ag} \cdots \text{F} - \text{BF}_3 = 2.773(2)$  Å in **2**, and with O atoms of  $\text{SO}_2$  molecules link the complexes with the anions and the solvate molecules, respectively.

**Key words:** Silver Complexes, Sulfur Dioxide, Thianthrene Complexes, Weakly Coordinating Anions, Crystal Structure

## Introduction

Thianthrene (TA) has been the focus of extensive research since it exhibits interesting properties. Its crystal structure has been determined several times [1–3]. The two planar aromatic rings define the dihedral angle of the molecule which is folded along the S–S axis by  $127^\circ$  at 163 K and  $128^\circ$  at 295 K. Solution  $^1\text{H}$  NMR studies show a substantially larger angle of  $140.2(2)$  and  $141.6(2)^\circ$  in two different nematic phases [4]. With a dihedral angle of  $131^\circ$  electron diffraction studies in the gas phase indicate a molecular shape similar to that in the crystalline state [5, 6]. Thianthrene shows a remarkable electrochemistry. It can reversibly be oxidized to the stable radical cation, which is of planar molecular shape [7].

Many efforts have been made to prepare complex compounds with the butterfly-shaped molecule acting as a ligand towards various metal atoms. However, only few reports have been published containing crystallographically supported data for TA-metal complex structures. Most of the complex structures have been



Molecular formula of thianthrene (TA).

proposed indirectly based on spectroscopic data or on the mode of chemical reactions [8, 9].

The crystal structure determination of  $[\text{Au}(\text{TA})\text{Cl}_3]$  showed that the planar coordinated gold(III) ion is bound to TA *via* one sulfur atom; TA is thus acting as a monodentate ligand [10]. The (cyclopentadienyl iron) $^+$  fragment in  $[(\text{Cp})(\text{TA})\text{Fe}][\text{PF}_6]$  is bound *via* one  $\eta^6$ -coordinating phenyl ring to the bent TA molecule [11]. As both its sulfur atoms are separated by 3.2 Å, TA is a potential bidentate chelate ligand which can coordinate either one metal atom in  $\eta^2$  mode or two metal centers simultaneously in  $\kappa^2\text{S}$  mode. To date there are only two crystal structures showing that TA can act as such a bidentate ligand.  $[\text{Ag}_2(\text{TA})_2][\text{ClO}_4]_2$  is built of dinuclear complexes [12]. Two  $\text{Ag}^+$  ions are coordinated by TA in an  $\eta^2$  fashion. Additionally,  $\pi$ -arene interactions between two carbon atoms of the phenyl

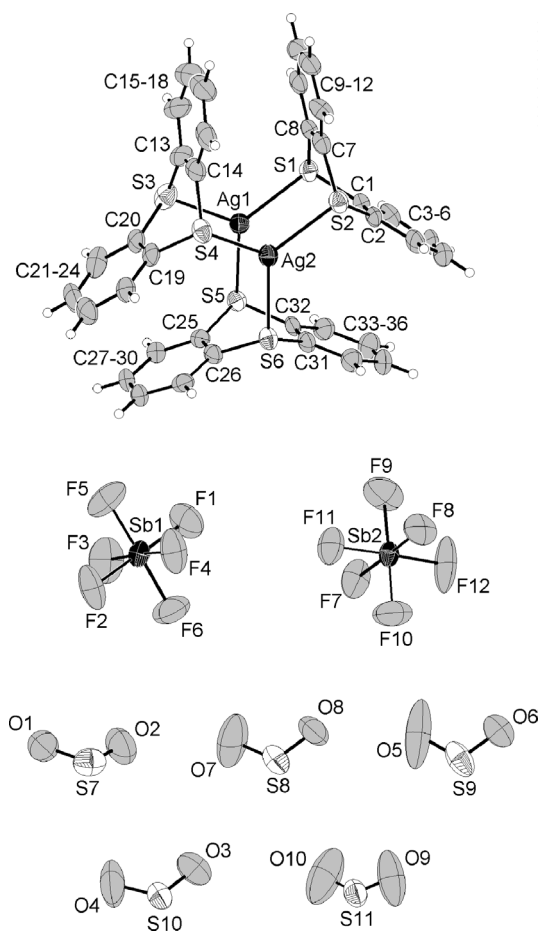


Fig. 1. The complex cations  $[\text{Ag}_2(\text{TA})_3]^{2+}$ , the two independent  $[\text{SbF}_6]^-$  anions and the five independent  $\text{SO}_2$  molecules in the structure of  $[\text{Ag}_2(\text{TA})_3][\text{SbF}_6]_2 \cdot 5 \text{SO}_2$  (**1**). The thermal ellipsoids for the non-hydrogen atoms are drawn at the 70% probability level. The Sb–F bonds in the  $[\text{SbF}_6]^-$  ions are in the range from 1.857(4) to 1.891(4) Å, the S–O bonds in the  $\text{SO}_2$  molecules from 1.313(8) to 1.445(8), the respective O–S–O angles from 115.8(5) to 121.9(7)°.

rings and the Ag atoms are present. Thianthrenophane ( $\text{TA} = \text{C}(\text{CH}_3)=\text{C}(\text{CH}_3)-$ )<sub>2</sub> coordinates  $\text{Ag}^+$  ions in a similar fashion and forms a coordination polymer [13].

In the present work we studied the coordination behavior of TA considering the influence of weakly coordinating anions and a weakly coordinating solvent. In ligand exchange reactions the ‘stronger’ ligand replaces the ‘weaker’ one from the metal center. To increase the coordinating tendency of TA towards metal ions we used the poorly coordinating solvent liquid  $\text{SO}_2$ , which forms very labile  $[\text{M}(\text{SO}_2)_y]^{x+}$  complexes and keeps metal ions in a highly reactive, al-

Table 1. Selected bond lengths (Å) and angles (°) in **1**.

Ag1–S1	2.528(2)	Ag1–S3	2.535(2)
Ag1–S5	2.541(2)	Ag2–S2	2.520(2)
Ag2–S4	2.533(2)	Ag2–S6	2.543(2)
Ag2–Ag1	2.9113(7)		
S1–C1	1.793(5)	S1–C8	1.786(6)
S2–C7	1.789(6)	S2–C2	1.785(6)
S3–C20	1.780(6)	S3–C13	1.782(7)
S4–C14	1.797(6)	S4–C19	1.777(6)
S5–C25	1.782(5)	S5–C32	1.787(5)
S6–C31	1.791(5)	S6–C26	1.792(6)
S1–Ag1–S3	123.09(5)	C1–S1–C8	101.5(3)
S1–Ag1–S5	117.55(5)	C2–S2–C7	102.0(3)
S3–Ag1–S5	118.19(5)	C13–S3–C20	102.1(3)
S2–Ag2–S4	115.36(5)	C14–S4–C19	101.6(3)
S2–Ag2–S6	124.39(5)	C25–S5–C32	101.2(2)
S4–Ag2–S6	118.53(5)	C26–S6–C31	101.7(3)

most uncoordinated or naked form, hence prone to ligand and attack. Moreover, this solvent accentuates the role of weakly coordinating anions present in the solution which can be chosen to form even weaker complexes with the metal ions than  $\text{SO}_2$  does, such that their influence on the complexation reaction can be minimized.

The metal ion used in this study was silver, since it is known to form complexes with TA, and we chose the anions  $[\text{BF}_4]^-$  and  $[\text{SbF}_6]^-$  known to coordinate very weakly. In comparison with  $[\text{BF}_4]^-$ ,  $[\text{SbF}_6]^-$  is more bulky and shows an even weaker coordinating ability [14].

## Results and Discussion

Colorless single crystals of complexes **1** and **2** were grown from solutions in liquid  $\text{SO}_2$  containing the respective silver salt and TA. The  $\text{SO}_2$  solutions in all experiments were, however, not colorless but showed a pink to violet color. This indicates a partial oxidation of thianthrene to the respective radical cation which is deeply colored and in higher concentrations gives the solutions in  $\text{SO}_2$  a dark violet appearance. The nature of this reaction is presently under investigation.

The crystal structure of tris( $\mu$ -thianthrene- $\kappa^2\text{S}$ )-disilver(I) bis(hexafluoroantimonate)  $[\text{Ag}_2(\text{TA})_3][\text{SbF}_6]_2 \cdot 5 \text{SO}_2$  (**1**) consists of dinuclear complex cations, octahedral  $[\text{SbF}_6]^-$  anions, and five  $\text{SO}_2$  molecules per formula unit. Fig. 1 illustrates the structure of the  $[\text{Ag}_2(\text{TA})_3]^{2+}$  complex unit, the two crystallographically independent  $[\text{SbF}_6]^-$  anions and the five independent  $\text{SO}_2$  molecules with the atom numbering scheme. Table 1 lists selected structural parameters. The  $[\text{Ag}_2(\text{TA})_3]^{2+}$  complex consists of three TA units each bridging two  $\text{Ag}^+$

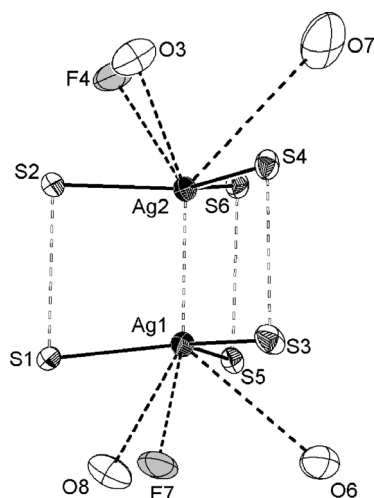


Fig. 2. A detailed view of the core unit of the  $[\text{Ag}_2(\text{TA})_3]^{2+}$  complex in the structure of **1**. Shown are the two  $\text{Ag}^+$  ions, the six S atoms of the three thianthrene ligands, all F and O atoms which exhibit distances to the  $\text{Ag}^+$  ions of less than 4.2 Å. The black, broken lines indicate weak, coordinative bonds. The broken lines connecting the sulfur atoms do not represent bonds, but are only guidelines for the eye. Distances (Å): Ag1–F7 2.862(4), Ag1–O6 3.382(5), Ag1–O8 3.347(6), Ag2–F4 3.010(4), Ag2–O3 3.551(6), Ag2–O7 3.782(9).

ions. Despite exhibiting no crystallographic symmetry, the complex deviates only slightly from point group  $D_{3h}$  symmetry with the threefold rotation axis running along the Ag1–Ag2 axis. Each  $\text{Ag}^+$  ion has a trigonal coordination environment by three sulfur atoms of three TA molecules. The two  $\text{Ag}^+$  ions are located close to the centers of the triangular faces of a distorted trigonal prism made up of the six sulfur atoms of the three thianthrene molecules (Fig. 2). It is remarkable that the two  $\text{Ag}^+$  ions are shifted by 0.159 Å (Ag1) and 0.192 Å (Ag2) out of the plane of the three coordinating sulfur atoms towards each other, resulting in an Ag...Ag separation of 2.911 Å, explicitly shorter than the average S...S separation, which amounts to 3.277 Å. Although the Ag...Ag separation is longer than the sum of the ionic radii of  $\text{Ag}^+$  (2.46 Å [15]), it is within the range assumed for significant  $d^{10}\cdots d^{10}$  interactions in Ag(I) compounds [16, 17]. The Ag–S bond lengths are in the narrow range from 2.520 to 2.543 Å, with an average of 2.533 Å, considerably shorter than in the related complexes  $[\text{Ag}_2(\text{TA})_2][\text{ClO}_4]_2$  (Ag–S = 2.631 and 2.791 Å [12]) and in the chainlike polymer based on thianthrenophane  $[\text{Ag}\{(\text{TA}-\text{C}(\text{CH}_3)=\text{C}(\text{CH}_3)-)_2\}][\text{ClO}_4]$  (Ag–S = 2.81 Å [13]). The TA

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

Ag–S1	2.481(1)	Ag–S2 <sup>I</sup>	2.475(1)
Ag1–Ag1 <sup>I</sup>	2.9250(5)	S1–C1	1.770(3)
S1–C12	1.772(3)	S2–C6	1.774(4)
S2–C7	1.771(4)		
B1–F1	1.363(5)	B1–F2	1.357(5)
B1–F3	1.242(7)	B1–F4	1.269(7)
B1–F5	1.565(9)	B1–F6	1.537(8)
S3–O1	1.420(3)	S3–O2	1.420(3)
S4–O3	1.438(10)	S4–O4	1.375(8)
S1–Ag–S2 <sup>I</sup>	171.04(3)	C1–S1–C12	101.5(2)
C6–S2–C7	101.6(2)	C1–S1–Ag	105.7(1)
C12–S1–Ag	109.8(1)	C6–S2–Ag1 <sup>I</sup>	109.7(1)
C7–S2–Ag1 <sup>I</sup>	107.4(1)		
F1–B1–F2	114.0(3)	F1–B1–F3	119.1(5)
F1–B1–F4	116.7(6)	F1–B1–F6	100.9(4)
F2–B1–F3	118.7(4)	F2–B1–F4	122.3(5)
F3–B1–F6	104.5(6)	F4–B1–F5	103.3(7)
O1–S3–O2	118.0(2)	O3–S4–O4 <sup>II</sup>	116.5(6)

molecules bound to Ag in the structure of **1** show wider dihedral angles (132.62°, 132.89° and 130.53°) between the phenyl rings compared with free TA (127° [8]). This flattening of the ligand molecules is accompanied by longer S–S distances (averaged 3.277 Å) within the three complexed TA molecules compared to free TA (3.193 Å [3]). Additionally, weak coordinative bonds of F atoms of the  $[\text{SbF}_6]^-$  anions and of the O atoms of  $\text{SO}_2$  molecules to the  $\text{Ag}^+$  ions are present (Fig. 2). Each  $\text{Ag}^+$  ion has contacts to one F atom of a neighboring  $[\text{SbF}_6]^-$  ion and to two O atoms of two neighboring  $\text{SO}_2$  molecules. The respective distances are shorter for Ag1 than for Ag2 (Ag1...F7–SbF5 = 2.862(4), Ag2...F4–SbF5 = 3.010(4) Å).

The arrangement of the molecules in the unit cell shows a clear separation in an organic, positively charged part, made up of the  $[\text{Ag}_2(\text{TA})_3]^{2+}$  complexes, and an inorganic, negatively charged part, made up of  $[\text{SbF}_6]^-$  ions and  $\text{SO}_2$  molecules. All  $[\text{Ag}_2(\text{TA})_3]^{2+}$  complexes are arranged in layers parallel to the *ab* plane of the crystal structure (Fig. 3). The packing of the phenyl rings determines this arrangement. The complexes form the motif of a cubic close packing with the stacking sequence ABC perpendicular to the *ab* plane. Between these layers, the  $[\text{SbF}_6]^-$  anions and the  $\text{SO}_2$  molecules are located. Since each  $\text{Ag}^+$  ion has a close contact to one  $[\text{SbF}_6]^-$  anion, the anions are located in the tetrahedral voids.

The crystal structure of bis( $\mu$ -thianthrene- $\kappa^2\text{S}$ )-disilver(I) bis(tetrafluoroborate)  $[\text{Ag}_2(\text{TA})_2][\text{BF}_4]_2 \cdot 3 \text{SO}_2$  (**2**) consists of dinuclear complex cations, tetrahedral  $[\text{BF}_4]^-$  anions and three  $\text{SO}_2$  molecules

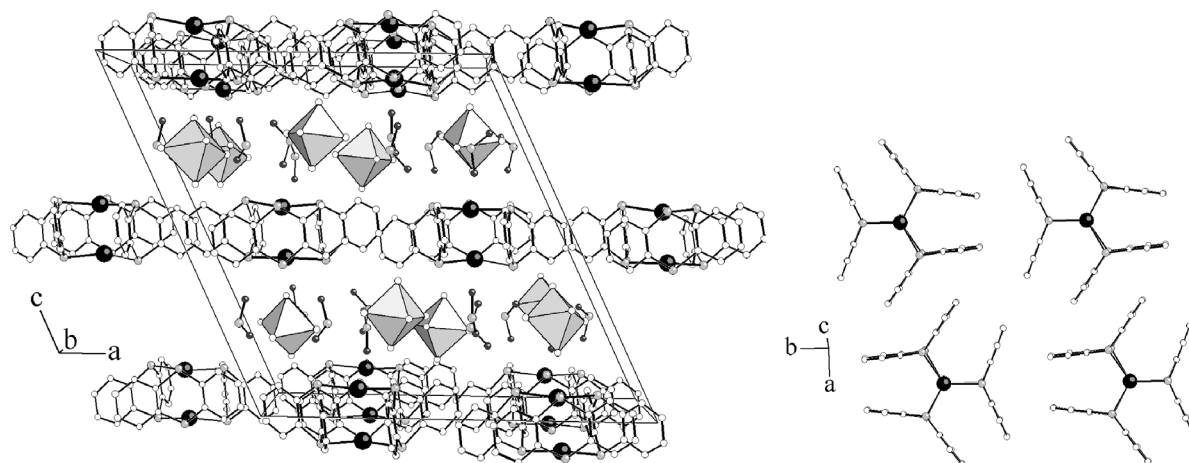


Fig. 3. The unit cell of  $[\text{Ag}_2(\text{TA})_3][\text{SbF}_6]_2 \cdot 5 \text{SO}_2$  (**1**) in a perspective view along the  $b$  axis showing the separation of the structure into layers of the complex cations, the  $[\text{SbF}_6]^-$  anions and the  $\text{SO}_2$  molecules (left), and the arrangement of the  $[\text{Ag}_2(\text{TA})_3]^{2+}$  complexes by the view onto one layer along the  $\text{Ag} \cdots \text{Ag}$  axes of the cations (right).

per formula unit. Fig. 4 shows the structure of the  $[\text{Ag}_2(\text{TA})_2]^{2+}$  coordination unit, the tetrafluoroborate ion and the two independent  $\text{SO}_2$  molecules. Selected structural parameters are listed in Table 2. The  $[\text{Ag}_2(\text{TA})_2]^{2+}$  complexes are built of two TA units each bridging two  $\text{Ag}^+$  ions. The complex ion has a crystallographic inversion center, but the overall symmetry is only slightly distorted from point group  $D_{2h}$  symmetry. Each  $\text{Ag}^+$  ion is almost linearly coordinated by two S atoms with an angle  $\text{S1} - \text{Ag} - \text{S2}^{\text{I}} = 171.04(3)^\circ$ . The two  $\text{S} - \text{Ag} - \text{S}$  units are bent inwards resulting in a  $\text{Ag} \cdots \text{Ag}$  separation of 2.925 Å, almost identical to the one observed in the structure of **1**, and considerably shorter than the  $\text{S} \cdots \text{S}$  separation  $\text{S1} - \text{S2} = 3.264$  Å. The  $\text{Ag} - \text{S}$  bond lengths (2.47 and 2.48 Å) are even shorter than in the structure of **1**. This shortening, however, is expected, since the coordination number of the  $\text{Ag}$  atoms is smaller in the structure of **2**. The TA ligand molecules have dihedral angles of  $133.0^\circ$  and are thus flattened – as in complex **1** – with respect to the uncoordinated molecule.

The  $[\text{BF}_4]^-$  anion and one of the two  $\text{SO}_2$  molecules show disorder (Fig. 4). In the structure refinements, the smeared electron density around the B atom was refined assuming two fully occupied and four only half occupied F atom positions. For the  $\text{SO}_2$  molecule located on a special position on a twofold axis ( $\text{O3} - \text{S4} - \text{O4}$ ) two closely neighboring O positions were refined. Both units,  $[\text{BF}_4]^-$  and  $\text{S(4)O}_2$ , appear to occupy statistically two positions with B and S4 as the pivot atoms, since reasonable B–F and S–O bond

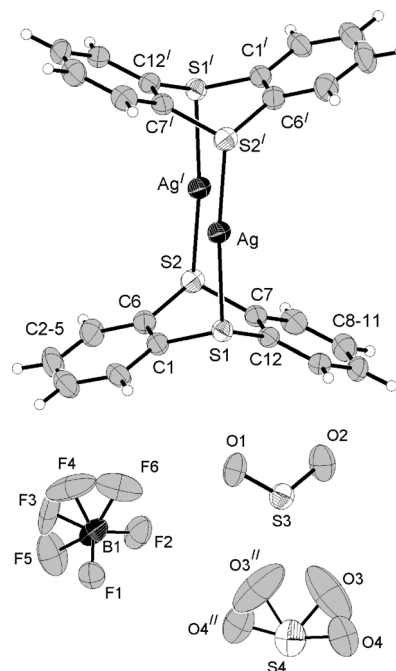


Fig. 4. The complex cation  $[\text{Ag}_2(\text{TA})_2]^{2+}$ , the  $[\text{BF}_4]^-$  anion and the two independent  $\text{SO}_2$  molecules in the structure of  $[\text{Ag}_2(\text{TA})_2][\text{BF}_4]_2 \cdot 3 \text{SO}_2$  (**2**). The thermal ellipsoids for the non-hydrogen atoms are drawn at the 50 % probability level. The atoms F3, F4, F5, F6 of the  $[\text{BF}_4]^-$  ions and the atoms O3 and O4 of one of the  $\text{SO}_2$  molecules were refined with occupation factors of only 0.5, assuming positional disorder of these two molecules. The S–O bonds in the  $\text{SO}_2$  molecules are in the range from 1.375(8) to 1.438(10) Å, the respective O–S–O angles from  $116.5(9)$  to  $118.0(2)^\circ$ . Symmetry operations:  $^{\text{I}}1.5 - x, 0.5 - y, 1 - z$ ;  $^{\text{II}}2 - x, y, 1.5 - z$ .

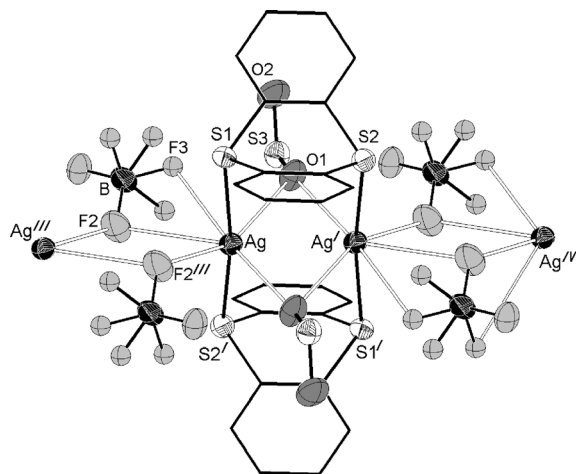


Fig. 5. A detailed view of the  $[\text{Ag}_2(\text{TA})_2]^{2+}$  complex cations in the structure of **2** and their concatenation by  $\text{Ag}\cdots\text{F}$  interactions. The thermal ellipsoids are drawn at the 50 % probability level. The four F atoms of each  $[\text{BF}_4]^-$  ion with occupation factors of 0.5 are drawn as spheres, the C atoms of the two thianthrene molecules are shown only schematically. Selected distances (Å): Ag–O1 2.952(3), Ag<sup>I</sup>–O1 2.824(3), Ag–F2 2.827(2), Ag–F2<sup>III</sup> 2.772(2), Ag–F3 2.968(6). Symmetry operations: <sup>III</sup>  $1.5 - x, 1.5 - y, 1 - z$ ; <sup>IV</sup>  $x, -1 + y, z$ .

lengths and F–B–F and O–S–O angles are present (Tab. 2).

The  $\text{Ag}^+$  ions in the  $[\text{Ag}_2(\text{TA})_2]^{2+}$  complexes are coordinated additionally by O atoms of  $\text{SO}_2$  molecules and by F atoms of  $[\text{BF}_4]^-$  anions as illustrated in a detailed view in Fig. 5. Taking into account all Ag–O and Ag–F distances up to 3 Å each  $\text{Ag}^+$  ion gains besides the two Ag–S bonds two Ag–O bonds and three Ag–F bonds. Two  $\text{SO}_2$  molecules act as bridging ligands each with one O atom coordinated to both  $\text{Ag}^+$  ions of one complex. The Ag–F interactions link the  $[\text{Ag}_2(\text{TA})_2]^{2+}$  complexes to one-dimensional chains which run along the crystallographic *b* axis (Fig. 6).

## Conclusion

Two complexes were synthesized from thianthrene and silver salts with weakly coordinating anions in the poorly coordinating solvent liquid  $\text{SO}_2$ . Both complexes are dinuclear and are built of pairs of  $\text{Ag}^+$  ions with short Ag–Ag distances of 2.9 Å. Thianthrene acts as a bridging ligand in the so far unobserved  $\kappa^2\text{S}$  mode. The differences between the two complexes are obviously the result of the differences between the two used anions. The more weakly coordinating anion  $[\text{SbF}_6]^-$  allows for the complexation of the Ag–Ag dumbbell

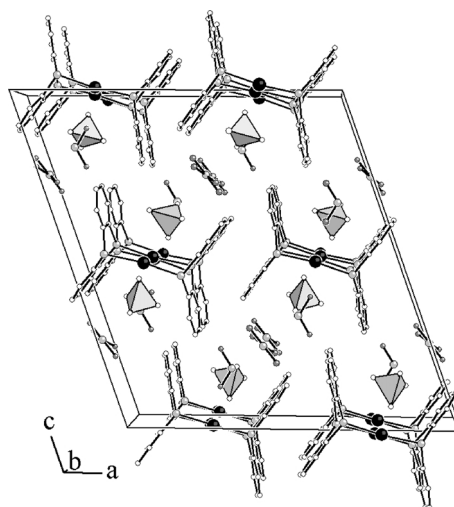


Fig. 6. View of the unit cell of  $[\text{Ag}_2(\text{TA})_2][\text{BF}_4]_2 \cdot 3 \text{SO}_2$  (**2**). Only one position of the disordered  $[\text{BF}_4]^-$  anions is shown.

by three thianthrene molecules while the smaller and slightly more nucleophilic anion  $[\text{BF}_4]^-$  causes the complexation by only two thianthrene ligands, which allows for a stronger additional complexation of the  $\text{Ag}^+$  ions by  $\text{SO}_2$  and by the F atoms of the anions.

## Experimental Section

Silver tetrafluoroborate (Aldrich) and silver hexafluoroantimonate (Acros) were used as purchased. Thianthrene (Aldrich) was purified by recrystallization from ethanol-toluene before use. Sulfur dioxide (Air Products) was stored over  $\text{P}_4\text{O}_{10}$  and freshly distilled into the reaction vessel. H-shaped, two-compartment, thick walled glass reaction vessels equipped with teflon screw cocks (Young) and a glass frit between the two tubes were used for all reactions. These vessels withstand the equilibrium pressure (approx. 3 bars) of liquid  $\text{SO}_2$  at ambient temperature and are described in detail in [18].

### Preparation of $[\text{Ag}_2(\text{TA})_3][\text{SbF}_6]_2 \cdot 5 \text{SO}_2$ (**1**)

79.4 mg (0.23 mmol)  $\text{Ag}[\text{SbF}_6]$  and 50 mg (0.23 mmol) thianthrene were placed separately into the bulbs of an H-shaped vessel under argon atmosphere and with protection from intensive sunlight. 30 mL of  $\text{SO}_2$  was then distilled into the bulb containing TA which dissolved completely to give a yellow solution. The vessel was closed with the teflon valves. After having reached r. t. the solution was poured into the other bulb which contained the silver salt. The solution darkened within a few days and finally reached a pink to light violet color. Colorless crystals began to grow on the walls of the vessel after one day.

Formula	$[\text{Ag}_2(\text{C}_{12}\text{H}_8\text{S}_2)_3][\text{SbF}_6]_2 \cdot 5 \text{SO}_2$ ( <b>1</b> )	$[\text{Ag}_2(\text{C}_{12}\text{H}_8\text{S}_2)_2][\text{BF}_4]_2 \cdot 3 \text{SO}_2$ ( <b>2</b> )
$M_r$	1656.32	1014.15
Cryst. size, mm <sup>3</sup>	$0.196 \times 0.178 \times 0.172$	$0.054 \times 0.282 \times 0.036$
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$C2/c$
$a$ , Å	21.644(3)	21.0045(6)
$b$ , Å	12.4216(4)	7.4553(2)
$c$ , Å	21.934(3)	22.6024(6)
$\beta$ , deg.	115.038(10)	109.65(0)
$V$ , Å <sup>3</sup>	5342.7(11)	3333.32(16)
$Z$	4	4
$D_{\text{calcd}}$ , g cm <sup>-3</sup>	2.06	2.02
$\mu(\text{MoK}\alpha)$ , cm <sup>-1</sup>	22.5	17.0
$F(000)$ , e	3200	1984
$hkl$ Range	$h = \pm 28, -16 \leq k \leq 15, l = \pm 28$	$h = \pm 27, k = \pm 9, l = \pm 29$
$((\sin \theta)/\lambda)_{\text{max}}$ , Å <sup>-1</sup>	0.9532	1.0518
Refl. measured	191011	45162
Refl. unique	12277	3804
$R_{\text{int}}$	0.1260	0.0776
Param. refined	658	249
$R(F)/wR(F^2)$ (all reffs.)	0.046/0.095	0.034/0.076
GoF ( $F^2$ )	1.076	1.112
$\Delta\rho_{\text{fin}}$ (max/min), e Å <sup>-3</sup>	1.08/−1.13	0.58/−0.60

Table 3. Crystal Structure data for **1** and **2**.

#### Preparation of $[\text{Ag}_2(\text{TA})_2][\text{BF}_4]_2 \cdot 3 \text{SO}_2$ (**2**)

45 mg (0.23 mmol)  $\text{Ag}[\text{BF}_4]$  and 50 mg (0.23 mmol) thianthrene were placed separately into the bulbs of an H-shaped vessel under argon atmosphere and with protection from sunlight. The reaction was performed as described for **1**. The final color of the solution was pink, and colorless crystals appeared after one day.

#### X-Ray structure determinations

The crystal selection from the vessels was performed under a stream of cold nitrogen. Crystals were transferred into a cold (200 K) perfluorinated oil. The selected single crystals were mounted on a Bruker-Nonius Kappa-CCD diffractometer equipped with an Oxford Cryostream cooling device. Crystal structures were solved by Direct Methods and refined using the SHELX-97 program suite [19]. A semi-empirical absorption correction by the multi-scan method was applied to both data sets [20]. Hydrogen atoms were refined as riding

on their attached carbon atoms with isotropical displacement factors fixed to 1.2 times the value of the respective C atoms. In the structure determination of **2**, partially occupied positions of F atoms in the  $[\text{BF}_4]^-$  anions and of O atoms of one of the  $\text{SO}_2$  molecules were observed. The atomic positions of F3, F4, F5, F6, O3, O4 were refined with occupation factors fixed to 0.5. Crystal data and details of the structure determinations for both compounds are summarized in Table 3.

CCDC 646102 (**1**) and CCDC 646101 (**2**) contain 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](http://www.ccdc.cam.ac.uk/data_request/cif).

#### Acknowledgement

We thank Dr. Jörg Daniels, Institute for Inorganic Chemistry of Bonn University, for the collection of X-ray diffraction data.

- |   |   |
|---|---|
| <p>[1] H. Lyndon, E.G. Cox, <i>J. Chem. Soc.</i> <b>1956</b>, 4887–4895.</p> <p>[2] I. Rowe, B. Post, <i>Acta Crystallogr.</i> <b>1958</b>, <i>11</i>, 372–374.</p> <p>[3] S.B. Larson, S.H. Simonsen, G.E. Martin, K. Smith, S. Puig-Torres, <i>Acta Crystallogr.</i> <b>1984</b>, <i>C40</i>, 103–106.</p> <p>[4] H. Fujiwara, A. Kawamura, T. Takagi, Y. Sasaki, <i>J. Amer. Chem. Soc.</i> <b>1983</b>, <i>105</i>, 125–126.</p> <p>[5] K.L. Gallaher, S.H. Bauer, <i>J. Chem. Soc., Faraday Trans. 2</i>, <b>1975</b>, <i>71</i>, 1173–1182.</p> <p>[6] V.S. Mastryukov, K.-H. Chen, S.H. Simonsen, N.L.</p> | <p>Allinger, J.E. Boggs, <i>J. Mol. Struct.</i> <b>1997</b>, <i>413–414</i>, 1–12.</p> <p>[7] H. Bock, A. Rauschenbach, Ch. Näther, M. Kleine, Z. Havlas, <i>Chem. Ber.</i> <b>1994</b>, <i>127</i>, 2043–2049.</p> <p>[8] W.-L. Kwik, S.-F. Tan, <i>J. Chem. Soc., Dalton Trans.</i> <b>1976</b>, 1072–1075.</p> <p>[9] S.-F. Tan, W.-L. Kwik, K.-P. Ang, <i>J. Less-Common. Met.</i> <b>1980</b>, <i>75</i>, 29–35.</p> <p>[10] N.W. Alcock, K.P. Ang, K.F. Mok, S.F. Tan, <i>Acta Crystallogr.</i> <b>1978</b>, <i>B34</i>, 3364–3366.</p> |
|---|---|

- [11] K. A. Abboud, V. M. Lynch, S. H. Simonsen, A. Porko, R. G. Sutherland, *Acta Crystallogr.* **1990**, *C46*, 1018–1022.
- [12] M. Munakata, S. G. Yan, I. Ino, T. Kuroda-Sowa, M. Maekawa, Y. Suenaga, *Inorg. Chim. Acta* **1998**, *271*, 145–150.
- [13] S. Amthor, Ch. Lambert, B. Graser, D. Leusser, C. Selinka, D. Stalke, *Org. Biomol. Chem.* **2004**, *2*, 2897–2901.
- [14] I. Krossing, I. Raabe, *Chem. Eur. J.* **2004**, *10*, 5017–5030.
- [15] R. D. Shannon, *Acta Crystallogr., A* **1976**, *32*, 751–767. The coordination number of the Ag<sup>+</sup> ions in both complexes was estimated to be 5, taking into account three S atoms, one Ag atom and the three distant coordinations by O and F as one additional ligand.
- [16] M. Jansen, *Angew. Chem. Int. Ed.* **1987**, *26*, 1098–1110.
- [17] P. Pyykkö, *Chem. Rev.* **1997**, *97*, 597–636.
- [18] J. Beck, F. Steden, *Z. Naturforsch.* **2003**, *58b*, 711–714.
- [19] G. M. Sheldrick, SHELXS/L-97, Programs for Crystal Structure Determination, University of Göttingen, Göttingen (Germany) **1997**.
- [20] R. H. Blessing, *Acta Crystallogr.* **1995**, *A51*, 33–38.