

## Crystal Structure and NMR Study of Tetrakis(acetonitrile)silver(I) Fluorosulfonate $[\text{Ag}(\text{CH}_3\text{CN})_4]^+[\text{SO}_3\text{F}]^-$

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The title compound  $[\text{Ag}(\text{CH}_3\text{CN})_4]^+[\text{SO}_3\text{F}]^-$  crystallizes in the orthorhombic space group  $Pna2_1$ ,  $a = 24.383(24)$ ,  $b = 8.632(11)$ ,  $c = 20.755(17)$  Å,  $V = 4368(6)$  Å<sup>3</sup>,  $Z = 12$ , with three independent formula units in the unit cell. A comparison with the isostructural compound  $[\text{Ag}(\text{CH}_3\text{CN})_4]^+[\text{ClO}_4]^-$  is given. The salt has also been characterized by solution <sup>1</sup>H and <sup>19</sup>F NMR spectroscopy and the data compared to that of fluorosulfonic acid.

**Key words:** Crystal Structure, Silver(I), Fluorosulfonate, NMR, Acetonitrile

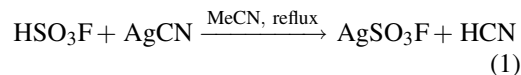
### Introduction

The salt  $\text{AgSO}_3\text{F}$  is a well known compound in the literature, however only few spectroscopic studies were carried out [1–4]. The fluorosulfonate anion ( $\text{SO}_3\text{F}^-$ ) was one of the first weakly coordinating anions used in organic and also in inorganic chemistry due to its unexpected remarkable stability against hydrolysis [5].

Hayek *et al.* reported in 1956 a convenient route to synthesize  $\text{AgSO}_3\text{F}$  from silver cyanide ( $\text{AgCN}$ ) and fluorosulfonic acid ( $\text{HSO}_3\text{F}$ ) in acetonitrile [6]. The authors described  $\text{AgSO}_3\text{F}$  as colorless crystals, which include coordinating molecules of acetonitrile. Grochala *et al.* recently published another solid-state study of  $\text{AgSO}_3\text{F}$ , synthesized from silver fluoride ( $\text{AgF}$ ) and fluorosulfonic acid ( $\text{HSO}_3\text{F}$ ) [7], but the X-ray structure of  $\text{AgSO}_3\text{F} \cdot 4 \text{CH}_3\text{CN}$  has remained unknown.

### Results and Discussion

The silver salt of fluorosulfonic acid was synthesized as described in the literature according to Eq. 1 [6].



The product was recrystallized from acetonitrile to obtain crystals suitable for X-ray structure analysis. Also NMR spectra were recorded from these crystals dissolved in  $\text{CDCl}_3$ . In the <sup>19</sup>F NMR spectrum the fluorine signal was detected at 24.5 ppm. Compared to the <sup>19</sup>F NMR spectrum of  $\text{HSO}_3\text{F}$  in  $\text{CDCl}_3$  ( $\delta(^{19}\text{F}) = 43.5$  ppm) the resonance of the fluorine atom is shifted by about 19 ppm to higher field.

$[\text{Ag}(\text{CH}_3\text{CN})_4]^+[\text{SO}_3\text{F}]^-$  (**1**) crystallizes in the orthorhombic space group  $Pna2_1$  with twelve formula units in the unit cell. A view of the molecular structure is shown in Fig. 1. Table 1 contains selected geometric parameters. The asymmetric unit of the crystals of **1** is composed of three  $[\text{Ag}(\text{CH}_3\text{CN})_4]^+$  cations and three  $\text{SO}_3\text{F}^-$  anions (Fig. 1). In the anion  $\text{SO}_3\text{F}^-$  it is very difficult to exclude a disorder between oxygen and fluorine atoms by X-ray diffraction analysis. Such difficulties are well known and were also described

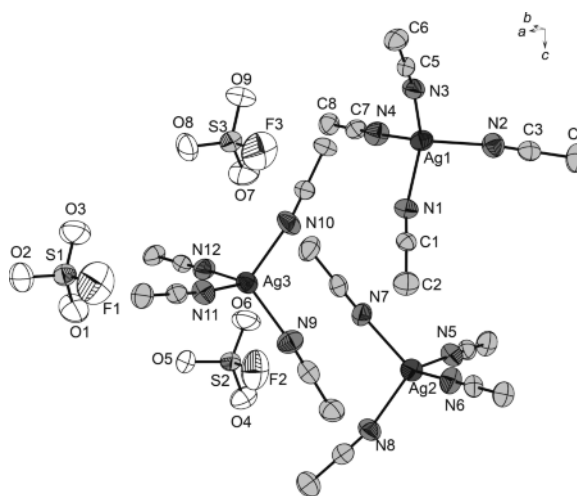


Fig. 1. View of the molecular structure of  $[\text{Ag}(\text{CH}_3\text{CN})_4]^+[\text{SO}_3\text{F}]^-$  (**1**) in the crystal with displacement ellipsoids at the 50% probability level.

Table 1. Selected bond lengths (Å) and angles (deg), for **1** with estimated standard deviations in parentheses.

<b>1</b>			
Distances			
Ag–N <sup>av</sup>	2.272	S2–O5	1.413(5)
N–C <sup>av</sup>	1.127	S2–O6	1.413(6)
C–C <sup>av</sup>	1.453	S2–F2	1.560(6)
S1–O1	1.429(7)	S3–O7	1.432(7)
S1–O2	1.424(5)	S3–O8	1.409(6)
S1–O3	1.417(7)	S3–O9	1.435(7)
S1–F1	1.500(6)	S3–F3	1.516(7)
S2–O4	1.430(7)		
Angles			
N–Ag1–N	104.6(2)–111.2(2)	F2–S2–O5	103.4(3)
N–Ag2–N	104.7(2)–111.9(2)	O4–S2–O5	115.1(4)
N–Ag3–N	106.7(2)–113.6(2)	O5–S2–O6	114.6(4)
F1–S1–O2	107.2(4)	O4–S2–O6	114.0(4)
F1–S1–O3	106.5(4)	F3–S3–O9	104.8(4)
F1–S1–O1	106.2(4)	F3–S3–O7	105.7(4)
O1–S1–O3	111.9(4)	F3–S3–O8	106.4(4)
O2–S1–O3	112.1(4)	O8–S3–O9	112.7(4)
O1–S1–O2	112.4(4)	O7–S3–O8	113.0(4)
F2–S2–O6	104.5(4)	O7–S3–O9	113.3(4)
F2–S2–O4	103.3(4)		

for other crystals with the  $\text{SO}_3\text{F}^-$  anion [7, 8], as well as for the  $\text{SO}_2\text{F}^-$  anion [9, 10]. In the present case the S–O bond lengths are in the range between 1.413(5) and 1.435(7) Å. However the S–F bond lengths are clearly longer, in the range of 1.500(6) and 1.560(6) Å (see Table 1), in the same range as compared to other literature known fluorosulfonate anions [7, 8, 11, 12]. In this structure all three  $\text{SO}_3\text{F}^-$  anions have the same orientation. The fluorosulfonate anions show the expected tetrahedral geometry with angles O/F–S–O/F 103.3(4)–115.1(4)°. The Ag atoms are surrounded slightly distorted tetrahedrally by four acetonitriles with Ag–N distances in the range of 2.238(6)–2.313(5) Å the same as in the isostructural complex  $[\text{Ag}(\text{CH}_3\text{CN})_4]^+[\text{ClO}_4]^-$  described in the literature [13, 14] and also agree well with those of other known structures containing  $[\text{Ag}(\text{CH}_3\text{CN})_4]^+$  [15–18]. The N–C (1.112(7)–1.136(9) Å) and C–C distances (1.442(9)–1.471(9) Å) have the expected values.

## Conclusion

This study shows the crystal structure of the adduct of  $\text{AgSO}_3\text{F}$  with four molecules of acetonitrile, confirming the results of Hayek *et al.* [6]

The fluorosulfonate salt  $[\text{Ag}(\text{CH}_3\text{CN})_4]^+[\text{SO}_3\text{F}]^-$  (**1**) crystallizes isostructurally to the perchlorate salt  $[\text{Ag}(\text{CH}_3\text{CN})_4]^+[\text{ClO}_4]^-$  described in the literature [13, 14]. In addition, solution  $^{19}\text{F}$  NMR chemical shift data of the  $\text{SO}_3\text{F}^-$  anion are presented for comparison with that of  $\text{HSO}_3\text{F}$ .

## Experimental Section

Synthesis and sample handling was performed by employing standard Schlenk techniques. The NMR spectra were recorded with a Delta Jeol 400 ECX instrument at room temperature.

### Synthesis of $\text{AgSO}_3\text{F}\cdot 4\text{CH}_3\text{CN}$ (**1**) [6]

Silver cyanide (AgCN, 10 mmol, 1.34 g) was dissolved in acetonitrile (50 mL) and the solution stirred for 10 min. Then fluorosulfonic acid  $\text{HSO}_3\text{F}$  (10 mmol, 1.00 g) was slowly added to the mixture which was refluxed at 95 °C for 8 h. After 1 d colorless crystals formed in a saturated solution. At room temperature the crystals lose acetonitrile rapidly.

Table 2. Crystal structure data for **1**.

<b>1</b>	
Empirical formula	$\text{C}_8\text{H}_{12}\text{AgFN}_4\text{O}_3\text{S}$
$M_r$	371.16
Crystal size, mm <sup>3</sup>	$0.3 \times 0.15 \times 0.1$
Crystal system	orthorhombic
Space group	<i>Pna</i> 2 <sub>1</sub>
<i>a</i> , Å	24.383(24)
<i>b</i> , Å	8.632(11)
<i>c</i> , Å	20.755(17)
<i>V</i> , Å <sup>3</sup>	4368(6)
<i>Z</i>	12
$D_{\text{calcd.}}$ , g cm <sup>−3</sup>	1.69
$\mu$ , mm <sup>−1</sup>	1.5
$\lambda(\text{MoK}\alpha)$ , Å	0.7107
<i>F</i> (000), e	2208
<i>hkl</i> range	−30 : 29; −10 : 9; −21 : 25
$\theta_{\text{min/max}}$ , deg	4.2/26.0
Refl. measured	18049
Refl. unique	7694
$R_{\text{int}}$	0.0583
Param. refined	489
$R(F)^a/wR(F^2)^b$ (all reffs.)	0.0577/0.0920
Weighting scheme A/B <sup>b</sup>	0.0279/0.0
GoF ( $F^2$ ) <sup>c</sup>	1.027
<i>x</i> (Flack)	0.22(3)
$\Delta\rho_{\text{fin}}$ (max/min), e Å <sup>−3</sup>	0.69/−0.57

<sup>a</sup>  $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ ; <sup>b</sup>  $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$ ,  $w = [\sigma^2(F_o^2) + (AP)^2 + BP]^{-1}$ , where  $P = (\text{Max}(F_o^2, 0) + 2F_c^2)/3$  and A and B are constants adjusted by the program; <sup>c</sup>  $\text{GoF} = S = [\Sigma w(F_o^2 - F_c^2)^2/(n_{\text{obs}} - n_{\text{param}})]^{1/2}$ , where  $n_{\text{obs}}$  is the number of data and  $n_{\text{param}}$  the number of refined parameters.

–  $^1\text{H}$  NMR (270 MHz,  $\text{CDCl}_3$ , 20 °C, TMS):  $\delta = 1.99$  (s,  $\text{NCCCH}_3$ ). –  $^{19}\text{F}$  NMR (270 MHz,  $\text{CDCl}_3$ , 20 °C,  $\text{CFCl}_3$ ):  $\delta = 24.5$  (s,  $\text{SO}_3\text{F}$ ).

#### X-Ray structure determination

The low-temperature X-ray diffraction of **1** was performed on an Oxford XCalibur3 diffractometer equipped with a Spellman generator (voltage 50 kV, current 40 mA) and a KappaCCD detector, operating with  $\text{MoK}\alpha$  radiation ( $\lambda = 0.7107 \text{ \AA}$ ). Data collection at 100 K was performed using the CRYVALIS CCD software [19], the data reductions

were carried out using the CRYVALIS RED software [20]. The solution and refinement of the structure was performed with the programs SHELXS [21, 22] and SHELXL-97 [21, 22] implemented in the WINGX software package [23, 24] and finally checked with the PLATON software [25, 26]. The absorption correction was performed with the SCALE3 ABSPACK multi-scan method [27]. Selected data and parameters of the X-ray analysis are given in Table 2.

CCDC 960265 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](http://www.ccdc.cam.ac.uk/data_request/cif).

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