AgS$_2$O$_6$CF$_3$: the first trifluoromethylsulfonylsulfate(vi)† ‡

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We describe the synthetic route towards a novel class of salts, trifluoromethylsulfonylsulfates, as exemplified by the silver(i) derivative (AgS$_2$O$_6$CF$_3$). Formation proceeds via direct reaction between a triflate precursor, AgSO$_3$CF$_3$, and SO$_3$. The title compound crystallizes in the $P2_1/c$ unit cell with $a = 5.15746(14)$ Å, $b = 25.8563(9)$ Å, $c = 5.53970(14)$ Å and $\beta = 101.1749(19)°$. The structure is layered with the puckered [AgS$_2$O$_6$] 2D sheets; the terminal CF$_3$ groups are separated by the van der Waals gap, as seen also for related metal triflates. The compound is very fragile thermally and it decomposes endothermally to AgSO$_3$CF$_3$ with concomitant evolution of SO$_3$ even at 65 °C or upon grinding in an agate mortar; thus it may serve as a solid store of – otherwise volatile and corrosive – SO$_3$. The IR and Raman spectra of AgS$_2$O$_6$CF$_3$ have been tentatively assigned based on similarities to those of related Ag$_2$SO$_4$ and AgSO$_3$CF$_3$ and phonon calculations. Synthesis and properties of K$_2$O$_6$CF$_3$ are also briefly described.

Introduction

Strong solid Lewis acids and superacids are very important groups of compounds due to their numerous applications in heterogeneous and homogeneous catalyses. The common examples are AlCl$_3$, sulfated zirconia or silver trifluoromethane-sulfonate (AgOTF), to mention just a few. Many solid superacids are the salts of weakly coordinating anions, such as SbF$_6^-$, Sb$_2$F$_{11}^-$, SO$_3$CF$_3^-$ or SO$_3$F$^{-}$. The central metal cation coordinated by these anions is prone to attach to any Lewis base of basicity greater than that of its parent anion. This is the reason why solid Lewis acids may form adducts even with weak Lewis bases, as exemplified by commercialized ether solutions of AlCl$_3$ or solutions of AgOTf in benzene/acetonitrile.

Due to their practical importance, the search for novel solid superacids is of value. One of the methods of obtaining new superacids is to further decrease the basicity of already known weakly coordinating anions. To achieve this, one may react them with very strong Lewis acids. One nice example is provided by SO$_3$, which is known to react with H$_2$SO$_4$ yielding a much stronger Brønsted and Lewis acid, H$_2$SO$_5$. Many pyrosulfates and quasi-binary salts of this acid have been prepared and characterized in the past. The related fluorosulfuric acid, HSO$_3$F, also reacts with SO$_3$, yielding a poorly characterized fluorodisulfuric acid, H$_2$SO$_5$F. Some of its salts have been prepared. The trifluoromethylated or methylated analogues of H$_2$SO$_5$F were reported to form when SO$_3$ was dissolved in CH$_3$SO$_2$H or CF$_3$SO$_2$H. Both H$_2$SO$_5$CF$_3$ and H$_2$SO$_5$CH$_3$ are unstable. Interestingly, reactions between metal triflates or metal methylsulfonates and SO$_3$ have not yet been reported.

In the article we describe the facile synthetic route to the first trifluoromethylsulfonylsulfate salt – Ag(i)S$_2$O$_6$CF$_3$. The structural and thermal features as well as lattice dynamics of this compound are analyzed, and attempts to prepare the related K$_2$O$_6$CF$_3$ are briefly described.

Experimental

Apparatus and reagents

Due to moisture sensitivity of the reagents used in the synthesis, all reactions were conducted in FEP (fluorinated ethylene-propylene) home-made reactors closed with tight-fitting PTFE stopcocks. The reagents were handled in an argon-filled glovebox (O$_2$ < 10 ppm, H$_2$O < 5 ppm in peak concentrations) provided by MBraun, equipped with a fridge providing a temperature of −35 °C. The reagents (>99% AgOTf, 99% SO$_3$ containing P$_2$O$_5$ as a stabilizer and 98% Cu(SO$_3$CF$_3$)$_2$) were purchased from Sigma-Aldrich. Ag$_2$O(SO$_3$CF$_3$)$_2$ was synthesised from KSO$_3$CF$_3$ (Sigma-Aldrich, 99%) and Ag(SbF$_6$)$_2$, according to a method described elsewhere. SO$_3$ was distilled and then

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†This work is dedicated to Prof. Darryl DesMarteau, in recognition of his contribution to fluoroine chemistry and his birthday.
‡Electronic supplementary information (ESI) available: Crystal structure solution and refinement, results of DFT calculations, correlation between calculated and experimental vibrational spectra. See DOI: 10.1039/c3dt50473e

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stored in an FEP container at −35 °C as a white fibrous solid. Tools used to handle AgOTf were made of FEP or stainless steel. Fibres of chilled Ni-coated tweezers at −35 °C to prevent sublimation of SO3. These precautions proved to be essential for synthesis of the thermally-fragile title product.

Vibrational spectra
IR spectra were recorded on a Bruker Vertex 80 vacuum spectrometer. The sample (ca. 1 mg) was gently smeared onto an agate pestle on either AgCl (for MIR range) or PE (for FIR range) windows.

Raman spectra were recorded with a Horiba-Yvon T64000 triple-grating spectrometer equipped with an Kr lamp and a PItXcel linear detector. The geometry used was DSH with a parallel beam equipped with a Gōbel mirror. The powder samples were sealed in quartz capillaries (Hilgenberg GmbH) of diameters ranging from 0.3 to 0.6 mm and a wall thickness of 0.01 mm. Preliminary data analysis was performed with CrystalSleuth.13 The best quality XRDP was obtained for the sample synthesised from 12 mg of SO3 and 36 mg of AgOTf (molar ratio 1.06 : 1) and loaded into a 0.6 mm thick capillary without grinding beforehand. We observed, based on the analysis of the obtained XRDPs, that manual grinding always resulted in partial decomposition of AgS2O6CF3 to AgOTf.

A thin layer of the powder was spread on the walls of the capillary to avoid strong absorption. There is a very small peak from an unknown phase in the diffractogram at ca. 7°, and the 2 theta interval from 6.63° to 7.23° was skipped. The peak is present only in one diffractogram, suggesting that it is only incidental contamination.

Indexation of the powder pattern was conducted by X-Cell14 implemented in the Materials Studio 5.0 package. The crystal structure of AgS2O6CF3 was solved in Jana2006.15 Isotropic thermal ellipsoids were refined with the constraint of the same \( U_{iso} \) for each type of atom. \( U_{aniso} \) was introduced only for the silver atom.16 The constraint on the bond length was applied to the C–F bonds (1.32 Å, s.u. 0.008 Å) but not for the S–O bonds. Additional information concerning processing of powder diffraction data and structure solution and refinement is presented in the ESI‡ Vesta17 was used for structure visualization.

Thermal analysis
Thermal analysis was performed with a Netzsch STA 409 PG which permits performing simultaneous thermogravimetric (TG)-differential scanning calorimetry (DSC)-evolved gas analysis (EGA) measurements. Evolved gases were analyzed by a mass spectrometer (Netzsch Aëolos QMS 403 C). The spectrometer was connected to the furnace chamber with a quartz capillary heated to 200 °C. The samples were loaded into Al2O3 crucibles with a pin hole in the lid. The loading was conducted in the glovebox. The sample mass was 15.14 mg, the applied heating rate was 4 °C min\(^{-1}\). Argon (99.999%) at 40 ml min\(^{-1}\) flow was used as a purging gas.

Theoretical calculations
Periodic Density Functional Theory (DFT) calculations were performed to determine unit cell vectors, fractional atomic coordinates as well as lattice dynamics (to support assignment of vibrational spectra). See the ESI‡ for technical details.

Results and discussion
AgOTf precursor
AgOTf is an unusual solid Lewis acid, which found numerous uses in organic chemistry, mainly as a substrate for metathetic (ligand-exchange) reactions, or as a catalyst. Screening of the CCSD database shows that over 400 adducts of AgOTf with Lewis bases have been structurally-characterized, while the number of similar compounds for which crystal structures have not been determined must be much larger than that.18 The hexagonal room temperature form of AgOTf has been recently thoroughly characterized. Having in mind the rich reactivity of AgOTf towards Lewis bases it seems justified that its reactions towards Lewis acids were not reported until now.

Synthesis of AgS2O6CF3
The synthesis of the title compound was realized by mixing a nearly stoichiometric amount of SO3 and AgOTf in a closed FEP reactor. The stoichiometric ratio was between 1 : 1 and 1.1 : 1. The amount of SO3 used for each batch was around 15 mg. The mixture was left for 12–24 hours at room temperature. After that time no traces of SO3 (present initially in the form of long fibres) were observed and only a white fine powder was left. The reaction equation is:

\[
\text{AgSO3CF}_3 + \text{SO}_3 \rightarrow \text{AgS}_2\text{O}_6\text{CF}_3
\] (1)

Use of a slight excess of SO3 was to prevent the product from contamination with unreacted triflate; the excess (<1 mg) of SO3 may easily be sublimed off at room temperature. XRDP of the product confirms the absence of any crystalline impurities (ESI‡).

Crystal structure
AgS2O6CF3 crystallizes in a centrosymmetric monoclinic \( P2_1/c \) unit cell (Fig. 1, Table 1). Similarly to its triflate precursor, it forms a layered structure with CF3 groups sticking out of the sheets and separated from one another by the van der Waals gap. However, the Ag sublattice is no longer hexagonal and flat (like for AgOTf), but rather rectangular and puckered. The
...F–F interactions between the neighbouring [AgS₂O₆CF₃]ₙ layers are weak; nevertheless, only slight preferred orientation of the crystallites in the capillary is observed (the March–Dollase parameter is equal to 0.97 for the preferred orientation direction [010]).

There is one symmetry-independent AgS₂O₆CF₃ structural unit inside the unit cell. The Ag atom is coordinated by seven oxygen atoms with the Ag–O distances falling between 2.37(2) Å and 2.91(2) Å. The bond valence sum for Ag1 is equal to 0.99(3), so silver is neither under- nor over-bonded. Within the [AgS₂O₆CF₃]ₙ layers the neighbouring [AgO₇] polyhedra share edges and form zigzag Ag⋯Ag chains which are separated from each other by S₄O₆CF₃ anions. Similarly as in silver(i) pyrosulfate, all O atoms except the one which bridges S atoms bind to Ag.

The geometry of the [S₄O₆] fragment of the S₄O₆CF₃ anion is similar to that found in the related S₄O₆²⁻ moiety (Fig. 2). The BVS for the O4 atom is very close to 2, which suggests that its fractional coordinate is reliable. The SOS bridge of the S₄O₆CF₃ anion is asymmetric with S1–O4 and S2–O4 distances of 1.70(3) Å and 1.56(3) Å and the S1–O4–S2 angle equal to 125.2(15)° (Table 1). Analogous bond length values for the S₄O₆²⁻ anion are 1.67(2) Å and 1.54(2) Å. The asymmetry of the SOS bridge of the S₄O₆CF₃ anion is thus more pronounced than in the case of Ag₃S₄O₁₁, i.e. in the pyrotrilate anion one can distinguish the SO₄ group which is only weakly bound to the triflate anion. This is consistent with the ease of the thermal decomposition of AgS₂O₆CF₃ (see the section Thermal analysis) which proceeds via elimination of SO₃ at temperatures as low as 65 °C. The fact that the inverse reaction (i.e. formation of AgS₂O₆CF₃ via insertion of SO₃ between a triflate anion and an Ag(i) cation) is also facile and proceeds with ca. 100% yield at room temperature points to a predominantly ionic character of the Ag–O bonding in AgOTf, in agreement with the previous description of this compound.

The DFT calculations nicely confirm the crystal structure with the discrepancy between measured and calculated unit cell vectors not exceeding 1% (ESI†).

### Vibrational spectra

IR and Raman (R) spectra of AgS₂O₆CF₃ are presented in Fig. 3, and their assignment is given in Table 2. The spectra do not contain any bands typical of AgOTf or SO₃ substrates, which testifies that the sample did not decompose during the spectroscopic measurements (e.g., in the laser beam). As expected from the large size of the anion (which consists of

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**Table 1** Crystallographic data for AgS₂O₆CF₃. Bold values refer to the O4 atom, which is bridging between sulphur atoms. BVS stands for the bond valence sum.

<table>
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<tr>
<th>Space group</th>
<th>( P2_1/c )</th>
<th>( \rho' (\text{g cm}^{-3}) )</th>
<th>( V (\text{Å}^3) )</th>
<th>( a (\text{Å}) )</th>
<th>( b (\text{Å}) )</th>
<th>( c (\text{Å}) )</th>
<th>( \rho (\text{mm}^{-1}) )</th>
<th>( U_{iso} ) (%)</th>
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<td>2.59(2)</td>
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</table>

\[ \text{BVS} \]

For S–O4 bonds.

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**Fig. 1** Crystal structure of AgS₂O₆CF₃. Left: view of the whole unit cell with layers with CF₃ groups sticking out; right, top: view of the anion with captioned S and O atoms and bond lengths of the SOS bridge; right, bottom: coordination of the Ag atom. Atom sizes proportional to \( S \) and \( O \) atoms and bond lengths of the SOS bridge; right, bottom: coordination of the Ag atom.

**Fig. 2** Comparison of geometry of the SO₆⁻, S₄O₆²⁻ and S₄O₆CF₃ anions in their Ag(i) salts. Dotted line emphasizes weak bonding between the triflate anion and the SO₃ group. Atom sizes proportional to \( U_{iso} \). Distances given in Å. Uncertainties skipped for clarity.

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12 atoms), its low local symmetry (point group C1), and the presence of 4 formula units inside the unit cell, each type of vibrational spectrum consists of a large number of bands.

As expected, the IR spectrum of AgS2O6CF3 bears similarities to those of AgOTf, AgS2O6 and K5S2O6F. Therefore vibrational spectra of triflates, pyrosulfates and fluorodisulfates are useful for the assignment of bands. Due to overlap of stretching and deformation modes of OSO and FCF groups, which is frequently encountered in triflate derivatives, unambiguous identification of vibrations was possible with help from theoretical computations (ESI) and Table 2.

The highest frequency bands above 1370 cm\(^{-1}\) can be attributed to the antisymmetric S–O stretching modes of the oxygen atom (O5) which is only weakly bound to silver at 2.91(2) Å.\(^{21}\) Those between 1260 and 1330 cm\(^{-1}\) come from the antisymmetric S–O stretching modes of the SO\(_2\) moiety bound to the Ag(i) cation; an admixture of the antisymmetric C–F stretching is calculated for the 1267 cm\(^{-1}\) IR-active mode. Bands at 1130–1260 cm\(^{-1}\) are assigned to C–S stretching coupled with diverse C–F stretching modes. The bands in the 1040–1060 cm\(^{-1}\) originate from the symmetric S–O stretching of the SO\(_2\) moiety attached to Ag(i).

A broad intense band in the IR spectrum ranging from 800 to 900 cm\(^{-1}\) (peaking at 873 cm\(^{-1}\)) and the weak Raman band at 893 cm\(^{-1}\) emerge from the SOS stretching vibrations.\(^{22}\) Indeed, for related AgS2O6 or K5S2O6 the region where \(\nu\)SOS bands are present falls between 700 and 900 cm\(^{-1}\). Moreover, metal triflates do not exhibit any vibrational bands above 850 cm\(^{-1}\). Thus, if the new modes appear in this region upon formation of the \(\text{S}_2\text{O}_6\text{CF}_3^-\) anion, they are related to vibrations of the SOS bridge (which is absent for triflates). The DFT calculations confirm this assignment.

A sharp peak around 773 cm\(^{-1}\) appears in both IR and R spectra of AgS2O6CF3, similar to those observed in the IR or R spectra of AgOTf,\(^{23}\) Ag(OTf)\(_2\),\(^{24}\) Au(OTf)\(_2\)\(^{25}\) or Fe(OTf)\(_2\).\(^{26}\) Based on this similarity, and on the DFT calculations, this band can be assigned to the CF\(_3\) deformation (umbrella) vibrations combined with the S–C stretching. Analogous umbrella deformations of the bridging SO\(_3\) group (between the terminal SO\(_3\))

### Table 2

<table>
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<th>(\text{AgS}_2\text{O}_6\text{CF}_3)</th>
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<th>DFT</th>
<th>Assignment</th>
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group with the CF$_3$ moiety) appear in the 630–660 cm$^{-1}$ in the IR spectra. Similar bands originating from δ(OSO) deformations are detected in spectra of KS$_2$O$_6$F above 600 cm$^{-1}$.

The bands corresponding to other FCF deformation modes, as well as complex deformation modes of the entire S$_2$O$_6$CF$_3$ anion, fall in the region of 400–600 cm$^{-1}$. Indeed, the δ(CF$_3$) bands are present in spectra of AgOTf below 600 cm$^{-1}$. According to the DFT calculations all bands appearing in the 400–600 cm$^{-1}$ region can be assigned to diverse FCF deformation modes admixed partially with the OSO deformations.

The spectral region between 200 and 400 cm$^{-1}$ is dominated by modes involving appreciable contribution from OAgO stretching and deformation, according to the phonon calculations. This is similar to the case of AgOTf. However, the shortest Ag–O bond of AgS$_2$O$_6$CF$_3$ (Table 1) is over 0.1 Å shorter than those of AgOTf (2.485(5) Å), hence the ν(Ag–O) and δ(Ago) bands reach out to higher wavenumbers for AgS$_2$O$_6$CF$_3$ (371 cm$^{-1}$) than for AgOTf (339 cm$^{-1}$). On the other hand, some of the δ(Ago) bands extend down to 50 cm$^{-1}$. Since these normal modes involve motion of the heavy Ag cation, they benefit from large polarizabilities changes of the AgO moiety and accordingly many of the bands in the 50–400 cm$^{-1}$ region have large intensities in the Raman spectrum. Deformations of the SOS bridge fall in a similar spectral range yielding IR bands at 174, 258 and 397 cm$^{-1}$.

The oscillations reminiscent of the hindered rotations of the CF$_3$ units yield two broad bands in the IR spectrum at 90 cm$^{-1}$ and 150 cm$^{-1}$. By necessity, these normal modes acquire some character from the AgO stretching and OAgO deformation. The corresponding wavenumbers for AgOTf are larger, 182–190 cm$^{-1}$. This comes from the fact that the more acidic S$_2$O$_6$CF$_3$ anion is less strongly bound to the Ag$^+$ cation as compared to the triflate anion for AgOTf (cf. the next section on Thermal analysis). For comparison, the hindered rotations of the CF$_3$ units fall, according to the DFT calculations, at 89 and 60–61 cm$^{-1}$ (they are not detected in the spectra due to low intensity) thus at somewhat higher wavenumbers than for AgOTf (43–52 cm$^{-1}$). This indicates that the energy barriers for free rotation of the CF$_3$ units are higher in the former case.

Finally, the low energy Ag–O modes, lattice modes (such as mutual motions of the entire cationic and anionic sublattices against each other), and various low-frequency librations are found at wavenumbers smaller than 55 cm$^{-1}$ and they appear as medium-intensity bands in the Raman spectrum. Energies of these lattice oscillations herald an enhanced room-temperature ionic conductivity in the Ag$^+$ compound studied; this supposition is now being tested in our laboratory for AgS$_2$O$_6$CF$_3$ but also for AgOTf and AgSO$_4$F with the anomalously low melting point of 156 °C for the last compound.

**Thermal analysis**

The TG and DSC curves for thermal decomposition of AgS$_2$O$_6$CF$_3$ are presented in Fig. 4.

Thermal decomposition of AgS$_2$O$_6$CF$_3$ commences at 65 °C. Mass spectra show that only SO$_3$ is evolved in the process. The shape of TG and DSC curves suggests that the process is at least a three-step one. The first mass loss (65–115 °C) is significantly endothermic, with the DSC peak at 100 °C and the integrated heat of decomposition of 100 kJ mol$^{-1}$. This value has been derived for the temperature region 65–115 °C while taking into account the degree of thermal decomposition. The heat of decomposition is of course larger than the heat of sublimation of SO$_3$ alone (56.2–68.1 kJ mol$^{-1}$ depending on the polymorphic form). Interestingly, the “thermodynamic value” of thermal decomposition temperature of AgS$_2$O$_6$CF$_3$ based on its heat of decomposition and absolute entropy of gaseous SO$_3$ (256.77 J mol$^{-1}$ K$^{-1}$) equals 116 °C, which is very close to the observed temperature at the end of the first step of decomposition. The rather small heat of decomposition, together with the rather low value of the temperature of thermal decomposition, reconfirms that SO$_3$ is bound very weakly to AgOTF.

Interestingly, heat effects related to subsequent mass losses are less pronounced. However, our attempts to obtain intermediates of the kind Ag[S$_2$O$_4$]SO$_3$CF$_3$ (0 < x < 1) via partial (temperature-controlled) thermal decomposition of AgS$_2$O$_6$CF$_3$ resulted only in the mixtures of AgOTf and AgS$_2$O$_6$CF$_3$ as judged from XRDPs. Therefore the complexity of the TG/DSC profiles can be attributed to inhomogeneity of the sample and to surface effects. Evolution of gaseous SO$_3$ from the grain surface is likely easier and faster than its diffusion from the bulk of crystallitles.

The mass loss is completed at 290 °C, slightly above the endothermic phase transition of AgOTf which is observed at 286 °C. At 290 °C the observed mass loss is 25% of the initial sample mass. The data match well with the reaction equation:

$$\text{AgS}_2\text{O}_6\text{CF}_3 \xrightarrow{65 \degree C} \text{AgS}_2\text{O}_4\text{CF}_3 + \text{SO}_3 \uparrow \text{ (theor. - 24.3%)}$$ (2)

The fact that the decomposition starts at 65 °C is consistent with the observed instability of AgS$_2$O$_6$CF$_3$ during hand grinding in an agate mortar, and it is a direct manifestation of weak bonding of SO$_3$ to the triflate anion. In the case of pyrosulfates of lower Lewis acidity the thermal decomposition commences at higher temperatures (170 °C for Ag$_2$S$_2$O$_6$, and even 380 °C...
for Na$_2$S$_2$O$_3$.$^{26}$ However, the closest relatives of trifluoromethylsulfonyl sulfates – the fluorodisulfates evolve SO$_3$ under similarly mild temperature conditions ($<$100 °C for Na$_2$S$_2$O$_3$F, K$_2$S$_2$O$_3$F). The ease of thermal decomposition of trifluoromethylsulfonylsulfates could be of practical use, since these compounds could be treated as solid sources of – otherwise volatile and very corrosive – SO$_3$.

**Stability of other metal pyrotriflates**

Successful preparation of AgS$_2$O$_3$CF$_3$ prompted us to investigate possible formation of its analogues, notably K(i), Ag(i) and Cu(ii) derivatives.

K(i) trifluoromethylsulfonylsulfate forms easily at room temperature via a reaction similar to that used for the preparation of Ag(i) salts. Indexation of the XRD pattern of the sample (loaded without grinding of the powder) gave the monoclinic $P2_1/c$ cell with unit cell vectors: $a = 7.2014$ Å, $b = 25.6418$ Å, $c = 10.5941$ Å and $\beta = 124.879^\circ$. The volume of $1604$ Å$^3$ corresponds well to the expected volume of 8 structural units of K(i)S$_2$O$_3$CF$_3$ (as based on the volume of KSO$_3$ and the observed difference of structural unit volume between sulfates and pyrosulfates). The unit cell indexed is also similar to the unit cell of AgS$_2$O$_3$CF$_3$ (shorter cell dimensions are now larger, as expected from cationic radii: K(i) > Ag(i)), which suggests isomorphism of the two compounds.

Thermal decomposition of K(i)S$_2$O$_3$CF$_3$ begins at 105 °C and ends at 225 °C. The observed mass loss (37%) is larger than expected based on the evolution of SO$_3$ (30%), which suggests a complex scenario for thermal decomposition. Indeed, an unidentified phase(s) is detected in the XRD pattern of the sample partially decomposed during manual grinding. A relative lack of thermal stability of K(i)S$_2$O$_3$CF$_3$ suggests that SO$_3$ is bound rather weakly to K(i)OTf and that syntheses of metal trifluoromethylsulfonylsulfates from even more Lewis-acidic triflate precursors may be problematic.

Indeed, all attempts to obtain Ag(i)(S$_2$O$_3$CF$_3$)$_2$ and Cu(ii)-(S$_2$O$_3$CF$_3$)$_2$ at room temperature have failed. This is probably not only due to kinetic reasons (the metal–oxygen bonds in the corresponding triflates are rather short, strong and covalent,$^{1,2,27}$ thus hampering the SO$_3$ insertion between metal and oxygen atoms) but also due to unfavourable thermodynamics.

**Conclusions**

The paper presents a convenient synthetic route to two novel salts: trifluoromethylsulfonylsulfates of Ag(i) and K(i). These salts can be obtained via direct reaction of the corresponding metal triflates and SO$_3$ at room temperature. Both compounds are thermally unstable above 65 °C or 105 °C, respectively. SO$_3$ is rather weakly bound in these materials, as evidenced also from some features in the vibrational spectra of AgS$_2$O$_3$CF$_3$ compared to those of the related AgOTf Lewis base. AgS$_2$O$_3$CF$_3$ has been characterized structurally. Its crystal structure is monoclinic and it exhibits well pronounced two-dimensional character with CF$_3$ groups separated by the van der Waals gap. K$_2$S$_2$O$_3$CF$_3$ is isostructural with the silver(i) salt. Attempts to obtain more acidic Ag(i)(S$_2$O$_3$CF$_3$)$_2$ and Cu(ii)-(S$_2$O$_3$CF$_3$)$_2$ have failed, likely due to both kinetic and thermodynamic reasons.

Trifluoromethylsulfonylsulfates contain the S$_2$O$_3$CF$_3^−$ polyanion and they are related to fluorodisulfates and disulfates. It is conceivable that many more trifluoromethylsulfonylsulfates – in particular Group 1 and Group 2 metals – could be prepared and characterized. It is also of interest whether systems could be prepared which contain higher (SO$_3$)$_2$CF$_3^−$ polyanions ($n > 2$).

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**Notes and references**

4. Since there are several different borderlines in the literature for labelling of anions as “weakly coordinating”, in this
work we reserve this term for anions forming Brønsted acids which are stronger than H$_2$SO$_4$.


16 $U_{iso}$ parameters for atoms of the CF$_3$ group are much larger than those for other atoms. It is in accordance with the fact that the group is terminal and its vibrations are less restrained than for other atoms. Obtaining single crystals would enable more precise determination of thermal ellipsoids but due to technical difficulties, powder XRDP currently remains the only convenient method for structure determination.


18 P. J. Leszczyński, A. Budzianowski and W. Grochala, database search was conducted in spring 2012.


21 The discussion should also include the S–O distances, but due to small differences in their lengths and large uncertainties, only Ag–O distances will be considered here.

22 In the spectra of KS$_2$O$_6$F the $\nu$(SOS) vibrations were tentatively assigned to the bands at wavenumbers as low as 700 cm$^{-1}$ and the bands at ca. 870 cm$^{-1}$ were assigned to the $\nu$(S–F) modes. The assignment for this compound should, we think, be reconsidered.


25 It is provisionally assumed, despite the pressure of SO$_3$ over the sample being not equal to 1 bar, that the conditions of thermodynamic equilibrium are fulfilled; hence: $\Delta H = T_{dec} \Delta S$. Here, $\Delta H$ has been approximated by the measured heat of the decomposition reaction, while $\Delta S$ by the absolute entropy of the only gaseous product, SO$_3$.
