

## Pentafluorooxosulfate

A Versatile Silver(I) Pentafluorooxosulfate Reagent for the Synthesis of OSF<sub>5</sub> Compounds

Axel Haupt,\* Daniel Duvinage, Enno Lork, Maksym Ponomarenko, and Gerd-Volker Rösenthaller

**Abstract:** Herein, we report the preparation of silver(I) pentafluorooxosulfate from commercially available AgF and OSF<sub>4</sub>. The compound is surprisingly stable in a MeCN solution. Apart from that, AgOSF<sub>5</sub> has been stabilised by the addition of 2,2'-bipyridine ligands. Starting from solutions of the unstabilised silver(I) salt, OSF<sub>5</sub> complexes with Ni<sup>II</sup>, Cu<sup>I</sup>, and Cu<sup>II</sup>-centres have been obtained. In addition, AgOSF<sub>5</sub> has proven to be generally capable of mediating the transfer of OSF<sub>5</sub> groups to arylene moieties, thus furnishing a new and safe method for the preparation of OSF<sub>5</sub>-substituted arenes. X-ray crystal structure analysis of selected transition-metal OSF<sub>5</sub> compounds have revealed distorted octahedral [OSF<sub>5</sub>]<sup>-</sup> anions which are extensively stabilised by hydrogen bonding.

The existence of pentafluorooxochalcogenate salts [OEF<sub>5</sub>]<sup>-</sup> (E = S, Se, Te) has been known for many years. However, the stability and thus the accessibility of these species differ.<sup>[1]</sup> The most investigated element in this series is tellurium, since the corresponding acid HOTeF<sub>5</sub> and its salts are readily available.<sup>[2]</sup> There are numerous publications on compounds containing the OTeF<sub>5</sub> substituent, for example B(OTeF<sub>5</sub>)<sub>3</sub> or Xe(OTeF<sub>5</sub>)<sub>2</sub>, which are used for the synthesis of further OTeF<sub>5</sub> derivatives.<sup>[3]</sup> Other examples include tetra- and hexavalent xenon compounds, such as Xe(OTeF<sub>5</sub>)<sub>4</sub>, which is so far the only stable xenon(IV) species besides XeF<sub>4</sub>.<sup>[4]</sup> More recently, derivatives based on Al and Ga have been published.<sup>[5]</sup> Selenium analogues containing the [OSeF<sub>5</sub>]<sup>-</sup> anion are slightly less stable, but can still be prepared from the free acid HOSeF<sub>5</sub>.<sup>[6]</sup> This is not the case for HOSF<sub>5</sub> which decomposes above -60 °C.<sup>[7]</sup> However, salts containing the

[OSF<sub>5</sub>]<sup>-</sup> anion are accessible from gaseous OSF<sub>4</sub> and ionic fluoride donors such as KF, CsF, or [NMe<sub>4</sub>]F, but not with LiF or NaF.<sup>[1,8,9]</sup> Fluorides with larger cations, such as [(Me<sub>2</sub>N)<sub>3</sub>S]<sup>+</sup>[SiMe<sub>3</sub>F<sub>2</sub>]<sup>-</sup> (TASF), have also been known to produce stable OSF<sub>5</sub> salts.<sup>[10]</sup> To the best of our knowledge, no transition-metal compounds containing [OSF<sub>5</sub>]<sup>-</sup> anions have been unambiguously described so far. However, a species Ag<sup>+</sup>OSF<sub>5</sub><sup>-</sup> has been proposed as intermediate in the fluorination of SOF<sub>4</sub>, giving rise to SF<sub>5</sub>OF or the peroxide (SF<sub>5</sub>O)<sub>2</sub>.<sup>[11]</sup> Structural data of the pentafluorooxosulfate anion are only published for the TAS salt [(Me<sub>2</sub>N)<sub>3</sub>S]<sup>+</sup>[OSF<sub>5</sub>]<sup>-</sup>, showing significant disorder.<sup>[10]</sup> Here we present syntheses of novel transition-metal salts including a crystallographic description of the [OSF<sub>5</sub>]<sup>-</sup> anion.

In terms of organic OEF<sub>5</sub> compounds, the situation is inverted, as a number of R-OSF<sub>5</sub> derivatives are known, whereas respective Se and Te analogues are only scarcely described.<sup>[9,12]</sup> Virtually all known OSF<sub>5</sub> arenes have been prepared in radical reactions, starting from the corresponding arene and SF<sub>5</sub>OOSF<sub>5</sub>.<sup>[13]</sup> It can be expected that the substitution with an OSF<sub>5</sub> group gives rise to compounds with interesting molecular properties, as it is well known for other fluorinated groups like -CF<sub>3</sub>, -OCF<sub>3</sub>, -SCF<sub>3</sub> or -SF<sub>5</sub>, which are typically found in pharmaceutical and agrochemical products.<sup>[14]</sup> For this purpose, a new synthetic approach towards aryl-OSF<sub>5</sub> compounds via aryne intermediates is introduced herein.

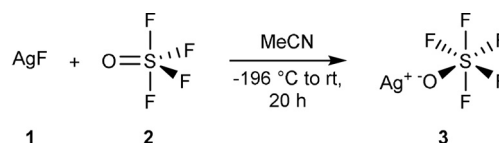
Isolated, non-stabilised transition metal salts M(OSF<sub>5</sub>)<sub>n</sub> are unknown, which has been rationalised by a readily occurring decomposition of the anion into F<sup>-</sup> and OSF<sub>4</sub>. However, the reaction of AgF **1** with OSF<sub>4</sub> **2** in MeCN quantitatively yields colourless solutions of AgOSF<sub>5</sub> **3** (Scheme 1). The anion has been unambiguously identified by <sup>19</sup>F-NMR spectroscopy, showing the expected AB<sub>4</sub>-type spectrum. Remarkably, there is no free OSF<sub>4</sub> left in the reaction mixture. Solutions of AgOSF<sub>5</sub> in MeCN are stable at room temperature and can be stored in standard laboratory glassware. A significant decomposition of the [OSF<sub>5</sub>]<sup>-</sup> anion is not observed, even after weeks.<sup>[15]</sup> Furthermore, the compound appears to be stable against light. However, attempts to isolate **3** by evaporation of the solvent have not been

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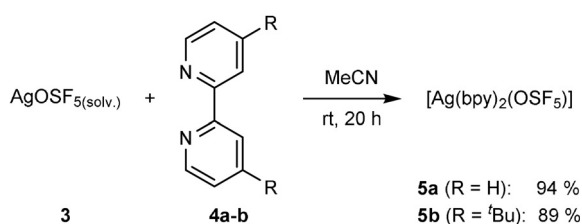
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Scheme 1. Preparation of silver(I) pentafluorooxosulfate **3**.

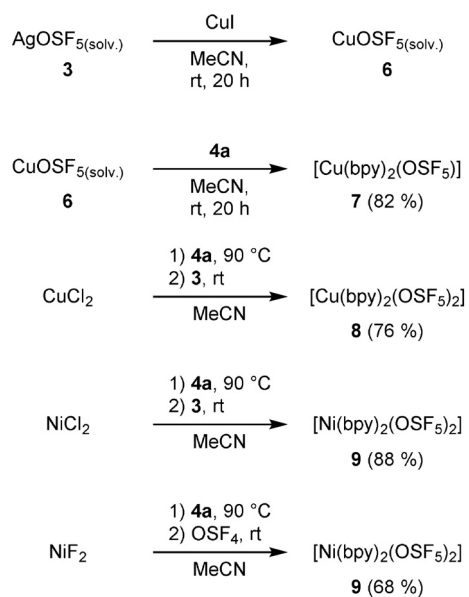
successful and resulted in decomposition. Cooling of MeCN solutions to  $-40^{\circ}\text{C}$  gives rise to colourless crystals, which melt below room temperature. Initial investigation of the crystals by X-ray crystallography did not furnish a suitable data set for a reliable structural description. Nevertheless, the silver cation has been proven to be solvated by MeCN, forming tetrahedral  $[\text{Ag}(\text{MeCN})_4]^+$  units, as it was expected. At this stage, this finding somewhat explains the stability of  $\text{AgOSF}_5$  in MeCN solutions and underlines the fact that non-stabilised transition-metal salts  $\text{M}(\text{OSF}_5)_n$  remain unknown.

Instead of rather labile MeCN, other N-donor ligands, such as 2,2'-bipyridines **4a,b**, efficiently stabilise  $\text{AgOSF}_5$ , even in the solid state. This allowed the preparation and isolation of two  $\text{AgOSF}_5$  complexes **5a,b** with differently substituted ligands (Scheme 2). They are both pale-yellow to ochre solids, which are stable against decomposition and can be indefinitely stored under inert conditions.



**Scheme 2.** Stabilisation of  $\text{AgOSF}_5$  by 2,2'-bipyridine ligands.

With the silver compounds **3** and **5** in hand, we explored the preparation of transition-metal derivatives by simple metathesis reactions with  $\text{MX}_n$  ( $\text{X} = \text{Cl}, \text{I}$ ), making use of the poor solubility of  $\text{AgX}$ . In a first approach, a MeCN solution of  $\text{AgOSF}_5$  **3** was treated with  $\text{CuI}$ , which quantitatively gave  $\text{CuOSF}_5$  **6** (Scheme 3). Similarly to the parent silver(I) compound, the copper(I) salt is stable in solution but

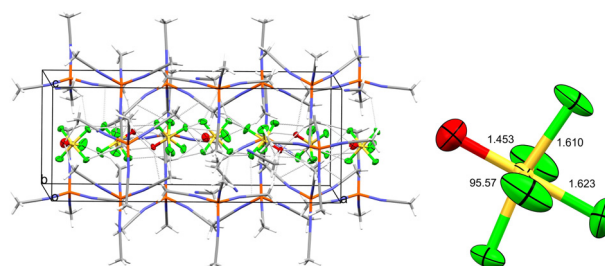


**Scheme 3.** Salt metathesis of transition-metal halides using  $\text{AgOSF}_5$  **3** and direct synthesis of nickel(II) complex **9**.

decomposes upon removal of the solvent. Treatment of a solution of  $\text{CuOSF}_5$  **6** with bipyridine **4a** and evaporation of the solvent gave rise to a stable, deep-red solid  $[\text{Cu}(\text{bpy})_2(\text{OSF}_5)]$  **7** (Scheme 3), which has been identified by NMR spectroscopy and mass spectrometry. The metathetical preparation of  $\text{OSF}_5$  compounds could be extended to the divalent metal chlorides  $\text{CuCl}_2$  and  $\text{NiCl}_2$ , however, the latter two had to be converted to their bpy complexes  $\text{M}(\text{bpy})_2\text{Cl}_2$  ( $\text{M} = \text{Cu}, \text{Ni}$ ) prior to the treatment with  $\text{AgOSF}_5$  (Scheme 3). The copper(II) complex  $[\text{Cu}(\text{bpy})_2(\text{OSF}_5)_2]$  **8** is a light-blue solid, whereas the nickel(II) derivative  $[\text{Ni}(\text{bpy})_2(\text{OSF}_5)_2]$  **9** has a salmon-pink colour in the solid state. The nickel(II) complex **9** has also been directly prepared from  $\text{NiF}_2$ , 2,2'-bipyridine, and  $\text{OSF}_4$ , thus avoiding the use of rather costly  $\text{AgF}$  and the generation of silver(I) halide waste (Scheme 3).

Interestingly, the  $^{19}\text{F}$  NMR spectra of all transition-metal compounds are very similar, revealing the pentet ( $\delta = 134\text{--}136$  ppm) and the dublet signals ( $\delta = 91\text{--}92$  ppm) in narrow chemical-shift segments.<sup>[15]</sup> Thus, it appears that the  $[\text{OSF}_5]^-$  anions dissociate from the metal centres in MeCN solution. Further evidence can be found in the NMR spectra of the  $\text{Cu}^{\text{II}}$  derivative **8**, where  $^1\text{H}$  and  $^{13}\text{C}$  signals cannot be observed due to paramagnetism of the  $d^9$  metal centre. In contrast, the corresponding  $^{19}\text{F}$  spectrum is only slightly broadened, whereas chemical shift and multiplicity of the signals remain unaffected. Overall, these findings clearly indicate that the  $[\text{OSF}_5]^-$  anion acts as a weakly coordinated ligand, which readily dissociates in ion-separating solvents like MeCN.

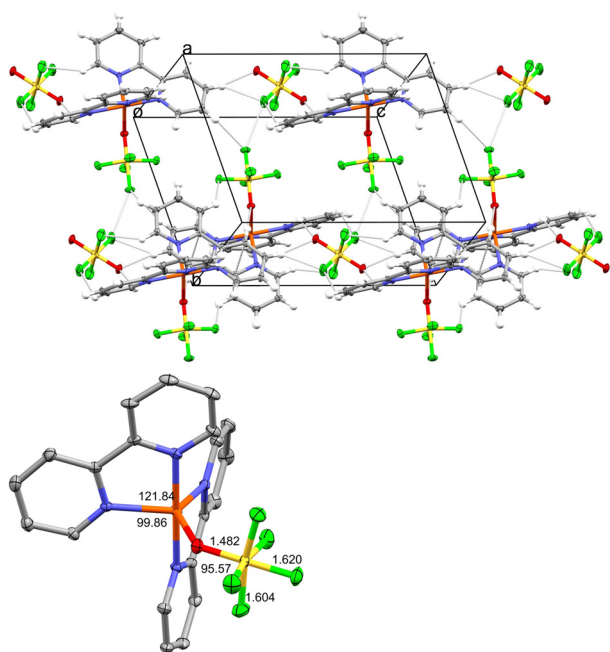
We were able to investigate the solid-state structures of compounds **6** and **8** by single-crystal X-ray analysis.<sup>[16]</sup> Cooling acetonitrile solutions of **6** to  $-40^{\circ}\text{C}$  yields colourless crystals, which have been shown to contain both solvated  $[\text{Cu}(\text{MeCN})_4]^+$  cations and distorted octahedral  $[\text{OSF}_5]^-$  anions (Figure 1). Additionally, another acetonitrile molecule is incorporated in the solid-state structure, where the packing is described by alternating areas of layers of cations and anions. The sheets of  $[\text{OSF}_5]^-$  anions are parallel to the *ab*-plane of the orthorhombic unit cell. Surprisingly, the structure of the anion does not show significant disorder, so that the oxygen atom can be unambiguously assigned to one of the axial positions, showing a decreased distance to the sulfur centre (1.45 Å). In contrast, the distance to the fluorine



**Figure 1.** Left: extract of the solid-state packing of  $[\text{Cu}(\text{MeCN})_4]^+[\text{OSF}_5]^- \cdots \text{MeCN}$  **6**, revealing layers of  $[\text{OSF}_5]^-$  anions, which are stabilised by numerous H-F and H-O contacts. For clarification, cations and free MeCN ligands with short contacts to the anions are shown exclusively using the stick model. Right: distorted octahedral  $[\text{OSF}_5]^-$  anion with selected bond lengths (in Å) and bonding angles. Ellipsoids are at a probability level of 50%.

substituent occupying the other apical position is very slightly elongated (1.62 Å) compared to the equatorial S–F bond lengths (1.61 Å). As expected, the sulfur atom is slightly shifted out of the equatorial plane towards the oxygen substituent, so that the angle O–S–F<sub>eq.</sub> amounts to 95.6°. In general, the solid-state structure of [Cu(MeCN)<sub>4</sub>][OSF<sub>5</sub>]<sub>2</sub>·MeCN shows a large number of H–F and H–O contacts between the anion and either free solvent molecules or MeCN ligands of the cation (Figure 1). Apparently, this leads to a significant stabilisation of the compound. Probably, a similar behaviour causes the stability of the Ag<sup>I</sup> derivative **3**.

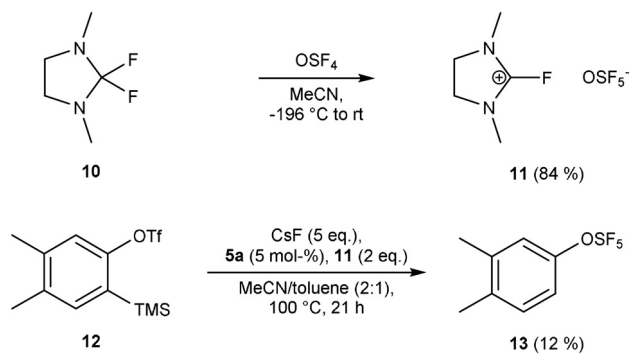
Single-crystal X-ray analysis of the copper(II) salt **8** revealed a five-coordinate structure (Figure 2), thus exhibiting a rather rare geometry for a Cu<sup>II</sup> compound. Since pentacoordinated metal centres typically adopt a geometry which lies in between the two extremes of a square pyramid and a trigonal bipyramid, geometric descriptors have been introduced to allow a better structural characterisation. For example, the angular structural parameter  $\tau$  is calculated based on the two largest angles  $\alpha$  and  $\beta$  by the formula  $\tau = (\beta - \alpha)/60$  and ranges from 0 (ideal square pyramid) to 1 (ideal trigonal bipyramid).<sup>[17]</sup> In the present case,  $\beta$  and  $\alpha$  amount to 178.85 and 138.29°, respectively, so that  $\tau$  has a value of 0.68. As a result, the structure of **8** can be clearly considered as distorted trigonal bipyramidal. One of the [OSF<sub>5</sub>]<sup>−</sup> anions is directly attached to an equatorial position of the metal centre via its oxygen atom. The remaining four positions of the coordination polyhedron are occupied by nitrogen atoms of the two bipyridine ligands. The bonding angles at the copper centre are significantly distorted, which is especially pro-



**Figure 2.** Top: extract of the solid-state packing of [Cu(bpy)<sub>2</sub>(OSF<sub>5</sub>)]<sup>+</sup>[OSF<sub>5</sub>]<sup>−</sup>·0.5 MeCN **8**, revealing the two different types of [OSF<sub>5</sub>]<sup>−</sup> anions. Bottom: distorted trigonal bipyramidal [Cu(bpy)<sub>2</sub>(OSF<sub>5</sub>)]<sup>+</sup> cation with selected bond lengths (in Å) and bonding angles. Hydrogen atoms are omitted for clarity; ellipsoids are at a probability level of 50%.

nounced for the equatorial substituents. The only rather regular value is observed for the N–Cu–N angle, which amounts to 121.8° and therefore only slightly deviates from ideal 120°. In contrast, the values for the N–Cu–O angles are found to be about 100 and 138°, respectively, where the larger angle arises from the steric congestion induced by the SF<sub>5</sub> group. Similarly to the solvated [OSF<sub>5</sub>]<sup>−</sup> anion in **6** (cf. Figure 1), the copper-bonded anion in **8** is distorted from ideal octahedral geometry, however, it seems to be only slightly stabilised by short contacts. Prominently, one can observe H–F interactions between the fluorinated anion and the ligands, in addition, there are also O–H and even F–F contacts. The latter are formed between the two types of [OSF<sub>5</sub>]<sup>−</sup> anions. Interestingly, the second type of anion is disordered and does not coordinate to any specific site, but occupies the cavities that are formed by packing of the [Cu(bpy)<sub>2</sub>(OSF<sub>5</sub>)]<sup>+</sup> units (Figure 2). In contrast to the Cu-bonded [OSF<sub>5</sub>]<sup>−</sup> anion, the “free” [OSF<sub>5</sub>]<sup>−</sup> exhibits a large number of H–F short contacts for stabilisation, as well as a few O–H and F–F interactions. Overall, the 3D packing structure of **8** can be summarised as an alternating arrangement of fluorinated and non-fluorinated parts, which are interconnected by H–F bridges. Therein, the layers are parallel to the *c*-axis.

Aromatic OSF<sub>5</sub> compounds are known to be quite robust and tolerant against many reagents and reaction conditions, except a strongly reductive environment.<sup>[13,18]</sup> Thus, they may not only remain an exotic footnote, but could potentially become interesting for applications, for example, in pharmaceuticals or agrochemicals. Of course, this requires convenient and reliable synthetic approaches, which have been limited to date. Some time ago, a long-chained aliphatic OSF<sub>5</sub> derivative was prepared by a S<sub>N</sub>2-type reaction.<sup>[12b]</sup> On the other hand, treatment of arynes with perfluorinated alkoxides, for example, CF<sub>3</sub>O<sup>−</sup>, has been shown to yield aryl trifluoromethyl ethers.<sup>[19]</sup> Therefore, we have tried to combine the latter two approaches for the synthesis of SF<sub>5</sub>O-substituted arenes. A few representative benzyne intermediates have been generated in situ following standard protocols and were reacted with different salts containing the [OSF<sub>5</sub>]<sup>−</sup> anion, such as **11**, which has been prepared from 2,2-difluoro-1,3-dimethylimidazolidine (DFI) **10** and OSF<sub>4</sub> (Scheme 4).<sup>[12b,20]</sup> However, probably due to the very poor nucleophilicity of the pentafluorooxosulfate anion, a nucleophilic attack on the aryne could not be observed.



**Scheme 4.** Synthesis of the stable OSF<sub>5</sub><sup>−</sup> salt **11** and preparation of OSF<sub>5</sub>-substituted dimethylbenzene **13**.

In the literature, one can find an example for an Ag-mediated introduction of -F, -CF<sub>3</sub> and -SCF<sub>3</sub> functions into aryne intermediates, which has been proposed to proceed via the formation of a cationic silver(I) complex.<sup>[21]</sup> Thus, we reacted 4,5-dimethyl-2-(trimethylsilyl)phenyl triflate **12**, the precursor to symmetric 4,5-dimethylbenzynes, with the stoichiometric [OSF<sub>5</sub>]<sup>-</sup> source **11** in presence of catalytic amounts of silver(I) complex **5a** and CsF (5 equiv) at 100 °C in a 2:1-mixture (v/v) of MeCN and toluene (Scheme 4). According to the <sup>19</sup>F NMR of the crude reaction mixture, the aforementioned conditions allow to furnish the SF<sub>5</sub>O-substituted *o*-dimethylbenzene **13** as main product. The compound is isolated and purified by column chromatography using *n*-pentane as eluent. It has been unambiguously characterised by NMR spectroscopy, revealing the expected AB<sub>4</sub> pattern in the <sup>19</sup>F NMR. However, the small yield of SF<sub>5</sub>O product **13** indicates that side-reactions are very likely to take place. For example, we identified two species in the <sup>19</sup>F NMR spectra of the crude mixtures, when the reaction was carried out in pure MeCN. Under these strongly polar conditions, side-products are formed by the addition of F<sup>-</sup> to the aryne and by a thia-Fries rearrangement of an intermediate anionic species, respectively, thus giving rise to an aryl fluoride and an *ortho*-trifluoromethylsulfonyl phenolate. The thia-Fries rearrangement is well known for aryl triflates and can be suppressed if reaction conditions are used which do not favour the stabilisation of anionic intermediates.<sup>[22]</sup> In the same way, the formation of aryl fluorides is disfavoured if the fluoride salt is less soluble in the reaction mixture. Thus, the use of a less polar solvent as well as the adjustment of the concentration of the reaction mixture have resulted in a significant but not complete suppression of these side-products. Apart from the formation of fluorine-containing species, it appears that there are probably more important side-reactions, which cannot be monitored by <sup>19</sup>F NMR spectroscopy, e.g., oligomerisation of the aryne intermediate. Therefore, further optimisations need to be conducted to improve the yields and selectivities of this synthetic approach. Nevertheless, the reaction of aryne substrates with [OSF<sub>5</sub>]<sup>-</sup> in presence of the silver catalyst **5a** is a starting point for a new and promising pathway towards aromatic pentafluorosulfanyloxy compounds. We are convinced that based on our findings reliable synthetic routes towards ArOSF<sub>5</sub> can be developed. Therefore, we will continue the optimisation of the synthetic protocol and also extend our efforts to mechanistic experiments.

In conclusion, we have presented novel pentafluoroosulfate compounds, which are based on the simple preparation of AgOSF<sub>5</sub> from AgF and OSF<sub>4</sub>. AgOSF<sub>5</sub> is remarkably resilient in acetonitrile and can be isolated upon treatment with 2,2'-bipyridine ligands. Salt metathesis of the silver salt with copper(I), copper(II), and nickel(II) halides gives rise to the corresponding transition-metal compounds. X-ray crystal structure analysis of the MeCN solvate of CuOSF<sub>5</sub> revealed a large number of H-F and H-O contacts between the distorted octahedral [OSF<sub>5</sub>]<sup>-</sup> anion and the solvent molecules. This finding gives a rough explanation for the stability of the copper(I) compound, which probably also holds for solvated AgOSF<sub>5</sub>. Moreover, the solid-state structure of a bpy-stabi-

lised Cu<sup>I</sup>-salt has been examined, revealing two different sorts of anions. One of them is coordinated to the distorted trigonal-bipyramidal copper centre, the other one is disordered and exhibits a large number of H-F and H-O contacts.

In addition, the stabilised silver(I) compound [Ag(bpy)<sub>2</sub>(OSF<sub>5</sub>)] has proven to be generally useful for the preparation of OSF<sub>5</sub>-substituted arenes via aryne intermediates. However, the reaction conditions apparently do not allow a clean product formation, so that the yield of the representative SF<sub>5</sub>O-substituted arene is so far rather poor. In following studies, we will work on the examination of improved synthetic pathways towards aromatic OSF<sub>5</sub> compounds.

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### Conflict of Interest

The authors declare no conflict of interest.

**Keywords:** arynes · chalcogens · fluorine · silver · synthetic methods

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- [15] For copies of NMR spectra, please see the Supporting Information.
- [16] Crystallographic data: **6** (CCDC 2088423), colourless block,  $0.2 \times 0.07 \times 0.05 \text{ mm}^3$ , orthorhombic,  $P2_12_12_1$ ,  $a = 21.7479(9)$ ,  $b = 27.5479(11)$ ,  $c = 8.5241(3) \text{ \AA}$ ,  $V = 5106.9(3) \text{ \AA}^3$ ,  $\rho_{\text{calcd}} = 1.607$ ,  $Z = 12$ , Mo- $K_{\alpha}$  radiation,  $\lambda = 0.71073 \text{ \AA}$ ,  $T = 100.0 \text{ K}$ ,  $\mu = 1.463 \text{ mm}^{-1}$ ,  $\theta_{\text{max}} = 36.23^\circ$ , 479897 measured reflexions, 20842 crystallographically independent reflexions,  $R_{\text{int}} = 0.0427$ , 638 parameters, GOOF = 1.090,  $R1 = 0.0280$ ,  $wR2 = 0.0722$ , refined as an inversion twin; **8** (CCDC 2082673), colourless block,  $0.23 \times 0.17 \times 0.13 \text{ mm}^3$ , triclinic,  $P-1$ ,  $a = 10.4126(5)$ ,  $b = 10.4331(5)$ ,  $c = 13.2642(6) \text{ \AA}$ ,  $\alpha = 70.3560(10)$ ,  $\beta = 70.5080(10)$ ,  $\gamma = 82.646(2)^\circ$ ,  $V = 1279.12(10) \text{ \AA}^3$ ,  $\rho_{\text{calcd}} = 1.825$ ,  $Z = 2$ , Mo- $K_{\alpha}$  radiation,  $\lambda = 0.71073 \text{ \AA}$ ,  $T = 100(2) \text{ K}$ ,  $\mu = 1.124 \text{ mm}^{-1}$ ,  $\theta_{\text{max}} = 33.212^\circ$ , 97401 measured reflexions, 9825 crystallographically independent reflexions,  $R_{\text{int}} = 0.0351$ , 402 parameters, GOOF = 1.132,  $R1 = 0.0392$ ,  $wR2 = 0.0890$ , refined as a 2-component twin. Structure solution by SHELXT<sup>[23]</sup> and full-matrix least square refinement using SHELXL.<sup>[24]</sup> Deposition numbers 2088423 (for **6**) and 2082673 (for **8**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.
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