A Versatile Silver(I) Pentafluorooxosulfate Reagent for the Synthesis of OSF₅ Compounds

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Abstract: Herein, we report the preparation of silver(I) pentafluorooxosulfate from commercially available AgF and OSF₅. The compound is surprisingly stable in a MeCN solvent. Apart from that, AgOSF₅ has been stabilised by the addition of 2,2'-bipyridine ligands. Starting from solutions of the unstaubilised silver(I) salt, OSF₅ complexes with Ni⁺, Cu¹, and Cu²-centres have been obtained. In addition, Ag(OSF₅)₂ has proven to be generally capable of mediating the transfer of OSF₅ groups to aryne moieties, thus furnishing a new and safe method for the preparation of OSF₅-substituted arenes. X-ray crystal structure analysis of selected transition-metal OSF₅ compounds have revealed distorted octahedral [OSF₅]⁻ anions that are extensively stabilised by hydrogen bonding.

The existence of pentafluorooxochalcogenate salts [OEF₅]⁻ (E = S, Se, Te) has been known for many years. However, the stability and thus the accessibility of these species differ.[¹] The most investigated element in this series is tellurium, since the corresponding acid HOTeF₅ and its salts are readily prepared in radical reactions, starting from the corresponding aryl derivatives.[³] Other examples include tetra- and hexavalent xenon compounds, such as Xe(OTeF₅)₄, which is so far the only stable xenon(IV) species besides XeF₄.[⁴] More recently, derivatives based on Al and Ga have been published.[⁵] Selenium analogues containing the [OSeF₅]⁻ anion are slightly less stable, but can still be prepared from the free acidi HOSeF₅.[⁶] This is not the case for HOSF₅, which decomposes above −60°C.[⁷] However, salts containing the [OSF₅]⁻ anion are accessible from gaseous OSF₅ and ionic fluoride donors such as KF, CsF, or [NMe₄]F, but not with LiF or NaF.[¹,⁸,⁹] Fluorides with larger cations, such as [(Me₂N)₃S]⁻[SiMe₃F₂]⁺(TASF), have also been known to produce stable OSF₅ salts.[¹⁰] To the best of our knowledge, no transition-metal compounds containing [OSF₅]⁻ anions have been unambiguously described so far. However, a species Ag⁺OSF₅⁻ has been proposed as intermediate in the fluorination of SOF₄, giving rise to SF₅OF or the peroxide (SF₅O)₂.[¹¹] Structural data of the pentafluorooxosulfate anion are only published for the TAS salt [(Me₂N)₃S]⁻[OSF₅]⁺, showing significant disorder.[¹⁰] Here we present syntheses of novel transition-metal salts including a crystallographic description of the [OSF₅]⁻ anion.

In terms of organic OEF₅ compounds, the situation is inverted, as a number of R-OSF₅ derivatives are known, whereas respective Se and Te analogues are only scarcely described.[⁹,¹²] Virtually all known OSF₅ arenes have been prepared in radical reactions, starting from the corresponding aryl and SF₅OOSF₅.[¹³] It can be expected that the substitution with an OSF₅ group gives rise to compounds with interesting molecular properties, as it is well known for other fluorinated groups like -CF₃, -OCF₃, -SCF₃ or -SF₅, which are typically found in pharmaceutical and agrochemical products.[¹⁴] For this purpose, a new synthetic approach towards aryl-OSF₅ compounds via aryne intermediates is introduced herein.

Isolated, non-stabilised transition metal salts M(OSF₅)₃, are unknown, which has been rationalised by a readily occurring decomposition of the anion into F⁻ and OSF₅. However, the reaction of AgF with OSF₅ in MeCN quantitatively yields colourless solutions of Ag(OSF₅)₃ (Scheme 1). The anion has been unambiguously identified by ¹⁹F-NMR spectroscopy, showing the expected AB₄-type spectrum. Remarkably, there is no free OSF₅ left in the reaction mixture. Solutions of Ag(OSF₅)₃ in MeCN are stable at room temperature and can be stored in standard laboratory glassware. A significant decomposition of the [OSF₅]⁻ anion is not observed, even after weeks.[¹⁵] Furthermore, the compound appears to be stable against light. However, attempts to isolate 3 by evaporation of the solvent have not been successful.

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Scheme 1. Preparation of silver(I) pentafluorooxosulfate 3.
CuOSF₅ cation has been proven to be solvated by MeCN, forming a reliable structural description. Nevertheless, the silver below room temperature. Initial investigation of the crystals of AgOSF₅ poor solubility of AgX. In a first approach, a MeCN solution to crystals of AgOSF₅ by 2,2'-bipyridyl ligands. They are both pale-yellow to ochre solids, which are stable against decomposition and can be indefinitely stored under inert conditions.

Instead of rather labile MeCN, other N-donor ligands, such as 2,2'-bipyridines 4a,b, efficiently stabilise AgOSF₅, even in the solid state. This allowed the preparation and isolation of two AgOSF₅ complexes 5a,b with differently substituted ligands (Scheme 2). With the silver compounds 3 and 5 in hand, we explored the preparation of transition-metal derivatives by simple metathesis reactions with MX₂ (X = Cl, I), making use of the poor solubility of AgX. In a first approach, a MeCN solution of AgOSF₅ 3 was treated with CuI, which quantitatively gave CuOSF₅ 6 (Scheme 3). Similarly to the parent silver(I) compound, the copper(I) salt is stable in solution but decomposes upon removal of the solvent. Treatment of a solution of CuOSF₅ 6 with bipyridine 4a and evaporation of the solvent gave rise to a stable, deep-red solid [Cu(bpy)₂(OSF₅)₂] 7 (Scheme 3), which has been identified by NMR spectroscopy and mass spectrometry. The metathetical preparation of OSF₅ compounds could be extended to the divalent metal chlorides CuCl₂ and NiCl₂, however, the latter two had to be converted to their bppy complexes M(bpy)₂Cl₂ (M = Cu, Ni) prior to the treatment with AgOSF₅ (Scheme 3). The copper(II) complex [Cu(bpy)₂(OSF₅)₂] 8 is a light-blue solid, whereas the nickel(II) derivative [Ni(bpy)₂(OSF₅)₂] 9 has a salmon-pink colour in the solid state. The nickel(II) complex 9 has also been directly prepared from NiF₂, 2,2'-bipyridine, and OSF₅, thus avoiding the use of rather costly AgF and the generation of silver(I) halide waste (Scheme 3).

Interestingly, the ¹⁹F NMR spectra of all transition-metal compounds are very similar, revealing the pentet (δ = 134–136 ppm) and the doublet signals (δ = 91–92 ppm) in narrow chemical-shift segments.[15] Thus, it appears that the [OSF₅]⁻ anions dissociate from the metal centres in MeCN solution. Further evidence can be found in the NMR spectra of the CuII derivative 8, where ¹H and ¹³C signals cannot be observed due to paramagnetism of the d⁹ metal centre. In contrast, the corresponding ¹⁹F spectrum is only slightly broadened, whereas chemical shift and multiplicity of the signals remain unaffected. Overall, these findings clearly indicate that the [OSF₅]⁻ 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.[16] Cooling acetonitrile solutions of 6 to −40°C yields colourless crystals, which have been shown to contain both solvated [Cu(MeCN)₄]⁺ cations and distorted octahedral [OSF₅]⁻ 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 [OSF₅]⁻ anions are parallel to the a-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

**Scheme 2.** Stabilisation of AgOSF₅ by 2,2'-bipyridine ligands.

**Scheme 3.** Salt metathesis of transition-metal halides using AgOSF₅ and direct synthesis of nickel(II) complex 9.
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$_{eq}$ amounts to 95.6°. In general, the solid-state structure of [Cu(MeCN)$_4$][OSF$_5$]·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$_4$ 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 CuІІ 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 bipyramidal).\(^{[13]}\) 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$_5$]$^-$ 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 pronounced 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$_5$ group. Similarly to the solvated [OSF$_5$]$^-$ 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$_5$]$^-$ 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)$_2$(OSF$_5$)]$^+$ units (Figure 2). In contrast to the Cu-bonded [OSF$_5$]$^-$ anion, the “free” [OSF$_5$]$^-$ 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$_5$ compounds are known to be quite robust and tolerant against many reagents and reaction conditions, except a strongly reductive environment.\(^{[13, 14]}\) 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$_5$ derivative was prepared by a S$_{N}$2-type reaction.\(^{[12c]}\) On the other hand, treatment of arynes with perfluorinated alkoxides, for example, CF$_3$O$^-$, has been shown to yield aryl trifluoromethyl ethers.\(^{[19]}\) Therefore, we have tried to combine the latter two approaches for the synthesis of SF$_5$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$_5$]$^-$ anion, such as 11, which has been prepared from 2,2-difluoro-1,3-dimethylimidazolidine (DFI) 10 and OSF$_5$(Scheme 4).\(^{[12n, 20]}\) However, probably due to the very poor nucleophilicity of the pentfluorooxoosulfate anion, a nucleophilic attack on the aryne could not be observed.

![Figure 2. Top: extract of the solid-state packing of [Cu(bpy)$_2$(OSF$_5$)$_3$][OSF$_5$]·0.5 MeCN 8, revealing the two different types of [OSF$_5$]$^-$ anions. Bottom: distorted trigonal bipyramidal [Cu(bpy)$_2$(OSF$_5$)$_3$]$^+$ cation with selected bond lengths (in Å) and bonding angles. Hydrogen atoms are omitted for clarity; ellipsoids are at a probability level of 50%.](image-url)
In the literature, one can find an example for an Ag-mediated introduction of -F, -CF₃, and -SCF₃ functions into aryl intermediates, which has been proposed to proceed via the formation of a cationic silver(I) complex. Thy thus, we reacted 4,5-dimethyl-2-(trimethylsilyl)phenyl triflate 12, the precursor to symmetric 4,5-dimethylbenzylcine, with the stochiometric [OSF₅]⁻ 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 ᵈF NMR of the crude reaction mixture, the aforementioned conditions allow to furnish the SF₅O-substituted ortho-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 AB₃ pattern in the ᵈF NMR. However, the small yield of SF₅O product 13 indicates that side-reactions are very likely to take place. For example, we identified two species in the ᵈF 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⁻ to the arylene and by a thia-Fries rearrangement of an intermediate anonic 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. Thy 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 ᵈF NMR spectroscopy, e.g., oligomerisation of the arylene intermediate. Therefore, further optimisations need to be conducted to improve the yields and selectivities of this synthetic approach. Nevertheless, the reaction of arene substrates with [OSF₅]⁻ in presence of the silver catalyst 5a is a starting point for a new and promising pathway towards aromatic pentafluorosulfanyl compounds. We are convinced that based on our findings reliable synthetic routes towards ArOSF₅ 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 pentafluoroxosulfinate compounds, which are based on the simple preparation of AgOSF₅ from AgF and OSF₅. AgOSF₅ 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 CuOSF₅ revealed a large number of H–F and H–O contacts between the distorted octahedral [OSF₅]⁻ ion and the solvent molecules. This finding gives a rough explanation for the stability of the copper(I) compound, which probably also holds for solvated AgOSF₅. Moreover, the solid-state structure of a bpy-stabilised Cu(II)-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)₂-(OSF₅)]⁻ has proven to be generally useful for the preparation of OSF₅-substituted arenes via arylene intermediates. However, the reaction conditions apparently do not allow a clean product formation, so that the yield of the representative SF₅O-substituted arene is so far rather poor. In following studies, we will work on the examination of improved synthetic pathways towards aromatic OSF₅ 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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[16] Crystallographic data: 6 (CCDC 2088423), colourless block, 0.2 × 0.07 × 0.05 mm³, orthorhombic, P2₁2₁2₁, a = 21.7479(9), b = 27.5479(11), c = 8.5241(3) Å, V = 5106.9(3) Å³, ρcalc = 1.607, Z = 12, Mo-Kα radiation, λ = 0.71073 Å, T = 100.0 K, μ = 1.463 mm⁻¹, θmax = 36.23°, 479897 measured reflections, 20842 crystallographically independent reflections, Rint = 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 × 0.17 × 0.13 mm³, triclinic, P–1, a = 10.4126(5), b = 10.4331(5), c = 13.2642(6) Å, α = 70.3560(10), β = 70.5080(10), γ = 82.646°, V = 1279.12(10) Å³, ρdata = 1.825, Z = 2, Mo-Kα radiation, λ = 0.71073 Å, T = 100(2) K, μ = 1.124 mm⁻¹, θmax = 33.21°, 97401 measured reflections, 9825 crystallographically independent reflections, Rint = 0.0351, 402 parameters, GOOF = 1.132, R1 = 0.0392, wR2 = 0.0890, refined as a 2-component twin. Structure solution by SHELXT [23] and full-matrix least square refinement using SHELXL [16]. 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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