

The synthesis and vibrational spectra of fluorosulfate derivatives of titanium, zirconium and hafnium

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Abstract

The syntheses of the binary fluorosulfates, $Zr(SO_3F)_4$ and $Hf(SO_3F)_4$, by oxidation of the corresponding metal powders with bis(fluorosulfonyl) peroxide, $S_2O_6F_2$, in fluorosulfuric acid, HSO_3F , are described. The resulting products are white hygroscopic solids which are not sufficiently soluble in HSO_3F to allow electrical conductivity and NMR studies or Hammett acidity function (H_0) determinations in order to evaluate their use as Lewis acids in conjugate superacid systems. Oxidation of titanium under similar conditions resulted in the formation of a greenish-yellow resin-like material of limited thermal stability with the approximate composition $Ti(SO_3F)_4$. However, infrared spectra indicated the presence of small amounts of HSO_3F . In addition, the solvolysis of $ZrCl_4$ in an excess of HSO_3F at 25 °C has been investigated as a potential route to $Zr(SO_3F)_4$. The results indicate that short reaction times of 1–2 d yielded incompletely substituted products of the approximate composition $ZrCl_x(SO_3F)_{4-x}$ ($x=0.22$), while prolonged reaction times of 3–4 weeks gave rise to partially decomposed materials of approximate composition $ZrO_{0.5}F_{1.5}(SO_3F)_{1.5}$. The ability of all three tetrakis(fluorosulfato) metallates to act as SO_3F^- ion acceptors is evident from the isolation of thermally stable salts of the composition $Cs_2[M(SO_3F)_6]$ ($M=Ti, Zr$ or Hf) when the metal oxidation was carried out in the presence of 2 mol equiv. of $CsSO_3F$. All the materials were characterized by their vibrational spectra, which are extremely similar and closely resemble those of previously reported cesium hexakis(fluorosulfato) metallates.

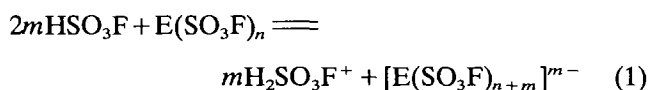
Introduction

Among very strong protonic or Brønsted acids and superacids [1], the highest acidities are observed in conjugate superacid systems. These systems usually consist of a strong protonic acid and an equally strong Lewis acid [2]. Anhydrous hydrogen fluoride (HF) and fluorosulfuric acid (HSO_3F) have emerged as the two strongest Brønsted acids with identical Hammett (H_0) values [3] of -15.1 reported for both [2, 4]. Both have found extensive use in many conjugate superacid systems [2]. Because of the wider liquid range, greater ease of purification by distillation at atmospheric pressure [5], compatibility with glass and the large number of easily utilizable physical and spectroscopic techniques available, the use of HSO_3F [6, 7] offers clear advantages over the use of HF [8].

Various binary element pentafluorides, particularly those of the elements in Group 5 (Nb and Ta) and Group 15 (As and Sb), have found frequent use as Lewis acids in conjugate superacids, with either hydrogen fluoride or fluorosulfuric acid as Brønsted acids [2]. The conjugate superacid system HSO_3F-SbF_5 ,

termed 'Magic Acid', is widely employed in the generation and stabilization of a wide range of electrophilic cations, even though both the facile fluoride versus fluorosulfate exchange and the concentration dependent solute association via SO_3F^- and F-bridges cause the presence of several anions in solution and introduce some complexity [8–11]. Both processes limit the use of such systems in the synthesis of salts with electrophilic cations.

Some of this inherent complexity may be avoided in conjugate superacid systems of the type $HSO_3F-E(SO_3F)_n$, where a high oxidation state binary fluorosulfate acts as a Lewis acid and where, according to the general equilibrium:



stable fluorosulfate complexes are readily formed and isolated. In the past, four such conjugate superacids have been developed by us, although some disadvantages have emerged in all four systems. The use of the conjugate superacids $HSO_3F-Au(SO_3F)_3$ [12] and $HSO_3F-Pt(SO_3F)_4$ [13] is limited by the high price of the metals and the oxidizing ability of Au^{III} and Pt^{IV} . In the case of the $HSO_3F-Au(SO_3F)_3$ system, the

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reduction of Au^{III} by either gold powder or carbon monoxide has produced very interesting species such as Au²⁺_(solv) [14], Au(CO)SO₃F [15] and [Au(CO)₂]⁺ [15, 16], and it appears now that Pt(SO₃F)₄ is also reduced by CO to give *cis*-[Pt(CO)₂(SO₃F)₂] [17]. In conjugate superacid systems such redox reactions are undesirable, since they imply the loss of superacidity on reduction of the Lewis acid, Au(SO₃F)₃ or Pt(SO₃F)₄.

In two recently reported superacid systems, i.e. HSO₃F–Nb(SO₃F)₅ and HSO₃F–Ta(SO₃F)₅ [18], interference from redox reactions involving Nb^V and Ta^V is improbable. However, the two Lewis acids Nb(SO₃F)₅ and Ta(SO₃F)₅ are generated *in situ* and exhibit limited thermal stability. They both decompose via SO₃ elimination, resulting in the formation of fluoride-fluorosulfates of Nb^V and Ta^V [18, 19].

To increase the number of potential conjugate superacid systems in HSO₃F, syntheses of Lewis acids of the type M(SO₃F)₄ (M = Ti, Zr or Hf) were attempted in this study. To demonstrate the intrinsic fluorosulfate ion acceptor ability of these binary fluorosulfates, the syntheses, thermal stabilities and vibrational characteristics of their ternary fluorosulfato derivatives of the type Cs₂[M(SO₃F)₆] were also studied. Of the binary compounds, only one has been reported so far. The binary fluorosulfate Zr(SO₃F)₄ was synthesized by the solvolysis of Zr(CO₂CF₃)₄ in an excess of fluorosulfuric acid, and an infrared spectrum has been reported [20].

Experimental

Chemicals

Titanium (100 mesh, 99.9%), zirconium (80 mesh, 99.9%, packed under water), and hafnium (325 mesh, 99.6%, containing 2%–3% Zr) were obtained from Alfa Products, Thiokol/Ventron Division. Cesium chloride (99.9%) was obtained from BDH Chemicals. HSO₃F technical grade (Orange County Chemicals) was purified by double distillation at atmospheric pressure as described previously [5]. Bis(fluorosulfuryl) peroxide was prepared by the catalytic (AgF₂) fluorination of SO₃ [21].

Caution: Finely divided powders of Group 4 metals are known to be pyrophoric. Although there were no explosions or violent reactions during the course of our studies, these metal powders should be used in small quantities, with suitable safeguards.

Instrumentation

Infrared spectra were recorded on a Perkin-Elmer 598 grating spectrophotometer or a Bomem Michelson MB102 FT-IR spectrometer, with the solid samples pressed as thin films between AgBr windows (Harshaw Chemicals) or IR grade silicon wafers (Wacker Chemie).

Raman spectra were obtained on a Spex Ramalog 5 equipped with an argon ion laser (Spectra Physics 164) using the 514.5 nm line for excitation. The samples were held in 2 mm o.d. melting point capillaries. Melting points were taken on a Gallenkamp melting point apparatus. Standard vacuum line techniques were used for the manipulation and handling of volatile reagents and products. All solids and non-volatile liquids were manipulated inside a nitrogen-filled Vacuum Atmospheres Corporation Dri-Lab model HE-493 dry box equipped with a model HE-493 Dri-Train purifier. Except where mentioned, most of the reactions were carried out in 50 ml Pyrex round-bottom flasks fitted with 4 mm Kontes Teflon stem stopcocks and standard taper B10 ground glass cones.

Synthetic reactions

(i) Ti(SO₃F)₄

To 53 mg (1.106 mmol) of Ti metal, contained in the reaction vessel, about 5 ml of HSO₃F was added *in vacuo*. After warming, the mixture was allowed to stir at room temperature for 15 min. After cooling the flask to –196 °C, about 5 ml of S₂O₆F₂ was transferred *in vacuo*. The resulting mixture was left stirring at room temperature overnight. After 24 h, the mixture had a light green colour and stirring was continued until all the metal had been consumed (10 d). Upon opening the reactor at –196 °C, there was some residual pressure due to O₂ as identified by mass spectrometry. The reactor was warmed to room temperature and with pumping the product became more viscous and eventually remained at constant weight (495 mg, 1.115 mmol). The residue was green and had a resin-like consistency. Attempts to redissolve the product in HSO₃F were unsuccessful because the resin-like material appeared immiscible in this solvent. No satisfactory analysis of the material could be obtained because of the viscous nature of the product.

(ii) Zr(SO₃F)₄

Prior to use, the Zr powder was dried *in vacuo* to remove all traces of water. In a typical reaction, 93 mg (1.020 mmol) of Zr metal was sealed in the reaction vessel and about 5 ml of fluorosulfuric acid was added by vacuum-transfer. The reactor was briefly warmed to 100 °C. The mixture was left stirring and allowed to cool to room temperature. After briefly pumping on the reactor, about 5 ml of S₂O₆F₂ was vacuum-transferred into it. The reaction mixture was allowed to warm up to room temperature and left stirring overnight. The temperature was raised to 120 °C and after 3 weeks all the Zr metal had been consumed and a white powder was suspended in the solution. Volatile materials were pumped off at room temperature leaving 434 mg (0.890 mmol) of a white solid behind. During the reaction

the reactor had been corroded, hence the weight balance must be regarded as unreliable. Analysis: Calc. for $Zr(SO_3F)_4$: F, 15.64; S, 26.31; Zr, 18.71%. Found: F, 16.4; S, 25.2; Zr, 17.69%.

(iii) $Hf(SO_3F)_4$

About 5 ml of HSO_3F was added by vacuum-transfer to 235 mg (1.317 mmol) Hf metal. The mixture was heated briefly to 100 °C and allowed to cool to room temperature with stirring. About 5 ml of $S_2O_6F_2$ was vacuum-transferred to the reactor and the mixture allowed to warm up to room temperature overnight with stirring. The temperature was raised to 60 °C for 24 h, 100 °C for 1 week and finally to 120 °C for 1 week, after which all the metal had been consumed. A white solid was observed suspended in the liquid mixture of HSO_3F and $S_2O_6F_2$. The reactor was cooled to -196 °C and the oxygen removed *in vacuo*. The rest of the volatiles were pumped off with the reactor at room temperature leaving behind a white solid weighing 804 mg (1.399 mmol). Analysis: Calc. for $Hf(SO_3F)_4$: F, 13.22; S, 22.32; Hf, 31.06%. Found: F, 13.9; S, 22.05; Hf, 31.94%.

(iv) $Cs_2[Ti(SO_3F)_6]$

Titanium (53 mg, 1.106 mmol) and 513 mg (2.212 mmol) of $CsSO_3F$ were weighed out in the reaction vessel. About 5 ml of HSO_3F was transferred to this mixture in the dry box. About 5 ml of $S_2O_6F_2$ was added to the solution via vacuum-transfer and the reactor allowed to warm to room temperature. During this stage, some bubbling occurred at the metal surface and the bottom of the reactor was warm to the touch. Stirring was continued for *c.* 5 d with the reactor at room temperature. The reactor was then evacuated at room temperature leaving a whitish-pale green solid weighing 979 mg (1.078 mmol) behind. Analysis: Calc. for $Cs_2[Ti(SO_3F)_6]$: S, 21.18%. Found: S, 21.35%.

(v) $Cs_2[Zr(SO_3F)_6]$

Zirconium (202 mg, 2.214 mmol) and 1.032 g (4.449 mmol) of $CsSO_3F$ were weighed out in a 2 mm wall thickness Pyrex ampoule of 2 cm diameter. The ampoule was connected to the vacuum line via an ampoule key as described previously [22]. About 5 ml each of HSO_3F and $S_2O_6F_2$ were vacuum-transferred to the ampoule and it was then sealed off. The mixture was left stirring at 110 °C for 2 d when all the Zr had been consumed. Upon allowing the mixture to stand at room temperature, two layers were observed. With time at this temperature, the lower layer converted to a waxy solid, along with what appeared to be small crystals. Maintaining the mixture at 4 °C for *c.* 10 weeks did not yield any crystals. The ampoule was cooled to -196 °C and opened *in vacuo*. It was then evacuated overnight with

warming to room temperature leaving behind 2.099 g (2.206 mmol) of a white solid. Analysis: Calc. for $Cs_2[Zr(SO_3F)_6]$: F, 11.98; S, 20.22; Zr, 9.59%. Found: F, 12.1; S, 20.80; Zr, 9.82%.

(vi) $Cs_2[Hf(SO_3F)_6]$

Hafnium (180 mg, 1.008 mmol) and 369 mg (2.191 mmol) of $CsCl$ were weighed out into a 50 ml Pyrex round-bottom flask fitted with a 4 mm Kontes Teflon stopcock and a B10 ground glass joint. About 5 ml HSO_3F was vacuum-transferred to the reactor and the mixture allowed to warm up to room temperature with stirring. After 30 min, the reactor was pumped on to remove the HCl formed. About 5 ml of $S_2O_6F_2$ was then vacuum-transferred to the reactor and the reaction mixture left stirring at 100 °C for *c.* 10 d when all the Hf had been consumed. A white solid, insoluble in the $HSO_3F/S_2O_6F_2$ mixture, was suspended in the flask. The volatiles were pumped off leaving behind a white solid weighing 1.083 g (1.043 mmol). Analysis: Calc. for $Cs_2[Hf(SO_3F)_6]$: F, 10.97; S, 18.52; Hf, 17.18%. Found: F, 10.9; S, 18.55; Hf, 19.86%.

Results and discussion

(a) Synthesis

According to a recent review [23], two general routes to binary and ternary fluorosulfates of the types $M(SO_3F)_4$ and $Cs_2[M(SO_3F)_6]$ ($M = Ti, Zr$ or Hf) may be contemplated: (i) ligand substitution of suitable MX_4 or $[MX_6]^{2-}$ precursors ($X = \text{halide, alkoxide or carboxylate}$) by HSO_3F , its anhydride $S_2O_5F_2$ or, in the case of $X = Cl$, by bis(fluorosulfonyl) peroxide ($S_2O_6F_2$) or bromine(I) fluorosulfate ($BrSO_3F$); and (ii) metal oxidation using $S_2O_6F_2$ as oxidizer and HSO_3F as the reaction medium, either in the absence or presence of stoichiometric amounts of $CsSO_3F$.

Previous attempts to synthesize binary fluorosulfates of the type $M(SO_3F)_4$ ($M = Ti, Zr$) have been restricted to the use of route (i) and have met with mixed success. The solvolysis of zirconium tetrakis(trifluoroacetate), $Zr(O_2CCF_3)_4$, in an excess of HSO_3F has reportedly allowed the isolation of $Zr(SO_3F)_4$ in an analytically pure form [20]. In most other instances, either incomplete substitution or complex decomposition of the initial products was observed; for example, the solvolyses of MCl_4 in HSO_3F ($M = Ti$ and Zr) studied by Hayek *et al.* have yielded $TiCl_2(SO_3F)_2$ and ZrF_3SO_3F , respectively [24]. The compound $TiCl_2(SO_3F)_2$ was also formed in the reaction of $TiCl_4$ with a slight excess of $S_2O_6F_2$ at -20 °C. When higher temperatures and a large excess of $S_2O_6F_2$ were used, more extensive chloride substitution led to poorly defined, chloride-containing materials [25]. Finally, the reaction of $Ti(OCH_3)_4$

with an excess of bis(fluorosulfonyl)oxide, $S_2O_5F_2$, resulted only in disubstitution and allowed the isolation of $Ti(OCH_3)_2(SO_3F)_2$ [26].

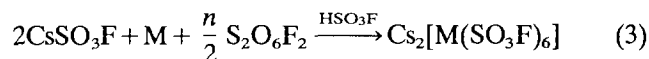
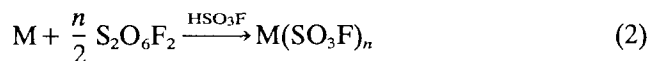
Of all these reactions, the reported formation of ZrF_3SO_3F via the solvolysis of $ZrCl_4$ with HSO_3F at $100^\circ C$ [24] is puzzling in the light of the corresponding reaction of $ZrCl_4$ with the related acid HSO_3CF_3 . Here complete substitution occurred at $50^\circ C$ to give $Zr(SO_3CF_3)_4$ which is thermally stable to $207^\circ C$ [27]. The same authors reported the formation of $TiCl(SO_3CF_3)_3$ from $TiCl_4$ and HSO_3CF_3 under similar conditions [24]. A recent reinvestigation of this reaction under more forcing conditions (and with the anhydride, $S_2O_5(CF_3)_2$ added to HSO_3CF_3) led to the formation of a chloride-containing product with the composition $TiCl_{0.75}(SO_3CF_3)_{3.25}$ [28]. The same study also provided evidence for $(NO_2)_2[Ti(SO_3CF_3)_6]$, an anionic trifluoromethylsulfato complex of titanium, which is formed in the reaction of $Ti(NO_3)_4$ with a mixture of HSO_3CF_3 and its anhydride $S_2O_5(CF_3)_2$ [28].

Before turning to the study of metal oxidation reactions, it seemed useful to re-investigate the outcome of the reaction between $ZrCl_4$ and HSO_3F at room temperature and after short exposure (1–2 d) to an excess of HSO_3F . The white solid product obtained has the approximate composition $ZrCl_x(SO_3F)_{4-x}$ ($x=0.22$) and its vibrational spectrum (discussed below) is not markedly different from that of $Zr(SO_3F)_4$. It must be concluded that $ZrCl_4$ undergoes more extensive substitution of chloride by fluorosulfate or trifluoromethylsulfate than does $TiCl_4$ when either HSO_3F or HSO_3CF_3 are used [27, 28]. However, it appears that the substitution of Cl by SO_3F is still incomplete.

In order to achieve complete substitution, the reaction time was extended to 3 weeks with the reaction mixture held at room temperature. While the resulting white solid product isolated after removal of all volatiles *in vacuo* was now free of chloride, the mass fell well short of that expected for $Zr(SO_3F)_4$. The analytical data (S, 17.45; F, 20.5%) suggest an F/S ratio of 2:1 and best fit the composition $ZrO_{0.5}F_{1.5}(SO_3F)_{1.5}$ (where S, 17.4; F, 20.63%). It must be concluded that decomposition of some of the fluorosulfate groups with elimination of SO_3 , and quite possibly of $S_2O_5F_2$, must have occurred; both are viable decomposition modes for metal fluorosulfates. In addition, the infrared and Raman spectra of this material (*vide infra*) were now much simpler and appeared to contain only bands which were attributable to a bidentate, presumably bridging, configuration of the SO_3F group.

The alternative synthetic route to $Zr(SO_3F)_4$ and the remaining Group 4 fluorosulfates, i.e. metal oxidation by bis(fluorosulfonyl) peroxide ($S_2O_6F_2$), may be carried out with reaction temperatures up to $150^\circ C$ to yield either binary or ternary fluorosulfates according to the

following general reactions:



This approach has been used previously for a number of metals (Pt [13], Nb, Ta [18], Pd [29], Ir [30], Ru [31], Sn and Ge [32]), all of which form ternary $Cs_2[M(SO_3F)_6]$ compounds as well. Cesium fluorosulfate was chosen in all instances, because an incomplete reaction would result in residual $CsSO_3F$ which is readily recognized by the occurrence of an infrared band at 728 cm^{-1} , assigned to ν_2 the sulfur–fluorine stretching vibration [31]. For the fluorosulfates of other Group 1 metals, $\nu(S-F)$ is found at gradually increasing wavenumbers [33] which makes an unambiguous assignment more difficult. In addition, the vibrational spectra of the $Cs_2[M(SO_3F)_6]$ salts are less complex than those of the corresponding compounds with other more strongly polarizing Group 1 cations or heterocations such as ClO_2^+ , or NO^+ [13, 29–32] on account of the larger, spherical shape of Cs^+ and its low ionization potential. For $M=Zr$, a number of attempts were made to obtain the anions $[Zr(SO_3F)_7]^{3-}$ or $[Zr(SO_3F)_8]^{4-}$ by analogy with the fluoro anions ZrF_7^{3-} [34] and ZrF_8^{4-} [35] by using $CsSO_3F/Zr$ stoichiometric ratios of 3:1 and 4:1, respectively, but in all instances the infrared spectra of the resulting solid products indicated the presence of uncomplexed $CsSO_3F$, which implies that potentially seven- or eight-coordinate anionic complexes may not be obtainable in a pure form. It is interesting to note that analogous reactions with $M=Nb$ or Ta both produced the $[M(SO_3F)_7]^{2-}$ salts of cesium while those with $[M(SO_3F)_8]^{3-}$ as the anion were not formed [18].

Details of the oxidation of Ti, Zr and Hf by $S_2O_6F_2$ in HSO_3F are summarized in Table 1. The results are compared with previous studies [13, 29–32] with respect to reaction times, reaction temperatures and the thermal stability of the resulting products. As can be seen, all three binary fluorosulfates and their cesium salts were obtained and all, except for $Ti(SO_3F)_4$, are hygroscopic white solids. The rather long reaction times required to oxidize Zr and Hf were, in part, a result of the careful approach taken during the initial stages of the reactions on account of the well-documented pyrophoric nature of the metal powders. In all our reactions, however, the metal powders reacted sluggishly and complete oxidation required extended reaction times and relatively high temperatures. It is felt that initial passivation due to surface oxidation is the reason for the observed but unexpected lack of reactivity of the metal powders towards a strong oxidizing agent. In

TABLE 1. Binary and ternary metal fluorosulfate derivatives obtained by oxidation with $S_2O_6F_2$ in HSO_3F

Compound	Temperature (°C)	Time (d)	Thermal stability	Description	Ref.
<i>(a) M(SO₃F)_n</i>					
Ti(SO ₃ F) ₄	25–60	10		yellow viscous liquid	tw ^e
Zr(SO ₃ F) ₄	25–120	21	up to 180 °C	white solid	tw
Hf(SO ₃ F) ₄ ^a	25–120	21	up to 190 °C	white solid	tw
Sn(SO ₃ F) ₄	25	0.5	up to 196 °C	white solid	32
Pt(SO ₃ F) ₄	120	2	dec. pt. 220 °C	yellow-orange solid	13
Ir(SO ₃ F) ₄ ^b	60–140	6.5	up to 150 °C	dark brown solid	30
Pd(SO ₃ F) ₃ ^c	25–120	3	up to 180 °C	black brown solid	29
Ru(SO ₃ F) ₃	60	1	up to 140 °C	red brown solid	31
GeF ₂ (SO ₃ F) ₂ ^d	50	3	dec. pt. 146 °C	white solid	32
<i>(b) Cs₂[M(SO₃F)₆]</i>					
Cs ₂ [Ti(SO ₃ F) ₆]	25	5	dec. pt. 60–65 °C	white solid	tw
Cs ₂ [Zr(SO ₃ F) ₆]	25–110	1–2	dec. pt. 260–265 °C	white solid	tw
Cs ₂ [Hf(SO ₃ F) ₆]	100	10	dec. pt. 262 °C	white solid	tw
Cs ₂ [Sn(SO ₃ F) ₆]	25	0.5	dec. pt. 249–253 °C	white solid	32
Cs ₂ [Pt(SO ₃ F) ₆]	80	3	dec. pt. 260 °C	light yellow solid	13
Cs ₂ [Ir(SO ₃ F) ₆]	150	10	dec. pt. ~150 °C	pale orange solid	30
Cs ₂ [Pd(SO ₃ F) ₆]	120	3	up to 200 °C	dark red solid	29
Cs ₂ [Ru(SO ₃ F) ₆]	60	1	not stated	orange solid	31
Cs ₂ [Ge(SO ₃ F) ₆]	50	2	dec. pt. 242 °C	white solid	32

^aContains 2%–3% Zr(SO₃F)₄.

^bObtained by oxidation of Ir(SO₃F)₃ with S₂O₆F₂ [30].

^cFormulated as Pd^{II}[Pd^{IV}(SO₃F)₆].

^dObtained in 75%–80% yield when Ge was oxidized by S₂O₆F₂ in HSO₃F [32].

^etw = this work.

some instances, where high temperatures were required, O₂ was produced as a byproduct, possibly by reaction of SO₃F[•] radicals at elevated temperatures with the walls of the reactor as reported previously [36]. The formation of O₂ together with bis(fluorosulfonyl) oxide, S₂O₅F₂, has also been reported during the oxidation of iridium [30] and rhodium [37], where prolonged reaction times and reaction temperatures of 140–150 °C were also employed.

As observed for all the reactions summarized in Table 1, shorter reaction times and lower reaction temperatures were required when CsSO₃F was present in the reaction mixture. The occasional observation of two liquid phases during the initial stages of the reaction has recently been investigated during a study of the HSO₃F–S₂O₆F₂ system [38]. The addition of CsSO₃F, or another alkali metal fluorosulfate, to fluorosulfuric acid reduces the acidity of HSO₃F and limits the solubility of S₂O₆F₂, which is found to behave as weak base in HSO₃F [38]. In these mixtures, the upper phase was found to consist almost solely of S₂O₆F₂ while the lower phase was initially a solution of CsSO₃F in HSO₃F.

Two apparent inconsistencies during the syntheses of Zr(SO₃F)₄ and Hf(SO₃F)₄ require an explanation. The final weight of Zr(SO₃F)₄ appeared slightly less than expected. This behaviour is explained by the corrosion of the inner walls of the reactor during the

prolonged reaction times, which is also consistent with the formation of SiF₄ (detected by IR spectroscopy) during the reaction. Nevertheless, the analytical data indicate that under these conditions extensive dissociation of the product did not occur despite the high reaction temperatures, provided the product was isolated as soon as all the metal had been consumed. On the other hand, the weight of Hf(SO₃F)₄ obtained appears to be slightly higher, suggesting the formation of 1.399 mmol of product rather than the expected 1.317 mmol. As stated in the Experimental section, according to the supplier the hafnium powder employed contained 2%–3% zirconium which should produce 2%–3% Zr(SO₃F)₄ in the final product, thus explaining the observed weight difference and the inaccurate microanalytical results for hafnium (tetrakis)fluorosulfate and the cesium salt. Both Zr(SO₃F)₄ and Hf(SO₃F)₄ are white hygroscopic powders of comparable thermal stability, and both gave nearly identical infrared spectra. It was therefore not possible to detect the presence of a small amount of Zr(SO₃F)₄ in hafnium(IV) fluorosulfate.

The appearance and thermal stability of Zr(SO₃F)₄ agrees reasonably well with the previous report [20] of its synthesis from Zr(O₂CCF₃)₄ and HSO₃F. However, the appearance of Ti(SO₃F)₄ is unprecedented. Whilst in all the cases summarized in Table 1 and discussed

elsewhere [23] binary fluorosulfates are relatively high-melting, hygroscopic solids, $\text{Ti}(\text{SO}_3\text{F})_4$ is found to be a waxy, resin-like material which does not redissolve in HSO_3F . This does not allow recrystallization nor permit sublimation. The yellow-greenish colour of the product is not surprising since all titanium(IV) chlorosulfonates are described as yellow solids [24, 25, 27, 28].

There is some evidence to be discussed subsequently that $\text{Ti}(\text{SO}_3\text{F})_4$ obtained in the manner described above may not be pure despite the good weight balance. All samples of $\text{Ti}(\text{SO}_3\text{F})_4$ studied by IR spectroscopy were found to attack silver halide windows, in contrast to $\text{Zr}(\text{SO}_3\text{F})_4$ or $\text{Hf}(\text{SO}_3\text{F})_4$. The spectra obtained on samples pressed between silicon discs showed a broad absorption band at *c.* 3100 cm^{-1} . The presence of this band suggests the retention of a small amount of acid in the sample. All attempts to remove the acid by heating the sample *in vacuo* resulted in some sample decomposition and extensive weight loss. The situation is reminiscent of the oxidation of Nb or Ta in HSO_3F by $\text{S}_2\text{O}_6\text{F}_2$ which leads to the *in situ* formation of $\text{M}(\text{SO}_3\text{F})_5$ ($\text{M}=\text{Nb}$ or Ta). Both are too labile towards dissociation to give SO_3 to permit isolation from solution [18] by solved evaporation *in vacuo*.

The high thermal stability of the ternary fluorosulfates $\text{Cs}_2[\text{M}(\text{SO}_3\text{F})_6]$ where $\text{M}=\text{Zr}$, Hf , Ge [32], Sn [32] or Pt [13], all of which have decomposition points at *c.* $250\text{ }^\circ\text{C}$, is surprising. The similarity in their vibrational spectra (discussed below) to those reported previously points to structural similarities. The high thermal stability of all anionic complexes may also be taken as an indication of the acceptor ability of the binary fluorosulfates, even though the $\text{M}(\text{SO}_3\text{F})_4$ compounds have not been isolated for $\text{M}=\text{Pd}$, Ru and Ge [13, 29–32], where the tris(fluorosulfates), $\text{Ru}(\text{SO}_3\text{F})_3$ [31], $\text{Pd}(\text{SO}_3\text{F})_3$ (or more accurately $\text{Pd}^{\text{II}}[\text{Pd}^{\text{IV}}(\text{SO}_3\text{F})_6]$ [29]) and $\text{GeF}_2(\text{SO}_3\text{F})_2$ [32], have been obtained instead.

In all instances, the Group 4 fluorosulfates exhibited very low solubility in fluorosulfuric acid while the cesium salts showed moderate solubility in HSO_3F . This precluded electrical conductivity, NMR or Hammett acidity studies in this solvent. It appears that bridging by fluorosulfate groups leads to polymers similar to those suggested for $\text{Sn}(\text{SO}_3\text{F})_4$ by ^{119}Sn Mössbauer and vibrational spectra [39]. It is unclear why decomposition with the formation of $\text{S}_2\text{O}_5\text{F}_2$ and SO_3 takes place in the solvolysis of ZrCl_4 in HSO_3F , although metal oxidation leads to $\text{Zr}(\text{SO}_3\text{F})_4$ which is thermally stable to $180\text{ }^\circ\text{C}$.

(b) Vibrational spectra

The band positions and estimated intensities for both compounds are collected in Table 2 and compared to the previously reported IR spectra of $[\text{Au}(\text{SO}_3\text{F})_3]_2$ [12,

40], and of the tetrakis(fluorosulfates) of Sn [39], Pt [13] and Ir [29]. Also included in this comparison are the previously published spectra of $\text{Zr}(\text{SO}_3\text{F})_4$ [20] and those of the product of the solvolysis ZrCl_4 in an excess of HSO_3F , either after short or long exposure time.

The most intriguing observation is the very close similarity in band positions, intensities and shapes for both compounds. Only in the low-wavenumber region (below 500 cm^{-1}) do small discrepancies emerge. The identical oxidation states, atomic and covalent radii for Zr and Hf [41], which are responsible for many identical chemical and structural features of their compounds, are seen as the reason for the observed spectral similarity. This observation strongly suggests a common molecular structure for both compounds.

The spectrum of $\text{ZrCl}_x(\text{SO}_3\text{F})_{4-x}$ ($x=0.22$) is identical with that of $\text{Zr}(\text{SO}_3\text{F})_4$ obtained by the metal oxidation of Zr , except for very slight differences in band shape and an additional band of medium intensity at 408 cm^{-1} possibly due to a $\text{Zr}-\text{Cl}$ stretch. The contention that chloride is almost completely replaced by SO_3F is also consistent with a rather low residual chlorine content of 1.6% as determined by microanalysis.

The IR spectrum of $\text{Zr}(\text{SO}_3\text{F})_4$ obtained by solvolysis of $\text{Zr}(\text{O}_2\text{CCF}_3)_4$ in HSO_3F reported by Singh *et al.* [20] is different and, particularly in the SO_3 stretching region where only three bands are reported, much simpler than the IR spectra of all the metal fluorosulfates summarized in Table 2. While it appears likely that differences in instrumentation, spectral resolution or sample preparation techniques may have contributed to these discrepancies, there is however a different explanation. The product obtained by us from the solvolysis of ZrCl_4 in HSO_3F after reaction times of 3 weeks shows a strong spectral similarity to the one reported by Singh *et al.* [20]. All the vibrations in the SO_3F stretching range may be assigned to a bidentate, possibly bridging SO_3F group in both instances. It therefore appears that the $\text{Zr}(\text{SO}_3\text{F})_4$ initially formed was degraded in much the same manner as the solvolysis product of ZrCl_4 in HSO_3F obtained in this study.

For all $\text{M}(\text{SO}_3\text{F})_4$ compounds, oligomeric or polymeric structures are expected consistent with their limited solubility in HSO_3F . This should result in complex vibrational spectra. The presence of two different types of fluorosulfate groups, unidentate and bidentate bridging, was confirmed for dimeric gold(III) fluorosulfate by an X-ray diffraction study [40] and is also suspected for the remaining fluorosulfates listed in Table 2 on the basis of the observed spectral similarities.

The presence of only a bidentate bridging fluorosulfate group in some tin(IV) derivatives, confirmed for $(\text{CH}_3)_2\text{Sn}(\text{SO}_3\text{F})_2$ [42] by X-ray diffraction and suggested for $\text{SnCl}_2(\text{SO}_3\text{F})_2$ [39] and $\text{SnF}_2(\text{SO}_3\text{F})_2$ [43] from their ^{119}Sn Mössbauer spectra, aids in the

TABLE 2. Infrared spectra of $[\text{Au}(\text{SO}_3\text{F})_3]_2$ and the tetrakis(fluorosulfates) of zirconium, hafnium, tin, platinum and iridium and related compounds

$[\text{Au}(\text{SO}_3\text{F})_3]_2^a$		$\text{Zr}(\text{SO}_3\text{F})_4$		$\text{Hf}(\text{SO}_3\text{F})_4$		$\text{Sn}(\text{SO}_3\text{F})_4^b$		$\text{Pt}(\text{SO}_3\text{F})_4^c$		$\text{Zr}(\text{SO}_3\text{F})_4^d$		$\text{Zr}_2\text{OF}_3(\text{SO}_3\text{F})_3$		Approximate description of bands
$\bar{\nu}$ (cm^{-1})	Int.	$\bar{\nu}$ (cm^{-1})	Int.	$\bar{\nu}$ (cm^{-1})	Int.	$\bar{\nu}$ (cm^{-1})	Int.	$\bar{\nu}$ (cm^{-1})	Int.	$\bar{\nu}$ (cm^{-1})	Int.	$\bar{\nu}$ (cm^{-1})	Int.	
1442	vs	1418	s, sh	1415	s, sh	1438	s	1440	vs, b	1403	s	1395	m	} $\nu(\text{SO}_3)$ asym, bridging and terminal SO_3F group
1425	s	1393	vs	1390	s	1411	s	1440	vs, b	1403	s	1395	m	
		1380	vs	1378	vs	1395	w, sh	1225	s	1116	s	1140	m, b	} $\nu(\text{SO}_3)$ sym, terminal SO_3F group } $\nu(\text{SO}_3)$ asym, bridging SO_3F group
1240	s	1274	s	1269	s	1232	s	1150	vs	1116	s	1140	m, b	
1220	s, sh	1170	w, sh	1180	w	1130	s	1150	vs	1116	s	1140	m, b	
		1150	vs	1150	vs	1130	s	1150	vs	1116	s	1140	m, b	
1135	ms							1070	vs	1068	ms	1060	s	} $\nu(\text{SO}_3)$ sym, bridging
		1110	s, sh	1120	s, sh	1085	s	1070	vs	1068	ms	1060	s	
		1073	m, sh	1078	m, sh	1085	s	1070	vs	1068	ms	1060	s	} $\nu(\text{SO}-\text{M})$, terminal SO_3F groups
1055	s	1022	m	1018	m, w	980	w, sh	1000	vs	862	m	835	s	
960	s, b	972	w, sh	970	vw, sh	920	m	900	vs, b	862	m	835	s	} $\nu(\text{SF})$, bridging and terminal groups
920	s, sh	862	s, sh	860	s, sh	850	m	900	vs, b	862	m	835	s	
895	s, b	853	s	853	s	832	s	670	s, b	658	m	650	m	} $\nu(\text{M}-\text{O})$ + deformation mode
820	s	853	s	853	s	832	s	640	s, b	658	m	650	m	
682	s	642	w, sh	640	w	657	w	670	s, b	593	m	590	m	} $\delta(\text{SO}_3)$ bending vibrations
670	s, sh	633	m	628	m	628	m	640	s, b	593	m	550	m	
		600	s	594	s	585	m	580	s	563	m	550	m	} various deformation modes for rocking vibrations and M-O skeletal vibrations
610	w	570	s	564	s	550	s	540	m	563	m	550	m	
590	s									474	br	440	w	
582	s, sh									430	w	440	w	
550	s									320	w	295	s	
		475	s	470	m	460	w	460	w	474	br	440	w	
460	m	465	s, sh	460	m, sh	438	m	438	m	430	w	440	w	
		430	vw	420	vw	427	vw	427	vw	430	w	440	w	
		385	m	358	m	328	m	328	m	320	w	295	s	
		380	m, sh	335	m	328	m	328	m	320	w	295	s	

Abbreviations: s = strong; m = medium; w = weak; v = very; b = broad; sh = shoulder; $\bar{\nu}$ = wavenumber; ν = stretch; δ = bend; sym = symmetric, asym = asymmetric.^aRef. 12.^bRef. 39.^cRef. 13.^dRef. 20.

TABLE 3. Vibrational spectra of $Cs_2[M(SO_3F)_6]$, with $M = Ti, Zr, Hf$ and Sn .

$\bar{\nu}$ (cm^{-1})	M = Ti; IR		M = Ti; Ra		M = Zr; IR		M = Hf; IR		M = Hf; Ra		M = Sn, Ra ^a		Approximate description of bands
	Int.	$\Delta\nu$ (cm^{-1})	Int.	$\bar{\nu}$ (cm^{-1})	Int.	$\bar{\nu}$ (cm^{-1})	Int.	$\bar{\nu}$ (cm^{-1})	$\Delta\nu$ (cm^{-1})	Int.	$\Delta\nu$ (cm^{-1})	Int.	
1400	vs, b	1405	w, b	1420	m, sh	1390	s, sh	1398	1398	w	1407	m	} $\nu(SO_2)$ asym
1276	w	1278	vs	1359	vs, b	1370	vs	1382	1382	m	1399	m	
1211	vs	1210	w	1215	vs, b	1265	w	1280	1280	s	1270	s	} $\nu(SO_2)$ sym
1110	vw			1204	s, sh	1218	vs	1215	1215	m	1218	w	
980	vs, b	990	ms, b	1109	m, s	1150	vw	1106	1106	m	1091	s	} $\nu(SO-M)$
790	s, sh	970	m, sh	1077	w, sh	1110	m	1050	1050	s, sh	995	s, sh	
700	vw			1050	vs	1015	vs	1028	1028	s	828	m	} $\nu(SF)$
651	mw	625	m	~1020	m, sh	810	vs	858	858	s	811	m	
619	w			844	ms	795	s, sh	770	770	w			} $\nu(M-O)$ + deformation mode
~580	m, sh	580	vw	620	m, s	620	m	625	625	m, sh	625	s	
566	s	563	ms	585	m, sh	575	s, sh	570	570	m	578	ms	$\delta(SO_2)$ asym + $\delta(SO_2)$ sym combination bands
520	vw			567	s	565	m	555	555	m	560	ms	
430	ms	423	ms, b	495	vw, sh	415	vw, sh	415	415	m	431	m	M-O skeletal vibrations $\rho(SO_3F)$
420	m, sh			425	ms	405	w	415	415	w	418, 407	w	
		259	s	405	s	405	w	345	345	w	345	w	M-O skeletal vibrations + deformation modes
		170	w	240	ms	240	ms	260	260	m	260	m	

^aRef. 32(b); for abbreviations, see Table 2.

approximate band assignments listed in Table 2. For both coordination modes of the fluorosulfate group with local symmetry C_s or even lower, three bands are expected in the SO_3 stretching region for each coordination mode with different band positions. For unidentate, terminal fluorosulfate groups, the three bands are usually found at 1500–1420, 1270–1220 and 1000–850 cm^{-1} , while bidentate groups are best recognized by bands at 1420–1350, 1170–1100 and 1080–1060 cm^{-1} . A similarly clear differentiation between deformation modes is not possible on account of the rather narrow wavenumber range (600–400 cm^{-1}) and extensive band overlap in this area. While the infrared spectra summarized in Table 2 provide evidence for the presence of fluorosulfate-bridged polymers or oligomers, they offer no clear clues as to why three of the metal fluorosulfates, i.e. $[Au(SO_3F)_3]_2$ [12], $Pt(SO_3F)_4$ [13] and $Ir(SO_3F)_4$ [29], two of which act as Lewis acids in conjugate superacid systems [12, 13], are well soluble in HSO_3F while the rest are virtually insoluble in fluorosulfuric acid.

There must however be some very limited solubility for all metal fluorosulfates in HSO_3F when $CsSO_3F$ is present, in order to allow for the formation of ternary fluorosulfates of the type $Cs_2[M(SO_3F)_6]$ for $M=Ti, Zr$ or Hf . Their vibrational spectra are summarized in Table 3 and compared to the Raman spectrum of $Cs_2[Sn(SO_3F)_6]$ [32] for which the ^{119}Sn Mössbauer spectrum has indicated an octahedral coordination for tin. Again the spectra are all very similar with the principal SO_3F stretching vibrations giving rise to bands at 1400, 1280–1210, 1110–970 and 860–770 [$\nu(SF)$], indicative of anionic, unidentate SO_3F groups in the various anions. Some band proliferation (probably as a result of vibrational coupling) gives rise to the formation of shoulders in the IR spectra in particular. Very similar vibrational spectra are reported for all the other $Cs_2[M(SO_3F)_6]$ salts listed in Table 1 and the vibrational assignment is adopted from ref. 32.

Both infrared and Raman spectra obtained for $Cs_2[Ti(SO_3F)_6]$ are in complete agreement with the spectra listed in Table 3 and those published previously [13, 29–32]. The binary fluorosulfate $Ti(SO_3F)_4$ was, however, not isolated in a pure form. The IR spectrum of the resin-like material obtained shows SO_3 stretches at 1390 (vs), 1251 (ms), 1110 (w), 1050 (vs), 960 (vs, sh) and 880 cm^{-1} in the stretching range, with deformation vibrations giving rise to bands at 640 (s), 585 (ms), 551 (m) and 450 (s) cm^{-1} all similar to bands observed in the IR spectra of $Zr(SO_3F)_4$ and $Hf(SO_3F)_4$. In addition, a medium–weak broad band at *c.* 3100 cm^{-1} was observed which suggests the presence of residual amounts of HSO_3F . The presence of HSO_3F may be responsible for the difference in appearance of $Ti(SO_3F)_4$.

Conclusion and summary

The oxidation of the Group 4 metals Ti, Zr and Hf by $S_2O_6F_2$ in HSO_3F provides a simple, versatile synthetic route to the corresponding fluorosulfates of composition $M(SO_3F)_4$, $M=Ti, Zr$ or Hf . While the zirconium and hafnium compounds are extremely similar in their appearance and give identical infrared spectra, $Ti(SO_3F)_4$ is a greenish-yellow resin-like material which retains small amounts of HSO_3F .

All three binary fluorosulfates appear to be virtually insoluble in fluorosulfuric acid. The intrinsic acceptor ability towards SO_3F^- ions is demonstrated for all three materials by their isolation and relatively high thermal stability (to *c.* 260 °C) of ternary fluorosulfates of composition $Cs_2[M(SO_3F)_6]$, $M=Ti, Zr$ or Hf , which appear to be isostructural to other $Cs_2[M(SO_3F)_6]$ salts with $M=Ru, Ir, Pd, Pt, Ge$ and Sn , as is evident from the data listed in Table 3.

It should be remembered that the intrinsic acceptor ability of the metal centre may be demonstrated in two ways: (i) the ability to form polymers with polydentate bridging anionic groups (this ability is expected to be strengthened by anionic groups that show a strong tendency to function as polydentate ligands, such as fluorosulfate groups); and (ii) the propensity to function as Lewis acids towards weakly basic donor ligands such as the SO_3F^- ion.

Only where there is a limited tendency towards polymer formation as, for example, in $Au(SO_3F)_3$ which is dimeric in the solid state [40] and quite possibly also in HSO_3F solution [44], is it feasible to use binary fluorosulfates in conjugate HSO_3F superacid systems. It is interesting to note that the two binary fluorosulfates that meet these criteria, i.e. $Au(SO_3F)_3$ [12] and $Pt(SO_3F)_4$ [13], were first synthesized by Cady and his students [45].

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