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NIOBIUM(V) AND TANTALUM(V) FLUORIDE DERIVATIVES OF FLUOROSULFURIC AND TRIFLUOROMETHYLSULFURIC ACIDS

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SUMMARY

The syntheses and characterizations of three niobium(V)- and tantalum(V) fluoro derivatives of the sulfonic acids HSO_3F and HSO_3CF_3 are described. All are white, solid, seemingly polymeric sulfonato bridged materials, which are of interest as Lewis acids in super acid systems. $NbF_2(SO_3F)_3$ forms as a byproduct in the oxidation of niobium by bis(fluorosulfuryl)peroxide in HSO_3F as a polymeric solid. $TaF_4(SO_3CF_3)$ results from the addition of triflic acid, HSO_3CF_3, to $Ta(SO_3F)_5$ dissolved in HSO_3F, while $TaF_4(SO_3F)$ forms in a ligand redistribution reaction of $Ta(SO_3F)_5$ with a four-fold amount of TaF_5 in HSO_3F as solvent. Infrared and Raman spectra of the compounds are reported.

INTRODUCTION

The pentafluorides of niobium and tantalum have a common cis-fluorine bridged tetrameric structure[1] and display very similar chemical behaviour[2]. Their importance in chemical reactions centers on their ability to function as Lewis acids. Both NbF_5 and even more so TaF_5 have

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found use in superacid systems in conjunction with strong protonic acids like anhydrous HF, HSO_3F and HSO_3CF_3, in spite of their limited solubility in these protonic solvents[3]. Both are effective fluoride ion acceptors and the existence of complex anions of the type $[MF_7]^{2-}$ and $[MF_8]^{3-}$ in addition to $[MF_6]^-$, with M = Nb or Ta, in HF solution and in the form of alkali metal salts[2][5] illustrates the ability of the central atom to expand its coordination sphere beyond the octahedral configuration.

With the exception of hydrolysis, ammonolysis and similar solvolysis reactions, very few ligand substitution reactions are known [2][5], and only a limited number of mixed ternary compounds of the type $MF_nX_{(5-n)}$ exist, with M = Nb or Ta and X = a uninegative anionic ligand. The fluoride-fluorosulfates $MF_3(SO_3F)_2$ are two of these rare examples[6]. They are obtained by the reaction of an excess of SO_3 with the pentafluorides as clear, colourless, viscous liquids and have the actual composition $NbF_5 \cdot 2.1\ SO_3$ and $TaF_5 \cdot 2.6\ SO_3$, respectively. It was claimed that excess SO_3 is only incompletely removed, but spectroscopic or structural information was not reported [6].

Our interest in materials of this kind stems from the recent development of the two superacid systems HSO_3F-$Ta(SO_3F)_5$ and HSO_3F-$Nb(SO_3F)_5$[7]. The two pentakis(fluorosulfates) are obtained by oxidation of the corresponding metals with bis(fluorosulfuryl) peroxide, $S_2O_6F_2$, in HSO_3F. Both compounds are extremely soluble in fluorosulfuric acid and attempts at their isolation result in decomposition, supposedly with SO_3 elimination. In particular, $Nb(SO_3F)_5$ displays this tendency. To confirm the decomposition mode, it is of interest to isolate well defined fluoride-fluorosulfates of both niobium and tantalum, and to characterize these materials by spectroscopic means.

We have previously reported on the synthesis and characterisation of a number of fluoride-fluorosulfates, capable of functioning as Lewis acids: polymeric solids of the type $MF_2(SO_3F)_2$ with M = Sn[8] or Ge[9], and clear, viscous liquids of the composition $MF_3(SO_3F)_2$ with M = As[10] or Sb[11]. Antimony forms two additional compounds in this group, $SbF_4(SO_3F)$[11][12] and $Sb_2F_9(SO_3F)$[11], both colorless viscous liquids. The principal routes of synthesis, the oxidation of lower valent fluorides such as AsF_3 or SbF_3 by $S_2O_6F_2$[11], or in case of SbF_3 by fluorine fluorosulfate FSO_3F[11], or even chloride replacement of $SnCl_2F_2$ by $S_2O_6F_2$ [8], are however, not applicable here, because suitable precursors are either unknown or difficult to obtain for both niobium and tantalum [2][5]. Only the isolation of $GeF_2(SO_3F)_2$ in about 70% yield during the oxidation of Ge by $S_2O_6F_2$ in HSO_3F may be seen as a precedent[9].

There appears to be only one single fluoride-trifluoromethylsulfate reported so far, $GeF_2(SO_3CF_3)_2$, formed quantitatively by the solvolysis of $GeF_2(SO_3F)_2$ in a large excess of triflic acid, HSO_3CF_3[13].

EXPERIMENTAL

a) Chemicals

Niobium and tantalum powder of-60 mesh and 99.99% purity are obtained from the Ventron Corporation. Tantalum(V) fluoride of 99% purity is obtained from Ozark-Mahoning (Pennwalt) and trifluoromethylsulfuric acid from the 3M-company. HSO_3CF_3 is purified by distillation from conc. H_2SO_4 at reduced pressure. Fluorosulfuric acid of technical grade is obtained from Orange County Chemicals and is purified by double distillation at atmospheric pressure, as described before[14]. Bis(fluorosulfuryl) peroxide is prepared by catalytic fluorination of SO_3 over AgF_2[15].

b) Instrumentation and Methods of Analysis

Chemical analyses were carried out by Analytische Laboratorien, Gummersbach, F.R.G., except for the carbon and sulfur analyses which were provided by Mr. P. Borda of this department. The equipment used for synthetic reactions followed published precedents[16]. The invertible filtration apparatus used to isolate the solids was similar in design to an apparatus described by Shriver[17]. Manipulation of all materials was done in a Vacuum Atmospheres Corp. Dri lab model HE-493 filled with dry N_2 and equipped with an HE-493 Dri-Train circulating unit. Methods and instruments used to obtain infrared and Raman spectra have also all been described[16].

c) Synthetic reactions

(i) Niobium(V) difluoro tris(fluorosulfate), $NbF_2(SO_3F)_3$

a) Crystalline $NbF_2(SO_3F)_3$

394 mg (4.24 mmols) niobium metal powder was treated with 3.17 ml (27.6 mmols) $S_2O_6F_2$ and 2.31 ml (39.8 mmols) HSO_3F and allowed to react at 25°C for 3 days, by which time all the metal had been consumed and a colorless, slightly murky solution was obtained. Excess $S_2O_6F_2$ was removed in vacuo at 0°C and the solution was stored in the drybox for two months, during which time a crystalline product precipitated from solution. The crystals were isolated by slowly removing the liquid, first in vacuo at 0°C and then by passing a stream of dry N_2 over the product for a total of 4 days. The white, hygroscopic $NbF_2(SO_3F)_3$ melted at 126-129°C.

b) Finely powdered $NbF_2(SO_3F)_3$

1.289 g (13.87 mmols) niobium metal powder was treated with about 9 ml $S_2O_6F_2$ and 13 ml HSO_3F and stirred at 25°C for 4 days, during which time the metal was completely consumed and a turbid, colorless solution was obtained. Excess $S_2O_6F_2$ was removed in vacuo at -5°C. A fine, white powder precipitated out of solution within 24 hours and was collected by vacuum filtration. The product was dried in vacuo at 25°C overnight and obtained in 15% yield. $NbF_2(SO_3F)_3$ melted at 126-129°C.

Analysis:	Calc. for $NbF_5S_3O_9$:	Nb,21.70; S,22.47 and F,22.19.
	Found	Nb,21.40; S,22.52 and F,21.85.

(ii) Tantalum(V) tetrafluoro fluorosulfate, $TaF_4(SO_3F)$

1.50 g (5.44 mmol) TaF_5 was added to 0.73 ml of a 1.88 M $Ta(SO_3F)_5$ solution, prepared from Ta and $S_2O_6F_2$ in HSO_3F[7] corresponding to 1.36 mmol $Ta(SO_3F)_5$, in the drybox. The heterogeneous mixture was stirred for 18 hours at room temperature, by which time all of the TaF_5 had dissolved and a clear, colourless solution resulted. A white, powdery product was isolated in 52% yield by pumping on the solution for 2 days at room temperature and thus removing all volatiles. $TaF_4(SO_3F)$ decomposed at 210-220°C.

Analysis:	Calc. for TaF_5SO_3:	Ta,50.83; S,9.01 and F,26.68.
	Found:	Ta,51.10; S,9.16 and F,26.54.

(iii) Tantalum(V) tetrafluoro(trifluoromethyl) sulfate, $TaF_4(SO_3CF_3)$

Onto a 1.54 M solution of $Ta(SO_3F)_5$ in 1.14 ml HSO_3F about 5 ml of HSO_3CF_3 were distilled in vacuo and the resulting mixture was stirred for one week at 25°C. By this time a precipitate had formed. The excess acid and any other volatile by-products were removed in vacuo at room temperature overnight. The white, amorphous solid was isolated in quantitative yield. $TaF_4(SO_3CF_3)$ melted at 312-318°C and appeared to go through a physical change at 255-265°C.

Analysis:	Calc. for TaF_7CSO_3:	Ta,44.57; S,7.90; C,2.96 and F,32.76.
Found:		Ta,44.70; S,8.20; C,2.76 and F,32.42.

Infrared bands obtained on a solid film: 1410s,sh, ~1355s,b, 1235m,sh, 1210s,b, 1170m,sh, 1150m, 1090w,sh, 980ms,b, 860m,b, 770w, ~680m,b, 605m,sh, 572s, 512s, 480m,sh, 465s.

RESULTS AND DISCUSSION

a) Synthesis

The formation of $NbF_2(SO_3F)_3$ from solutions of $Nb(SO_3F)_5$ in HSO_3F occurs with time or if high concentrations of $Nb(SO_3F)_5$ are obtained by oxidation of niobium by $S_2O_6F_2$ in HSO_3F[7]. Its separation from solution is possible on account of the lack of solubility in fluorosulfuric acid displayed by $NbF_2(SO_3F)_3$. Both solvent removal or filtration are possible methods of isolation. The rather low yield of 15% obtained when filtration is applied after a reaction time of 4 days indicates that either undissociated $Nb(SO_3F)_5$, or other soluble products like $NbF(SO_3F)_4$ remain in solution, or $NbF_2(SO_3F)_3$ may have limited solubility.

The composition is established by microanalysis as $NbF_2(SO_3F)_3$. Attempts to obtain an X-ray diffraction single crystal structure on crystalline $NbF_2(SO_3F)_3$ are not successful, because clusters of twinned and disordered crystals are encountered. Both the crystalline and the finely powdered form have identical melting points and analytical data. There is in essence no chemical or structural difference between the two forms, and the difference in appearance is the result of the conditions of their formation from solution. It hence appears that solutions of $Nb(SO_3F)_5$ in HSO_3F are unstable and will undergo successive loss of SO_3. Of the products resulting from SO_3 elimination, $NbF_2(SO_3F)_3$ has limited solubility and will eventually precipitate while shifting the decomposition equilibrium further to the right:

$$Nb(SO_3F)_{5(solv.)} \rightleftharpoons NbF(SO_3F)_{4(solv.)} + SO_3 \rightleftharpoons NbF_2(SO_3F)_3(s) + 2SO_3 \quad (1)$$

In dilute solution, the overall process will be slow, allowing the growth of crystals. In concentrated solution, more finely divided material forms quickly in about 15% isolated yield. The first intermediate $NbF(SO_3F)_{4(solv.)}$ seemingly remains in solution and is not isolated. With the formation of solid $NbF_2(SO_3F)_3$, reaction (1) comes to an end and materials like $NbF_3(SO_3F)_2$ or $NbF_4(SO_3F)$ are not obtained in this manner. There is a precedent for a material of this composition, $UF_2(SO_3F)_3$[18], obtained from the reaction of UF_6 with SO_3. The same reaction yields at lower temperature $UF(SO_3F)_4$, while $UF_3(SO_3F)_2$ results from the reaction of UF_5 with SO_3[19].

Formation of $TaF_4(SO_3CF_3)$ is rather unexpected and is the result of an attempt to convert solvated $Ta(SO_3F)_5$ to $Ta(SO_3CF_3)_5$ in the hope of obtaining a less soluble and hence isolable tantalum(V) compound. The solvolysis of binary fluorosulfates in an excess of triflic acid according to the generalized equation:

$$E(SO_3F)_n + nHSO_3CF_3 \longrightarrow E(SO_3CF_3)_n + nHSO_3F \quad (2)$$

is convenient and many precedents for various bonding types of the fluorosulfate group are reported[13], all employing solid fluorosulfates of known composition as starting materials.

Such solvolytic conversion of fluorosulfates into trifluoromethylsulfates is based on the mutual degradation of the SO_3F-group and HSO_3CF_3, with the latter present in excess. This degradation, best illustrated by the interaction of the two acids HSO_3F and HSO_3CF_3 [20][21], results in the formation of mostly volatile products such as $CF_3SO_3CF_3$, CF_3SO_3F,

CF_2O, CO_2, SO_2, SiF_4 and by inference HF and H_2O. It is hence expected that when solvated $Ta(SO_3F)_5$ is reacted with an excess of HSO_3CF_3, HF will form and take part in the conversion reaction, resulting in the formation of Ta-F bonds and consequently the isolation of $TaF_4(SO_3CF_3)$. The formation of Ta-F bonds by SO_3 - elimination from Ta-SO_3F groups is also possible during the complex conversion reaction. In any event, after all volatiles are removed in vacuo, $TaF_4(SO_3CF_3)$ remains behind as a solid residue and is identified by chemical analysis. The analogous solvolytic conversion attempt of solvated $Nb(SO_3F)_5$ by an excess of HSO_3CF_3 does not yield a pure product. The solid residue obtained after removal of all volatiles analyses as $NbF_{4.3}(SO_3CF_3)_{0.5}(SO_3F)_{0.2}$. The synthesis of $TaF_4(SO_3F)$ differs from the formation reactions of $NbF_2(SO_3F)_3$ and $TaF_4(SO_3CF_3)$, which are rather accidental. Formation of $TaF_4(SO_3F)$ according to:

$$Ta(SO_3F)_5 + 4TaF_5 \xrightarrow{HSO_3F} 5TaF_4(SO_3F) \qquad (3)$$

is viewed as a planned synthesis, with the composition of the reaction product determined by the stoichiometry of the reactants, and HSO_3F acting as reaction medium.

The successful isolation of $TaF_4(SO_3F)$ as an analytically pure, high melting solid allows the following conclusions: (i) Ligand redistribution of F^- and SO_3F^- must occur during the reaction. (ii) The presence of $Ta(SO_3F)_{5(solv.)}$ allows the dissolution of large quantities of TaF_5 in HSO_3F, which by itself as stated is only sparingly soluble in this solvent[3]. (iii) Formation of other tantalum(V) fluoride-fluorosulfates should be possible according to the generalized equation:

$$(5-n)Ta(SO_3F)_5 + nTaF_5 \longrightarrow 5\ TaF_n(SO_3F)_{(5-n)} \qquad (4)$$

with n = 2, 3 or 4, and (iv) Similar redistribution reactions should be possible for $Nb(SO_3F)_{5(solv.)}$.

However, there is a rather unexpected and surprising aspect to reaction (4) and the isolation of $TaF_4(SO_3F)$ as a high melting, non-volatile solid by removal of all volatiles in vacuo: the yield of analytically pure $TaF_4(SO_3F)$ is only about 50%, which in turn implies that not all $TaF_4(SO_3F)$ crystallizes and another volatile Ta(V) - compound of identical composition forms as well. From the IR spectrum discussed below it appears that solid TaF_4SO_3F is polymeric and nonvolatile. Solvation by HSO_3F seems to prevent polymerisation partly, resulting in a volatile product. We have so far not been able to identify this material, which is removed together with excess HSO_3F.

Before wider use of this synthetic route to novel Lewis acids can be made, it will be necessary to fully understand the formation reaction of $TaF_4(SO_3F)$, including identification of the volatile Ta(V) compound. This conclusion also applies to the conversion of $MF_n(SO_3F)_{5-n}$ compounds, with M = Nb or Ta and n = 1 - 4, into the corresponding triflates by solvolysis in an excess of HSO_3CF_3.

All three materials isolated and characterized in the course of this study are solids and appear to be polymeric. Any similarity to the previously described viscous oils of the type $MF_3(SO_3F)_2$[6] is not apparent. There is of course the difference in composition between the previously reported materials and those obtained by us, but the presence of incompletely removed SO_3, as the authors suggest[6], remains as a plausible explanation for the apparent differences, as does the actual stoichiometry, which may indicate a complex mixture of several fluoride-fluorosulfates of both Nb and Ta.

b) Vibrational spectra

Both Raman and infrared spectra on solid films are obtained for $NbF_2(SO_3F)_3$ and $TaF_4(SO_3F)$. They are listed in Tables I and II, respectively. For $TaF_4(SO_3CF_3)$, strong fluorescence prevents the recording of a

TABLE I

Vibrational frequencies of $NbF_2(SO_3F)_3$

Raman ($\Delta\nu$, cm^{-1})		IR (ν, cm^{-1})		Approx. Assignment
~1435	vw,b	1434	s	ν_{as} (SO_3)
		1407	s	
		1394	s,sh	
		1378	s	
		1216	s,b	ν_s (SO_3)
1161	m	1164	s	
~1112	w,b,sh	1115	m,b,sh	
1104	m			
1080	w	1090	s,sh	ν (SO_2 + O-SO_2F)
1070	w	1069	s	
~1050	w,b	1046	s,sh	
1006	s	1002	s	
		~970	m,vb,sh	
884	m,sh	888	m,b,sh	ν (S-F)
874	m	854	s,b	
869	m,sh	837	s,b,sh	
		712	m,b	ν_{as} (Nb-F)
669	vw,b	666	s	
		634	m,sh	ν_s (Nb-O) + δ (SO_3F)
		621	s	
		605	m,sh	
		592	m	
566	vw,b	571	m,sh	δ (SO_3F)
561	vw,b	562	m	
		475	w	ν_{as} (Nb-O) + δ (SO_3F)
		450	w	
386	vw,b			lattice vibrations + torsion modes
310	w,b			
288	w			
269	m			
250	m			

Abbreviations: s=strong, m=medium, w=weak, sh=shoulder, b=broad, v=very, as=asymmetric, s=symmetric, ν=stretch, δ=deformation.

TABLE II

Vibrational frequencies of $TaF_4(SO_3F)$

Raman ($\Delta\nu$, cm^{-1})		IR (ν, cm^{-1})		Approx. Assignment
		1403	m	ν_{as} (SO_3)
1191	w	1180	s	ν (SO_3)
1123	s	1112	s,b	
1105	w,sh			
1083	m	1075	s,sh	
		895	m,sh	ν (S-F)
		879	m,sh	
748	vs			ν_s (Ta-F)
725	m	733	m	ν (Ta-F) + ν_s (Ta-O) + δ (SO_3F)
716	m	708	m	
691	m	684	m	
671	m			
660	vw,sh	663	m,sh	
648	w	644	m	
620	vw,b	611	w	
488	w	486	w	ν_{as} (Ta-O) + δ (SO_3F)
470	w	464	vw,sh	
308	w			lattice vibrations + torsion modes
283	m,sh			
268	m			
241	w			
228	w			
220	w,sh			
200	w			

Abbreviations: see Table I.

Raman spectrum and the IR spectrum of the high melting solid is very poorly resolved. Attempts to use Nujol as a mulling agent are unsatisfactory, because 'new' very intense bands, not found in the solid film spectrum, are observed and reaction of the solid with Nujol is suggested. Some of the more prominent broad bands observed on the solid film of $TaF_4(SO_3CF_3)$ are listed in the experimental section, but this listing may be incomplete.

Even for the remaining two fluoride-fluorosulfates, $NbF_2(SO_3F)_3$ and $TaF_4(SO_3F)$, very few conclusions can be made safely for a number of reasons: (i) The quality of the spectra obtained is not optimal. Some of the asymmetric vibrations are not observed in the Raman spectra or are found to be very weak. In the region between 500 and 600 cm^{-1}, where SO_3 deformation modes occur, the infrared spectrum of $TaF_4(SO_3F)$ shows only a broad shoulder with a very weak peak at about 570 cm^{-1} and another very weak shoulder at ~530 cm^{-1}. (ii) It cannot be assumed safely that the central atoms will have coordination number six, as has been the case previously for fluoride-fluorosulfates studied by us [8][11] with main-group elements as central atoms. (iii) Support from other physical techniques, for example ^{119}Sn Mössbauer spectroscopy in the case of $SnF_2(SO_3F)_2$ and related compounds [8], is not available. (iv) A spectral comparison with precedents is not very helpful. The vibrational spectra reported for liquid $SbF_4(SO_3F)$[11] are far less complex than those for $TaF_4(SO_3F)$. On the other hand, there is some limited similarity, particularly in the SO_3F stretching region, between the spectra found for $NbF_2(SO_3F)_3$ and those reported for $UF_2(SO_3F)_3$[18] and $UF(SO_3F)_4$ [19]. However, these authors do not reach any definitive conclusions which could be of use in our interpretation. A similar spectral complexity for the U(V) and Nb(V) species is not surprising, since both central atoms together with Ta(V) may well expand their coordination number to 7 or 8.

Under these circumstances, only an approximate band description is possible. Employing an assignment rationale reported by us some time ago[22], it appears that the presence of both ionic or monodentate SO_3F groups can be eliminated for both compounds. For $TaF_4(SO_3F)$, which gives a simpler spectrum, SO_3 stretching modes at ~1403, 1180 and 1075 cm^{-1} suggest a bidentate configuration, while bands at 1180 (assuming band overlap) and 1120 cm^{-1} may be attributed to tridentate modes. There are also two distinct ν S-F bands observed.

A number of strong IR bands between ~640 and 740 cm^{-1} are in part due to Ta-F stretches and it appears that terminal rather than bridging fluoride is present. A Raman band at 748 cm^{-1}, also attributed to ν Ta-F, is clearly the most intense band in the spectrum. There are additional puzzling observations, such as the absence of the ν SO_3 band at 1400 cm^{-1} and of both ν S-F bands in the Raman spectrum, as well as the previously discussed absence of distinct bands in the region 500-600 cm^{-1} in both the IR and Raman spectra. It seems reasonable to assume the presence of bridging SO_3F - groups rather than of bridging fluoride in this compound, and judging by the complexity and relative band intensity, the possible presence of more than one coordination environment cannot be ruled out.

The vibrational spectra observed for $NbF_2(SO_3F)_3$ reflect an even greater complexity in the diagnostic SO_3F-stretching region and at least three different fluorosulfate groups are suggested by the observation of three distinct ν S-F bands at ~850 cm^{-1} in both the Raman and IR spectrum. The Nb-F stretching region appears to be simpler, with bands at 666 and 712 cm^{-1} in the infrared. Again, terminal fluorines are suggested while band positions in the SO_3-stretching region suggest bi- and possibly tridentate fluorosulfate groups.

It is hoped that once more compounds in this group become available, distinct features will emerge in their vibrational spectra to permit a more detailed discussion.

CONCLUSIONS

Of the three new compounds reported here, only one is obtained as the result of an intentional, directed synthesis. The method used, ligand redistribution between solvated $Ta(SO_3F)_5$ and TaF_5, appears to be of general use and may be applicable also to the synthesis of corresponding niobium compounds. The unexpectedly low yield of $TaF_4(SO_3F)$ remains a puzzle that needs to be solved. On the other hand, $TaF_4(SO_3F)$ can be redissolved in HSO_3F, giving rise to a new superacid system which deserves further study.

Well defined $NbF_2(SO_3F)_3$ is found to be the only isolable product of the Nb metal oxidation by $S_2O_6F_2$ in HSO_3F. Its isolation is possible because $NbF_2(SO_3F)_3$ is insoluble in HSO_3F which in turn precludes formation of other materials in the series $NbF_n(SO_3F)_{5-n}$ with n = 3, 4 or 5.

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