indicates that the oxidation product is diamagnetic and that all three ligands are equivalent. Diamagnetism must result either from strong spin–spin coupling between the paramagnetic metal and radical ligand or from charge delocalization within the cationic complex. This observation further suggests that the positively charged complex, which may form initially in the hydrolysis reaction between MO_4^- and catechol in reaction 1, is the Tc(VI) species $Tc^{VI}(DBSQ)(DBCat)_2^+$ rather than $Tc^{VII}(DBCat)_3^+$. Given the negative value of the DBSQ/DBCat couple, catecholate reduction of Tc(VII) to Tc(VI) would be quite favorable.

Discussion

Two unusual examples of Tc(VI) have been obtained from the reaction between NH_4TcO_4 and 3,5-di-*tert*-butylcatechol. Other well-characterized complexes of Tc(VI) are confined to the nitrido anions $TcNX_4^-$ (X = Cl, Br, TcF_6) and the polymeric oxyhalides $TcOX_4$ (X = F, Cl).[10,15,16] In the reaction, catechol serves as an acid to hydrolyze oxo ligands of the pertechnetate ion, as a chelating agent with the metal, and as a reducing agent for Tc(VII). Both $Tc(DBCat)_3$ and $Tc(DBCat)_2(DBAP)$ show well-resolved 10-line EPR spectra in solution at room temperature. Electrochemical characterization has been used to show the stability of the neutral Tc(VI) complexes relative to Tc(V) and Tc(IV) forms and to evaluate the accessibility of cationic forms of the complexes.

Empirical studies have shown that complexes with a single positive charge are particularly effective as heart-imaging agents. Spheroidal complexes appear to bind most effectively with myocardial receptors and the hexakis(isonitrile)technetium(I) complexes are among the most effective myocardial-imaging agents.[17] The *tert*-butylisonitrile complex $Tc(t\text{-}BuNC)_6^+$ provides high-quality images but accumulates in the liver, blocking exposure to the heart. Derivatives with methoxy substituents have shown lower liver accumulation and higher miocardial specificity. Clathrochelating triglyoxime complexes of Tc(III) have been tested with some success,[18] cationic complexes containing phosphine and arsine ligands have been investigated,[19] and even dibenzenetechnetium(I) has been considered for heart-imaging applications.[20]

The catecholate complexes of technetium and rhenium may be of interest in imaging applications. They can be synthesized by procedures that should be easily adapted to a field kit, and they are chemically and kinetically stable in solution. The DBCat complexes included in our present investigation undergo $Tc^{VI}(DBSQ)(DBCat)_2^+/Tc^{VI}(DBCat)_3$ reduction at positive potentials. They are probably too strong as oxidants for use as myocardial-imaging agents, and the lipophilic character of the neutral complexes may promote transfer to the liver. However, catechols are readily available with a wide variety of different substituents, which may be used to shift electrochemical potentials, solubility properties, and stereochemical features. The catechol/pertechnetate reaction could prove useful as a practical route to technetium catecholate complexes that may be of interest as radiopharmaceuticals.

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Supplementary Material Available: Tables containing details of the structure determination and refinement, anisotropic thermal parameters, a complete list of bond distances and angles, and hydrogen atom positions for $Tc(DBCat)_3$ (14 pages); observed and calculated structure factors (20 pages). Ordering information is given on any current masthead page.

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(15) Holloway, J. H.; Selig, H. *J. Inorg. Nucl. Chem.* **1968**, *30*, 473.

(16) (a) Edwards, A. J.; Jones, G. R.; Sills, R. J. C. *J. Chem. Soc. A* **1970**, 2521. (b) Guest, A.; Lock, C. J. L. *Can. J. Chem.* **1972**, *50*, 1807.

(17) (a) Jones, A. G.; Kronauge, J. F.; Davison, A. *J. Nucl. Med. Allied Sci.* **1985**, *29*, 200. (b) Linder, K. E.; Davison, A.; Jones, A. G. *J. Nucl. Med. Allied Sci.* **1985**, *29*, 203.

(18) Thompson, M.; Nunn, A. D.; Treher, E. N. *Anal. Chem.* **1986**, *58*, 3100.

(19) (a) Hurst, R. W.; Heineman, W. R.; Deutsch, E. *Inorg. Chem.* **1981**, *20*, 3298. (b) Vanderheyden, J.-L.; Heeg, M. J.; Deutsch, E. *Inorg. Chem.* **1985**, *24*, 1666.

(20) Dean, R. T.; Wester, D. W.; Nosco, D. L.; Adams, M. D.; Coveney, J. R.; Robbins, M. S.; McElvany, K. D.; DeJong, R. *Technetium in Chemistry and Nuclear Medicine 2*; Nicolini, M., Bandoli, G., Mazzi, U., Eds.; Cortina International: Verona, Italy, 1986; p 147.

The Novel Superacid Systems $HSO_3F\text{–}Nb(SO_3F)_5$ and $HSO_3F\text{–}Ta(SO_3F)_5$

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Abstract: The in situ oxidation of niobium and tantalum in HSO_3F by bis(fluorosulfuryl) peroxide, $S_2O_6F_2$, results in the formation of solvated Lewis acids $M(SO_3F)_5$, M = Nb or Ta. Both solutes behave as moderately strong, monoprotonic acids, based on electrical conductivity measurements over the concentration range 0–0.05 *m* and on conductometric titrations against KSO_3F. These measurements suggest a general order of acidity, $Au(SO_3F)_3 > Ta(SO_3F)_5 \geq SbF_5 > Nb(SO_3F)_5 > NbF_5$, all giving rise to monoprotonic acids. Supporting evidence comes from ^1H, ^{19}F, and ^{93}Nb NMR spectroscopy and the successful isolation and characterization of complexes of the type $Cs_n[M(SO_3F)_{5+n}]$, with M = Nb or Ta and n = 1 or 2, from these solutions.

1. Introduction

After initial observation by Woolf in 1959,[1] the superacid system $HSO_3F\text{–}SbF_5$, later termed "magic acid",[2] was first investigated in 1965 by means of conductometry, cryoscopy, and ^{19}F nuclear magnetic resonance[3] and applied to the generation of carbonium cations[4] at about the same time. Following these early reports, the system has been subsequently extensively studied[5] and even

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(1) Woolf, A. A. *J. Chem. Soc.* **1955**, 433.

(2) Olah, G. A.; Prakash, G. K. S.; Sommer, J. *Science* **1979**, *206*, 13.

(3) Thompson, R. C.; Barr, J.; Gillespie, R. J.; Milne, J. B.; Rothenbury, R. A. *Inorg. Chem.* **1965**, *4*, 1641.

(4) Olah, G. A.; Comisarow, M. B.; Cupas, C. A.; Pittman, C. U. *J. Am. Chem. Soc.* **1965**, *87*, 2997.

0002-7863/89/1511-4328$01.50/0 © 1989 American Chemical Society

more widely used[6] to generate a large variety of carbocations with numerous applications in organic synthesis. In spite of the excellent properties of HSO_3F[7] and the high Lewis acidity of SbF_5,[8] facile F vs SO_3F interchange as well as concentration- and temperature-dependent association via SO_3F[3] or F bridges[5] have been responsible for rather complex equilibria, involving in particular the anions and their corresponding protonated acids. The absence of a single anion has restricted the use of magic acid and of related HSO_3F–MF_5 systems in the synthesis of novel compounds with extremely electrophilic cations.

We report on recent results of our studies into the development of viable alternatives to the HSO_3F–SbF_5 superacid, the HSO_3F–$Ta(SO_3F)_5$ and the HSO_3F–$Nb(SO_3F)_5$ systems, where only SO_3F groups are present. The Lewis acids TaF_5 and NbF_5 have so far found limited use in superacid studies.[9] Their lack of solubility in HSO_3F,[7] and more so in HF,[10] as well as the low acidity of the resulting solutions[6,11] has contributed to this lack of interest.

Earlier attempts by us to use binary metal fluorosulfates as acidic solutes in HSO_3F[7,12] have led to the development of the superacid systems HSO_3F–$Au(SO_3F)_3$[13] and HSO_3F–$Pt(SO_3F)_4$.[14] Even though these systems show high acidity and good thermal stability, the high cost of the metals involved restricts any widespread synthetic application. On the other hand, the lack of appreciable solubility of $Sn(SO_3F)_4$ in HSO_3F has precluded a solution study and a confirmation of its suspected superacidity in HSO_3F.[15]

2. Synthesis

In order to expand the range of binary fluorosulfates with potential Lewis acidity, the preparation of tantalum(V) and niobium(V) fluorosulfates was undertaken. Binary fluorosulfates of the type $M(SO_3F)_5$ have, to our knowledge, not been prepared so far. The formation of oxyfluorosulfates of the composition $MO(SO_3F)_3$, with M being V, Nb, or Ta, has been observed in the reactions of MCl_5 with bis(fluorosulfuryl) peroxide, $S_2O_6F_2$.[16a] On the other hand, the reaction of SO_3 with both NbF_5 and TaF_5 yields materials of the composition $NbF_5 \cdot 2.1SO_3$ and $TaF_5 \cdot 2.6SO_3$,[16b] which are viewed as $MF_3(SO_3F)_2$ with incompletely removed excess of SO_3.[9b]

A general synthetic route to binary metal fluorosulfates,[13–15] which combines the oxidizing power of bis(fluorosulfuryl) peroxide ($S_2O_6F_2$) with the solvating ability of HSO_3F, is applied to prepare the desired species. The reaction proceeds according to

$$2M + 5S_2O_6F_2 \xrightarrow[40\ ^\circ C]{HSO_3F} 2M(SO_3F)_5(solv) \qquad M = Nb \text{ or } Ta \qquad (1)$$

and yields clear, colorless solutions after approximately 3 days. More concentrated solutions (>1 M) are of a gellike consistency, but unlike the synthesis of $Pt(SO_3F)_4$[14] or $Sn(SO_3F)_4$[15] no precipitate forms during synthesis. Excess $S_2O_6F_2$ is readily removed in vacuo at room temperature, whereas complete removal of excess HSO_3F fails because of the extremely high solubility and limited thermal stability of the solutes, which does not allow heating during solvent removal in vacuo.

The observation at ambient temperature of a single ^{19}F NMR resonance at 40.9 ppm relative to $CFCl_3$ for a 1 M solution of $Nb(SO_3F)_5$ and at 42.0 ppm for a 0.9 M solution of $Ta(SO_3F)_5$ is consistent with rapid fluorosulfate exchange between solute and solvent. The observed difference of 1.1 ppm in the resonance positions, with both bands downfield from the solvent resonance at 40.74 ppm, suggests different concentrations of $H_2SO_3F^+$ in both cases.

Evidence for the presence of $M(SO_3F)_5$, M = Nb or Ta, in solution is based on a detailed ^{19}F NMR resonance integration of the combined solvent–solute resonance and the band due to excess $S_2O_6F_2$ at low temperatures and, in the case of $Nb(SO_3F)_5$ solutions, on the observation of a single ^{93}Nb resonance at −80 ppm relative to NbF_6^-. Support comes also from the isolation, analysis, and characterization of cesium salts of the type $Cs[M(SO_3F)_6]$ and $Cs_2[M(SO_3F)_7]$, M = Nb or Ta, upon addition of 1 or 2 mol of $CsSO_3F$ to the $M(SO_3F)_5$ solutions, as described below.

Both types of salts, $Cs[M(SO_3F)_6]$ and $Cs_2[M(SO_3F)_7]$, M = Nb or Ta, are obtained by the general route

$$2nCsSO_3F + 2M + 5S_2O_6F_2 \xrightarrow{HSO_3F} 2Cs_n[M(SO_3F)_{5+n}] \qquad (2)$$

$$n = 1 \text{ or } 2;\ M = Nb \text{ or } Ta$$

This route has precedents, e.g. for M = Pt[14] or Sn,[15] but the anion in the isolated salts is $[M(SO_3F)_6]^{2-}$ with octahedral coordination of tin evident from the ^{119}Sn Mössbauer spectrum.[15] There are, to our knowledge, no precedents for anions of the type $[M(SO_3F)_7]^{2-}$, but coordination expansion is not unexpected for niobium and tantulum.[9] Product isolation by filtration is chosen, because the very high solubility of $CsSO_3F$ in HSO_3F[3] would preclude interpretation of isolated salts of the composition $Cs_2[M(SO_3F)_7]$ as 1:1 mixtures of $CsSO_3F$ and $Cs[M(SO_3F)_6]$. The isolated yields for the four salts range from 64 to 77%. Some solubility of the salts in the HSO_3F–$S_2O_6F_2$ mixture is seen as a contributing cause for this variation in yields. All four salts will redissolve in HSO_3F once isolated to form up to 0.2 M solutions.

The synthesis of salts of the composition $Cs_2[M(SO_3F)_7]$ is in part suggested by the known fluorocomplexes of the type $M^I_2[MF_7]$,[9] with M^I = an alkali metal or NH_4 and M = Nb or Ta. Attempts to extend the general route in eq 2 to other alkali-metal salts are not successful. The reactions with KSO_3F lead to waxy, poorly crystallized materials, while with $LiSO_3F$ as base in HSO_3F, viscous oils are obtained. Likewise attempts to synthesize $Cs_3[Ta(SO_3F)_8]$ lead to inhomogeneous mixtures only.

The infrared spectra listed in the Experimental Section serve "fingerprinting" purposes. They allow two relevant comments: (i) The characteristic stretching vibrations of $CsSO_3F$,[17] in particular the intense S–F stretch at 715 cm^{-1}, are absent. (ii) Both band positions and relative intensity for $Cs_2[M(SO_3F)_7]$ are rather similar to reported spectral data for $Cs_2[Sn(SO_3F)_6]$,[15] while band patterns found for $Cs[M(SO_3F)_6]$, M = Nb or Ta, are somewhat more complicated, particularly in the SO_3 stretching region.

The composition of all four salts is established by chemical analysis. The close correspondence argues against partial decomposition with evolution of either $S_2O_5F_2$ to give oxyfluorosulfato or SO_3 to give fluorofluorosulfato complexes. In particular, the observed S:F molar ratio of very close to 1 is in all four instances helpful in ruling out the latter mode of decomposition.

The thermal stability, judged by the melting or decomposition points, seems to decrease from $Cs[M(SO_3F)_6]$ to $Cs_2[M(SO_3F)_7]$, almost independent of the central metal, and even for the former they are considerably lower than found for either $Cs_2[Sn(SO_3F)_6]$ (249 °C) or $Cs_2[Ge(SO_3F)_6]$ (242 °C).[15] Not surprisingly, all

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(5) Gillespie, R. J.; Peel, T. E. *Adv. Phys. Org. Chem.* **1972**, *9*, 1.

(6) Olah, G. A.; Prakash, G. K. S.; Sommer, J. *Superacids*; Wiley: New York, 1985; and references herein.

(7) Thompson, R. C. In *Inorganic Sulphur Chemistry*; Nickless, G., Ed.; Elsevier: Amsterdam, The Netherlands, 1968.

(8) Fabre, P. L.; Devnyk, J.; Tremillon, B. *Chem. Rev.* **1982**, *82*, 591.

(9) (a) Fairbrother, F. *The Chemistry of Niobium and Tantalum*; Elsevier: London, 1967. (b) Brown, D. *Chemistry of Niobium and Tanatalum in Comprehensive Inorganic Chemistry*; Pergamon Press: New York, 1973; Vol. 3, p 565.

(10) Dove, M. F. A.; Clifford, A. F. In *Chemistry in Non-Aqueous Ionizing Solvents*; Jander, J., Spandau, H., Addison, C. C., Eds.; Vieweg: Wiesbaden, FRG, 1971; Vol. 2.1.

(11) McCauley, D. A.; Higley, S. W.; Lien, A. P. *J. Am. Chem. Soc.* **1956**, *78*, 3009.

(12) Gillespie, R. J. *Acc. Chem. Res.* **1968**, *1*, 202.

(13) (a) Lee, K. C.; Aubke, F. *Inorg. Chem.* **1979**, *18*, 389. (b) Lee, K. C. Ph.D. Thesis, University of British Columbia, 1980.

(14) Lee, K. C.; Aubke, F. *Inorg. Chem.* **1984**, *23*, 2124.

(15) Mallela, S. P.; Lee, K. C.; Aubke, F. *Inorg. Chem.* **1984**, *23*, 653.

(16) (a) KleinKopf, G. C.; Shreeve, J. M. *Inorg. Chem.* **1964**, *3*, 607. (b) Clark, H. C.; Emeleus, H. J. *J. Chem. Soc.* **1958**, 190.

(17) Ruoff, A.; Milne, J. B.; Kaufmann, G.; Leroy, M. *Z. Anorg. Allg. Chem.* **1970**, *372*, 119.

Table I. Specific Conductances in HSO_3F at 25 °C

$Nb(SO_3F)_5$		$Ta(SO_3F)_5$	
10^2m, mol/kg	$10^4\kappa$, Ω^{-1} cm^{-1}	10^2m, mol/kg	$10^4\kappa$, Ω^{-1} cm^{-1}
0.000	1.57	0.000	1.55
0.101	1.92	0.119	2.84
0.338	2.97	0.312	4.79
0.546	3.89	0.566	7.37
0.847	5.29	0.822	9.76
0.867	5.38	1.173	13.12
1.175	6.73	1.541	16.37
1.378	7.79	1.770	18.27
1.648	9.18	2.002	20.23
1.660	9.25	2.276	22.48
1.908	10.57	2.549	24.36
2.200	11.72	2.761	26.50
2.416	12.60	2.915	27.53
2.626	13.48	4.002	36.41
2.827	14.33		
3.037	15.27		
3.275	16.36		
3.522	17.44		
3.724	18.40		
3.914	19.30		
4.105	20.18		
4.183	20.56		

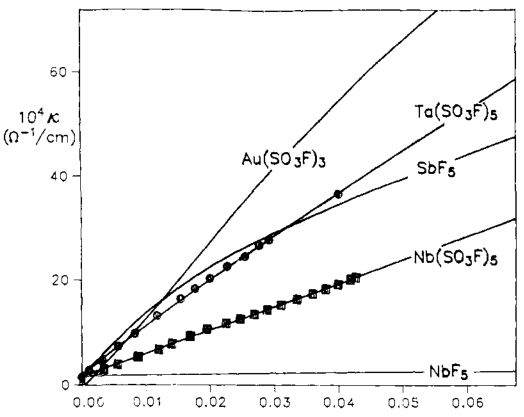

Figure 1. Concentration-dependent specific electrical conductivities of $Ta(SO_3F)_5$ and $Nb(SO_3F)_5$, compared to other monoprotonic acids in HSO_3F at 25 °C: SbF_5, ref 3; $Au(SO_3F)_3$, ref 13; NbF_5, ref 20.

four salts are very moisture sensitive.

3. Electrical Conductance and Solution Studies

Electrical conductivity measurements are used to provide direct evidence for acidic behavior of $Nb(SO_3F)_5$ and $Ta(SO_3F)_5$ in HSO_3F after removal of all excess $S_2O_6F_2$, which reportedly behaves as a nonelectrolyte in HSO_3F.[18] Reduction of the volume of stock solutions in vacuo by about 50% is successful, as judged by ^{19}F NMR and Raman spectroscopy, where the absence of the very intense ν_{O-O} at 801 cm^{-1} [19] is probed. Both $Nb(SO_3F)_5$ and $Ta(SO_3F)_5$ behave as strong electrolytes in HSO_3F, indicated by the concentration-dependent increase in their specific conductance listed in Table I and shown in Figure 1 together with the corresponding plots of the related acidic solutes $Au(SO_3F)_3$,[13] SbF_5,[3] and NbF_5.[20]

If acidic behavior is assumed, the proton jump mechanism suggests the acidium ion $H_2SO_3F^+$ to be the principle cause of the observed conductivities. It follows then that the differences in the slope of the κ vs concentration plot (Figure 1) reflect differences in $H_2SO_3F^+$ concentration and hence in acidity for the concentration range shown. Hence, the slopes of the various plots suggest the following order of solute acidity: $Au(SO_3F)_3 > Ta(SO_3F_5) \geq SbF_5 > Nb(SO_3F)_5 > NbF_5$. Furthermore, the strong curvature of the SbF_5 plot, ascribed to association effects,[3] is not observed for any of the other solutes. Interestingly also, $Nb(SO_3F)_5$, albeit the weakest fluorosulfato acid, appears to be considerably stronger than NbF_5.[20]

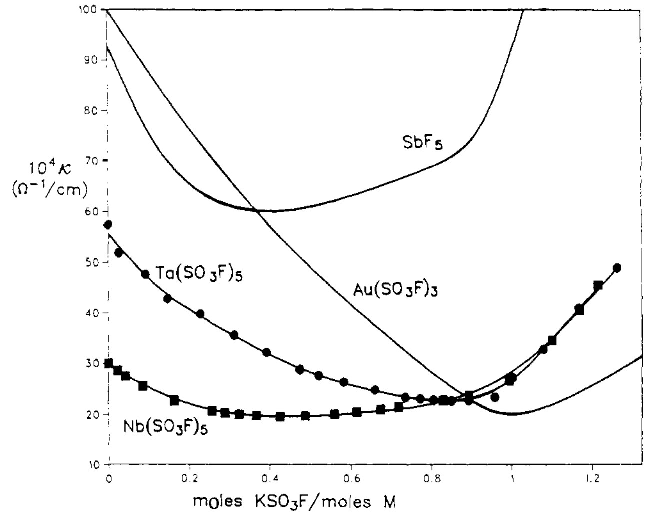

Figure 2. Conductometric titrations of $Ta(SO_3F)_5$, $Nb(SO_3F)_5$, $Au(SO_3F)_3$,[13] and SbF_5[3] in HSO_3F against KSO_3F at 25 °C.

Acidic behavior of $Ta(SO_3F)_5$ and $Nb(SO_3F)_5$ in HSO_3F is confirmed by titration with KSO_3F as base. The resulting curves, together with those for SbF_5[3] and $Au(SO_3F)_3$,[13] are shown in Figure 2. The minimum specific conductances occur here at $KSO_3F-Ta(SO_3F)_5 = 0.85$ and $KSO_3F-Nb(SO_3F)_5 = 0.43$, respectively, whereas the equivalence or inversion points are at about 1.00 in both cases. This suggests that both solutes behave as moderately strong, monoprotonic acids in HSO_3F, with $Ta(SO_3F)_5$ significantly stronger than $Nb(SO_3F)_5$.

The reported titration curve for SbF_5[3] vs KSO_3F, shown also in Figure 2 for purpose of comparison, starts at a considerably higher acid concentration than was used in our measurements. The similarity in shape to the $Nb(SO_3F)_5$ vs KSO_3F titration curve is nevertheless recognizable. The almost symmetrical shape of the curve for $Au(SO_3F)_3$ vs KSO_3F,[13] typical for a strong acid–strong base reaction, with equivalence point and point of lowest conductivity nearly coinciding at a 1.0 ratio, is consistent with the acidity order based on the conductivity data. The acidic behavior of both solvated Ta(V) and Nb(V) species in HSO_3F may be expressed by the equation

$$2HSO_3F + M(SO_3F)_5(solv) \xrightleftharpoons{HSO_3F} H_2SO_3F^+(solv) + [M(SO_3F)_6]^-(solv) \quad (3)$$

where M = Ta or Nb, consistent with ambient-temperature single ^1H NMR resonances at 11.84 or 10.60 ppm relative to TMS for 0.9 and 1.0 M solutions of $Ta(SO_3F)_5$ and $Nb(SO_3F)_5$, respectively, due to rapid proton exchange. In agreement with observations in the system $KSO_3F-HSO_3F-Sn(SO_3F)_4$,[15] independent ^{19}F NMR resonances for the solutes $M(SO_3F)_5$ and the solvent HSO_3F are not observed even at lower temperatures, due to rapid SO_3F exchange. Upon addition of KSO_3F or $CsSO_3F$, separate solute signals for both the tantalum and the niobium system are detected in the expected range for SO_3F compounds,[20] but only at temperatures below −20 °C. Solutions of the strongly acidic $Au(SO_3F)_3$ in HSO_3F on the other hand show a second resonance line due to $[Au(SO_3F)_4]^-$ at room temperature even before KSO_3F is added.[13]

4. Conclusions

Isolation of salts of the type $Cs_2[M(SO_3F)_7]$, M = Nb or Ta, and the results of the conductometric titration where both $Nb(SO_3F)_5$ and $Ta(SO_3F)_5$ behave as monoprotonic acids with [M-

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(18) Gillespie, R. J.; Milne, J. B.; Thompson, R. C. *Inorg. Chem.* **1966**, *5*, 468.

(19) Qureshi, A. M.; Levchuk, L. E.; Aubke, F. *Can. J. Chem.* **1971**, *15*, 2544.

(20) Gillespie, R. J.; Ouchi, R.; Pez, G. P. *Inorg. Chem.* **1969**, *8*, 63.

(21) Hohorst, F. A.; Shreeve, J. M. *Inorg. Chem.* **1966**, *5*, 2069.

$(SO_3F)_6]^-$ formed (see eq 3) appear to be contradictory on first sight. It must be remembered that the heptakis(fluorosulfato) species are only obtained with an excess of the base ion SO_3F^- whereas only a weakly basic medium is generated during the acid–base titration. Conversely, $[M(SO_3F)_7]^{2-}$ is expected to be strongly basic and may not exist in HSO_3F in the absence of base ions due to the equilibrium

$$[M(SO_3F)_7]^{2-}(solv) \xrightleftharpoons{HSO_3F} [M(SO_3F)_6]^-(solv) + SO_3F^-(solv),\ M = Nb \text{ or } Ta \quad (4)$$

Analogously, the superacid systems HF–NbF_5 and HF–TaF_5 are viewed as monoprotonic acids[6,8,10] even though salts like K_2NbF_7 and K_2TaF_7 exist.[9] The superacid system HSO_3F–Pt-$(SO_3F)_4$ studied by us previously[14] remains the only diprotonic superacid system so far.

In addition to the above-stated similarities between the two new superacid systems and magic acid, the former appear to hold some significant advantages, such as the absence of complex association via mixed bridging ligands and the successful isolation of distinct alkali salts, which has not been possible with the SbF_5 system.[22]

On the other hand, the limited solubility of NbF_5 and TaF_5[6] in either anhydrous HF or HSO_3F is not found for the corresponding fluorosulfates, generated in situ.

5. Experimental Section

Published methods were used for the synthesis of KSO_3F[3] and $S_2O_6F_2$,[23] while $CsSO_3F$ was generated by solvolysis from CsCl and HSO_3F. Technical-grade HSO_3F was purified by double distillation[3] with particular care taken for the acid used in conductivity studies. Tantalum and niobium powder, both −60 mesh, were obtained from the Ventron Corp. Chemical analysis was carried out by Analytische Laboratories, Gummersbach, FRG. Equipment used for synthetic reactions followed published precedents.[14,15] The invertible filtration apparatus used to isolate the salts was similar in design to an apparatus described by Shriver.[24] 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. The conductivity cells used and methods for their calibration[3] and our conductivity bridge and constant temperature bath[3,13] as well as methods and instruments used to obtain infrared and Raman spectra have also all been described.[14,15] A Varian XL-300 multinuclear spectrometer was used to obtain the ^1H and ^{19}F NMR spectra (with $CDCl_3$ as the external lock source in each case), as well as the ^{93}Nb NMR data, with the spectrometer operating at 73.329 MHz for the latter.

Synthesis. (i) $Ta(SO_3F)_5$ in HSO_3F Solution. Typically, 411 mg (2.27 mmol) of tantalum metal powder is treated with a ~7-mL mixture of $S_2O_6F_2$ and HSO_3F (2:1 by volume) and allowed to react at 40 °C for 5 days, by which time all the metal is consumed and a colorless solution is obtained. Excess $S_2O_6F_2$ is removed in vacuo at room temperature.

(ii) $Nb(SO_3F)_5$ in HSO_3F Solution. Typically, 321 mg (3.46 mmol) of niobium metal powder is treated with a ~6-mL mixture of $S_2O_6F_2$ and HSO_3F (2:1 by volume) and allowed to stir at 40 °C for 2 days, by which time all the metal is consumed and a colorless solution is obtained. Excess $S_2O_6F_2$ is removed in vacuo at room temperature.

(iii) $Cs[Nb(SO_3F)_6]$. Typically, 265 mg (2.85 mmol) of niobium metal powder is added to 661 mg (2.85 mmol) of $CsSO_3F$ to which is then vacuum distilled about 4 mL of $S_2O_6F_2$ and about 3 mL of HSO_3F. The gray slurry is allowed to stir for 2 days at room temperature, by which time all the metal is consumed and the slurry appears white. The white powder is collected by vacuum filtration. Excess $S_2O_6F_2$ is removed, and the product is dried in vacuo for 24 h at room temperature (isolated yield 77%). Anal. Calcd for $CsNbS_6O_{18}F_6$: Nb, 11.33; S, 23.45; F, 13.90. Found: Nb, 10.95; S, 23.46; F, 14.11. S:F = 1.0003. Mp: 115–119 °C dec. IR (cm^{-1}): 1425 (s, vb), 1257 (m, sh), 1217 (s, b), 1153 (m, sh), 912 (s, vb), 831 (s, vb), 646 (m), 554 (m, b), 434 (m, sh), 423 (m), 410 (m, sh). Abbreviations: s = strong, m = medium, w = weak, v = very, b = broad, sh = shoulder.

(iv) $Cs[Ta(SO_3F)_6]$. A total of 617 mg (3.41 mmol) of tantalum metal powder is added to 781 mg (3.37 mmol) of $CsSO_3F$ to which is then distilled 5 mL of $S_2O_6F_2$ and 4 mL of HSO_3F in vacuo. The mixture is allowed to stir at 35 °C for 3 days, by which time the dark gray metal powder is completely consumed and a white slurry has formed. The fine white powder is collected by vacuum filtration. Excess $S_2O_6F_2$ is removed, and the product is dried in vacuo for 24 h at room temperature (64% isolated yield). Anal. Calcd for $CsTaS_6O_{18}F_6$: Cs, 14.63; Ta, 19.92; S, 21.18; F, 12.55. Found: Cs, 14.45; Ta, 20.00; S, 20.96; F, 12.31. S:F = 0.991. Mp: 120–124 °C dec. IR (cm^{-1}): 1433 (s, b), 1263 (m), 1222 (s, b), 1155 (s, sh, b), 1121 (s, sh, b), 928 (s, vb), 830 (s, vb), 633 (m, br), 540 (m, vb), 435 (m), 413 (m).

(v) $Cs_2[Nb(SO_3F)_7]$. Typically, 227 mg (2.44 mmol) of niobium metal powder is added to 1.105 g (4.76 mmol) of $CsSO_3F$ to which is then vacuum distilled about 4 mL of $S_2O_6F_2$ and 3 mL of HSO_3F. The gray slurry is stirred at room temperature for 3 days, by which time all the metal is consumed and a thick white slurry appears. The reaction vessel is cooled to 0 °C for 1 h, and a fine white powder is collected by vacuum filtration. Excess $S_2O_6F_2$ is removed, and the product is dried in vacuo for 24 h at room temperature (70% isolated yield). Anal. Calcd for $Cs_2NbS_7O_{21}F_7$: Nb, 8.83; S, 21.33; F, 12.64. Found: Nb, 9.10; S, 21.46; F, 12.85. S:F = 1.016. Mp: 78–82 °C. IR (cm^{-1}): 1410 (s, vb), 1337 (m, sh), 1255 (m, sh), 1217 (s), 1085 (w, sh), 980 (m, vb), 915 (m, vb, sh), 830 (b), 640 (w, vb), 555 (m), 433 (w), 424 (w), 412 (w).

(vi) $Cs_2[Ta(SO_3F)_7]$. Typically, 309.9 mg (1.711 mmol) of tantalum metal powder is added to 824 mg (3.55 mmol) of $CsSO_3F$ to which is then vacuum distilled about 3 mL of $S_2O_6F_2$ and 2 mL of HSO_3F. The mixture is allowed to stir at 40 °C for 2 days, by which time all the dark gray metal is consumed and a white slurry appears. The reaction vessel is cooled to 0 °C. A fine white powder is collected by vacuum filtration. Excess $S_2O_6F_2$ is removed, and the product is dried in vacuo for 3 days at room temperature (isolated yield 70%). Anal. Calcd for $Cs_2TaS_7O_{21}F_7$: Ta, 15.87; S, 19.68; F, 11.66. Found: Ta, 15.60; S, 19.40; F, 11.61. S:F = 1.010. Mp: 77–79 °C dec. IR (cm^{-1}): 1410 (s, vb), 1215 (s), 1070 (w, sh, b), 955 (s, vb), 825 (m, vb), 670 (w, vb), 558 (w), 430 (vw), 415 (vw).

Caution! Some of the materials involved in this study require careful and safe handling. HSO_3F and HF, its possible byproduct, are extremely reactive with the skin. SO_3, another byproduct, is strongly oxidizing. Its anhydride, disulfuryl difluoride, $S_2O_5F_2$, is extremely toxic when inhaled.[25] The purification of HSO_3F should be carried out in a well-ventilated fumehood, and protective gloves should be worn. Bis(fluorosulfuryl) peroxide, $S_2O_6F_2$, may be stored safely in glass vessels with greaseless valves but must be kept away from oxidizable material. Its preparation by catalytic fluorination of SO_3[23] may produce the extremely hazardous byproduct fluorine fluorosulfate, $FOSO_2F$. A cautionary note and advise on how to avoid collecting this compound has been published[26] and should be consulted.

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(22) Wilson, W. W.; Aubke, F. *J. Fluorine Chem.* **1979**, *13*, 431.

(23) Cady, G. H.; Shreeve, J. M. *Inorg. Synth.* **1963**, *7*, 124.

(24) Shriver, D. F. *The Manipulation of Air-Sensitive Compounds*; McGraw-Hill: New York, 1969.

(25) Muetterties, E. L.; Coffman, D. D. *J. Am. Chem. Soc.* **1958**, *80*, 5914.

(26) Cady, G. H. *Inorg. Synth.* **1968**, *11*, 155.