enhancement has been calculated to be $\sim 10^{10}$ at 650 K.

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Registry No. $SmCl_3$, 10361-82-7; $SmCl_2$, 13874-75-4; $SmAl_3Cl_{12}$, 68645-74-9; Sm_2O_3, 12060-58-1; Al_2Cl_6, 13845-12-0.

Supplementary Material Available: Table I, determination of molar absorptivity, Table III, absorbances, partial pressures, and equilibrium constants for the Sm^{III}–Al–Cl system, Table VI, absorbances and partial pressures of the Sm^{II}–Al–Cl system, and Table VII, vapor density experiments (4 pages). Ordering information is given on any current masthead page.

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Gold(III) Fluorosulfate, Its Solution Behavior in HSO_3F, and the Tetrakis(fluorosulfato)aurate(III) Ion

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Gold(III) fluorosulfate is found to be a good fluorosulfate ion acceptor. The tetrakis(fluorosulfato)aurate(III) ion, $[Au(SO_3F)_4]^-$, is found in solid, crystalline materials of the composition $M[Au(SO_3F)_4]$, with M = Cs, K, Li, NO, or ClO_2. Their syntheses and vibrational spectra are discussed. Ionic formulation as $M^+[Au(SO_3F)_4]^-$ is suggested. The ability of $Au(SO_3F)_3$ to accept SO_3F^- ions extends also to the system HSO_3F–$Au(SO_3F)_3$. This system is investigated by electrical conductance measurements and by UV–visible, Raman, and NMR (^{19}F and ^1H) spectroscopy. Gold(III) fluorosulfate is thought to be monosolvated and acts as a moderately strong acid in HSO_3F according to $H[Au(SO_3F)_4] + HSO_3F \rightleftharpoons [Au(SO_3F)_4]^- + H_2SO_3F^+$.

Introduction

The chemistry of gold provides many examples where the metal exhibits a formal oxidation state of +3. As expected for a d^8 electron configuraton, a regular or slightly distorted square-planar stereochemistry around gold is commonly found, resulting in diamagnetic compounds.

The square-planar environment for gold is accomplished either by polymerization, as in AuF_3,[1] or by complex formation. Both anionic complexes of the type AuX_4^-, where X is a uninegative, monodentate ligand, and neutral complexes of the type AuX_3L, where L is an electron pair donor ligand, are commonly found.

Of the binary gold(III) compounds of the type AuX_3, the fluorosulfate $Au(SO_3F)_3$, first reported in 1972 by Johnson, Dev, and Cady[2] appears to be the only well documented oxyacid derivative of gold(III).

We became interested in this compound for two reasons: (a) $Au(SO_3F)_3$ should act as a fluorosulfate ion acceptor, allowing the syntheses of complexes containing the anion $[Au(SO_3F)_4]^-$ with hopefully a wide variety of catons, and (b) $Au(SO_3F)_3$ may remove fluorosulfate ions from the self-ionization equilibrium of fluorosulfuric acid[3] (eq 1) and hence

$$2HSO_3F \rightleftharpoons H_2SO_3F^+ + SO_3F^- \qquad (1)$$

act as an acid in HSO_3F. Such behavior would not be unexpected, because solutions of AuF_3 in HSO_3F have been reported to show acidic behavior.[4]

Experimental Section

Chemicals. Commercially available chemicals of analytical reagent or of reagent grade were generally used without purification. Technical grade HSO_3F (Baker and Adamson) was purified by double distillation at atmospheric pressure as described previously. Gold powder, 100 mesh, 99.995% pure, was obtained from Ventron Corp.

The following compounds were synthesized according to published methods: bis(fluorosulfuryl) peroxide, $S_2O_6F_2$,[5] bromine(I) fluorosulfate, $BrSO_3F$,[6] chlorine dioxide, ClO_2,[7] chloryl fluorosulfate, ClO_2SO_3F,[8] and potassium fluorosulfate KSO_3F.[3] $AuBr_3$ was obtained from the reaction of gold with Br_2 at 80 °C.

A direct route to $Au(SO_3F)_3$ will be described below in detail.

Instrumentation. Raman spectra were obtained with either a Cary 81 or a Spex Ramalog spectrophotometer, equipped with a heli-

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um–neon laser (Spectra Physics Model 125) at λ 632.8 nm or an argon ion laser (Spectra Physics Model 164) at λ 514.5 nm, respectively.

Infrared spectra were obtained on a Perkin-Elmer 457 grating spectrophotometer or on a Pye Unicam SP 1100 instrument. Silver chloride and bromide were used as window materials. For HSO_3F solutions, thin Teflon films were used. Due to the reactivity of the samples, no mulling agents could be used and spectra were obtained on thin films. ^{19}F NMR spectra were obtained on a XL-100 spectrometer (Varian Associates) and a Varian T-60 was used for ^1H NMR spectra. ^{19}F chemical shifts are reported with respect to $CFCl_3$ and with shifts to lower fields considered positive.

Both mull and solution spectra in the UV–visible region were obtained on a Cary 14 spectrophotometer. HSO_3F was used as a solvent.

Magnetic measurements were performed on solid samples by the Gouy method.

Electrical conductance measurements were carried out with a Wayne-Kerr Universal Bridge, Type B221. The measuring temperature of 25.00 ± 0.01 °C was maintained in an oil bath equipped with a Sargent Thermonitor Model ST temperature control unit. The conductivity cell, similar in design to the one described by Barr et al.,[3] was scaled down in size to allow measurement on small volumes (~50 mL). The cell constant of 5.374 cm^{-1} was determined by the method of Lind et al.[9] and checked before and after each run. Additions of solutions of $Au(SO_3F)_3$ in HSO_3F and of solid KSO_3F were made in a manner described previously.[3]

All reactions were performed in Pyrex reaction vials of about 40-mL capacity, fitted with Kontes Teflon stem valves. Volatile materials were handled using vacuum-line techniques. Solids were handled in a Vacuum Atmospheres Corp. "Dri Lab" Model No. HE-43-2, filled with purified dry nitrogen and equipped with a "Dri-Train" Model No. HE-93-B circulating unit.

Syntheses. Gold(III) Fluorosulfate. $Au(SO_3F)_3$ is prepared directly by the oxidation of gold powder (0.579 g or 2.94 mmol) with an excess of bis(fluorosulfuryl) peroxide, $S_2O_6F_2$ (about 4 g or 20 mmol), in the presence of approximately 6 g of fluorosulfuric acid as solvent. The reaction proceeds at room temperature with the gold dissolving over a period of about 3 h to give an orange solution. Removal of all volatile materials in vacuo with the reactor first at room temperature and later at +60 °C allows the isolation of 1.460 g or 2.94 mmol of $Au(SO_3F)_3$.

Cesium Tetrakis(fluorosulfato)aurate(III). $Cs[Au(SO_3F)_4]$ is prepared by the reaction of a stoichiometric (1:1) mixture of gold powder and cesium chloride with either an excess of bromine(I) fluorosulfate or a mixture of $S_2O_6F_2$ and HSO_3F, similar to the one used in the synthesis of gold(III) fluorosulfate. In a typical reaction 0.287 g of gold powder and 0.245 g of cesium chloride (1.46 mmol) yield 1.044 g (1.44 mmol) of $Cs[Au(SO_3F)_4]$ after removal of all volatile materials. $Li[Au(SO_3F)_4]$ and $K[Au(SO_3F)_4]$ are prepared in an identical manner.

Chloronium Tetrakis(Fluorosulfato)aurate(III). $ClO_2[Au(SO_3F)_4]$ is prepared by the addition of an excess (about 3 g) of ClO_2SO_3F to 0.224 g (0.453 mmol) of $Au(SO_3F)_3$. The solid gold(III) fluorosulfate dissolves readily and subsequent removal of all excess ClO_2SO_3F in vacuo yields 0.288 g (0.436 mmol) of yellow crystalline ClO_2 $[Au(SO_3F)_4]$.

Nitrosonium Tetrakis(fluorosulfato)aurate(III). $NO[Au(SO_3F)_4]$ is prepared by reacting $NO[AuCl_4]$ with a large excess of bromine(I) fluorosulfate and heating the reaction mixture at +80 °C for 30 min. In a typical reaction 0.209 g (0.567 mmol) of $NO[AuCl_4]$ yields 0.348 g (0.558 mmol) of $NO[Au(SO_3F)_4]$.

$NO[AuCl_4]$ is prepared by the reaction of $AuBr_3$ with a large excess of nitrosyl chloride at +80 °C. The reaction is followed by weight.

Analytical Data and Physical Properties. Quantitative analyses were performed by A. Bernhardt, Microanalytical Laboratories, Elbach, West Germany. All analytical data quoted are in percent.

$Au(SO_3F)_3$ was obtained as orange to yellow needles, melting at +140 °C with decomposition. The needles are sublimable at +100 °C in vacuo and are diamagnetic and hygroscopic. IR spectrum (AgCl windows), values in cm^{-1}, intensities estimated: 1442 (vs), 1425 (s, sh), 1240 (s), 1220 (s, sh), 1135 (ms), 1055 (s), 960 (s, b), 920 (s, sh), 895 (s, b), 820 (s), 682 (s), 670 (s, sh), 610 (w), 590 (s), 582 (s), 550 (ms), 460 (m). A Raman spectrum and the chemical analyses have been reported.[2]

$K[Au(SO_3F)_4]$ is a yellow crystalline solid, melting with decomposition at +230 °C. Anal. Calcd for $K[Au(SO_3F)_4]$: K, 6.18; Au, 31.15; F, 12.02. Found: K, 6.42; Au, 30.80; F, 12.28.

$Cs[Au(SO_3F)_4]$ was obtained as a yellow crystalline solid, mp +105 °C, which decomposes at ~300 °C; it is hygroscopic. Anal. Calcd for $Cs[Au(SO_3F)_4]$: Cs, 18.30; Au, 27.13; F, 10.47. Found: Cs, 18.14; Au, 26.98; F, 10.30.

$Li[Au(SO_3F)_4]$ is a yellow crystalline solid and does not melt below +280 °C; it is hygroscopic. Anal. Calcd for $Li[Au(SO_3F)_4]$: Li, 1.16; Au, 32.87; F, 12.66. Found: Li, 1.21; Au, 32.59; F, 12.51.

$ClO_2[Au(SO_3F)_4]$ is a yellow crystalline solid, mp 101–103 °C, and decomposes at +170 °C; it is hygroscopic. Anal. Calcd for $ClO_2[Au(SO_3F)_4]$: Cl, 5.37; Au, 29.81; S, 19.41. Found: Cl, 5.23; Au, 30.00; S, 19.24.

$NO[Au(SO_3F)_4]$ was obtained as a light yellow crystalline solid which melts at 192–195 °C to a clear orange liquid. Decomposition begins at 260 °C. Anal. Calcd for $NO[Au(SO_3F)_4]$: N, 2.25; Au, 31.61; F, 12.19. Found: N, 2.10; Au, 31.85; F, 12.32.

Results and Discussion

Synthesis. For the intended solution study on $Au(SO_3F)_3$ in HSO_3F a convenient and fast synthetic route to very pure gold(III) fluorosulfate was needed. The original synthesis,[2] involving the oxidation of gold with an excess of bromine(I) fluorosulfate, yields gold(III) fluorosulfate only after controlled thermal decomposition of a solid intermediate reported to have the approximate composition $Au(SO_3F)_3\cdot 2BrSO_3F$. In addition, all samples of $Au(SO_3F)_3$ obtained by us using this method were very weakly paramagnetic.

Even though the reaction of bis(fluorosulfuryl) peroxide and gold results only in a slow surface attack, the addition of HSO_3F as solvent to the reaction mixture allows the synthesis of very pure, diamagnetic $Au(SO_3F)_3$ in a fast and efficient manner. As an additional advantage, this method allows the convenient preparation of solutions of gold(III) fluorosulfate in HSO_3F using nearly stoichiometric amounts of gold and of bis(fluorosulfuryl) peroxide. Generally a slight excess of $S_2O_6F_2$ is necessary in order to reduce the reaction time. A variation of this synthetic method can be adopted to the preparation of alkali metal tetrakis(fluorosulfato)aurates(III). Stoichiometric mixtures of gold and MCl, where M = Li, K, or Cs, react rapidly with $S_2O_6F_2$ in HSO_3F to give the corresponding $M^I[Au(SO_3F)_4]$ after removal of all volatile materials. The direct reaction of ClO_2SO_3F with $Au(SO_3F)_3$ without a solvent affords a stable heterocation complex $ClO_2[Au(SO_3F)_4]$.

Alternative routes to $Au(SO_3F)_3$ or $K[Au(SO_3F)_4]$ use gold(III) chloride as the starting material (eq 2 and 3).

$$2AuCl_3 + 6BrSO_3F \rightarrow 2Au(SO_3F)_3 + 3Cl_2 + 3Br_2 \qquad (2)$$

$$KCl + AuCl_3 + 4BrSO_3F \rightarrow K[Au(SO_3F)_4] + 2Cl_2 + 2Br_2 \qquad (3)$$

However, these methods offer no distinct advantage over the others. A variation of this method is used in the conversion of $NO[AuCl_4]$ into $NO[Au(SO_3F)_4]$ by using an excess of $BrSO_3F$.

All tetrakis(fluorosulfato)aurate(III) complexes show relatively high thermal stabilities, when moisture is excluded.

Vibrational Spectra. The Raman spectrum of $K[Au(SO_3F)_4]$ is shown in Figure 1. The observed Raman shifts for $NO[Au(SO_3F)_4]$, $ClO_2[Au(SO_3F)_4]$, $Li[Au(SO_3F)_4]$, and $Cs[Au(SO_3F)_4]$ are listed in Table I together with their estimated intensities. The infrared data for $Cs[Au(SO_3F)_4]$ in the AgCl transmission range is shown here.

Except for some shoulders and occasional small splittings of bands due possibly to solid state effects, identical spectra are obtained for all $[Au(SO_3F)_4]^-$ complexes independent of the cation. Both band positions and intensities agree well with previously[10] reported Raman data for $K[I(SO_3F)_4]$ and $K[Br(SO_3F)_4]$, suggesting some structural similarities. The presence of monodentate OSO_2F groups is indicated in all complexes by the observed spacing of the SO_3-stretching

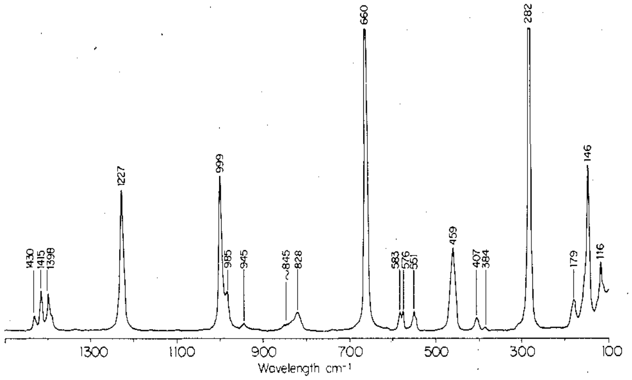

Figure 1. Raman spectrum of $K[Au(SO_3F)_4]$.

Table I. Vibrational Frequencies ($\Delta\nu$, cm^{-1}, and Intensities[a]) for $M[Au(SO_3F)_4]$

M = NO	M = ClO_2	M = Li	M = Cs	
Raman[b]	Raman[b]	Raman	Raman	IR
	1425 s, sh	1434 w		
1417 ms	1415 ms	1409 w, sh	1404 ms	1400 s, b
1395 m	1383 mw	1400 mw	1380 vw, sh	
		1390 w, sh		
1231 vs	1228 vs	1242 vs	1239 vs	1245 s
1204 w	1208 w	1210 w, sh	1205 w, sh	1208 vs
1018 s	1025 s	1029 s	1011 s	1010 w, sh
978 w	985 m, sh	985 w		970 s, sh
	974 m	~950 vw, b	960 vw, b	930 vs, b
933 vw	922 vw			
846 m	835 m	835 mw	830 mw	830 s, sh
818 m	818 m	815 m	814 w	810 s
				678 s
651 s	643 vs	642 vs	649 vs	
643 s				
580 w	587 w	582 w	580 w	585 ms
573 w	576 w			
	555 w	555 w	550 w	550 s
546 w	546 w, sh			
455 m	448 s	453 s	452 s	456 ms
445 m	417 w	415 w	405 vs	
402 vw, b	353 vw	391 w	391 w	
278 vs	277 vs	280 vs	282	
			279 vs	
150 w, sh	162 w	151 w	150 m	
133 m	125 w		127 m	

[a] Abbreviations: s = strong, m = medium, w = weak, b = broad, v = very, sh = shoulder. [b] Cation bands for NO^+ at 2331 cm^{-1} and for ClO_2^+ at 1296, 1050, and 518 cm^{-1} are omitted here.

Table II. Specific Conductances at 25 °C

$Au(SO_3F)_3$		$K[Au(SO_3F)_4]$	
10^2m, mol/kg	$10^4\kappa$, Ω^{-1} cm^{-1}	10^2m, mol/kg	$10^4\kappa$, Ω^{-1} cm^{-1}
0.644	6.24	0.075	1.62
1.128	13.06	0.282	2.98
1.531	19.83	0.826	6.22
1.906	25.90	1.295	8.76
2.199	30.42	1.707	10.93
2.346	32.41	2.168	13.36
2.571	35.58	2.746	16.45
3.071	42.67	3.240	19.47
3.365	46.54	3.845	24.34
3.808	51.81	4.487	30.00
4.092	55.35		
4.410	59.11		
4.701	62.34		

modes, and a square-planar environment for gold, consistent with the observed diamagnetism, is suggested. Similar band positions in the SO_3-stretching modes are also found for other fluorosulfato anions, e.g., $[Sn(SO_3F)_6]^{2-}$.[11] In general, a good correspondence between Raman and IR bands is found, reflecting the low symmetry of the fluorosulfate group. Strong intensity differences between IR and Raman bands in the 950- and 1230-cm^{-1} regions indicate vibrational coupling, producing in-phase and out-of-phase vibrations.

Noncoincidence of IR and Raman bands is found for bands in the 640–680-cm^{-1} range, where internal OSO_2F bands are commonly not observed. Strong contributions from AuO_4 skeletal stretching vibrations may explain the mutual exclusion of IR and Raman bands in this region. In addition to Raman bands at ~650 cm^{-1}, other rather intense Raman bands are found at about 450 and 275 cm^{-1} for all $[Au(SO_3F)_4]^-$ complexes. They also may involve AuO_4 skeletal motions coupled with internal OSO_2F vibrations, as would be expected for such a complex molecule.

The presence of the $[Au(SO_3F)_4]^-$ ion in all complexes is supported by the band positions for the heterocations ClO_2^+ and NO^+. The fundamentals for the chloronium cation are found at 1296, 1050, and 518 cm^{-1}, in good agreement with published precedents.[12] The NO stretching frequency, generally known to be anion dependent,[13] is raised by about 30 cm^{-1} to 2331 cm^{-1} for $NO[Au(SO_3F)_4]$ compared with that of $NOSO_3F$.[14]

Finally, the similarities in vibrational spectra extend also to $Au(SO_3F)_3$[2] and the halogen compounds $I(SO_3F)_3$ and $Br(SO_3F)_3$.[10] The complexity of the spectra of these compounds in the sulfur–oxygen stretching range suggests polymeric structures with both mono- and bidentate fluorosulfate groups. A detailed assignment is beyond the intention of this study.

In summary, the vibrational spectra are consistent with the ionic formulation as $M^+[Au(SO_3F)_4]^-$ and the presence of a square-planar AuO_4 grouping. A X-ray diffraction study on $K[Au(NO_3)_4]$[15] had provided a precedence for such a square-planar coordination around gold.

Solution Studies in Fluorosulfuric Acid. All tetrakis(fluorosulfato)aurate(III) salts are very soluble in HSO_3F at 25 °C. As expected for a polymeric material, gold(III) fluorosulfate will dissolve only very slowly at room temperature; however, clear, diamagnetic solutions are obtained when the initially produced suspensions are allowed to stand for several hours.

On the other hand, when $Au(SO_3F)_3$ is prepared directly in a solution of HSO_3F, very concentrated solutions (molalities of ~7 mol/kg of solvent) may be obtained, before a precipitate forms.

All solutions are yellow to deep orange, depending on the concentrations. Both $Au(SO_3F)_3$ and $Cs[Au(SO_3F)_4]$ give identical absorption spectra in HSO_3F solution with λ_{max} at 278 nm and ϵ_{max} of approximately 15000 M^{-1} cm^{-1}. This rather broad band, best interpreted as due to charge transfer, extends well into the visible region and prevents the observation of any bands due to d–d transitions.

The results of electrical conductance measurements on dilute solutions of $K[Au(SO_3F)_4]$ and $Au(SO_3F)_3$ in HSO_3F at 25 °C are shown in Table II. While both solutes behave as electrolytes in fluorosulfuric acid, indicated by the concentration dependent increase in specific conductance, their effects on the self-ionization equilibrium $2HSO_3F \rightleftharpoons H_2SO_3F^+ + SO_3F^-$ are different: $K[Au(SO_3F)_4]$ behaves as a weak base, but $Au(SO_3F)_3$ is a moderately strong acid. The mode of ionization is confirmed by conductometric titration with the standard base KSO_3F.[3] The results of the titration of $Au(SO_3F)_3$ vs. KSO_3F are plotted in Figure 2. As with the titration of $SbF_2(SO_3F)_3$[16]—the strongest known acid in HSO_3F—with KSO_3F, the conductance decreases gradually upon addition of KSO_3F solution and the equivalence point at $KSO_3F/Au(SO_3F)_3 = 0.996$ coincides with the point of lowest specific conductance (13.28×10^{-4} Ω^{-1} cm^{-1}). This behavior is typical for a strong, monobasic acid. In contrast,

Table III. Raman Shifts ($\Delta\nu$, cm^{-1}, and Intensities) for HSO_3F Solutions of $Au(SO_3F)_3$ and $Cs[Au(SO_3F)_4]$

$HSO_3F(l)^a$	$Cs[Au(SO_3F)_4]$, ~1 *m* in HSO_3F	$Au(SO_3F)_3$, ~0.15 *m* in HSO_3F	$Au(SO_3F)_3$, ~2.3 *m* in HSO_3F	$Au(SO_3F)_3$, ~7 *m* in HSO_3F
1443 mw	~1440 m, b, sh	1430 ms		
	1420 m	~1420 m, sh	1412 m, b	1420 m, b
			~1360 m, b	1360 vw
1230 ms, b	1232 s	1228 vs	1227 vs	1226 vw
1178 x	1190 ms, sh	~1185 s, sh	~1190 vw, sh	
				1090 vw
	1026 ms	1020 m	1024 ms	1030 m
960 s	958 m	960 s	960 w, sh	997 m, sh
				960 m
	910 vw	910 vw	910 w, b	912 m
850 vs	849 s	848 s	846 m	840 m
	~820 m, sh		830 m, sh	825 m, sh
	649 vs	647 vs	647 vs	647 vs
560 vs	~570 s, sh	~570 s, sh	580 w, sh	~570 m, sh
555 sh	553 s	550 s	547 m	546 s
	453 s	455 m	457 s	457 s
405 s	406 s	~395 ms, b	~400 w, b	400 w, b
393 s, sh	392 s			~350 vw, b
	278 vs	276 vs	276 vs	276 vs
	150 m	150 mw	151 mw	148 mw

[a] Reference 20.

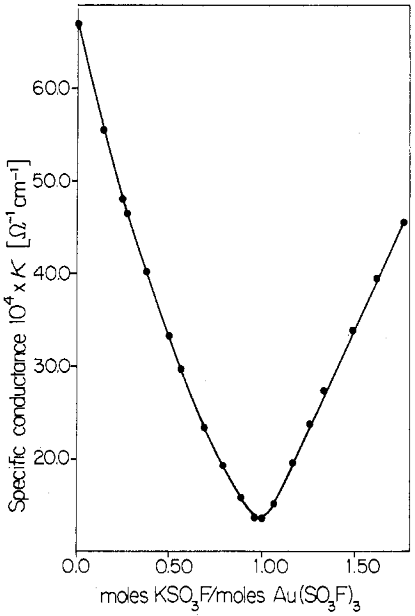

Figure 2. Conductometric titration of $Au(SO_3F)_3$ with KSO_3F in HSO_3F at +25 °C.

the weaker acid SbF_5 has a minimum conductance at $KSO_3F/SbF_5 \approx 0.4$ with the equivalent point at $KSO_3F/SbF_5 = 0.97$.[16]

If the titration is formulated as in eq 4, the observed

$$KSO_3F + Au(SO_3F)_3 \xrightarrow{HSO_3F} K[Au(SO_3F)_4] \quad (4)$$

minimum conductance must be primarily caused by K^+_{solv} and $[Au(SO_3F)_4]^-_{solv}$, with an expected concentration of 24.6×10^{-3} mol/kg. The measured conductance is in reasonable agreement with an interpolated value of approximately 14.9×10^{-4} Ω^{-1} cm^{-1} for $K[Au(SO_3F)_4]$ in HSO_3F at this concentration.

The specific conductance vs. concentration plot for $Au(SO_3F)_3$ in HSO_3F is shown in Figure 3 together with plots obtained from published data, for $SbF_2(SO_3F)_3$,[16] SbF_5,[16] and $I(SO_3F)_3$.[17] The data allow an approximate estimate of the degree of ionization of these solutes in HSO_3F and hence their acidities. However, $I(SO_3F)_3$ is so weakly ionized in fluorosulfuric acid that a clear distinction between acidic or basic behavior has not been possible.[17] A more unambiguous estimation of the acidity of HSO_3F–$Au(SO_3F)_3$ systems will have to await the determination of the Hammett acidity function. Corresponding data for HSO_3F–SbF_5 and HSO_3F–SbF_5–SO_3 systems have been published.[18] The obtained straight line for $Au(SO_3F)_3$ indicates the absence of solute association with increasing concentration, in contrast to the behavior of SbF_5.[16]

A direct quantitative comparison between our electrical conductance measurements and an earlier study[4] of AuF_3 in HSO_3F is not possible since only a conductometric titration with KSO_3F was reported. The end point at $KSO_3F \approx 2AuF_3$ indicates a greater complexity in the HSO_3F–AuF_3 system.

^{19}F NMR spectra of solutions of $Au(SO_3F)_3$ in HSO_3F (about 2 M) show two broad single lines at 41.2 and 46.5 ppm relative to $CFCl_3$ (external). The first line is attributed to HSO_3F, with the resonance of the pure solvent at 40.6 ppm. Solutions of $Cs[Au(SO_3F)_4]$ produce two rather sharp single lines at 40.8 and 45.4 ppm, respectively. Line broadening is also observed in the ^1H NMR spectrum of $Au(SO_3F)_3$ solutions in HSO_3F. The signal at 9.97 ppm (relative to Me_4Si (external)) found for the solvent, solutions of $Cs[Au(SO_3F)_4]$, and dilute solutions of $Au(SO_3F)_3$ moves downfield to −10.30 ppm for the 2 M solution of $Au(SO_3F)_3$ in HSO_3F.

The observation of only one proton resonance indicates rapid proton exchange between solvent and solute. A precedent for the observed downfield shift of the ^1H signal in HSO_3F–$Au(SO_3F)_3$ depending on solute concentration is found for the superacid system H_2SO_4–$H[B(SO_4H)_4]$.[19]

The observation of two ^{19}F NMR signals at room temperature argues against rapid SO_3F-group exchanges between solvent and solute, whether the solute is $Au(SO_3F)_3$ or $Cs[Au(SO_3F)_4]$. A similar observation is reported for solutions of $Cs_2[Sn(SO_3F)_6]$ in HSO_3F;[11] however, $I(SO_3F)_3$ exchanges rapidly with HSO_3F even at −90 °C.[17] The appearance of a single ^{19}F NMR resonance for the solute in $Au(SO_3F)_3$ solutions is consistent with the presence of a monomeric species, rather than a SO_3F-bridged polymer; the absence of appreciable SO_3F exchange suggests a coordinatively saturated species, such as $H[Au(SO_3F)_4]$. Proton exchange and acidic behavior may be expressed by equilibrium 5. The presence

$$H[Au(SO_3F)_4] + HSO_3F \rightleftharpoons H_2SO_3F^+ + [Au(SO_3F)_4]^- \quad (5)$$

of protonated species, $H[Au(SO_3F)_4]$ and $H_2SO_3F^+$ in equilibrium with $[Au(SO_3F)_4]^-$ and HSO_3F, respectively, may

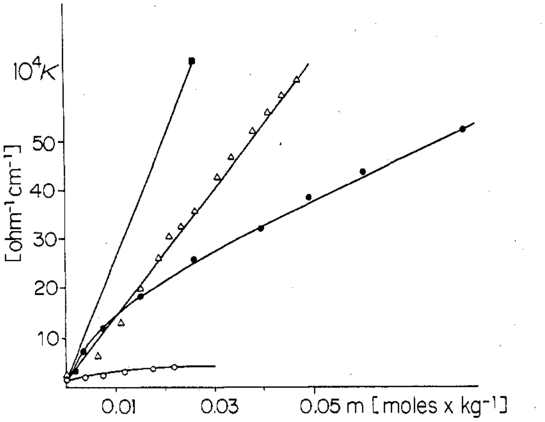

Figure 3. Specific conductivities of acids in HSO_3F at +25 °C: (■) $SbF_2(SO_3F)_3$,[16] (△) $Au(SO_3F)_3$, (●) SbF_5,[16] (○) $I(SO_3F)_3$.[17]

account for the observed downfield ^{19}F NMR shift of both the solute and the solvent for solutions of $Au(SO_3F)_3$ vs. those of $Cs[Au(SO_3F)_4]$.

Raman spectra were obtained on solutions of $Au(SO_3F)_3$ in HSO_3F at various concentrations and also on a solution of $Cs[Au(SO_3F)_4]$ in fluorosulfuric acid. The observed Raman shifts are listed in Table III, together with estimated relative intensities and previously published Raman data on HSO_3F.[20]

As expected for solution spectra, the observed bands are rather broad and since the fluorosulfate group is common to both the solvent and the solute, some overlap between solvent and solute bands is encountered. However, the fluorosulfato–gold species in solution is found to be an excellent Raman scatterer, allowing the observation of solute bands even at concentration as low as 0.15 molal. At higher concentrations of $Au(SO_3F)_3$ the solvent bands are gradually supressed, thus accounting for differences in relative band intensities with increasing concentrations. This fact allows some interesting conclusions: The spectra of $Au(SO_3F)_3$ in HSO_3F are rather similar to the one obtained on $Cs[Au(SO_3F)_4]$ in the same solvent. Furthermore, the most prominent solute bands at ~645, ~450, and ~275 cm^{-1} are all found in the solid-state spectra of $M[Au(SO_3F)_4]$ listed in Table II with similar relative intensities. The solution spectra, if we take band overlaps into account, may be regarded as composite spectra of HSO_3F and the $[Au(SO_3F)_4]^-$ moiety. Any polymeric fluorosulfate-bridged species in the HSO_3F–$Au(SO_3F)_3$ system is not detected, even at high solute concentrations. New bands, observed only at the highest concentration, at 1360, 1090, and 350 cm^{-1} are extremely weak and may be caused by a laser-induced decomposition of the sample.

The concentration range covered by the Raman experiments on the $Au(SO_3F)_3$–HSO_3F systems overlaps well with the concentrations of solute used to obtain NMR spectra. However, more dilute solutions were used to obtain electronic spectra and to measure electrical conductivities. It seems rather unlikely that polymers of $Au(SO_3F)_3$ should exist at those very low concentrations and the results presented here suggest that the species in solution is best described as $H[Au(SO_3F)_4]$ in equilibrium with $[Au(SO_3F)_4]^-$ as formulated in eq 5.

Finally, as previously reported for HSO_3F,[20] bands due to OH stretching vibrations could not be detected in the solution Raman spectra. Infrared spectra, obtained by using perfluoropolyethylene (Teflon) as the window material, show a shift of the solvent band at 3125 cm^{-1}[21] to ~2950 cm^{-1} for the 2.3 molal solution; however the extreme broadness of the band makes it difficult to attach much significance to the frequency shift.

Conclusions

The results presented here indicate that $Au(SO_3F)_3$ is indeed an excellent fluorosulfate ion acceptor. It should therefore be possible to stabilize unusual cations with the $[Au(SO_3F)_4]^-$ ion. Work in this direction is currently being undertaken.[22]

The HSO_3F–$Au(SO_3F)_3$ system may be classified as a superacid system. Even though the HSO_3F–$SbF_2(SO_3F)_3$ system appears to be more acidic, the usefulness of our system is based on the noted lack of oxidizing ability (thus allowing the study of oxidizable cations) and the rather uncomplicated ^{19}F NMR spectrum.

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Registry No. $Au(SO_3F)_3$, 36735-27-0; $K[Au(SO_3F)_4]$ (salt form), 68213-01-4; $K[Au(SO_3F)_4]$ (coordination form), 68213-05-8; $Cs[Au(SO_3F)_4]$ (salt form), 68213-02-5; $Cs[Au(SO_3F)_4]$ (coordination form), 68213-06-9; $Li[Au(SO_3F)_4]$ (salt form), 68213-03-6; $Li[Au(SO_3F)_4]$ (coordination form), 68213-07-0; $ClO_2[Au(SO_3F)_4]$, 68213-09-2; $NO[Au(SO_3F)_4]$, 68213-10-5; $S_2O_6F_2$, 13709-32-5; ClO_2SO_3F, 24114-30-5; $NO[AuCl_4]$, 68213-11-6; $BrSO_3F$, 13997-93-8.

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