sulfonating and oxidizing agent.[2-5] Peroxydisulfuryl difluoride has now been found to react with cerium(III) carbonate to form oxobis(fluorosulfato)cerium(IV), while peroxydisulfuryl difluoride and bromine(I) fluorosulfate each react with cerium(III) fluoride giving trifluoro(fluorosulfato)cerium(IV).

Experimental Section

Materials.—Peroxydisulfuryl difluoride was prepared by the reaction of fluorine with sulfur trioxide[6] and purified by prolonged pumping of the crude product held at −78°. Infrared analysis and vapor density measurements indicated that the product was substantially pure. Bromine(I) fluorosulfate was prepared by the method of Aubke and Gillespie.[7]

Cerium(III) carbonate was prepared by dissolving Ce_2O_3 in dilute HCl and precipitating $Ce_2(CO_3)_3 \cdot 5H_2O$ by the addition of sodium bicarbonate solution. The pentahydrate was made anhydrous by heating it to 100–110° in an oven and subsequently drying under dynamic vacuum at about 70° for several hours. Cerium(III) fluoride was used as received from the American Potash and Chemical Corp. without further purification.

Infrared spectra of the solid compounds were obtained using Nujol mulls held between silver chloride disks. Spectra of the gaseous products were obtained with a 10-cm Pyrex glass cell fitted with silver chloride windows and a cold finger. The instrument used was a Beckman IR-10 spectrometer.

Reaction of Peroxydisulfuryl Difluoride with Cerium(III) Carbonate.—Cerium(III) carbonate, 0.0693 g, was placed in a 100-ml glass reaction vessel fitted with a Fischer-Porter LabCrest valve closed with a Teflon stopper. After evacuating and cooling the vessel to −183°, an excess of peroxydisulfuryl difluoride was added by distillation. The vessel was then brought slowly to room temperature and allowed to stand overnight. The volatile products were removed by pumping and were shown by a combination of distillation and infrared spectroscopic techniques to be CO_2, $S_2O_6F_2$, $S_2O_5F_2$, O_2, and a trace of SiF_4. After pumping to constant weight at room temperature, the vessel contained 0.1028 g of an orange solid. The calculated weight for $CeO(SO_3F)_2$ was 0.1067 g.

For analysis, a weighed sample of the solid was digested at 100° in an excess of a solution 0.1 *M* in NaOH and 0.1 *M* in Na_2CO_3. The cerium carbonate which precipitated was removed by filtration. The filtrate was then neutralized and treated with oxalic acid. Any cerium oxalate which precipitated was removed and combined with the carbonate. After igniting at about 800°, the resulting CeO_2 was weighed. Sulfur was determined by weighing as $BaSO_4$ and fluorine was determined using a distillation technique similar to that of Willard and Winter[8] followed by titration with 0.1 *N* $Th(NO_3)_4$. A fluoride ion selective electrode was used to observe the end point. *Anal.* Calcd for $CeO(SO_3F)_2$: Ce, 39.6; S, 10.7; F, 18.1. Found: Ce, 39.8; S, 10.5; F, 16.5.

Reaction of Peroxydisulfuryl Difluoride with Cerium(III) Fluoride.—Cerium(III) fluoride, 0.1882 g, was placed in a 100-ml glass vessel like that described in the previous paragraph. An excess of peroxydisulfuryl difluoride, 0.8223 g, was condensed onto the CeF_3, while the vessel was held at −183°. The reaction vessel was then placed behind a safety shield and brought to room temperature. A visible reaction took place. After the vessel had stood for 16 hr to allow all of the cerium(III) fluoride to react, the volatile materials were removed by pumping until the remaining yellowish brown solid had a constant weight of 0.2810 g. The theoretical weight for CeF_3SO_3F was 0.2830 g.

Reaction of Bromine(I) Fluorosulfate with Cerium(III) Fluoride.—Cerium(III) fluoride, 0.1547 g or 0.785 mmol, was placed in a vessel similar to that described above. Bromine(I) fluorosulfate, 1.4663 g or 8.20 mmol, was condensed onto the CeF_3 while the vessel was held at −183°. The reaction vessel was slowly warmed to room temperature behind a safety shield. The reaction proceeded to completion at room temperature when left overnight. There was no oxygen found among the volatile products. The vessel was held at room temperature and pumped to constant weight. A yellowish brown crystalline solid having a weight of 0.2342 g remained. The expected weight for $CeF_3(SO_3F)$ was 0.2326 g. This product had the same properties as that of the previous paragraph. *Anal.* Calcd for CeF_3SO_3F: Ce, 47.3; S, 10.8; F, 25.7. Found: Ce, 46.8; S, 10.4; F, 26.1.

TABLE I

IR SPECTRA OF $CeO(SO_3F)_2$ AND $CeF_3(SO_3F)$

KSO_3F[a]	$CeF_3(SO_3F)$	$CeO(SO_3F)_2$	Assignments[b]
1280 s	1270 vs, br	1346 vs	ν_4(e) SO_3 asym st
		1224 vs, br	
1080 s	1112 s, br	1160 s, br	ν_1(a) SO_3 sym st
		1045	
750 s	841 s	873 s	ν_2(a) S–F st
	725 m, br	720 m, br	
		652 m	
590 s	598 w	604 s	ν_5(e) SO_3 asym def
	583 m	579 s	
570 sh	560 s	564 s	ν_3(a) SO_3 sym def
408 vw	420 m, vbr	416 w	ν_6(e) S–F def
138 m, br			Lattice vib

[a] Reported in ref 9. [b] Assignments are tentative and are based on those found in ref 9: s, strong; m, medium; v, very; w, weak; br, broad; sh, shoulder; def, deformation; sym, symmetric; asym, asymmetric; st, stretch; vib, vibration.

Infrared Spectra (Nujol Mulls).—The infrared spectrum of $CeF_3(SO_3F)$ is much simpler than that of $CeO(SO_3F)_2$. The region of the $CeO(SO_3F)_2$ spectrum between 1400 and 1000 cm^{-1} consists of a strong broad absorption centered at about 1250 cm^{-1} with some fine structure superimposed on it. The spectrum of $CeF_3(SO_3F)$ also has a strong broad peak in the S–O stretching region, but this band takes up only the region from about 1400 to 1150 cm^{-1} and is centered at about 1265 cm^{-1}. It has much less fine structure than that of $CeO(SO_3F)_2$. The location of the S–F stretching peak is at 873 and 841 cm^{-1} in the $CeO(SO_3F)_2$ and $CeF_3(SO_3F)$ spectra, respectively. The $CeO(SO_3F)_2$ spectrum also has more peaks than does the $CeF_3(So_3F)$ spectrum in the region 725–560 cm^{-1}. The peaks are listed in Table I along with the spectrum of KSO_3F and assignments reported by Gobeau and Milne.[9] From splitting of the E modes (ν_4 and ν_5) in the spectrum for $CeO(SO_3F)_2$ and an apparent lack of splitting for $CeF_3(SO_3F)$, it seems that the SO_3F groups in the former compound have lost the C_{3v} symmetry they possess in $Ca(SO_3F)_2$[9] whereas the symmetry seems to have been retained in $CeF_3(SO_3F)$. This, together with the higher frequency of the S–F stretching mode of $CeO(SO_3F)_2$ relative to that of $CeF_3(SO_3F)$, may mean that the former is a more covalent material than the latter.[9-12]

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Reaction of Bromine(I) Fluorosulfate with Gold and with Platinum

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The reaction of bromine(I) fluorosulfate with gold and platinum was discovered almost accidentally.

Other studies made of bromine(I) fluorosulfate had given indications of some molecular association in the liquid state.[1-3] With this in mind it was decided to obtain a mass spectrum of the vapor of bromine(I) fluorosulfate to see whether a species with a mass greater than that of the monomeric parent ion could be found. The mass spectrometer was equipped with a leak made of gold; therefore, an experiment was run to determine whether gold would react with bromine(I) fluorosulfate. A reaction was found to occur. The study was later extended to the reaction of platinum. The products obtained were gold(III) fluorosulfate and platinum(IV) fluorosulfate.

Both gold and platinum have been reported to be inert even in boiling fluorosulfuric acid.[4] Attempts made in these laboratories to cause gold, tin, or zinc to react extensively with peroxydisulfuryl difluoride at room temperature also were unsuccessful. Rhenium has been shown to react.[5]

Gold(III) fluorosulfate was found in this work to combine with $BrSO_3F$ to form the solid adduct $Au(SO_3F)_3 \cdot 2BrSO_3F$. When this was warmed under vacuum, bromine(I) fluorosulfate was lost. Probably the solid $Au(SO_3F)_3 \cdot BrSO_3F$ was produced as an intermediate, but this, too, lost $BrSO_3F$ and left $Au(SO_3F)_3$. Platinum(IV) fluorosulfate also formed solid adducts with $BrSO_3F$. The work did not clearly indicate their stoichiometry but it strongly suggested that both $Pt(SO_3F)_4 \cdot 4BrSO_3F$ and $Pt(SO_3F)_4 \cdot 2BrSO_3F$ were formed.

Experimental Section

Bromine(I) fluorosulfate was prepared by the method of Aubke and Gillespie.[1] Gold wire and platinum foil were used as received.

Gold and platinum in the respective compounds were determined as metals.[6] For the determination of sulfur and fluorine, a known weight of the compound was allowed to react with a solution of sodium hydroxide. Sulfur was weighed as barium sulfate and fluorine was determined by titration with 0.1 *N* $Th(NO_3)_4$ solution using an Orion fluoride ion selective electrode to find the end point.

Reaction of Bromine(I) Fluorosulfate with Gold.—Gold wire, 0.0550 g (0.279 g-atom), was placed in a 100-ml glass vessel equipped with a Fischer-Porter Lab-Crest valve having a Teflon stem. An excess of bromine(I) fluorosulfate, 0.6805 g (3.80 mmol), was distilled into the vessel and the latter was then allowed to stand at about 65° overnight. The gold dissolved in the liquid, and bromine was formed, as shown by the color of the vapor. The vessel was then weighed, cooled to −183°, and pumped. This produced no change in weight and showed that oxygen was not produced by the reaction. The vessel was then held at room temperature while volatile materials were removed by dynamic vacuum. From time to time the vessel was weighed. At first, the loss of weight was rapid, but this rate decreased and the weight fell to the substantially constant value of 0.234 g. The product was a crystalline solid having a composition close to $Au(SO_3F)_3 \cdot 2BrSO_3F$ (theoretical weight 0.238 g).

When the resulting solid was held at 55° and pumping was continued, the weight again fell rather rapidly at first, but the rate of loss continually decreased. After about 3 hr the weight had dropped to 0.188 g (the theoretical value for $Au(SO_3F)_3 \cdot BrSO_3F$) but it continued to fall slowly. The vessel was then held at 100° while pumping was continued. After 75 min the weight had fallen to 0.144 g, where it remained constant (theoretical weight for $Au(SO_3F)_3$ 0.138 g). This experiment indicates that the crystalline compound $Au(SO_3F)_3 \cdot 2BrSO_3F$ was obtained at room temperature and that it decomposed when heated under vacuum, giving $Au(SO_3F)_3$ with the probable formation of $Au(SO_3)_3 \cdot BrSO_3F$ as an intermediate.

Other experiments established that gold interacts slowly at room temperature with $BrSO_3F$ liquid and vapor. The latter case caused the entire supply of liquid $BrSO_3F$ held in a separate bulb to distil, over a period of several weeks, into the finger holding the gold compound produced by the reaction.

Gold(III) fluorosulfate is bright orange-yellow and the solid melts at about 94°. *Anal.* Calcd for $Au(SO_3F)_3$: Au, 39.8; S, 19.4; F, 11.5. Found: Au, 38.2; S, 19.3; F, 11.0. A qualitative test for bromine was negative.

Reaction of Bromine(I) Fluorosulfate with Platinum.—Platinum (0.1610 g, 0.825 g-atom) was placed in a vessel like that described above. An excess, 1.274 g (7.13 mmol), of bromine(I) fluorosulfate was transferred into the vessel at −183° and the reactor was then brought to room temperature. No visible reaction took place, even after standing for a few days. The reaction vessel was then kept at about 95° for 3 weeks, after which all of the platinum had reacted. The reactor then contained a liquid phase and a crystalline solid. The possible evolution of oxygen during the reaction was checked as before, but none was found. Volatile products were then pumped away, while the vessel was held at room temperature, and the reactor was removed from the vacuum line and weighed periodically. At first the weight decreased rather rapidly, but the rate of removal of $BrSO_3F$ kept decreasing and the weight remained almost constant after the molar ratio of $BrSO_3F$ to $Pt(SO_3F)_4$ in the reactor had fallen from 3.5 to 1. The material was then completely solid. Pumping was then continued with the vessel held at 60°. The weight again fell, and the rate of removal of $BrSO_3F$ decreased to a slow but substantially constant value after the molar ratio of $BrSO_3F$ to $Pt(SO_3)F)_4$ dropped below 2.20. When the vessel was later held at 90° and evacuated for 10 hr, the ratio fell to 0.49–1. Finally, pumping was continued for an additional 22 hr with the temperature at 110°. The weight of the material fell to 0.480 g (theoretical weight for $Pt(SO_3F)_4$ was 0.488 g). Pumping was stopped at this point to avoid decomposition of the platinum(IV) fluorosulfate. The substance was a dark brown solid and a sample melted at 182°. *Anal.* Calcd for $Pt(SO_3F)_4$: Pt, 33.0; S, 21.6; F, 12.9. Found: Pt, 31.9; S, 21.1; F, 12.3; Br, 0.0.

The above experiment shows clearly that platinum(IV) fluorosulfate is produced by the reaction of platinum with bromine(I) fluorosulfate and that solid adducts are formed. It appears probable that formulas for two of these adducts are $Pt(SO_3F)_4 \cdot 4BrSO_3F$ and $Pt(SO_3F)_4 \cdot 2BrSO_3F$.

Spectra.—The Raman spectrum of solid $Au(SO_3F)_3$ was recorded using the 6471-Å exciting line of a Coherent Model 52 mixed-gas ion laser in conjunction with a Spex 1401 double spectrometer and a thermoelectrically cooled FW-130 phototube. The spectrum is reported in Table I. The solid was sealed in a capillary tube under anhydrous conditions. Unsuccessful attempts were made to obtain Raman spectra of $Pt(SO_3F)_4$ and of the adducts formed with $BrSO_3F$.

TABLE I

RAMAN SPECTRUM OF $Au(SO_3F)_3$

Freq, cm^{-1}	Rel intens	Freq, cm^{-1}	Rel intens
1485	0.1	607	1.1
1492	0.7	576	0.4
1420	0.4	545	0.6
1224	3.5	460	2.6
1100	0.2	441	1.0
1050	0.8	347	1.4
955	sh	295	10.0
928	3.8	287	9.2
896	2.1	235	0.3
870	0.9	189	1.4
819	0.9	170	2.4
662	2.6	149	1.9
648	7.2	96	2.7

A Varian Model V-4311 spectrometer equipped with a 56.4-MHz oscillator was used to obtain the ^{19}F nmr spectrum of an

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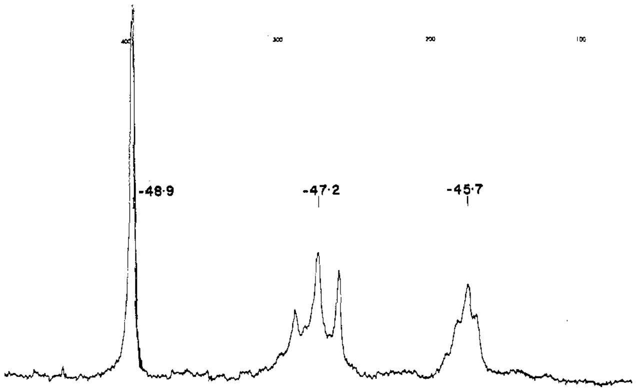

Figure 1.—Part of the ^{19}F nmr spectrum of a liquid made by mixing $BrSO_3F$ with $Au(SO_3F)_3$ in an 8:1 molar ratio. Chemical shifts are in ppm with respect to $CFCl_3$ as an external standard.

8:1 molar ratio liquid mixture of bromine(I) fluorosulfate with gold(III) fluorosulfate at room temperature. Fluorotrichloromethane was used as an external reference. Part of the spectrum is shown in Figure 1.

Discussion

While compounds of stoichiometry $Au(SO_3F)_3$ and $Pt(SO_3F)_4$ are in harmony with the other chemistry of the two noble metals, it is somewhat surprising that $BrSO_3F$ reacts so readily. The adducts of $BrSO_3F$ with $Au(SO_3F)_3$ and $Pt(SO_3F)_4$ are of sufficient interest to merit further study.

The nmr spectrum of the 1:8 liquid mixture of $Au(SO_3F)_3$ with $BrSO_3F$ contains a sharp single peak at a chemical shift of -37.9 ppm. Other peaks are shown in Figure 1. Relative areas of the bands centered at -37.9, -45.7, -47.2, and -48.9 ppm are approximately 5:2.2:4:3. It is apparent that fluorosulfate groups are present in several environments and that exchange among at least some of these is slow enough to allow several bands to appear in the spectrum. Since the quadrupole moments of both gold and bromine are high, it is unlikely that the ^{19}F nmr spectrum shows evidence of coupling with the spins of Br or Au.[7,8] The spectrum is not interpreted in terms of possible molecular structures.

The Raman spectrum of solid $Au(SO_3F)_3$ reported in Table I has some of the characteristics of spectra of substances containing the SO_3F^- ion. There are marked differences, however, which make it appear that gold(III) fluorosulfate is covalent and probably polymeric. This state of affairs is in agreement with the structure of other gold(III) compounds. Complex vibrational spectra of several fluorosulfates have been interpreted to indicate the existence of polymers.[9,10] Fluorosulfate groups may serve as bridges.

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Acid-Catalyzed Exchange of Oxalate Oxygen between Oxalatotetraaquochromium(III) Ion and Solvent Water

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In a continuation of our interest in metal–oxalato complexes[1] we have undertaken an examination of acid-catalyzed exchange of oxygen between oxalate in $Cr(H_2O)_4C_2O_4^+$ and solvent water. The results add to those obtained by others[2–4] on some closely related chromium(III) complexes. All oxalate oxygens in $Cr(H_2O)_4C_2O_4^+$ exhibit kinetic equivalence in their exchange with solvent, as has been found for all chromium(III) oxalato complexes thus far examined. The present experimental results on $Cr(H_2O)_4C_2O_4^+$, together with predictions which can be made about the kinetics of oxygen exchange between coordinated water and solvent, enable one to limit considerably the mechanistic possibilities for the exchange processes. As a by-product of the study we conclude that cerium(IV) perchlorate oxidation of $Cr(H_2O)_4C_2O_4^+$ in acidic solution to produce carbon dioxide involves Cr–O bond cleavage without accompanying C–O bond cleavage.

Experimental Section

Reagents.—Materials were reagent grade in quality except where otherwise specified. Water enriched in ^{18}O was obtained from Yeda Research and Development Co., Inc. Solutions of perchloric acid and sodium perchlorate, prepared by standard procedures,[1] were used to control acidity and ionic strength.

An aqueous solution of $[Cr(H_2O)_4C_2O_4]ClO_4$ was prepared by allowing $[Cr(H_2O)_6](ClO_4)_3$ (G. F. Smith) to react with sodium oxalate.[5]. Equal volumes of 0.10 *M* solutions were mixed, the pH was adjusted into the range 3–4, and the solution was heated to incipient boiling for 0.5 hr. The cooled solution was diluted approximately 20-fold with 0.01 *M* $HClO_4$ and passed onto a Dowex-50W-X8 column in the hydrogen ion form. The column was washed with 0.01 *M* $HClO_4$ and then eluted with 0.1 *M* $HClO_4$ until the violet band due to the complex passed off the column. A middle fraction of this effluent solution was carefully concentrated by rotary evaporation at room temperature. During this process the pH was periodically adjusted to 3–4 with $KHCO_3$. After the preparation had been cooled overnight in a refrigerator, the $KClO_4$ produced was filtered from the final solution.

Chromium was analyzed[6] by converting the complex to CrO_4^{2-} and, for solutions which were 0.1 *M* in NaOH, comparing the absorbance at 372 nm with values given by standard solutions also in 0.1 *M* NaOH. The oxalate concentration was determined by the method of Hamm.[7] The oxalate to chromium ratio was found to be 1.006 to 1.000.

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