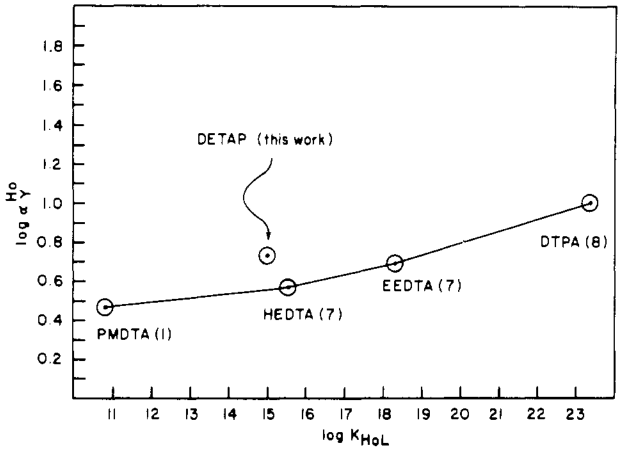

Figure 3. Ho^{3+}–Y^{3+} separation factors as a function of affinity.

of Ho^{3+}, exhibits a ligand affinity depressed to the point that it appears that Y^{3+} would elute nearly in coincidence with the light lanthanon Ce^{3+} (log K_{YL} = 14.28; log K_{CeL} = 14.26). This is a position later in the elution sequence than Y^{3+} has ever been observed to elute. Yttrium elutes between Tb and Dy when EDTA is the eluant and nearly (but not quite) in coincidence with Nd when either EEDTA or HEDTA is the eluant. If one first removed Ce, e.g. via solvent extraction in its +4 oxidation state, it would appear that Y^{3+} could then be removed rather easily from the other (tervalent) lanthanons since the closest Ln^{3+} neighbor would then be Pr^{3+}, and the Pr–Y separation factor would be ca. 2.1.

As for the estimation of the minimum Am–Ln separation factor (Am^{3+} from Sm^{3+} or Eu^{3+}), if one presumes from an interpolation (see Figure 2) that the Am^{3+}–Nd^{3+} $\Delta \log K_{ML}$ is 0.61 (about the same as in the case of TEDTA) and subtracts 0.49 (log K_{SmL} – log K_{NdL}), the Am–Sm separation factor can be inferred to be antilog (0.12) = 1.3. When Ho^{3+}–Y^{3+} separation factors are plotted in a similar manner (Figure 3) against the logarithm of the Ho–L affinity, the Ho–Y separation factor for DETAP is seen to be abnormally high···well off the trend established by the other data. Because log K_{YL} in the case of DETAP is abnormally low relative to log K_{HoL}, one wonders if log K_{AmL} might not be abnormally high relative to log K_{NdL}. If so, log α_{Nd}^{Am} could be considerably larger than the interpolated value of 0.61 (Figure 2), and the Am–Sm separation factor (minimum Am–Ln separation factor) would then be substantially higher than the 1.3 that has been estimated in a conservative way above. This possibility needs to be checked out via the elution chromatographic technique.[7–9]

Registry No. DETAP, 97592-02-4.

(7) Mackey, J. L.; Hiller, M. A.; Powell, J. E. *J. Phys. Chem.* **1962**, *66*, 311.
(8) Harder, R.; Chaberek, S. *J. Inorg. Nucl. Chem.* **1959**, *11*, 197.
(9) Powell, J. E.; Johnson, D. A.; Burkholder, H. R.; Vick, S. C. *J. Chromatogr.* **1973**, *87*, 437.

Contribution from the Department of Chemistry,
The University of British Columbia, Vancouver, B.C. V6T 1Y6, Canada

Fluorosulfate Derivatives of Manganese and Rhenium

S. P. MALLELA and F. AUBKE*

Received July 10, 1984

The oxidation of manganese by bis(fluorosulfuryl) peroxide ($S_2O_6F_2$) in HSO_3F allows the preparation of $Mn(SO_3F)_3$ and the ternary fluorosulfates $M'_2[Mn(SO_3F)_5]$ (M′ = K or Cs), with manganese oxidized to the +3 oxidation state. The oxidation of $Mn_2(CO)_{10}$ by $S_2O_6F_2$, or the further oxidation of $Mn(SO_3F)_2$ by $S_2O_6F_2$, in either the absence or the presence of HSO_3F provides alternate routes to $Mn(SO_3F)_3$. Solutions of $M'_2[Mn(SO_3F)_5]$ in HSO_3F are unstable and produce polymeric $Mn(SO_3F)_2$. Rhenium is oxidized to the +7 oxidation state, and a yellow oil of the composition $ReO_2(SO_3F)_3$ is identified as one of the reaction products. The reaction of Re_2O_7 with $S_2O_6F_2$ provides an alternate route to $ReO_2(SO_3F)_3$. The metal carbonyl fluorosulfates $Re(CO)_5SO_3F$ and $Mn(CO)_5SO_3F$ are obtained from the reaction of $Re(CO)_5Cl$ and $Mn(CO)_5Br$, respectively, with $AgSO_3F$ in CH_2Cl_2. Controlled pyrolysis of $Mn(CO)_5SO_3F$ at ~70 °C allows isolation of $Mn(CO)_4SO_3F$.

Introduction

A number of fluorosulfate derivatives of both manganese and rhenium have been reported previously. Manganese(II) fluorosulfate is conveniently prepared by a displacement reaction of the type

$$MnX_2 + 2HSO_3F \rightarrow Mn(SO_3F)_2 + 2HX \quad (1)$$
$$X = \text{acetate or benzoate}^{1,2}$$

Interestingly, solvolysis of manganese(III) acetate in HSO_3F also produces $Mn(SO_3F)_2$ in what appears to be a redox reaction.[1] Limited structural information on $Mn(SO_3F)_2$ is available. A magnetic moment, μ_{eff}, of 5.8 μ_B at 293 K suggests[3] a high-spin configuration for Mn^{2+}, and the vibrational spectra[2] suggest a three-dimensional polymer with O-tridentate fluorosulfate groups and a regular octahedral environment for the central atom, a rather common structural type for $M(SO_3F)_2$.[2,4] Bis(fluorosulfuryl) peroxide ($S_2O_6F_2$) has been found[5] to produce quantitatively an oxo fluorosulfate of the composition $MnO(SO_3F)$ when reacted with $MnCO_3$. On the other hand, the reaction of dimanganese decacarbonyl ($Mn_2(CO)_{10}$) with a large excess of $S_2O_6F_2$ is said[6] to afford quantitatively manganese tetrakis(fluorosulfate) ($Mn(SO_3F)_4$). Since both reactions are said to proceed smoothly at room temperature with comparable reaction times, it is not immediately obvious why there should be a difference in the oxidizing ability of $S_2O_6F_2$, reflected in the different oxidation states of manganese in the resulting products.

The oxidation of rhenium metal by $S_2O_6F_2$[7] does lead to oxo fluorosulfates of rhenium. Depending on the reaction conditions, $Reo_3(SO_3F)$, described as a yellow liquid, or $ReO_2(SO_3F)_3$, a white solid, forms with Re in the +7 oxidation state.

Our interest in these systems is focused primarily on $Mn(SO_3F)_4$[6] for two reasons: (a) binary Mn(IV) oxyacid salts and halides appear to be quite rate,[8] and very little is known about

(1) Woolf, A. A. *J. Chem. Soc. A* **1967**, 335.
(2) Alleyne, C. S.; O'Sullivan-Mailer, K.; Thompson, R. C. *Can. J. Chem.* **1974**, *52*, 336.
(3) Edwards, D. A.; Stiff, M. J.; Woolf, A. A. *Inorg. Nucl. Chem. Lett.* **1967**, *3*, 427.
(4) Mallela, S. P.; Aubke, F. *Can. J. Chem.* **1984**, *62*, 382.
(5) Dev, R.; Cady, G. H. *Inorg. Chem.* **1971**, *10*, 2354.
(6) Brown, S. D.; Gard, G. L. *Inorg. Chem.* **1978**, *17*, 1363.
(7) Kleinkopf, G. C.; Shreeve, J. M. *Inorg. Chem.* **1964**, *3*, 607.

electronic spectra[9] or magnetic properties[10] of Mn(IV) compounds; (b) we have for some time been interested in medium- to high-valent binary fluorosulfates of transition metals as SO_3F^- ion acceptors and potential ansolvo superacids in HSO_3F. Previous work on $HSO_3F/Au(SO_3F)_3$[11] and on $HSO_3F/Pt(SO_3F)_4$[12] had provided strong evidence for superacidity in both instances, but the high prices of Au and Pt pose limitations to extensive usage and the $HSO_3F/Mn(SO_3F)_4$ system appeared economically more attractive. Metal oxidation by $S_2O_6F_2$ in HSO_3F as reaction medium appears to be a convenient synthetic route that offers many advantages, producing binary metal fluorosulfates such as $Au(SO_3F)_3$[11] or $Pt(SO_3F)_4$,[12] as well as ternary fluorosulfates of the general type $M'_n[M(SO_3F)_{m+n}]$, where M' is an alkali metal. Alkali-metal fluorosulfates, conveniently obtained in situ by the solvolysis of the corresponding chlorides in HSO_3F, are present in stoichiometric amounts and the overall reaction follows the general equation

$$nM'Cl + nHSO_3F + M + (m/2)S_2O_6F_2 \xrightarrow[HSO_3F]{} M'_n[M(SO_3F)_{m+n}] + nHCl \quad (2)$$

Examples of such ternary fluorosulfates include $K[Au(SO_3F)_4]$,[11] $K_2[Pt(SO_3F)_6]$,[12] and $Cs_2[Pd(SO_3F)_6]$.[13] The latter compound is interesting, because it is easily formed, while a binary $Pd(SO_3F)_4$ is not obtainable.[13]

Similar anionic complexes of manganese are of interest for two reasons: (a) the acceptor ability of a binary metal fluorosulfate $M(SO_3F)_n$, the basic requirement for superacidity, is best illustrated by the isolation and structural characterization of such anionic complexes; (b) their preparation appears to be a synthetic challenge, because no ternary fluorosulfates of any 3d-block metal appear to have been reported.

It is also hoped that the oxidation of rhenium by $S_2O_6F_2$ in HSO_3F will take a different course, hopefully resulting in the formation of binary or ternary fluorosulfates rather than the oxofluorosulfates reported previously.[7]

The preparation of metal carbonyl fluorosulfates of both Mn and Re became an additional objective. Compounds like $Mn(CO)_5SO_3F$ or $Mn(CO)_4SO_3F$ may be viewed as intermediates in the reaction of $Mn_2(CO)_{10}$ with $S_2O_6F_2$, and $Fe(CO)_4(SO_3F)_2$, the only reported[6] transition-metal carbonyl fluorosulfate, is indeed obtained from $Fe(CO)_5$ and $S_2O_6F_2$. However, the silver salt method, the reaction of $M(CO)_5X$ (M = Mn, Re; X = Cl, Br) with $AgSO_3F$ in a suitable solvent, is viewed as a more promising route. Only a very brief mention of $Mn(CO)_5SO_3F$ is made in a conference report.[14] A number of derivatives having groups isoelectronic with the SO_3F group are reported. These include $Mn(CO)_5ClO_4$,[15] $Mn(CO)_5PO_2F_2$,[15] $Mn(CO)_5NSOF_2$,[16] and $Re(CO)_5NSOF_2$.[16] All are obtained by the silver salt method.

Experimental Section

Chemicals. The following chemicals were obtained from the chemical sources given in parentheses and were used without further purification: $Mn(CO)_5Cl$, $Re(CO)_5Cl$, Re_2O_7, $Mn_2(CO)_{10}$ (all from Pressure Chemicals Inc.); $Mn(CO)_5Br$ (Strem Chemicals Inc.); Re powder, 99.99% pure (Ventron Corp.); Mn powder 50–325 mesh (MCB); HSO_3CF_3 (3M Co.); SO_3 (Allied Chemicals); F_2 (Air Products); $AgCO_2CF_3$ (Aldrich Chemicals). Technical grade HSO_3F was purified by double distillation at atmospheric pressure,[17] and spectral grade CH_2Cl_2 was dried over Linde 4A molecular sieves. The following materials were synthesized according to published methods: $S_2O_6F_2$, catalytic fluorination (AgF_2) of SO_3;[18] $AgSO_3F$, solvolysis of $AgCO_2CF_3$ in purified HSO_3F;[19] $Mn(SO_3F)_2$, solvolysis of $Mn(O_2CC_6H_5)_2{\cdot}2H_2O$ (kindly supplied by Professor R. C. Thompson of our department) in HSO_3F.[2]

Instrumentation. Our instrumentation used to obtain Raman, ^{19}F NMR, and infrared spectra has been described recently.[20] Infrared spectra were recorded on thin solid films, spread between silver halide windows (Harshaw Chemicals). In one instance ($ReO_2(SO_3F)_3$) the sample's reactivity dictated the use of BaF_2 windows (Harshaw Chemicals).

Magnetic susceptibilities were determined by using a Gouy apparatus described before.[21] Measurements were made at constant field strengths of approximately 4500 and 8000 G. All susceptibilities measured were found to be independent of field strength. Calibrations were carried out by using $HgCo(CNS)_4$.[22] Diamagnetic corrections were obtained from the literature.[10] The diamagnetic correction for SO_3F^- was assumed to be identical with the value for SO_4^{2-} (-40.1×10^{-6} cm^3 mol^{-1}). Electronic spectra were recorded on either a Cary 14 or a Perkin-Elmer Model 124 spectrophotometer. Differential scanning calorimetry (DSC) studies were made by using a Mettler DSC 20 cell and a Mettler TC 10 TA processor.

All moisture-sensitive solids and nonvolatile ligands were handled in a Vacuum Atmospheres Corp. "Dri-Lab", Model He-43-2, described before.[20] Reactions were carried out in glass reaction vials of an approximate volume of 50 mL, fitted with Kontes Teflon-stem stopcocks and equipped with Teflon-coated stirring bars. Where large amounts of highly volatile mterials (O_2, CO_2) evolved, the reactions were carried out in thick-wall reaction vials. All reactions were monitored by weighing. Product isolation by filtration was carried out with an apparatus described by Shriver.[23]

Microanalyses for metals, sulfur, and fluorine were performed by Analytische Laboratorien, Gummersbach, FRG. The carbon content was determined by P. Borda of this department.

Synthetic Reactions. (a) Manganese Tris(fluorosulfate) ($Mn(SO_3F)_3$). In a typical reaction, manganese powder (126.3 mg; 2.298 mmol) is treated with ~10 mL of a mixture of $S_2O_6F_2$ and HSO_3F (about 1:1 by volume) for about 30 days at 70 °C. The metal gradually disappears with formation of a light olive green precipitate. After all the metal has been consumed, all the volatiles are removed in vacuo. The solid residue, 657 mg or 1.866 mmol determined by weight differential, analyzes as $Mn(SO_3F)_3$. Anal. Calcd for $MnS_3O_9F_3$: Mn, 15.60; S, 27.32; F, 16.19. Found: Mn, 15.43; S, 27.03; F, 15.96.

$Mn(SO_3F)_3$ is an olive green, finely powdered hygroscopic solid, completely insoluble in HSO_3F at 25 °C. The compound changes color to light green at 220 °C and does not decompose up to 270 °C.

Two additional comments apply: (i) Due to the long reaction times with $T = 70$ °C, some slow glass attack by $S_2O_6F_2$ and the formation of volatiles such as SiF_4, $S_2O_5F_2$, and O_2 are noted. This requires occasional removal of the more volatile fraction and addition of more $S_2O_6F_2$. (ii) The oxidation of Mn to $Mn(SO_3F)_3$ proceeds quantitatively. The seemingly lower yield of ~81% is due to glass attack and product loss caused by "bumping" on evacuation.

(b) Cesium and Potassium Pentakis(fluorosulfato)manganates(III) ($Cs_2[Mn(SO_3F)_5]$, $K_2[Mn(SO_3F)_5]$). In a typical reaction, 89 mg (1.62 mmol) of manganese is added to a solution of 3.24 mmol of $CsSO_3F$ in HSO_3F, obtained by solvolysis of 545.7 mg of CsCl in excess HSO_3F (~5 mL) followed by removal of HCl in vacuo. An additional 5 mL of $S_2O_6F_2$ is added in vacuo, and the reaction mixture is kept at 60 °C for 3 days. The reaction mixture turns deep purple immediately, and after most of the metal powder is consumed, a dark purple precipitate begins to form. Removal of all of the volatile materials in vacuo yields 1275 mg (1.56 mmol) of $Cs_2[Mn(SO_3F)_5]$, according to chemical analysis. Anal. Calcd for $Cs_2MnS_5O_{15}F_5$: Cs, 32.58; Mn, 6.73; F, 11.64. Found: Cs, 32.45; Mn, 6.91; F, 11.47.

$Cs_2[Mn(SO_3F)_5]$ is a crystalline, hygroscopic purple solid. On heating the color changes at 120–130 °C to black-blue and decomposition is noted at 180 °C.

$K_2[Mn(SO_3F)_5]$ is prepared in an identical manner. At a reaction temperature of 60 °C, a slightly longer reaction time of 7 days is required. In a typical reaction, 153.7 mg (2.80 mmol) of manganese is

(8) "Gemlins Handbuch der Anorganischen Chemie"; Springer Verag: West Berlin, 1978 and 1976; Syst. No. 56, Vol. C5 and C6.
(9) Lever, A. B. P. "Inorganic Electronic Spectroscopy"; Elsevier: Amsterdam, 1968.
(10) Landolt-Börnstein. "Numerical Data and Functional Relationships in Science and Technology"; Springer Verlag: West Berlin, 1966 and 1976; Vol. II/2 and II/8.
(11) Lee, K. C.; Aubke, F. *Inorg. Chem.* **1979**, *18*, 389; **1980**, *19*, 119.
(12) Lee, K. C.; Aubke, F. *Inorg. Chem.* **1984**, *23*, 2124.
(13) Lee, K. C.; Aubke, F. *Can. J. Chem.* **1979**, *57*, 2058.
(14) Mews, R.; Glemser, O. "Abstracts of Papers", 7th International Symposium on Fluorine Chemistry, Santa Cruz, CA, July 15, 1973.
(15) Wimmer, F. L.; Snow, M. R. *Aust. J. Chem.* **1978**, *31*, 267.
(16) Mews, R.; Glemser, O. *J. Chem. Soc., Chem. Commun.* **1978**, 823.
(17) Barr, J.; Gillespie, R. J.; Thompson, R. C.; *Inorg. Chem.* **1964**, *3*, 1149.
(18) Cady, G. H.; Shreeve, J. M. *Inorg. Synth.* **1967**, *7*, 124.
(19) Leung, P. C.; Aubke, F. *Inorg. Chem.* **1978**, *17*, 1765.
(20) Mallela, S. P.; Lee, K. C.; Aubke, F. *Inorg. Chem.* **1984**, *23*, 653.
(21) Clark, H. C.; O'Brien, R. J. *Can. J. Chem.* **1961**, *39*, 1030.
(22) Figgis, B. N.; Nyholm, R. S. *J. Chem. Soc.* **1958**, 4190.
(23) Shriver, D. F. "The Manipulation of Air-Sensitive Compounds"; McGraw-Hill: New York, 1969.

converted to 1776.3 mg (2.82 mmol) of $K_2[Mn(SO_3F)_5]$. Anal. Calcd for $K_2MnS_5O_{15}F_5$: K, 12.44; Mn, 8.74; S, 25.51; F, 15.12. Found: K, 12.62; Mn, 8.90; S, 25.33; F, 15.08.

$K_2[Mn(SO_3F)_5]$ is a deep brown hygroscopic solid. On heating, the sample changes color to brownish purple and melts sharply at 198 °C.

(c) Dioxorhenium(VII) Tris(fluorosulfate) ($ReO_2(SO_3F)_3$). (i) From Re_2O_7. A large excess (about 10 mL) of $S_2O_6F_2$ is distilled in vacuo onto 2.277 g (4.70 mmol) of Re_2O_7, contained in a thick-walled reaction vessel. The reaction mixture is heated for 48 h at 80 °C. The reaction is interrupted periodically to remove oxygen in vacuo. All of the solid Re_2O_7 disappears gradually, and a yellow solution results. Excess $S_2O_6F_2$ is removed in vacuo, and 4.507 g (8.75 mmol) of a viscous yellow oil is obtained, which analyzes as $ReO_2(SO_3F)_3$. Anal. Calcd for $ReS_3O_{11}F_3$: Re, 36.14; S, 18.66; F, 11.06. Found: Re, 36.45; S, 18.43; F, 11.22.

(ii) From Re Metal. In a typical reaction, 9.253 g of HSO_3F is distilled onto 0.460 g of Re powder and 7.975 g of $S_2O_6F_2$ is added in vacuo. The reaction mixture is heated to 80 °C, and all of the metal is consumed within 12 h. A yellow solution results, from which yellow $ReO_2(SO_3F)_3$ is obtained after removal of all volatile materials. However, complete removal of all HSO_3F is tedious and time consuming.

In the absence of HSO_3F, 1.103 g of Re powder is converted to 3.281 g of $ReO_2(SO_3F)_3$ by an excess of $S_2O_6F_2$ within 48 h at a reaction temperature of 80 °C.

(d) Pentacarbonylmanganese(I) Fluorosulfate ($Mn(CO)_5SO_3F$). To 1.632 g (7.89 mmol) of $AgSO_3F$ is added 1.780 g (6.47 mmol) of $Mn(CO)_5Br$, and an excess (~20 mL) of dry CH_2Cl_2 is distilled onto this mixture. The reaction mixture, with the reactor wrapped in aluminum foil, is stirred magnetically at ambient temperature for 5 days. Filtration yields a greenish yellow solid and a clear yellow liquid. Removal of the solvent produces a yellow crystalline material, which analyzes as $Mn(CO)_5SO_3F$. Anal. Calcd for MnC_5O_8SF: Mn, 18.85; C, 20.42; S, 11.03; F, 6.39. Found: Mn, 18.68; C, 20.52; S, 10.90; F, 6.46.

$Mn(CO)_5SO_3F$ is a bright orange-yellow, highly hygroscopic solid. When it is heated in a melting point capillary, various color changes are noted: at ~65 °C from yellow-orange to orange, at 100–170 °C from orange to light yellow, and at 198 °C to white. No melting was noted up to 280 °C.

The corresponding rhenium compound $Re(CO)_5SO_3F$ is prepared from $Re(CO)_5Cl$ in an identical manner. The white crystalline solid melts between 95 and 120 °C to give first a white sludge. On further heating, a clear liquid forms between 122 and 130 °C. Its composition is established by chemical analysis as $Re(CO)_5SO_3F$. Anal. Calcd for ReC_5O_8SF: Re, 43.78; S, 7.54; F, 4.47; C, 14.12. Found: Re, 43.62; S, 7.46; F, 4.42; C, 14.92.

(e) Tetracarbonylmanganese(I) Fluorosulfate ($Mn(CO)_4SO_3F$). In an evacuated, carefully dried Pyrex reactor, 141.4 mg of $Mn(CO)_5SO_3F$ is heated to 70 °C and maintained at this temperature for 4 h. The reaction is monitored by the slow increase in pressure above the solid. An infrared spectrum shows changes in both the CO- and the SO_3-stretching region (to be discussed later). The resulting orange solid has the composition $Mn(CO)_4SO_3F$. Anal. Calcd for MnC_4O_7SF. Mn, 20.65; S, 12.05; F, 7.14; C, 18.06. Found: Mn, 20.39; S, 11.89; F, 6.93; C, 18.15; H, 0.0.

Results and Discussion

(a) Synthesis and Product Characterization. The oxidation of manganese metal by bis(fluorosulfuryl) peroxide ($S_2O_6F_2$) in fluorosulfuric acid (HSO_3F) as reaction medium is found to eventually produce in a rather slow reaction fluorosulfato derivatives of manganese(III). There are two variations of this oxidation reaction: (i) In "neutral" medium, with only the nonelectrolytes Mn and $S_2O_6F_2$[24] initially present, solid manganese(III) fluorosulfate ($Mn(SO_3F)_3$) forms in a rather slow reaction at 70 °C, according to

$$2Mn + 3S_2O_6F_2 \xrightarrow[HSO_3F]{70\ °C,\ 30\ days} 2Mn(SO_3F)_3 \quad (3)$$

(ii) In "basic" medium, due to the presence of $M'SO_3F$ with M' = K or Cs, at a Mn to $M'SO_3F$ ratio of 1:2, the ternary complexes $M'_2[Mn(SO_3F)_5]$ form at 60 °C within 3–7 days, according to

$$4M'SO_3F + 2Mn + 3S_2O_6F_2 \xrightarrow[HSO_3F]{60\ °C,\ 3-7\ days} 2M'_2[Mn(SO_3F)_5] \quad (4)$$

These ternary fluorosulfato complexes of Mn(III) show limited solubility in HSO_3F, which appears to be contributing to the substantially shorter reaction times. The relatively low reaction temperatures of 60–70 °C also contribute to the slow oxidation reactions. They are chosen to allow the isolation of $Mn(SO_3F)_4$, reportedly stable up to 105 °C,[6] or any of its fluorosulfato derivatives. However no evidence for the presence of Mn(IV) in the final products is obtained.

Table I. Magnetic Data for Manganese(III) Fluorosulfates

compd	temp, K	$10^{-6}\chi_M^{cor}$, $cm^3\ mol^{-1}$	μ_{eff}, μ_B
$Mn(SO_3F)_3$	305.8	10217.5	5.00
	108.0	27322	4.86
$Mn(SO_3F)_3$[a]	302.0	11576.5	5.29
$Cs_2[Mn(SO_3F)_5]$	305.6	9951.1	4.93
$K_2[Mn(SO_3F)_5]$	305.1	9710.8	4.87

[a] Prepared by the reported procedure.[6]

While $Mn(SO_3F)_3$ is insoluble in fluorosulfuric acid, the two fluorosulfato complexes give purple solutions with rather broad bands at 510 nm and broad shoulders at ~620 nm. The molar extinction coefficients for the 510-nm band vary slightly with ϵ = 55 L cm^{-1} mol^{-1} for the potassium compound and 65 L cm^{-1} mol^{-1} for $Cs_2[Mn(SO_3F)_5]$ in HSO_3F. All spectral features, including the rather high ϵ values, agree well with literature reports;[9,25] however, it is noted that the color fades with time, resulting in clear, colorless, slightly cloudy solutions. The broad band at 510 nm is best attributed to a $^5E_g \rightarrow {}^5T_{2g}$ transition in accordance with previous assignments.[9]

The ^{19}F NMR spectra show single lines at 42.2 ppm for $K_2[Mn(SO_3F)_5]$ and 43.2 ppm for $Cs_2[Mn(SO_3F)_5]$, relative to $CFCl_3$, suggestive of an octahedrally coordinated hexakis(fluorosulfato)manganate(III) species.

The magnetic data, shown in Table I, are indicative of Mn(III) in a high-spin configuration, and μ_{eff} between 4.9 and 5.0 μ_B for $M'_2[Mn(SO_3F)_5]$ and $Mn(SO_3F)_3$ is well within the range of previously reported values.[10] There appears to be no dramatic decrease in μ_{eff} with decreasing temperature. A measurement at 108 K yields a value of 4.86 μ_B. Invariance of μ_{eff} with temperature is consistent with either a ^5E_g or a ^5B_g ground state, assuming in both instances an octahedral environment for Mn(III) and in the latter case tetragonal elongation causing splitting of the ^5E_g ground state due to the Jahn–Teller effect.

Temperature invariance of μ_{eff} in octahedral complexes is expected also for both Mn(IV) ($^4A_{2g}$ ground state) and Mn(II) ($^6A_{1g}$ ground state), but the magnetic moments allow a clear differentiation. The rather scarce magnetic studies for Mn(IV)[10] suggest μ_{eff} values of 3.8–3.9 μ_B while for Mn(II) magnetic moments close to the spin-only value of 5.92 μ_B are expected and are found[10] in magnetically dilute systems.

There are alternate routes to both $Mn(SO_3F)_3$ and the complexes of the type $M'_2[Mn(SO_3F)_5]$. The former compound is formed when manganese(II) fluorosulfate, obtained by solvolyzing manganese(II) benzoate in HSO_3F,[2] is oxidized by $S_2O_6F_2$ according to

$$2Mn(SO_3F)_2 + S_2O_6F_2 \xrightarrow[HSO_3F]{60\ °C,\ 5\ days} 2Mn(SO_3F)_3 \quad (5)$$

The relatively short reaction time of approximately 5 days under comparable reaction conditions coupled with the facile conversion of manganese(II) carboxylates to fluorosulfates[1,2] points to a better and faster preparative route to $Mn(SO_3F)_3$. It hence appears that the initial oxidation of Mn metal is a rather slow process. In the absence of HSO_3F, reaction 5 proceeds somewhat slowly with reaction times of about 1 week while metal oxidation without HSO_3F at 70 °C for 5 days results in a conversion rate to $Mn(SO_3F)_3$ of only 1.7%.

An alternate route to ternary fluorosulfates of the type $M'_2[Mn(SO_3F)_5]$ should be the direct complexation of manganese(III) fluorosulfate according to

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

(25) Fackler, J. P., Jr.; Davis, T. S.; Chawla, I. D. *Inorg. Chem.* **1965**, *4*, 130.

$$2M'SO_3F + Mn(SO_3F)_3 \xrightarrow[HSO_3F]{25\ °C} M'_2[Mn(SO_3F)_5] \quad (6)$$

However, when a relatively small amount (0.43 mmol) of $Mn(SO_3F)_3$ is suspended in about 5 mL of a solution of 0.86 mmol of $CsSO_3F$ in HSO_3F, the characteristic purple color of $[Mn(SO_3F)_5]^{2-}$ fades quickly and within a few minutes all of the $Mn(SO_3F)_3$ is quantitatively converted to white, insoluble $Mn(SO_3F)_2$, identified by its infrared spectrum. Addition of about 2 mL of $S_2O_6F_2$ to such a suspension immediately restores the purple color of the solution, and within 1 h $Mn(SO_3F)_2$ is converted back to $Cs_2[Mn(SO_3F)_5]$, with all reactions occurring at room temperature. The initial net conversion reaction

$$2Mn(SO_3F)_3(s) \xrightarrow[HSO_3F/SO_3F^-]{25\ °C} 2Mn(SO_3F)_2(s) + S_2O_6F_2 \quad (7)$$

does not go to completion, when 0.73 mmol of $Mn(SO_3F)_3$ and 1.46 mmol of $CsSO_3F$ are dissolved in ~3 mL of HSO_3F. The liquid phase remains purple throughout, and a solid mixture of $Cs_2[Mn(SO_3F)_5]$ and $Mn(SO_3F)_2$ forms very quickly.

The reversible equilibrium encountered may hence be generally formulated as

$$2Mn^{3+}(solv) + 2SO_3F^-(solv) \underset{HSO_3F}{\overset{25\ °C}{\rightleftharpoons}} 2Mn^{2+}(solv) + S_2O_6F_2 \quad (8)$$

in good analogy to a similar equilibrium studied 35 years ago in 10 M aqueous HCl by Ibers and Davidson:[26]

$$2Mn^{3+}(solv) + 2Cl^-(solv) \rightleftharpoons 2Mn^{2+}(solv) + Cl_2(solv) \quad (9)$$

The strong oxidizing power of Mn(III) in aqueous sulfuric acid medium is reflected in the reported[27] oxidation–reduction potential of $E° = 1.51$ V for the Mn^{3+}/Mn^{2+} couple, which appears to be retained in HSO_3F. The postulated release (eq 8) of bis(fluorosulfuryl) peroxide from a HSO_3F solution of a transition-metal fluorosulfato complex is unprecedented. However, pyrolysis of $Ag(SO_3F)_2$ to $AgSO_3F$ at 215 °C[19] or of $Pd^{II}[Pd^{IV}(SO_3F)_6]$ to $Pd(SO_3F)_2$ at 160 °C[28] produces $S_2O_6F_2$ cleanly. Again $E°$ values of 1.98 V for the couple Ag^{2+}/Ag^+ and 1.288 V for $PdCl_6^{2-}/PdCl_4^{2-}$ indicate Pd^{4+} and Ag^{2+} to be as similarly strong oxidizers as Mn(III).

It appears then that oxidation of $Mn(SO_3F)_2$ by a large excess of $S_2O_6F_2$ in $CsSO_3F$–HSO_3F solution provides a fast and efficient route to $Cs_2[Mn(SO_3F)_5]$. The strong oxidizing ability of this material in HSO_3F solution and the suggested dissociation to form $S_2O_6F_2$ at 25 °C make it rather improbable that conditions may be found where further oxidation of manganese, perhaps to the +4 oxidation state, may occur. The oxidizing ability of Mn(III) in HSO_3F and the lack of appreciable solubility of $Mn(SO_3F)_3$ in fluorosulfuric acid both preclude any superacid studies in this system.

It may be recalled that the reported preparation of $Mn(SO_3F)_4$[6] by oxidation of $Mn_2(CO)_{10}$ with $S_2O_6F_2$ did not involve HSO_3F. Our attempts to repeat this reaction employing a large excess of $S_2O_6F_2$, with the starting material $Mn_2(CO)_{10}$ either neat or in a suspension of perfluorokerosene (PCR), were unsuccessful. A typical chemical analysis (15.72% Mn), a room-temperature magnetic moment of 5.29 μ_B, and the observed weight changes suggest formation of manganese(III) fluorosulfate as the principal reaction product with a small amount of $Mn(SO_3F)_2$ impurity present.

The scarcity of other binary maganese(IV) compounds also warrants scepticism regarding the existence of $Mn(SO_3F)_4$. Of the two closest analogues, MnF_4, a blue, very reactive hygroscopic solid, dissociates in a high vacuum at 0 °C to give MnF_3 and F_2.[29] Manganese(IV) sulfate ($Mn(SO_4)_2$), described as a black solid in the patent literature, appears to be rather a manganese oxide sulfate.[30] Only the oxide MnO_2 is sufficiently well established.

Attempts to synthesize other ternary fluorosulfates of manganese were unsuccessful. The oxidation of manganese in HSO_3F with only 1 or 3 equiv of $M'SO_3F$ present (M' = K, Cs) resulted in the formation of a mixture consisting largely of $M'_2[Mn(SO_3F)_5]$ and either unreacted metal or excess $M'SO_3F$. There are precedents for the anion $[MnX_5]^{2-}$ ($X = Cl^-, F^-$), but $[MnX_6]^{3-}$ is found as well as is $[MnF_4]^-$.[31]

An attempted reduction of a manganese(III) fluorosulfato complex according to

$$2Cs[Mn(SO_3F)_5] + Br_2 \xrightarrow[2\ days]{25\ °C} 2Cs_2[Mn(SO_3F)_4] + 2BrSO_3F \quad (10)$$

failed, and the reactants were recovered unchanged. An analogous route had allowed conversion of $Cs_2[Pd(SO_3F)_6]$ to $Cs_2[Pd(SO_3F)_4]$.[32]

The oxidation of rhenium metal by $S_2O_6F_2$ on the other hand proceeds very easily. The use of HSO_3F as reaction medium accelerates the oxidation considerably; however, the resulting yellow liquid is very difficult to separate from the fluorosulfuric acid by distillation in vacuo. Prolonged pumping affords a yellow viscous liquid, identified as $ReO_2(SO_3F)_3$ by chemical analysis.

The white solid, previously claimed to be $ReO_2(SO_3F)_3$,[7] is found in our reactions only when a small amount of $S_2O_6F_2$ is employed. Variable amounts of a yellow liquid are formed as well. Heating of the mixture to 80 °C irreversibly produces a viscous yellow oil, but no evolution of $S_2O_5F_2$[7] is noted. Since the white solid is not obtained in a pure form, its composition remains uncertain.

Since the metal oxidation to $ReO_2(SO_3F)_3$ by a large excess of $S_2O_6F_2$ produced bis(fluorosulfuryl) oxide ($S_2O_5F_2$) as a by-product, a cleaner preparative approach was developed: the reaction of Re_2O_7, with $S_2O_6F_2$ according to

$$Re_2O_7 + 3S_2O_6F_2 \xrightarrow[48\ h]{80\ °C} 2ReO_2(SO_3F)_3 + {}^3/_2O_2 \quad (11)$$

The reaction proceeds quite well, and progress can be monitored either by the evolution of O_2 or by the disappearance of the solid, yellow Re_2O_7. Again, the use of a small excess of $S_2O_6F_2$ over the required amount produces a solid–liquid mixture after removal of all excess $S_2O_6F_2$. Reaction with $S_2O_6F_2$ in large excess produces only a yellow oil, which analyzes as $ReO_2(SO_3F)_3$.

Preparation of both $Mn(CO)_5SO_3F$ and $Re(CO)_5SO_3F$ by the silver salt method using freshly prepared $AgSO_3F$ proceeds very smoothly. Separation from the silver halide is possible, because both the manganese and the rhenium carbonyl fluorosulfates are soluble in CH_2Cl_2. The general reaction

$$M(CO)_5X + AgSO_3F \xrightarrow[CH_2Cl_2]{25\ °C} M(CO)_5SO_3F + AgX \quad (12)$$
$$M = Mn, Re;\ X = Cl, Br$$

proceeds very quickly and efficiently in the case of M = Re (X = Cl, Br). $Mn(CO)_5Cl$ reacts very slowly, and even after prolonged reaction times and a reaction temperature of 40 °C, only incompletely converted materials are isolated. Complete halide substitution by SO_3F^- is found when $Mn(CO)_5Br$ is used as reagent. Reaction times of 5 days are needed to obtain bromide-free reaction products.

The thermal behaviors of the resulting fluorosulfates differ. Attempts to adopt controlled pyrolysis to fluorosulfates in order to obtain $M(CO)_4SO_3F$, a method well established in the preparation of dimeric carbonyl halides of the type $[M(CO)_4X]_2$[34,35]

(26) Ibers, J. A.; Davidson, N. J. Am. Chem. Soc. 1950, 72, 4744.
(27) Latimer, W. M. "The Oxidation States of the Elements and Their Potentials in Aqueous Solution", 2nd ed.; Prentice-Hall: Englewood Cliffs, NJ, 1952.
(28) Lee, K. C.; Aubke, F. Can. J. Chem. 1977, 55, 2473.
(29) Roesky, H. W.; Glemser, O.; Hellberg, K. H. Chem. Ber. 1965, 98, 2046.
(30) Sem, M.; Zeitschv, F. Elektrochem. Z. 1915, 21, 426.
(31) Hoppe, R.; Dahne, W.; Liebe, W. Z. Anorg. Allg. Chem. 1961, 307, 276.
(32) Lee, K. C.; Aubke, F. Can. J. Chem. 1981, 59, 2835.
(33) Abel, E. W.; Wilkinson, G. J. Chem. Soc. 1959, 1501.
(34) Abel, E. W.; Hargreaves, G. B.; Wilkinson, G. J. Chem. Soc. 1958, 3149.

Table II. Differential Scanning Calorimetric Data

sample	step	ΔH, J g^{-1}	peak temp, °C
$Mn(CO)_5SO_3F$	1	+9.70	65.1
	2	−35.70	93.7
	3	−595.16	136.6
$Mn(CO)_5Br$	1	+1.54	64.9
	2	+162.46	120.3
	3	−57.514	168.1

(M = Re, Mn; X = Cl, Br, I), are only successful for $Mn(CO)_5SO_3F$.

The rhenium analogue begins to release CO at 80 °C at a rather slow rate with melting to a grayish liquid at ~100 °C that subsequently solidifies to a gray solid. No consistent analytical data are obtained.

The thermal behavior of $Mn(CO)_5SO_3F$ was investigated by differential scanning calorimetry and contrasted with the behavior of $Mn(CO)_5Br$. The results are seen in Table II. The first steps for both compounds occur at nearly identical temperatures and are both endothermic processes. It seems reasonable to interpret the first step as being due to the loss of a single CO molecule, possibly with dimerization according to

$$2Mn(CO)_5X \xrightarrow[T \sim 65\ °C]{heat} [Mn(CO)_4X]_2 + 2CO \qquad X = Br, SO_3F \tag{13}$$

Two observations help in the interpretation of the second exothermic step for $Mn(CO)_5SO_3F$. The previously reported[14] pyrolysis in *n*-heptane (bp 98 °C) proceeds according to

$$4Mn(CO)_5SO_3F \rightarrow Mn_2(CO)_{10} + 2Mn(SO_3F)_2 + 10CO \tag{14}$$

Our attempts to sublime $Mn(CO)_5SO_3F$ at ~100 °C yielded crystalline $Mn_2(CO)_{10}$ instead. Identification was achieved by X-ray single-crystal analysis and comparison with the reported structural data.[35] The third exothermic step seems to involve further CO evolution and perhaps also combustion of some CO to give CO_2.

It seems the temperature range between 65 and 95 °C is suitable for the controlled pyrolysis of $Mn(CO)_5SO_3F$. Indeed, when a small amount of solid material (~0.2 g) is used and maintained at 70 °C for 4 h, $Mn(CO)_4SO_3F$ is obtained as the chemical analysis indicates. The reaction is monitored by the pressure increase, with the gas evolved identified by mass spectrometry.

Alternately, heating the sample for 30 min with a gradual increase in the temperature from 65 to 80 °C allows formation of $Mn(CO)_4SO_3F$ as well. Not unexpectedly, heating of $Mn(CO)_5SO_3F$ to temperatures between 65 and 100 °C for 60 min results in materials with a low carbon content (~11%) and detectable $Mn(SO_3F)_2$ in the solid residue by its infrared spectrum.[2] Incipient sublimattion is noted as well.

The dimeric formulation for $[Mn(CO)_4SO_3F]_2$ is conjecture. Not surprisingly, mass spectra reveal the fragmentation pattern of $Mn_2(CO)_{10}$.

(b) Vibrational Spectra. Structural information on all new manganese and rhenium fluorosulfate compounds is obtained through their vibrational spectra. There are some limitations however. For $Mn(SO_3F)_3$ and $M'_2[Mn(SO_3F)_5]$ the dark colors effectively prevent the use of Raman spectroscopy, while $ReO_2(SO_3F)_3$ on the other hand gives good and well-resolved Raman spectra but the reactivity of the material permits only the use of BaF_2 as window material.

The infrared absorption bands for $Mn(SO_3F)_3$, $Cs_2[Mn(SO_3F)_5]$, and $K_2[Mn(SO_3F)_5]$ together with estimated intensities are listed in Table III and compared to the previously published data for $Fe(SO_3F)_3$[36] and $Cs[Sn(SO_3F)_5]$.[20]

The striking feature of the IR spectrum of $Mn(SO_3F)_3$ is the extensive band splitting, not observed for $Fe(SO_3F)_3$[36] or any other metal tris(fluorosulfate) like $Ga(SO_3F)_3$[37] or $Cr(SO_3F)_3$.[38] The band centers at 1360, 1160, and 1015 cm^{-1} in the SO_3-stretching range, at ~840 cm^{-1} for ν_{SF}, and at ~650 cm^{-1} for the deformation modes show strong similarities among all these $M(SO_3F)_3$ species. The data suggest the presence of bidentate, presumably birdging fluorosulfate groups, resulting in polymeric structures and octahedral environments for the M(III) centers, with regular octahedral environments expected for Ga but also for $Cr(d^3)$ and $Fe(d^5$ high spin).[36] Extensive Jahn–Teller distortion is expected for $Mn(d^4)$ and appears to be the principal reason for the observed band proliferation.

Band proliferation for the Mn(III) complexes $Cs_2[Mn(SO_3F)_5]$ and $K_2[Mn(SO_3F)_5]$ is less pronounced. Presumably, the environment for Mn(III) is nonoctahedral. Any observed band splitting is now best explained by vibrational coupling, a feature commonly found for poly(fluorosulfato)metalate anions.[11,12,20]

A small but noticeable trend is observed in the SO_3^- and SF-stretching region: the positions of corresponding bands for $[Mn(SO_3F)_5]^{2-}$ are shifted consistently to frequencies lower than those observed for $[Sn(SO_3F)_5]^-$.[20] The higher negative charge for the former is seen as the principal reason for the trend.

If this shift is taken into consideration, the principal bands for bridging fluorosulfate, as observed for $Mn(SO_3F)_3$, are found as well at slightly lower wavelengths at ~1360, 1145, and 1020 (SO_3 stretching) and 830 (ν_{SF}) cm^{-1}, but they are now clearly a minor constituent. The major bands for $[Mn(SO_3F)_5]^{2-}$ are centered around 1330, 1200, and 1000 cm^{-1} in the SO_3-stretching range, and those at 780–800 cm^{-1} for ν_{SF} are best attributed to monodentate $-OSO_2F$ groups in anionic complexes.

The presence of both bidentate (presumably bridging) and predominantly monodentate fluorosulfate groups is consistent with the structure suggested for $[Sn(SO_3F)_5]^-$[20] as a fluorosulfate-bridged oligomer. Conclusions in this case were based on well-resolved Raman and ^{119}Sn Mössbauer spectra and are consistent with solution studies in HSO_3F.[20] Anionic complexes of the type $[MnX_5]^{2-}$ (X = F, Cl) provide percedents for both polymeric and monomeric anions. Fluoro complexes of the type $M'_2[MnF_5]$ (M' = NH_4, Li, Na)[39] or of the type $M'_2[MnF_5]-H_2O$ (M' = Rb,[40a] Cs[40b]), where the water is not coordinated to the metal, exhibit infinite chains of tetragonally elongated MnF_6 octahedra formed by trans-F bridges. Similar polymeric anions are suggested for complexes of the type $M'_2[MnCl_5]$[41] (M' = NH_4, Na, K). However with larger cations, like the phenanthrolinium ion, isolated, distorted square-pyramidal $[MnCl_5]^{2-}$ ions are found.[42] Seemingly, cation size has a profound effect here on the structure of the anion.

The Raman spectrum of $ReO_2(SO_3F)_3$ shows the following bands: 1460 m, 1406 mw, 1237 s, 1104 mw, br, 1015 vs, 995 s, sh, 924 m, 873 m, br, 696 m, 648 ms, 568 m, br, 550 m, sh, 465 w, 406 w, 294 s, 258 m cm^{-1}. The infrared spectrum, limited by the cutoff for BaF_2 at ~900 cm^{-1}, shows four rather broad bands at 1445, 1385, 1020, and 985 cm^{-1}.

The Raman spectrum is dominated by an extremely intense band at 1015 cm^{-1}, which in analogy to a reported band at 1024 cm^{-1} for matrix-isolated ReO_2F_3[43] is assigned as the symmetric ReO_2 stretch, with the asymmetric stretch found at 995 cm^{-1} for $ReO_2(SO_3F)_3$ and at 988 cm^{-1} for ReO_2F_3.[43] The occurrence of both bands in the infrared spectrum suggests a bent ReO_2 group in both instances. SO_3-stretching vibrations at 1460, 1237, and 924 cm^{-1} are attributed to monodentate OSO_2F groups, while

(35) Dahl, L. F.; Rundle, R. E. *Acta Crystallogr.* **1963**, *16*, 419.
(36) Goubeau, J.; Milne, J. B. *Can. J. Chem.* **1967**, *45*, 2321.
(37) Storr, A.; Yeats, P. A.; Aubke, F. *Can. J. Chem.* **1972**, *3*, 452.
(38) Brown, S. D.; Gard, G. L. *Inorg. Nucl. Chem. Lett.* **1975**, *11*, 19.
(39) (a) Emori, S.; Inoue, M.; Kishita, M.; Kubo, M. *Inorg. Chem.* **1969**, *8*, 1385. (b) Dingle, R. *Inorg. Chem.* **1965**, *4*, 1287.
(40) (a) Bukovec, P.; Kaucic, V. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1978**, *B34*, 3339. (b) Kaucic, V.; Bukovec, P. *Acta Crystallogr., Sect.* B: *Struct. Crystallogr. Cryst. Chem.* **1978**, *B34*, 3337.
(41) Crisp, R. I.; Seddon, K. R. *Coord. Chem. Rev.* **1981**, *37*, 167.
(42) (a) Bernal, I.; Elliot, N.; Lalancette, R. *J. Chem. Soc. D* **1971**, 803. (b) Witten, E. H.; Reill, W. M. *Inorg. Chim. Acta* **1980**, *41*, 227.
(43) Beattie, R.; Crocombe, R. A.; Ogden, J. S. *J. Chem. Soc., Dalton Trans.* **1977**, 1481.

Table III. Infrared Absorption Bands for $Mn(SO_3F)_3$, $Cs_2[Mn(SO_3F)_5]$, $K_2[Mn(SO_3F)_5]$, and Related Compounds[a]

$Mn(SO_3F)_3$ ν, cm^{-1}	$Fe(SO_3F)_3$[b] ν, cm^{-1}	$Cs_2[Mn(SO_3F)_5]$ ν, cm^{-1}	$K_2[Mn(SO_3F)_5]$ ν, cm^{-1}	$Cs[Sn(SO_3F)_5]$[c] ν, cm^{-1}
1415 w, sh				
		1402 w, sh	1408 s, sh	
1400 s, sh		1378 ms	1390 ms, sh	
1376 s, sh	1360 m	1358 ms	1365 s	1399 vs, br
1358 vs		1322 s	1330 ms, sh	
1280 vw				1251 m
		1215 s, sh	1215 s, br	1212 s
1182 s, sh		1190 vs	1195 s, sh	1186 w
1160 vs	1137 s			
1145 s		1145 mw, sh	1135 ms, sh	1111 w
1050 ms, sh		1090 vw		1095 w
1015 vs		1070 mw	1065 w, sh	1080 w
1005 s, sh				
		1020 s, sh	1025 s, br	1028 m, sh
		1006 s	999 s	990 s
856 ms	850 m	885 m, sh	890 w, sh	872 w
828 ms		~820 m, br	835 ms	851, 825 w
		788 vs	800 vs	807 s
665 vw				
655 s, sh		645 ms	645 ms	631 m, sh
648 s	630 m	618 mw	615 m, sh	620 s
636 s, sh				
595 w, sh		600 vw		
582 s	579 w	582 m	585 ms	580 m
560 s, sh		562 m, sh		
552 s	551 w	559 m, sh		555 m
450 ms	442 w	430 m, sh	440 m	
425 ms	419 w			
	318 m			

[a] Abbreviations (in this and the following table) for estimated intensities: s, strong; m, medium; w, weak; v, very; br, broad; sh, shoulder. [b] Reference 15. [c] Reference 20.

bands at 1406 and 1104 cm^{-1} are more indicative of bidentate fluorosulfate groups. It is implied that the third SO_3 stretch, expected at ~1050 cm^{-1}, is obscured by the extremely intense band at 1015 cm^{-1} and that both SF stretches for the two different fluorosulfate groups have coalesced into a rather broad band at 873 cm^{-1}. Molecular association of $ReO_2(SO_3F)_3$ via bridging fluorosulfate groups is not unexpected, since ReO_2F_3 also seems to dimerize even in the gas phase.[44]

The Raman spectrum of $ReO_2(SO_3F)_3$ gives no evidence for the presence of dissolved $S_2O_6F_2$, where the most intense band ν_{O-O} is found at 800 cm^{-1}. Hence interpretation of our analytical results as being due to an approximately equilmolar mixture of $S_2O_6F_2$ and ReO_3SO_3F, originally described as a yellow liquid,[7] appears unlikely. The presence of detectable amounts of bis-(fluorosulfuryl) oxide ($S_2O_5F_2$) is improbable because the sample for Raman studies is prepared from Re_2O_7 and $S_2O_6F_2$.

The vibrational spectra of the metal carbonyl fluorosulfates are listed in Table IV. Discussion will center around two general areas: (1) the vibrational characteristics of the SO_3F group in the various compounds and (2) the CO-stretching region. As can be seen from the listed IR absorption bands for $Re(CO)_5Cl$ in Table IV, the region between 1900 and 650 cm^{-1} is clear from fundamentals, due to the $Mn(CO)_5$ moiety. Hence a clear identification of SO_3F-stretching modes is possible.

However, the SO_3F-deformation modes below 650 cm^{-1} fall in the region of the CO deformation and metal–carbon stretching vibrations. A clear differentiation is difficult and not intended. The band positions for both $Re(CO)_5SO_3F$ and $Mn(CO)_5SO_3F$ in the SO_3- and SF-stretching regions are consistent with the presence of weakly bonded, monodentate $-OSO_2F$ groups. Evidence for weak bonding is found in two features: ν_{SF} and the symmetric SO_3 stretch in ionic fluorosulfates are found in nearly identical regions (e.g. for KSO_3F[36,45] 745 and 1079 cm^{-1}) in both $M(CO)_5$ fluorosulfates. Furthermore, splitting of the asymmetric SO_3stretch—observed at 1285 cm^{-1} for KSO_3F—indicative of departure from C_{3v} symmetry and removal of degeneracy for this e mode is only slight, in particular for the rhenium compound. A wider splitting of ~125 cm^{-1} is found for $Mn(CO)_5SO_3F$, suggesting stronger covalent interaction in this case. While the observed e-mode splitting appears to be too large to invoke site symmetry effects and ionic SO_3F^- as found in $NOSO_3F$,[45] the spectral features displayed in the SO_3F-stretching region differ markedly from the pattern displayed by other monodentate-OSO_2F groups (see e.g. the band positions for $[Mn(SO_3F)_5]^{2-}$ as discussed before).

In the CO-stretching region good correspondence with respect to band positions and intensities with reported spectra for $M(CO)_5X$[46,47] (X = Cl, Br, I) is found. The solution IR spectra for $Mn(CO)_5SO_3F$ show however more than the three (2 a_1 + e) fundamentals, reflecting a not unexpected departure from strictly C_{4v} symmetry for the $Mn(CO)_5$ moiety on account of the polyatomic nature of the fluorosulfate group. As a consequence, the e mode, expected at ~2050 cm^{-1}, is split into two components at 2060 and 2048 cm^{-1}. The Raman spectrum shows only a rather weak feature in this region. The two a_1 modes, assigned to a rather weak band at 2145 cm^{-1} and a more intense band at 2002 cm^{-1}, have strong Raman counterparts att 2161 and 2020 cm^{-1}. A strong Raman band at 2110 cm^{-1} is assigned to the b_1 vibration, which should be only Raman active, but a rather smeared out broad shoulder is noted in the IR spectrum as well. Two very weak infrared bands at 2030 and 1971 cm^{-1} are attributed to ^{13}C–O bands, in agreement with a previous report for $M(CO)_5X$.[46]

The infrared spectrum obtained on a Nujol mull of $Mn(CO)_5SO_3F$ is generally identical with the solution spectra, and for $Re(CO)_5SO_3F$, where a rather simple spectrum is obtained, a straightforward assignment of the three IR bands is possible. Interestingly no e-mode splitting is observed here.

For $Mn(CO)_4SO_3F$, different band patterns are observed in the CO- as well as in the SO_3F-stretching region. The four strong CO bands at 2130, 2020, 2000, and 1925 cm^{-1} correspond with respect to band position and relative intensity to reports for the

(44) Sunder, W. A.; Stevie, F. A. *J. Fluorine Chem.* **1975**, *6*, 449.
(45) Qureshi, A. M.; Carter, H. A.; Aubke, F. *Can. J. Chem.* **1971**, *49*, 35.
(46) El-Sayed, M. A.; Kaesz, H. D. *J. Mol. Spectrosc.* **1962**, *9*, 310.
(47) Orgel, L. E. *Inorg. Chem.* **1962**, *1*, 25.

Table IV. Vibrational Spectra of $Mn(CO)_5SO_3F$, $Re(CO)_5SO_3F$, $Mn(CO)_4SO_3F$, and Related Compounds

$Re(CO)_5Cl$ IR solid ν, cm^{-1}	$Re(CO)_5SO_3F$ IR solid ν, cm^{-1}	$Re(CO)_5Br$ IR solid ν, cm^{-1}	$Mn(CO)_5SO_3F$ IR Nujol mull ν, cm^{-1}	$Mn(CO)_5SO_3F$ IR CH_2Cl_2 ν, cm^{-1}	$Mn(CO)_5SO_3F$ Raman $\Delta\nu$, cm^{-1}	$Mn(CO)_4SO_3F$ IR solid ν, cm^{-1}
2160 w, sh	2160 w, sh	2150 vw	2140 vw	2140 w	2161 s (2161)[a]	2130 w
				~2100 w, sh	2110 s (2116)[a]	2020 vs, sh
2040 vs	2040 vs	2064 vs	2056 s, sh	2060 vs	2075 w	
				2048 s, sh		
1980 vs	1980 vs	2017 vs	2030 s, sh	2030 w, sh	2020 s (2038)[a]	
			2000 vs	2002 vs	1991 mw	2000 vs
			1972 w	1971 vw	1982 w	1925 vs
						1910 vw, sh
	1315 m		1346 s	1348 s		
						1290 m, sh
	1255 m		1221 s	1205 s		1240 s
	1170 w		1140 vw			
	1120 w					1130 s
	1030 m		1051 s	1042 s	1060 m	1070 s
			1000 vw			
			967 vw			
			878 w			878 m, br
	760 m		755 s, 715 sh		762 w, 705 w	755 vw
		639 s	635 s	635 s, sh	632 w	602 vs
			620 vs, 615 s, sh	624 vs	610 w	
			599 ms	600 ms		
590 s	590 s		582 ms	585 ms		585 ms
560 m	560 m		555 ms	555 ms		550 w, sh
		545 m	535 m	540 m	540 vw	535 w
					461 m	465 w
		410 m			415 m	420 w, 410 w
			385 m	395 m	388 m	
				384 w	368 m	
346 m	340 s					
240 m						

[a] Raman spectrum in CH_2Cl_2.

halogen-bridged dimers $[Mn(CO)_4X]_2$ (X = Cl, Br, I),[48] but do extend over a wider frequency range (2130–1910 cm^{-1}). While the four CO stretches suggest low local symmetry (D_{2h} or C_{2v}) for the $Mn(CO)_4$ moiety, the molecular nature of the SO_3F group and its expected higher electronegativity prevent vibrational coupling more effectively and produce a different electronic environment.

The SO_3F-stretching vibrations at ~1240, 1130, and 1070 cm^{-1} (ν_{SO_3}) and at 870 cm^{-1} (ν_{SF}) suggest a bidentate group. The rather low frequency observed for the band at 1240 cm^{-1} is unusual and suggests rather weak interaction between the metallic centers and the fluorosulfate groups. A fluorosulfato-bridged oligomer appears to be most consistent with the vibrational spectrum, but our inability to obtain either solution infrared or Raman spectra precludes a more extensive discussion. However the band pattern in the fluorosulfate-stretching region is inconsistent with the presence of detectable amounts of $Mn(SO_3F)_2$.[2] Likewise $Mn_2(CO)_{10}$[49] appears to be absent. Both are possible pyrolysis products as discussed before, but they should form at a higher decomposition temperature.

Conclusions

Manganese and rhenium display rather contrasting behavior toward oxidation by bis(fluorosulfuryl) peroxide. In the case of manganese, oxidation to the +3 oxidation state only is achieved with $M'_2[Mn(SO_3F)_5]$ (M′ = K, Cs) representing the first examples of anionic fluorosulfato complexes formed by a 3d-block element. On the other hand, rhenium is readily oxidized to the +7 oxidation state, but only oxofluorosulfates like $ReO_2(SO_3F)_3$ are isolated.

Rather complex thermal behavior is displayed by metal carbonyl fluorosulfates of the type $M(CO)_5SO_3F$ (M = Mn, Re). Only in the case where M = Mn is controlled thermal decomposition on a prepartive scale possible.

Acknowledgment. Financial support by the Natural Sciences and Engineering Research Council of Canada is gratefully acknowledged. We are also indebted to Ralph P. Hackl and Gerald A. Gordon, who did initial exploratory work on some of the compounds reported here as part of their undergraduate research project. Dr. R. C. Thompson and K. Oliver from this department are thanked for assistance in obtaining differential scanning calorimetry data with their instrument.

Registry No. $Mn(SO_3F)_3$, 97295-54-0; $Cs_2[Mn(SO_3F)_5]$, 97295-55-1; $K_2[Mn(SO_3F)_5]$, 97295-56-2; $ReO_2(SO_3F)_3$, 97295-57-3; $Mn(CO)_5SO_3F$, 97295-58-4; $Mn(CO)_5Br$, 14516-54-2; $Re(CO)_5SO_3F$, 97295-59-5; $Re(CO)_5Cl$, 14099-01-5; $Mn(CO)_4SO_3F$, 97295-60-8; $S_2O_6F_2$, 13709-32-5; Mn, 7439-96-5; Re, 7440-15-5.

(48) El-Sayed, M. A.; Kaesz, H. D. *Inorg. Chem.* **1963**, *2*, 158.
(49) Flintcroft, N.; Huggins, D. K.; Kaesz, H. D. *Inorg. Chem.* **1964**, *3*, 1123.