shift to lower frequencies of about 150 cm.$^{-1}$ in the position of ν_{CN} in $(C_5H_5)_3Fe_3(CO)_4(CH_2NCO)$ relative to $C_5H_5Mo(CO)_3CH_2NCO$ suggests that the isocyanate group in the iron complex is π-bonded to the iron atom.

A possible structure for $(C_5H_5)_3Fe_3(CO)_4(CH_2NCO)$ in agreement with these proton n.m.r. and infrared spectral data (Figure 1) and its negligible conductance is II. A key feature of this proposed structure II is an isocyanate group bridging between two metal atoms. In the indicated dipolar resonance structure the carbon–nitrogen triple bond is isoelectronic with the carbon–carbon triple bond in acetylenes which is known to act as a similar bridging group in compounds such as $(RC_2R)Co_2(CO)_6$[14] and $(RC_2R)[NiC_5H_5]_2$[15] obtained from acetylenes and $Co_2(CO)_8$ or $[C_5H_5NiCO]_2$, respectively.

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Enneafluoro-2-(fluorosulfato)butane and Trifluoroacetyl Fluorosulfate

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The reactive compounds fluorine fluorosulfate (FSO_3F) and peroxodisulfuryl difluoride ($S_2O_6F_2$) have been used to prepare a variety of fluorosulfate-containing compounds.[1–6] Fluorine fluorosulfate has been shown to react with haloolefins by cleaving the oxygen–fluorine bond. In this manner, FSO_3F was added across the carbon–carbon double bonds of tetrafluoroethylene, tetrachloroethylene, and perfluorocyclopentene to form the corresponding perhalofluorosulfates.[2] Also, peroxodisulfuryl difluoride has been added across the carbon–carbon double bonds of perhaloolefins to yield bis(fluorosulfato)perhaloalkanes.[4–6] Hexafluoro-1,2-bis(fluorosulfato)propane is prepared in such a manner.[5] When this latter compound is heated to 60° in the presence of potassium fluoride, it undergoes a novel defluorosulfurylization reaction to give tetrafluoro-2-(fluorosulfato)propionyl fluoride. When other bis(fluorosulfato) compounds, such as tetrafluorobis(fluorosulfato)ethane, hexafluoro-1,2-bis(fluorosulfato)cyclobutane, and octafluoro-2,3-bis(fluorosulfato)butane are similarly treated, total decomposition to SO_2F_2, CO, CO_2, O_2, and fluorocarbons is observed.[5]

Peroxodisulfuryl difluoride reacts with halomethanes containing fluorine and also a different halogen (*e.g.*, chlorine or bromine) to form perfluoromethyl fluorosulfates.[6] In contrast, carbon tetrachloride and $S_2O_6F_2$ give carbonyl chloride.[4] However, when the halomethane contains three fluorine atoms, there appears to be greater resistance to oxygenation and fluorosulfation occurs (*e.g.*, with CF_3Cl and CF_3Br).[6] It might be expected, then, that trifluoroacetyl bromide, under controlled conditions, would undergo replacement of the relatively labile bromine atom in the presence of $S_2O_6F_2$ to yield the acyl fluorosulfate. This was found to be the case and is thought to be the first example of this type of fluorosulfate.

Experimental Section

Reagents.—Fluorine fluorosulfate and peroxodisulfuryl difluoride were prepared by the catalytic fluorination of sulfur trioxide in the presence of silver(II) fluoride at 225 and 155°, respectively.[7,8] Purity was checked by vapor density measurements and infrared spectra. A mixture of *cis*- and *trans*-perfluoro-2-butene was obtained from the Matheson Company, Inc., and was used without further purification. Trifluoroacetyl bromide was synthesized from trifluoroacetic acid and phosphorus tribromide. Alkali fluorides were anhydrous and of reagent grade quality.

Sulfur was determined as barium sulfate after basic hydrolysis with 0.1 *N* sodium hydroxide at 100° for 2 weeks. Fluorine was determined by a null-point potentiometric method after fusion with sodium metal at 300° for 24 hr.[9,10] Vapor densities were determined by using Regnault's method with a Pyrex glass flask of 254.4-ml. volume, equipped with a 1.25-mm. Teflon stopcock (Fischer and Porter Co.). Reaction products were separated by fractional codistillation,[11] and vapor pressure measurements were obtained through the use of an apparatus similar to that described previously.[12] Infrared spectra were obtained by using a Perkin-Elmer Model 137 Infracord spectrophotometer. Infrared cells were constructed of Pyrex glass with a 5-cm. path length and sodium chloride windows. Mass spectra were obtained with a Consolidated Engineering Corp. Type 21-103 mass spectrometer. Nuclear magnetic resonance spectra were recorded through the use of a Varian Model 4311 B high-resolution spectrometer.

Preparation of Enneafluoro-2-(fluorosulfato)butane.—A 5:1 mixture of *cis*- and *trans*-perfluoro-2-butene and dry nitrogen was placed in a 1-l. Pyrex glass reaction vessel which was equipped with a 1.25-mm. Teflon stopcock and which was surrounded by an ice bath. An equimolar quantity of fluorine fluorosulfate was slowly titrated into the vessel and a colorless liquid gradually collected on the bottom of the vessel. The reaction

$$C_4F_8 + FSO_3F \xrightarrow{3^\circ} CF_3CF_2CF(SO_3F)CF_3$$

was rapid and exothermic. The yield of the reaction was about 91%, with only a small amount of unreacted C_4F_8 and SiF_4 found after separation by fractional codistillation.

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TABLE I

VAPOR PRESSURE OF $C_4F_9(SO_3F)$

P, mm.	*T*, °K.	*P*, mm.	*T*, °K.	*P*, mm.	*T*, °K.
26.2	266.0	283.6	316.3	515.6	332.3
55.5	280.0	338.5	320.8	582.4	335.7
106.8	294.5	408.8	325.8	678.8	340.2
155.4	301.1	446.5	328.1	714.9	341.7
198.6	307.9	454.0	328.7	803.5	354.4
231.2	311.1				

The compound is a clear, colorless liquid, which is inert toward mercury and which slowly dissolves fluorocarbon stopcock grease. Experimental measurements gave a molecular weight of 317 compared to a calculated value of 318 for $C_4F_9(SO_3F)$. The liquid density is 1.738 g./cc. at 22.2°; 1.805 at 0.1°; 1.780 at 7.8°; 1.756 at 16.0°; and 1.698 at 35.1°. A plot of the data gives the expression d (g./cc.) = $1.8056 - 0.0031t$ (°C.). The compound forms a cracked glass when cooled to −183°. A melting point could not be determined but the temperature at which the cracked appearance vanished was about −130°. The vapor pressure values, measured over the temperature range from 266.0 to 354.4°K., are given in Table I. A boiling point of 342.5°K. and a molar heat of vaporization of 7.7 kcal. are indicated by the data. The Trouton constant is 22.3. The infrared spectrum was obtained at 20 mm. pressure with a 5-cm. path length. Strong bands at 1500 cm.$^{-1}$ may be attributed to S–O stretch; at 1300–1225 cm.$^{-1}$ (complex) to S–O and C–F; at 1172 and 1130 cm.$^{-1}$ to C–F; and at 870–840 cm.$^{-1}$ (broad) to S–F. Other bands at 1085, 1060, 958, 900, and 738 cm.$^{-1}$ were not assigned. *Anal.* Calcd. for $C_4F_9(SO_3F)$: S, 10.1; F, 59.8. Found: S, 10.0; F, 59.6. The mass spectrum at an ionization potential of 70 v. had peaks attributed to the following species with the respective mass numbers and relative abundances shown: SO_2^+, 64, 5.3; SOF^+, 67, 13.8; CF_3^+ and $^{34}SOF^+$, 69, 100.0; SO_2F^+, 83, 89.9; $C_2F_3O^+$, 97, 31.4; $C_2F_4^+$, 100, 7.4; $C_2F_5^+$, 119, 29.8; $C_3F_5^+$, 131, 6.4; $C_2F_5SO_3^+$, 199, 6.4; $C_4F_9^+$, 219, 0.02; $C_3F_7SO_3^+$, 249, 3.2; and $C_4F_9SO_3^+$, 299, 0.5. The nuclear magnetic resonance spectrum of $C_4F_9(SO_3F)$ was run at 40 Mc. with $CFCl_3$ as the internal standard. Resonances were found at −51.3 p.p.m. due to the fluorine of the SO_3F group; +78.3 and +80.8 p.p.m. due to the two CF_3 groups; +124.5 p.p.m. due to the CF_2 of the CF_3CF_2 group; and +139.1 p.p.m. due to the CF of the CF_3CF group.

Reaction of Ennea-2-(fluorosulfato)butane with Cesium or Potassium Fluorides.—In the presence of either excess cesium or potassium fluoride at 70° for 16 hr., a 6.48-mmole sample of enneafluoro-2-(fluorosulfato)butane was partially converted to octafluoro-2-butanone, $CF_3CF_2COCF_3$, and SO_2F_2. The yield was about 31%. Separation and purification of C_4F_8O was accomplished by extended pumping for 48 hr. at −126°. The observed molecular weight was found to be 215 compared to a calculated value of 216. An infrared spectrum of this compound was taken at 20 mm. pressure. The following bands were identified: 1800 cm.$^{-1}$ (m), C=O stretch; 1310 (s), 1260–1185 (br, s), and 1075 cm.$^{-1}$ (m), C—F stretch. Other bands at 909 (ms), 885 (ms), and 720 cm.$^{-1}$ (s) were not assigned. Octafluoro-2-butanone was first synthesized in 15% yield by the fluorination of methyl ethyl ketone at 135° in the presence of copper.[13]

Preparation of Trifluoroacetyl Fluorosulfate.—Trifluoroacetyl bromide and dry nitrogen in a 1:3 mixture were introduced into a 1-l. Pyrex reaction vessel which was held at 3°. Peroxodisulfuryl difluoride was added slowly until the molar ratio of trifluoroacetyl bromide to $S_2O_6F_2$ was 2.5:2. After 20 min., a red-brown vapor began to appear. The cold bath was removed after 12 hr., and the contents of the vessel were separated by fractional codistillation. Each component was identified from its infrared spectrum. Since bromine and trifluoroacetyl fluorosulfate, $CF_3CO(SO_3F)$, were not separable by codistillation, the former was removed by contact of the gaseous mixture with mercury, which permitted the recovery of the pure $CF_3CO(SO_3F)$ in approximately 65% yield based on the CF_3COBr present initially. The equation for the reaction can be written as

$$2CF_3COBr + 2S_2O_6F_2 \xrightarrow{3^\circ} CF_3CO(SO_3F) + CF_3SO_3F + CO_2 + S_2O_5F_2 + Br_2$$

TABLE II

VAPOR PRESSURE OF $CF_3CO(SO_3F)$

P, mm.	*T*, °K.	*P*, mm.	*T*, °K.	*P*, mm.	*T*, °K.
24.6	249.8	171.9	286.1	505.7	308.8
49.2	262.5	184.0	286.5	632.8	314.4
68.3	268.7	208.3	288.6	675.6	316.2
116.0	277.2	280.3	295.4	721.5	318.0
133.4	280.4	356.9	301.7	770.0	319.6
160.6	283.8	439.3	305.9	785.8	320.5
167.4	284.6				

Trifluoroacetyl fluorosulfate is a clear, colorless liquid which hydrolyzes slowly with 0.1 *N* sodium hydroxide at 100° and which is inert toward mercury, at least for short periods of time. Experimental measurements resulted in a molecular weight of 195 compared to a calculated value of 196 for $CF_3CO(SO_3F)$. A liquid density of 1.618 g./cc. was found at 23.5°; other values obtained include: 1.672 at 6.7°, 1.654 at 12.6, 1.599 at 29.3°, and 1.595 at 31.5°. These data yield the expression d (g./cc.) = $1.6916 - 0.0031t$ (°C.). A melting point was not obtained. The point at which the compound loses the cracked glass appearance taken on when cooled to −183° was estimated to be −134 ± 2°. A boiling point of 319.5°K. is obtained from the vapor pressure data given in Table II. The molar heat of vaporization is 8.0 kcal., and the Trouton constant is 25.1. The infrared spectrum of $CF_3CO(SO_3F)$ is as follows: A band at 1850 cm.$^{-1}$ (s) corresponds to C=O stretch; at 1487 (vs) and 1250 cm.$^{-1}$ (s) to S—O; at 1303 (m) and 1200 cm.$^{-1}$ (s) to C—F; and at 862 and 830 cm.$^{-1}$ (s) to S—F stretch. Bands at 1040 (s) and 778 cm.$^{-1}$ (m) were not assigned. *Anal.* Calcd. for $CF_3CO(SO_3F)$: C, 12.2; S, 16.3; F, 38.8. Found: C, 15.1; S, 14.7; F, 37.5. The n.m.r. spectrum consisted of two resonances. The sulfur–fluorine and carbon–fluorine resonances occurred at shifts of −47.8 and +73.1 p.p.m., respectively, relative to $CFCl_3$, and had an area ratio of 1:3.

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Stepwise Hydrolysis of Hexafluoroantimonate(V)

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To explain the acidity of solutions resulting from the dissolving of hexafluoroantimonate(V) salts Lange and

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