for $C_{14}H_{30}O_2Sn$: C, 48.17; H, 8.66. Found: C, 48.47; H, 8.72. MS (EI): $m/z$ 350 ($M^+$, $^{120}Sn$).

## Results

The preparation and reactivity studies of new indiostannoxanes (**2a–d** and **3b**) treated in this paper are summarized in Scheme I. A characterization was undertaken for **2a–d** and **3b**, whose results are presented in Tables I and II. Finally, chemical and thermal reactivity studies were undertaken, and the results obtained are presented in Tables III and IV. These will be introduced at appropriate places in the section that follows.

## Discussion

Addition of **1c** or **1d** to dibutyltin oxide proceeded in an abnormal fashion. Thus new indiostannoxanes **2c,d** were obtained via a cleavage of the In–C bonds as illustrated in Scheme I, respectively. Vibrational absorption bands appeared at 1540 and 1400 $cm^{-1}$, and higher values of $\delta(^{13}CO)$ than 180 ppm indicated an existence of indium carboxylate linkages.[9] In addition fragment ion peaks observed at around 291 were assignable to $(Bu_3{}^{120}Sn)^{\bullet+}$. These spectral data reasonably suggested the presence of In–OCOEt bonds in **2c,d**. The reactions of **1a,b** with $Bu_2SnO$ also gave indiostannoxanes **2a,b**. Similarly, reactions of **1a,b** with $(Bu_3Sn)_2O$ were carried out, and indiostannoxanes **2a** and **3b** together with mixed tetrabutyltin were obtained. Consequently, it is assumed that the formation of **2** took place through a migration of a butyl group and not of a propionato group.

It is well-known that the reactions of organotin compounds with several organometallics including boron or thallium derivatives proceed via a migration of electronegative substituents such as halides or carboxylates to tin centers.[10] It should be remembered, however, that dibutyltin oxide sometimes behaves as an alkyl acceptor to give trialkyltin derivatives under specific conditions.[11] Further, certain dialkylindium derivatives donate their alkyls onto a neutral or less basic substrate such as triethylstibine oxide or thiobenzaldehyde, etc.[12] Thus, the butyl migration discussed in this article can be justified by a consideration that dibutyltin oxide and bis(tributyltin) oxide behave as an alkyl acceptor like triethylstibine sulfide.

Although $M^+ + 1$ peaks were detected in the FAB MS spectra for the indiostannoxanes **2a,b** and **3b**, their molecularity measurements showed that they formed a dimmeric aggregate in a solution. Perhaps, **2a,b** and **3b** exist in a ladder type dimer[9,13] but we could not clarify their structures in detail. In contrast the indiostannoxanes **2c,d** were monomeric in solution, because chelation by the carboxylato ligand prevented an intermolecular coordination. A formation of the chelation was confirmed by their values of $\nu_{as}(COOIn)$.[14] Meanwhile, the reaction of **1** with butanestannoic acid proceeded very fast even at room temperature but gave polymeric products that readily underwent a change into solid gels. Overall, the reactivities of the organotin oxides employed here were estimated as being $BuSnO_2H > (Bu_3Sn)_2O > Bu_2SnO$ with respect to the reaction temperatures. In contrast, it is curious that no reaction occurred in cases of **1** with diphenyltin oxide, dimethyltin oxide, bis(triphenyltin) oxide, benzenestannoic acid, and methanestannoic acid. We, however, could not explain the low reactivities of other organotin oxides than the butyl derivatives in view of their acidity and basicity.[15]

Next, we attempted a cleavage of In–O–Sn linkage by acetolysis. As shown in Table III, the reactions of **2a,b** with an equivalent amount of acetic acid gave the corresponding monoacetato derivatives, $Bu_2InOAc$ and $Bu_3SnOAc$, in somewhat low yields. In the reactions of **2a,b** with excess acetic acid, In–O–Sn linkages were cleaved quantitatively and the mixed tributyltin acetates **5** and $In(OAc)_3$ were obtained in quantitative yields. The formation of **5** also supported the proposed structures of **2** and **3** because of the absence of Sn–propionato linkage in **5**.

The indiostannoxanes **2** and **3** formed wet gels[16] via hydrolysis–polycondensation in benzene on standing for a week by an addition of the catalytic amounts of water (10 mol %). Thermal properties of **2a–d** were also investigated. These indiostannoxanes were found to release butyl groups at 260–280 °C with exotherms, and the thermal weight loss ended at 300–350 °C to give indium–tin oxide powders quantitatively. Consequently these results indicated that the indiostannoxanes are excellent precursors for indium–tin oxide (ITO) thin layers via the solution pyrolysis method.[5,17]

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# (Pentafluoro-λ⁶-sulfanyl)difluoromethanesulfonyl Fluoride and Derivatives

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## Introduction

Fluorinated-carbon-containing sulfonyl fluorides ($R_FSO_2F$) are of considerable interest.[2] The simplest member, trifluoromethanesulfonyl fluoride, $CF_3SO_2F$, has found multiple uses and is employed in the preparation of trifluoromethanesulfonic acid or triflic acid ($CF_3SO_3H$).[3]

We have prepared a number of fluorinated (pentafluoro-$\lambda^6$-sulfanyl)methanesulfonyl fluorides and their respective acids. In particular, we have previously prepared $SF_5CH_2SO_2F$ ($SF_5CH_2SO_3H\cdot H_2O$) and $SF_5CHFSO_2F$ ($SF_5CHFSO_3H$).[4,5] In addition, for the ethane series, the following $SF_5$ alkanesulfonic acids, $F_5SCH_2CH_2SO_3H$, $F_5SCH_2CF_2SO_3H\cdot H_2O$, and $F_5SCHFCF_2SO_3H\cdot H_2O$, are known.[6] We now report the successful preparation of the completely fluorinated member of the methane series, $SF_5CF_2SO_2F$, and its corresponding acid, ester, and salts.

## Results and Discussion

We have found that static fluorination of $SF_5CFHSO_2F$ under mild conditions and in the presence of NaF gave $SF_5CF_2SO_2F$ in good yield (57%):

$$SF_5CFHSO_2F + F_2 + NaF \rightarrow SF_5CF_2SO_2F + NaHF_2 \quad (1)$$

Compound **1** is a clear water-like liquid with a boiling point of 51 ± 1 °C. Basic hydrolysis of **1** gave the corresponding stable sulfonate salts (**2**):

$$2SF_5CF_2SO_2F + 2M(OH)_2 \rightarrow \underset{\mathbf{2}}{M(SF_5CF_2SO_3)_2} + MF_2 + 2H_2O \quad (2)$$

$$M = Ca\ (\mathbf{2a}),\ Ba\ (\mathbf{2b})$$

The corresponding acid was distilled from concentrated sulfuric

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acid as a colorless solid, mp 35 ± 1 °C.

$$M(SF_5CF_2SO_3)_2 + H_2SO_4(aq) \rightarrow \underset{\mathbf{3}}{2SF_5CF_2SO_3H\cdot 2.5H_2O} + MSO_4 \quad (3)$$

With $CF_3CH_2OLi$ and $SF_5CF_2SO_2F$ the following sulfonate ester was formed:

$$SF_5CF_2SO_2F + CF_3CH_2OLi \rightarrow \underset{\mathbf{4}}{SF_5CF_2SO_2OCH_2CF_3} + LiF \quad (4)$$

The infrared spectra for these compounds have common features with the presence of the $SF_5$ and $CF_2$ groups and their characteristic infrared absorption bands. Cross and co-workers reported that for compounds containing the $SF_5$ group the most intense bands should occur in the 850–920-cm$^{-1}$ region (S–F stretching modes) and in the region 600 cm$^{-1}$ (S–F deformation modes).[7] For the new compounds reported in this paper, absorption bands in the 832–907-cm$^{-1}$ region are assigned to the S–F stretching vibrations. One of the S–F deformation modes is found in the 588–596-cm$^{-1}$ region. For $SF_5CFHSO_2F$, $Ca(SF_5CHFSO_3)_2$, and $SF_5CFHSO_3H$, the corresponding absorption bands were found in the 858–914- and 586–598-cm$^{-1}$ regions.[4] The C–F stretching vibration of the $CF_2$ group for all compounds except the ester appears to be located in the 1234–1257-cm$^{-1}$ region. In general, it is expected that, for compounds containing a $CF_2$ group, the CF absorption will be in the 1050–1250-cm$^{-1}$ region.[8] In compound **4** the strong band at 1297 cm$^-$ is attributed to both the $CF_2$ and $CF_3$ groups.

The other functional groups also exhibit characteristic absorption bands. The asymmetric and symmetric $SO_2$ bands for compound **1** can be tentatively assigned to the 1479- and 1252-cm$^{-1}$ regions. For the sulfonyl fluoride group, the strong S–F absorption band is located at 801 cm$^{-1}$. This band disappears when the acid and salts are formed. The asymmetric and symmetric $SO_3$ stretching bands for **2a**, **2b**, and **3** are found in the 1257–1290- and 1055–1080-cm$^{-1}$ regions, respectively; for salts containing the $CF_3SO_3^-$ group, the corresponding assigned regions are 1266–1279 and 1025–1042 cm$^{-1}$. For the $SF_5CFHSO_3H$ acid and salts, the asymmetric and symmetric $SO_3$ stretching bands are located in the 1220–1276- and 1052–1100-cm$^{-1}$ regions, respectively.[4] For the new ester, **4**, the asymmetric/symmetric $SO_3$ stretching bands are located at 1452 and 1229 cm$^{-1}$, respectively; in $CF_3SO_3CH_2CF_3$, these absorptions are located at 1445 and 1231 cm$^{-1}$.[9]

The major mass spectral peaks for all new compounds are listed in the Experimental Section. The molecular ion peaks were not observed for any of the compounds listed; however many did show peaks such as $(M - F)^+$ and $(M - CF_3)^+$. For the Ca and Ba salts, the $[M(SF_5CF_2SO_3)_3]^-$ peak was observed. The acid did show a $(M + H_2O)^+$ peak as well as dimeric species such as $(M_2H)^+$, $(M_2)^+$ and $(M_2 - H)^+$. In general, appropriate fragments were found for all compounds and were supportive of the assigned structures.

For all compounds, the $SF_5$ fluorine NMR resonances consist of an $AB_4$ multiplet; the minimum between the B maxima is reported as the $SF_4$(eq) chemical shift while the SF(ax) chemical shift is reported as the center (line six) of its nine-line pattern. The magnitude of the coupling between the $CF_2$ group and the $AB_4$ system for all new compounds was consistent: $J_{F(A)CF_2}$ and $J_{SF_4(B)CF_2}$ values were 3.2–5.19 Hz and 12.0–14.8 Hz, respectively. For $J_{AB}$, values between 145 and 156 Hz were found. What is extremely interesting is the increased shielding found for the SF(ax), $SF_4$(eq), and $SO_2F$ groups when hydrogen is replaced by fluorine. For the series $SF_5CH_2SO_2F$, $SF_5CHFSO_2F$, and $SF_5CF_2SO_2F$, the corresponding values are as follows: SF(ax), 71.4, 65.2, and 60.6 ppm; $SF_4$(eq), 71.4, 55.2, and 47.2 ppm; and $SO_2F$, 58.5, 51.3, and 43.8 ppm. Also, for the perfluorinated systems, when the $SO_2F$ group is replaced by an $SF_5$ group ($SF_5CF_2SO_2F$ versus $SF_5CF_2SF_5$[10]) the values for SF(ax) and $SF_4$(eq) are relatively unchanged but the fluorines of the $CF_2$ group become significantly less shielded (from −83.9 to −68.4 ppm). The chemical shifts for $^{13}C$ in **1** (123.3 ppm) and **3** (127.2 ppm) are in the range reported for other similar systems: in $(SF_5)_2CF_2$ and $SF_5C_\alpha HFC_\beta F_2SO_3H$ the chemical shifts values were 130.6 and 105.6 ($C_\alpha$) ppm and 114.7 ($C_\beta$) ppm, respectively.[6,10] The $J_{CF}$ coupling constants of 342 and 336 Hz agree closely with that of 358 Hz found for $(SF_5)_2CF_2$; with $SF_5C_\alpha HFC_\beta F_2SO_3H$, the $J_{CF}$ coupling was lower (241.9 Hz) for the $C_\alpha HF$ group but did increase for the $CF_2$ site—for $C_\beta F$ and $C_\beta F'$, 294.8 and 282.0 Hz. For the ester compound **4**, the chemical shifts and coupling constants of the $SF_5CF_2$ group are in excellent agreement with those found for compounds **1** and **3**; values found for the $CF_3CH_2$ grouping also correspond well with literature values.[5]

## Experimental Section

**Materials.** The following compounds used in this work were obtained from commercial sources: $Ba(OH)_2\cdot 8H_2O$ and CaO (Merck); NaF (Riedel-deHaën); $F_2$ (Kali-Chemie). $LiOCH_2CF_3$ was prepared from lithium and $CF_3CH_2OH$ (PCR). $SF_5CFHSO_2F$ was synthesized by literature methods.[3]

**General Procedures.** Gases were manipulated in a conventional Pyrex glass vacuum apparatus equipped with a Leybold-Heraeus thermocouple gauge. Infrared spectra were obtained by using a 10-cm Pyrex gas cell with KBr windows or as solids/liquid between KBr or AgCl disks on a Nicolet 55DX-FT spectrometer. The NMR spectra were recorded with an AC 80 Bruker spectrometer operating at 80.0 MHz for proton and 75.4 MHz for fluorine resonances or on a WH360 Bruker spectrometer operating at 90.5 MHz for carbon-13 resonances; TMS, $CFCl_3$, and $CDCl_3$ were used as internal standards. The mass spectra were recorded with either a Varian MAT CH5 or a Finnigan MAT 8230 system operating at 70 eV.

Elemental analyses were determined by Beller Microanalytical Laboratory, Göttingen, West Germany.

**$SF_5CFHSO_2F$ with $F_2$.** Into a 500-mL prefluorinated Monel vessel equipped with a Hoke Monel valve and containing 331 mmol of dried NaF were added 21.9 mmol of $SF_5CFHSO_2F$ and 26.3 mmol of $F_2$. The reaction vessel was kept at room temperature (15 h). The vessel was cooled to −196 °C, and the excess $F_2$ was pumped away. Distillation of the products showed that unreacted $SF_5CFHSO_2F$ was still present. Since starting material was present, additional $F_2$ (26.3 mmol) was added and the reactants were heated at 39 °C (63 h). Distillation of the product mixture gave 12.5 mmol of $SF_5CF_2SO_2F$: 57% yield; bp 52 ± 1 °C.

The infrared spectrum gave the following absorption bands (cm$^{-1}$): 2720 (vw), 1600 (vw), 1535 (vw), 1479 (s), 1414 (vw), 1252 (ms), 1220 (s), 1173 (s), 1093 (vw), 1030 (vw), 971 (m), 907 (vs), 870 (s), 836 (vw), 801 (s), 750 (vw), 725 (vw), 697 (wm), 665 (m), 613 (m), 593 (s), 573 (s).

$^{19}F$ NMR spectral data ($CFCl_3$) for $F^ASF_4{}^BCF_2{}^CSO_2F^D$: $\phi_A$ 60.6 (nine-line pattern, t), $\phi_B$ 47.2 (d, m), $\phi_C$ −83.9 (d, d, p), $\phi_D$ 43.8 (m) ppm; coupling constants $J_{AB} = 149$ Hz, $J_{CD} = 4.4$ Hz, $J_{BC} = 12.0$ Hz, $J_{AC} = 3.2$ Hz, $J_{BD} = 4.8$ Hz.

$^{13}C$ NMR spectral data ($CDCl_3$): $\delta$ 123.3 (t, d, p, d) ppm; coupling constants $J_{C-SF_4} = 30.8$ Hz, $J_{C-SF(ax)} = 2.1$ Hz, $J_{C-SO_2F} = 37.9$ Hz, $J_{C-F_2} = 342.1$ Hz.

$EI^+$ mass spectral data (*m/e*, species): 203, $(M - 3F)^+$; 177, $(SF_5CF_2)^+$; 149, $(CF_3S_2O)^+$; 133, $(CF_2SO_2F)^+$; 127, $(SF_5)^+$; 120, $(CSF_4)^+$; 108, $(SF_4)^+$; 101, $(CSF_3)^+$; 89, $(SF_3)^+$; 83, $(SO_2F)^+$; 82, $(CSF_2)^+$; 70, $(SF_2)^+$; 69, $(CF_3)^+$; 67, $(SOF)^+$; 64, $(SO_2)^+$; 63, $(CSF)^+$; 51, $(SF)^+$; 50, $(CF_2)^+$; 48, $(SO)^+$; 44, $(SC)^+$; 32, $(S)^+$; 31, $(CF)^+$. $CI^-$ mass spectral data (*m/e*, species): 241, $(M - F)^-$; 146, $(CF_2S_2O_2)^-$; 129, $(C_2F_3SO)^-$; 127, $(SF_5)^-$; 83, $(SO_2F)^-$.

Anal. Calcd for $CF_8O_2S_2$: C, 4.62; F, 58.4; S, 24.65. Found: C, 4.78; F, 58.2; S, 24.70.

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**$SF_5CF_2SO_2F + LiOCH_2CF_3$.** Into a 105-mL Pyrex glass vessel equipped with a Teflon valve and Teflon stirring bar were added 6.04 mmol of $LiOCH_2CF_3$ and 5.77 mmol of $SF_5CF_2SO_2F$. The reaction was maintained at room temperature (16 h) and then heated to 40–45 °C (6 h). The volatile products were separated via trap to trap distillation. The pure ester product collected in the −40 to −50 °C trap, giving 3.91 mmol (68% yield).

The infrared spectrum gave the following absorption bands ($cm^{-1}$): 3062 (vw), 2997 (w), 1434 (ms with sh at 1415), 1287 (m with sh at 1302), 1228 (m), 1183 (s), 1158 (s), 1029 (ms), 965 (m), 885 (vs), 855 (vs), 809 (m with sh at 794), 692 (w), 662 (wm), 609 (w), 588 (ms), 567 (m), 527 (w), 493 (wm), 459 (w).

$^{19}F$ NMR spectral data ($CDCl_3$) for $F^ASF_4{}^BCF_2{}^CSO_2OCH_2{}^DCF_3{}^E$: $\phi_A$ 62.0 (nine-line pattern, t), $\phi_B$ 46.9 (d, m), $\phi_C$ −85.7 (m, p), $\phi_E$ −74.8 (t) ppm; coupling constants $J_{AB}$ = 156 Hz, $J_{AC}$ = 4.60 Hz, $J_{BC}$ = 12.6 Hz. $^1H$ NMR spectral data: $\delta_D$ = 4.73 ppm; $J_{DE}$ = 7.35 Hz.

The $^{13}C$ NMR spectral data ($CDCl_3$): $\delta$ 124.1 (t, p, d), 121.1 (q, t), 69.3 (t, q) ppm. The coupling constants are $J_{C-SF_4}$ = 28.7 Hz, $J_{C-SF(ax)}$ = 1.9 Hz, $J_{C-F_2}$ = 339.6 Hz, $J_{C-H_2}$ = 156.3 Hz, $J_{C-CF_3}$ = 39.8 Hz, $J_{C-F_3}$ = 277.3 Hz, and $J_{CH_2-CF_3}$ = 4.7 Hz.

$EI^+$ mass spectral data (*m/e*, species): 271, $(M - CF_3)^+$; 211, $(M - SF_5 - 2H)^+$; 193, $(M - SF_5 - HF)^+$; 177, $(SF_5CF_2)^+$; 163, $(CF_3CH_2SO_3)^+$; 147, $(CF_3CH_2SO_2)^+$; 127, $(SF_5)^+$; 97, $(C_2F_5O)^+$; 89, $(SF_3)^+$; 83, $(CF_3CH_2)^+$; 80, $(SO_3)^+$; 79, $(CF_2CHO)^+$; 69, $(CF_3)^+$; 64, $(SO_2)^+$; 63, $(CFS)^+$; 51, $(SF)^+$; 50, $(CF_2)^+$; 48, $(SO)^+$; 44, $(CHCF)^+$; 40, $(C_2O)^+$; 32, $(S)^+$.

Anal. Calcd for $C_3H_2F_{10}O_3S_2$: C, 10.59; H, 0.59; F, 55.9. Found: C, 10.84; H, 0.58; F, 55.1.

**$SF_5CF_2SO_2F$ + CaO(aq).** Into a 50-mL Pyrex glass round-bottom flask equipped with a Teflon stirring bar were added 17.0 mL of $H_2O$ (944 mmol), 27.8 mmol of CaO and 9.15 mmol of $SF_5CF_2SO_2F$. The mixture was heated to 50–60 °C (1 day) and 60–70 °C (40 min). Solid $CO_2$ was added; the mixture was filtered and water was removed by pumping through a trap cooled to −196 °C. The white solid product $Ca(SF_5CF_2SO_3)_2$, 2.81 mmol, was formed in 62% yield; dec pt >300 °C.

The infrared spectrum gave the following absorption bands ($cm^{-1}$): 1651 (w, br), 1256 (s, sh at 1278), 1180 (ms, sh at 1191), 1100 (w), 1068 (ms, sh at 1079), 963 (w), 876 (s, sh at 894), 837 (s), 670 (ms), 623 (m), 620 (m), 591 (s), 576 (ms), 537 (m).

$^{19}F$ NMR spectral data for $Ca(F^ASF_4{}^BCF_2{}^CSO_3)_2$ in $DC_3CN$: $\phi_A$ 69.5 (nine-line pattern, t), $\phi_B$ 45.0 (d, m), $\phi_C$ −85.1 (d, p) ppm; coupling constants $J_{AB}$ = 145 Hz, $J_{AC}$ = 5.14 Hz, $J_{BC}$ = 14.8 Hz.

$FAB^-$ mass spectral data (*m/e*, species): 811, $[Ca(SF_5CF_2SO_3)_3]^-$; 575, $(MH_2F)^-$; 574, $(MHF)^-$; 573, $(MF)^-$; 465, $(M - F_3O_2)^-$; 446, $(M - F_4O_2)^-$; 396, $(MH - SF_5 - 2O)^-$; 363, $(M - SF_4 - 4O)^-$; 335, $(M - SF_9O)^-$; 257, $(SF_5CF_2SO_3)^-$; 238, $(SF_5CF_2SO_3 - F)^-$; 227, $(M - CS_2F_9O_5)^-$; 219, $(SF_5CF_2SO_3 - 2F)^-$; 209, $(SF_5CF_2S)^-$; 177, $(SF_5CF_2)^-$; 158, $(SF_5CF)^-$; 149, $(CF_3S_2O)^-$; 131, $(CF_2SO_3H)^-$; 130, $(CF_2SO_3)^-$; 127, $(SF_5)^-$; 83, $(SO_2F)^-$; 80, $(SO_3)^-$.

Anal. Calcd for $C_2F_{14}O_6S_4Ca$: Ca, 7.23; F, 48.0. Found: Ca, 7.36; F, 46.8.

**$SF_5CF_2SO_2F + Ba(OH)_2{\cdot}8H_2O$.** In a manner analogous to that reported for the reaction with CaO, 12.9 mmol of $Ba(OH)_2{\cdot}8H_2O$, 20.2 mL of $H_2O$ (1122 mmol), and 10.8 mmol of $SF_5CF_2SO_2F$ were heated at 50–55 °C (16 h), 55–61 °C (3 h). An additional 2.4 mmol of $Ba(OH)_2{\cdot}8H_2O$ was added followed by heating at 61–64 °C for 1 h. Solid $CO_2$ was added to the reaction mixture; the solution was filtered, and excess water was removed by evaporation. The white solid product $Ba(SF_5CF_2SO_3)_2$, 3.22 mmol, was formed in 60% yield; dec pt >250 °C.

The infrared spectrum gave the following absorption bands ($cm^{-1}$): 1279 (vs, br), 1256 (vs), 1235 (vs), 1185 (s), 1077 (ms), 1059 (m), 965 (w), 904 (m), 860 (s, sh at 875), 837 (vs), 675 (m), 622 (wm), 614 (w), 596 (ms, sh at 573), 580 (w), 558 (w), 543 (w), 522 (wm), 459 (vw), 414 (vw).

$^{19}F$ NMR spectral data for $Ba(F^ASF_4{}^BCF_2{}^CSO_3)_2$ in $CD_3CN$: $\phi_A$ 69.5 (nine-line pattern, t), $\phi_B$ 45.0 (d, m), $\phi_C$ −85.1 (d, p) ppm; coupling constants $J_{AB}$ = 148 Hz, $J_{AC}$ = 5.19 Hz, $J_{BC}$ = 14.8 Hz.

The $FAB^-$ mass spectrum (*m/e*, species): 909, $[Ba(SF_5CF_2SO_3)_3]^-$; 673, $(MH_2F)^-$; 672, $(MHF)^-$; 671, $(MF)^-$; 563, $(M - F_3O_2)^-$; 544, $(M - F_4O_2)^-$; 494, $(MH - SF_5 - 2O)^-$; 455, $(M - F_7O_4)^-$; 433, $(M - SF_9O)$; 325, $(M - CS_2F_9O_5)^-$; 257, $(SF_5CF_2SO_3)^-$; 219, $(SF_5CF_2SO_3)^-$; 149, $(CF_3S_2O)^-$; 131, $(CF_2SO_3H)^-$; 130, $(CF_2SO_3)^-$; 127, $(SF_5)^-$; 99, $(CF_2SOH)^-$; 83, $(SO_2F)^-$; 80, $(SO_3)^-$.

Anal. Calcd for $C_2F_{14}O_6S_4Ba$. Ba, 21.08; F, 40.8. Found: Ba, 21.59; F, 40.2.

**$Ba(SF_5CF_2SO_3)_2 + H_2SO_4$.** Into a 5.0-mL round-bottomed flask were added 2.61 mmol of $Ba(SF_5CF_2SO_3)_2$ and 53 mmol of concentrated $H_2SO_4$. The mixture was heated (with stirring) for 1.5 h from 40 to 88 °C after which distillation was carried out two times under reduced pressure. The fraction boiling at 90 ± 1 °C (~1 Torr) was a colorless solid (2.05 mmol) of $SF_5CF_2SO_3H{\cdot}2.5H_2O$ and was obtained in 39% yield; mp 35 ± 1 °C.

The infrared spectrum gave the following absorption bands ($cm^{-1}$): 3325 (s, v br), 1724 (ms, br), 1290 (s), 1234 (s), 1188 (s), 1110 (m, sh at 1097), 1055 (s, sh at 1024), 962 (w), 872 (vs), 832 (s), 730 (w, sh at 715), 668 (vs, sh at 657), 594 (vs, sh at 616), 526 (w), 517 (w), 504 (w).

$^{19}F$ NMR spectral data ($CD_3CN$) for $F^ASF_4{}^BCF_2{}^CSO_3H{\cdot}2.5H_2O$: $\phi_A$ 69.3 (nine-line pattern, t), $\phi_B$ 44.8 (d, m), $\phi_C$ −85.3 (d, p) ppm; coupling constants $J_{AB}$ = 148 Hz, $J_{AC}$ = 5.16 Hz, $J_{BC}$ = 14.6 Hz.

$^1H$ NMR spectral data ($CD_3CN$): $\delta$ = 9.0 ppm (br s).

The $^{13}C$ NMR spectral data ($CD_3CN$): $\delta$ 127.2 (t, p, d) ppm; coupling constants $J_{C-SF_4}$ = 18.8 Hz, $J_{C-SF(ax)}$ = 2.5 Hz, $J_{C-F_2}$ = 336.3 Hz.

The $EI^+$ mass spectral data (*m/e*, species): 277, $(M + H_3O)^+$; 276, $(M + H_2O)^+$; 259, $(MH)^+$; 258, $(M)^+$; 257, $(M - H)^+$); 243, $(MH - O)^+$; 229, $(M + H_3O - 3O)^+$; 201, $(M - 3F)^+$; 131, $(M - SF_5)^+$; 127, $(SF_5)^+$; 89, $(SF_3)^+$; 82, $(CSF_2)^+$; 81, $(SO_3H)^+$; 70, $(SF_2)^+$; 69, $(CF_3)^+$; 67, $(SO)^+$; 65, $(SO_2H)^+$; other fragments including *m/e* 517 $(M_2H)^+$, 516 $(M_2)^+$, and 515 $(M_2 - H)^+$ due to the acid dimer were present in small amounts.

Anal. Calcd for $C_1H_6F_7O_{5.5}S_2$. C, 3.96; H, 1.99; F, 43.9; S, 21.15. Found: C, 4.11; H, 2.03; F, 40.7; S, 21.70.

**$Ca(SF_5CF_2SO_3)_2 + H_2SO_4$.** To a 5.0 mL Pyrex glass round-bottomed flask equipped with a Teflon stirring bar were added 1.82 mmol $Ca(SF_5CF_2SO_3)_2$ and 66 mmol of concentrated $H_2SO_4$. The mixture was distilled under reduced pressure (>$10^{-3}$ Torr). A solid hydrate (1.78 mmol) was formed in 49% yield. The melting point (35 ± 1 °C) and infrared and NMR spectra agreed with those found for the acid produced from the barium salt.

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