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A Pentafluorosulfur β-Sultone and Some Derivatives

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The new pentafluorosulfur β-sultone, $SF_4CFCF_2OSO_2$ (I), resulted from the reaction of sulfur trioxide with (trifluorovinyl)sulfur pentafluoride. In the presence of Et_3N, I underwent rearrangement of $SF_5CF(SO_2F)C(O)F$ (II), and with H_2O, I gave SF_5CFHSO_2F (III). Inorganic bases such as $Ca(OH)_2$ or NaOH with I formed the respective metal sulfonates, $Ca(SF_5CFHSO_3)_2$ (IV) and $Na(SF_5CFHSO_3)$ (V). IV was obtained also when $Ca(OH)_2$ was reacted with III. IV or V with sulfuric acid gave a new stable sulfonic acid, SF_5CFHSO_3H (VI). III and VI are hydrolytically stable.

Introduction

(Fluoroalkyl)sulfonic acids or salts continue to be subjects of considerable study. These acids are among the strongest acids known and have high thermal stabilities. Their salts (Na, K, Ba) have long liquid ranges. While many methods exist for preparing (fluoroalkyl)sulfonic acids/salts,[2-5] their utility in producing a sulfonic acid and its derivatives that contain a pentafluorosulfur (SF_5) group has not been demonstrated. For example, Temple prepared $(CF_3)_2CFSO_2F$ by reacting hexafluoropropene with SO_2F_2. Reaction with $Ca(OH)_2$ gives the corresponding calcium salt:[4]

$$CF_3CF{=}CF_2 + SO_2F_2 \xrightarrow{CsF} (CF_3)_2CFSO_2F$$

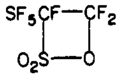
$$(CF_3)_2CFSO_2F + CaO(H_2O) \rightarrow [(CF_3)_2CFSO_3]_2Ca$$

All attempts to prepare a SF_5-containing sulfonic acid salt by analogy to the above reactions by using SO_2F_2 with (perfluorovinyl)sulfur pentafluoride ($SF_5CF{=}CF_2$) failed.

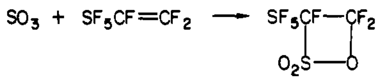
Sulfur trioxide reacts with fluoro olefins producing β-sultones.[5] Rearrangement of β-sultones to sulfonyl fluorides followed by addition of base should produce salts of sulfonic acids that upon acidification will yield the desired sulfonic acid. We report that this route is effective in producing the first SF_5-containing β-sultone, sulfonyl fluoride, sulfonic acid, and sulfonate salts.

Results and Discussion

The novel pentafluorosulfur β-sultone, 2-hydroxy-1-(pentafluoro-λ^6-sulfanyl)-1,2,2-trifluoroethanesulfonic acid sultone (I)

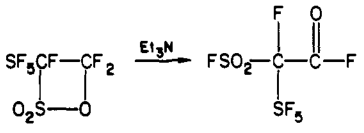


was prepared by reacting $SF_5CF{=}CF_2$ with distilled sulfur trioxide in a modified Carius tube under pressure and with mild heating (up to 100 °C):



I

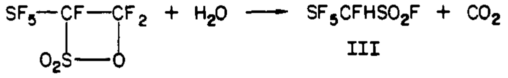
The β-sultone (I) is a colorless stable liquid that boils at 88 °C. Treatment of this sultone with a catalytic amount of triethylamine brought about a quantitative rearrangement to 2-(fluorosulfonyl)-2-(pentafluoro-λ^6-sulfanyl)-2-fluoroacetyl fluoride (II):



II

Possible mechanisms for the formation and rearrangement reactions are given in Scheme I.

An attempt to prepare the corresponding 2-(fluorosulfonyl)-2-(pentafluoro-λ^6-sulfanyl)-2-fluoroacetic acid derivative ($FSO_2CF(SF_5)COOH$) by reacting the β-sultone with water failed. Instead, the following reaction occurred, producing hydryl(pentafluoro-λ^6-sulfanyl)fluoromethanesulfonyl fluoride (III):



The mechanism in Scheme II is suggested to explain the formation of the sulfonyl fluoride.

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(1) Portland State University. (b) University of Idaho.
(2) Haszeldine, R. N.; Kidd, J. M. *J. Chem. Soc.* **1954**, 4228.
(3) Gramstad, T.; Haszeldine, R. N. *J. Chem. Soc.* **1957**, 2640.
(4) Temple, S. *J. Org. Chem.* **1968**, *33*, 344.
(5) England, D. C.; Dietrich, M. A.; Lindsey, R. V. *J. Am. Chem. Soc.* **1960**, *82*, 6181.

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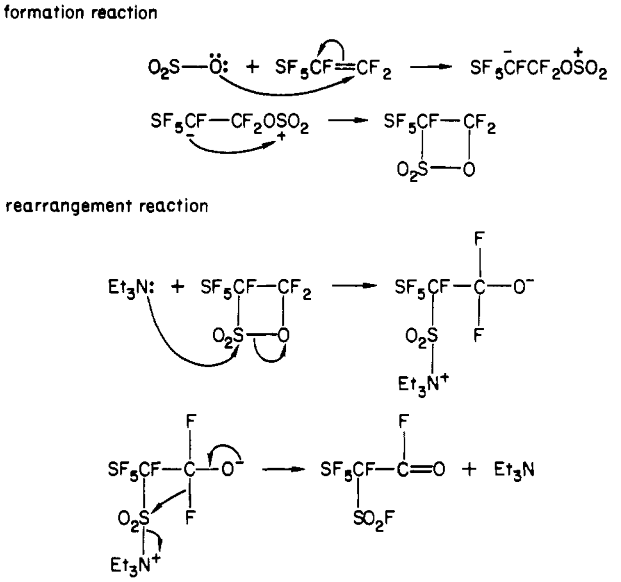
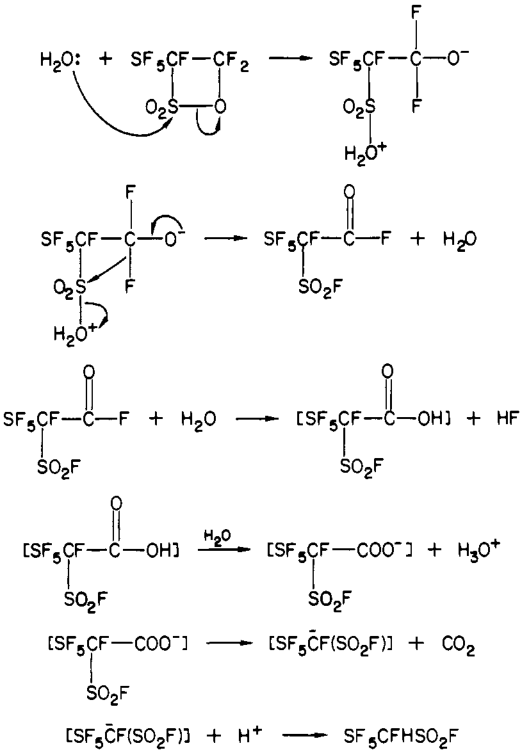
Scheme I



Scheme II



It was not possible to isolate the unstable formic acid intermediate. In a separate experiment, the reaction of $SF_5CF(SO_2F)C(O)F$ with water produced SF_5CFHSO_2F, CO_2, and HF. Although $SF_5CF(SO_2F)COF$ is hydrolytically unstable, it is thermally stable.

Treatment of the β-sultone (I) with a base, either $Ca(OH)_2$ or NaOH, produced the corresponding calcium or sodium hydryl(pentafluoro-λ^6-sulfanyl)fluoromethanesulfonates:

$$\mathrm{I} + Ca(OH)_2 \rightarrow \underset{\mathrm{IV}}{Ca(SF_5CFHSO_3)_2} + (CaF_2 + CaCO_3 + H_2O)$$

$$\mathrm{I} + NaOH \rightarrow \underset{\mathrm{V}}{Na(SF_5CFHSO_3)} + (NaF + Na_2CO_3 + H_2O)$$

The sulfonyl fluoride, SF_5CFHSO_2F (III), can be used in place of the β-sultone with $Ca(OH)_2$ to form the calcium salt.

$$2\mathrm{III} + 2Ca(OH)_2 \rightarrow Ca(SF_5CFHSO_3)_2 + CaF_2 + 2H_2O$$

The calcium or sodium salt with sulfuric acid gave an SF_5-containing sulfonic acid, hydryl(pentafluoro-λ^6-sulfanyl)fluoromethanesulfonic acid.

$$\mathrm{IV\ or\ V} + H_2SO_4 \rightarrow \underset{\mathrm{VI}}{SF_5CFHSO_3H} + CaSO_4\ (Na_2SO_4)$$

III does not react with water to form VI.

The infrared spectra for these derivatives have a common feature the presence of the SF_5 group and its characteristic infrared absorption bands. Cross and co-workers[6] reported that for compounds containing the SF_5 group the most intense bands should occur in the region 850–920 cm^{-1} (S–F stretching modes) and in the region 600 cm^{-1} (S–F deformation modes). For the new compounds reported in this paper, absorption bands in the 844–914-cm^{-1} region are assigned to the S–F stretching vibrations. The S–F deformation modes are found in 586–610-cm^{-1} region. The stretching vibration of the C–F group appears to be located in the 1096–1156-cm^{-1} region. In general, it is expected that for compounds containing a single C–F bond this absorption will be in the 1000–1110-cm^{-1} region.[7] For SF_5CFHCF_3, the C–F stretching vibration for the C–F group is assigned to the band at 1161 cm^{-1}.[8]

The other functional groups also exhibit characteristic absorption bands. The carbonyl band in $SF_5CH(SO_2F)COF$ is found at 1884 cm^{-1} and agrees closely with that found for $SF_5CF(CF_3)COF$.[9] The asymmetric and symmetric $-SO_2-$ bands in I–III can be tentatively assigned to the regions 1448–1472 and 1214–1250 cm^{-1}, respectively. This assignment is complicated by the appearance of strong carbon–fluorine absorption bands, particularly for the β-sultone, but, in any case, the above assignment agrees closely with that found for CF_3SO_2F and other sulfonyl derivatives.[9] For the sulfonyl fluoride group, the strong S–F absorption band is located near 786 cm^{-1} and is in the region found for other sulfonyl fluorides.[10] This band disappears when the acid/salts are formed from SF_5CFHSO_2F. The asymmetric and symmetric SO_3 bands for the sulfonic acid and salts are found in the 1220–1276- and 1052-1100-cm^{-1} regions, respectively (for salts containing the $CF_3SO_3^-$ group the respective regions are 1266–1279 and 1025–1042 cm^{-1}).[11] The C–H absorption bands for III–VI are located near 3000 cm^{-1} (for SF_5CFHCF_3 the C–H stretching frequency was located at 3007 cm^{-1}).[8]

The mass spectra for these compounds did not contain molecular ions, but appropriate fragment ions were found. The highest positive fragment ions were as follows: for I, $(M - 3F)^+$ and $(M - SO_3)^+$; for II, $(M - SF_5)^+$; for III, $(SF_5)^+$. The positive and negative ion spectra for the acid showed fragments not only for the monomer but for the dimer as well; the highest negative ion found for the monomer was $(M - H)^-$.

The NMR spectra (see Table I for chemical shift values) generally consist of complex multiplets. However, for some, first-order coupling constants could be determined, and these are listed in Table II.

The SF_5 fluorine resonance consists 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 reported $J_{1,3}$ coupling is the observed doubling of the nine-line A pattern

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(6) Cross, L. H.; Cushing, G.; Roberts, H. L. *Spectrochim. Acta* **1961**, *17*, 344.

(7) Brown, J. K.; Morgan, K. J. *Adv. Fluorine Chem.* **1965**, *4*, 256.

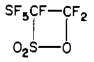
(8) Efner, H. F.; Kirk, R.; Noftle, R. E.; Uhrig, M. *Polyhedron* **1982**, *1*, 723.

(9) DeBuhr, R.; Howbert, J.; Canich, J. M.; White, H. F.; Gard, G. L. *J. Fluorine Chem.* **1982**, *20*, 515.

(10) Ham, N. S.; Hambly, A. N.; Laby, R. H. *Aust. J. Chem.* **1960**, *13*, 443.

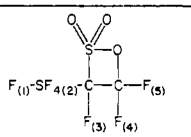
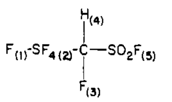
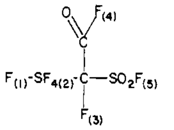
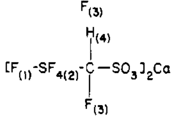
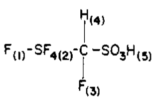
(11) Robinson, E. A. *Can. J. Chem.* **1961**, *39*, 247.

Table I. NMR Chemical Shifts[a]

compd	SF(ax)	SF_4(eq)	CF_2	CF	SO_2F	C(O)F	CH
 (I)	62.7	57.0	−80.6 (w) −81.8 (s) −83.0 (s) −84.2 (w)	−116.9			
$SF_5CF(SO_2F)COF$ (II)	59.9	58.6		−122	51.8	30.4	
SF_5CFHSO_2F (III)	65.2	55.2		−152	51.3[b]		6.31[c]
$Ca(SF_5CFHSO_3)_2$ (IV) in D_2O	77.5	55.6		−151.6			5.67
SF_5CFHSO_3H[d] (V) in CD_3CN	72.3	53.5		−153.2			5.43

[a] Fluorine chemical shifts in ppm from $CFCl_3$ and proton chemical shifts in ppm downfield from internal Me_4Si. [b] For CF_3CHFSO_2F the chemical shifts (ppm) are[13] SO_2F (+50.5) and CF (−189). [c] δ values:[13] $CF_2BrC\mathit{H}FSO_2F$, 5.84; $CF_2(OCH_3)C\mathit{H}FSO_2F$, 5.68; $CF_3C\mathit{H}FSO_2F$, 3.86. [d] The chemical shift for the proton of $-SO_3H$ is δ 11.37.

Table II

compd	coupling const, Hz	
	$J_{1,2} = 156.6$	
	$J_{1,2} = 141.3$ $J_{1,3} = 2.3$ $J_{2,4} = 4.8$	$J_{2,5} = 8.2$ $J_{3,4} = 42.9$
	$J_{1,2} = 100.1$ $J_{2,5} = 8.7$ $J_{3,4} = 19.6$	
	$J_{1,2} = 155.1$ $J_{1,3} = 2.5$ $J_{2,3} = 1.4$	$J_{2,4} = 5.1$ $J_{3,4} = 42.2$
	$J_{1,2} = 146.3$ $J_{1,3} = 2.5$ $J_{2,4} = 5.1$	$J_{2,4} = 5.1$ $J_{3,4} = 42.3$

and is assumed to be due to SF(ax) to CF(*vic*) coupling. Because of the complexity of the CF resonance, unambigous confirmation of the assignment cannot be documented. For III, IV, and VI the $J_{2,4}$ and $J_{3,4}$ values are consistent. The proton spectrum in each case is a doublet of pentets. The carbon–fluorine resonance is also a doublet of multiplets with a $J_{3,4}$ value around 42 Hz. The SF_5CFHCH_3, the $J_{3,4}$ ($J_{F,H}$) coupling value was found to be 43.5 Hz.[12] For the acid fluoride, II, the CF resonance consists of two poorly resolved multiplets with a doublet separation of 19.6 Hz. In $SF_5CF(CF_3)COF$, this coupling was found to be ~18 Hz.[9] The NMR spectrum of the β-sultone is complex, but there are several interesting features: (1) Only one isomer is present as the spectrum consists of single sets of resonances for the SF_5, CF, and CF_2 groups. (2) The CF_2 group that is present in an unsymmetrical ring exhibits a weak–strong–strong–weak combination of peaks (this pattern was observed for other fluorinated sultones[5]). (3) The NMR spectrum cannot unambiguously determine which isomer is present, but due to the fact that the rearranged product obtained by treating the β-sultone with Et_3N is $SF_5CF(COF)SO_2F$ and not $SF_5C(O)CF_2SO_2F$ or $FC(O)CF_2SO_2F$, it is possible to establish its structure as $SF_5CFCF_2OSO_2$.

Experimental Section

Materials. The compounds used in this work were obtained from commercial sources: SO_3, CsF, SO_2F_2 (Union Carbide); $(CH_3CH_2)_3N$ (MCB); CH_3CN (dry), diglyme (dry), NaOH, CaO (Mallinckrodt); fuming H_2SO_4, 95% H_2SO_4 (Baker). Except for SO_3, which was vacuum distilled, all reagents were used without further purification. $SF_5CF{=}CF_2$ was synthesized by literature methods.[14]

General Procedure. Gases were manipulated in a conventional Pyrex vacuum apparatus equipped with a Heise–Bourdon tube gauge and a Televac thermocouple gauge. Infrared spectra were obtained by using a 8.25-cm Monel cell with KBr or KRS-5 windows or as solids between KBr, KRS-5, or NaCl disks on a Perkin-Elmer 476 spectrometer. The spectra were calibrated with a polystyrene film. The NMR spectra were recorded with a Varian Model EM-390 spectrometer operating at 90.0 MHz for proton and 84.67 MHz for fluorine resonances. Me_4Si and F-11 were used as internal standards. The mass spectra were taken on a CEC 21-110 B double-focus mass spectrometer equipped with a 6-kV ion accelerator and operated at 70 V. Perfluorokerosene (PFK) was used as an internal standard.

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

Preparations. $SF_5CFCF_2OSO_2$ (I). To a 130-mL Carius tube equipped with a Kontes Teflon stopcock were added 88 mmol of freshly distilled SO_3 and 76 mmol of $SF_5CF{=}CF_2$. The vessel was warmed slowly to 80 °C over a period of 6 h and then heated at 100 °C for 36 h. Distillation of the mixture gave 43.7 mmol of the sultone: 58% yield; bp 88 °C (757 mm). The infrared spectra gave the following absorption bands (cm^{-1}): 1448 (s, with sh at 1460 and 1438), 1372 (w), 1346 (w), 1304 (s), 1240 (vs), 1214 (vs with sh at 1158), 1096 (s), 1020 (m), 896 (vs), 854 (vs), 788 (s), 692 (mw), 654 (ms), 632 (w), 610 (ms), 596 (ms), 570 (m), 532 (ms), 476 (w), 460 (w), 386 (vw).

The ^{19}F NMR spectrum (φ) gave the following relative peak areas: SF (1.0), SF_4 (3.9), CF (1.0), CF_2 (1.9). A molecular ion was not observed, but other appropriate fragment ions were found. Mass spectrum (*m/e*): 231 $(M - 3\ F)^+$, 219 $(M - CF_3)^+$, 208 $(M - SO_3)^+$, 181 $(M - CF_3 - 2\ F)^+$, 161 $(M - SF_5$ or $C_2F_3OS_2)^+$, 129 $(C_2F_3OS)^+$, 127 $(SF_5)^+$, 113 $(C_2F_3S)^+$, 108 $(SF_4)^+$, 101 $(SF_3C)^+$, 100 $(C_2F_4)^+$, 97 $(C_2F_3O)^+$, 89 $(SF_3)^+$, 81 $(C_2F_3)^+$, 80 $(SO_3)^+$, 70 $(SF_2)^+$, 69 $(CF_3)^+$, 66 $(COF_2)^+$, 64 $(SO_2)^+$, 60 $(SOC)^+$, 51 $(SF)_+$, 50 $(CF_2)^+$, 48 $(SO)^+$, 47 $(COF)^+$, 32 $(O_2\ S)^+$, 31 $(CF)^+$. Anal. Calcd: C, 8.34; F, 52.75. Found: C, 8.44; F, 52.4.

$SF_5CF(SO_2F)COF$ (II). To a 50-mL Pyrex vessel equipped with a Kontes Teflon valve and a Teflon-coated stirring bar were added 9.27 mmol of I and 0.25 mmol of Et_3N. The reaction mixture was allowed to warm slowly to 0 °C and maintained at 0 °C (18 h) and room temperature (3.5 h). The colorless liquid, $SF_5CF(SO_2F)COF$ (8.9 mmol), was formed in 96% yield. The infrared spectrum gave the following absorption bands (cm^{-1}): 1884 (s), 1472 (s) 1248 (m), 1232 (m), 1218 (m), 1148 (s), 904 (vs with sh at 934 and 962), 860 (s), 820 (m), 788 (s), 704 (w) 698 (w), 648 (w), 612 (w), 586 (s with sh at 576), 490 (w), 440 (w, b).

The ^{19}F NMR spectrum (φ) gave the following relative peak areas: SF_5 (4.9), C(O)F (1), SO_2F (1). A molecular ion was not observed, but other appropriate fragments were found. Mass spectrum (*m/e*): 161 $(M - SF_5)^+$, 149 $(SF_3CSO)^+$, 142 $(M - SF_6)^+$, 129 $(C_2F_3OS)^+$, 127 $(SF_5$ or $CFO_2S_2)^+$, 113 $(C_2F_3S)^+$, 108 $(SF_4)^+$, 101 $(SF_3C)^+$, 97 $(C_2F_3O)^+$, 89 $(SF_3)^+$, 91 $(C_2FOS)^+$, 83 $(SO_2F)^+$, 70 $(SF_2)^+$, 67 $(SOF)^+$, 64 $(SO_2)^+$, 60 $(SOC)^+$, 51 $(SF)^+$, 48 $(SO)_+$, 47 $(COF)^+$, 32 $(S)^+$, 31 $(CF)^+$. Anal. Calcd: 8.34; F, 52.75. Found: C, 8.47; F, 52.3.

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(12) De Marco, R. A.; Fox, W. B. *J. Fluorine Chem.* **1978**, *12*, 137.

(13) Dean, R. R.; Lee, J. *Trans. Faraday Soc.* **1968**, *64*, 1409.

(14) Steward, J.; Kegley, L.; White, H. F.; Gard, G. L. *J. Org. Chem.* **1969**, *34*, 760.

SF_5CFHSO_2F (III) from I. To a 40-mL Kel-F vessel equipped with a Teflon top and Whitey stainless-steel valve were added I (8.4 mmol) and H_2O (12 mmol). The reaction mixture was allowed to warm slowly to room temperature prior to heating at 50–60 °C for ~60 h. The materials, which were volatile at −78 °C (CO_2 and HF), were periodically removed from the reaction vessel. The product, SF_5CHFSO_2F (5.6 mmol), was formed: 67% yield; bp 78 °C (755 mm). Mol wt: calcd 242; found 243. The infrared spectrum gave the following absorption bands (cm^{-1}): 2994 (vw), 1470 (s), 1250 (m with sh at 1270), 1226 (m with sh at 1212), 1156 (ms), 914 (vs), 892 (vs), 828 (mw), 784 (s), 728 (mw), 678 (m), 620 (w), 586 (s), 504 (w), 468 (w), 438 (vw).

The ^{19}F NMR spectrum (ϕ) gave the following relative peak areas: SF (1.0), SF_4 (4.1), CF (1.0), SO_2F (1.0). A molecular ion was not observed, but other appropriate fragments were found. Mass spectrum (*m/e*): 127 $(SF_5)^+$, 108 $(SF_4)^+$, 101 $(SF_3C)^+$, 89 $(SF_3)^+$, 83 $(SO_2F, CHF_2S)^+$, 67 $(SOF)^+$, 64 $(SO_2, CHFS)^+$, 51 $(SF)^+$, 48 $(SO)^+$, 44 $(SC)^+$, 32 $(CHF, S, O_2)^+$, 31 $(CF)^+$. Anal. Calcd: C, 4.96; H, 0.42; F, 54.92. Found: C, 4.95; H, 0.45; F, 54.6.

SF_5CFHSO_2F (III) from II. To a 35-mL Kel-F vessel equipped with a Teflon top and Whitey stainless-steel valve were added 4.06 mmol of III and a total of 5.0 mmol of water. The reaction mixture was stirred under ambient conditions for 18 days. The product, 4.06 mmol of SF_5CFHSO_2F, was separated from HF and CO_2 as mentioned above; yield 100%. The infrared spectrum agreed with that found previously.

$Ca(SF_5CHFSO_3)_2$ (IV) from I. To a 25-mL Pyrex reaction vessel equipped with a Teflon stirring bar and Pyrex stopper were added 6.4 mmol of I, 0.96 mol of H_2O, and 13.2 mmol of CaO. After the mixture was stirred for 25 h, solid CO_2 was added to the mixture in order to precipitate unreacted CaO. The resulting mixture was filtered and $Ca(SF_5CHFSO_3)_2$ was recovered from the filtrate by removing the H_2O under vacuum. The white solid did not melt but decomposed at ~350 °C. The infrared spectrum gave the following absorption bands (cm^{-1}): 2999 (vw), 1316 (m), 1268 (s) 1236 (s with sh at 1250), 1144 (m), 1100 (m with sh 1086), 888 (s), 858 (s), 824 (m), 722 (m), 670 (m), 636 (m), 598 (m), 582 (w), 570 (w), 564 (w), 512 (w), 454 (w), 406 (w), 384 (m).

The ^{19}F NMR spectrum (ϕ) gave the following relative peak areas: SF (1.1), SF_4 (4.0), CF (1.0). Anal. Calcd: C, 4.63; H, 0.39; F, 43.98. Found: C, 4.86; H, 0.44; F, 43.8.

$Ca(SF_5CFHSO_3)_2$ (IV) from III. To a 25-mL Pyrex reaction vessel equipped with a Teflon stirring bar and Pyrex stopper were added 0.87 mmol of III and an excess of a saturated $Ca(OH)_2$ solution. After the mixture was stirred for ~1 h at room temperature, solid CO_2 was added in order to precipitate out any unreacted $Ca(OH)_2$ as $CaCO_3$. The mixture was filtered, and the filtrate was heated to evaporate off the water. IV was obtained in a 10% yield. The infrared spectrum agreed with that previously found by reacting I directly with CaO in water.

$Na(SF_5CFHSO_3)$ (V). To a 50-mL Pyrex glass round-bottomed flask that contained a Teflon-coated stirring bar were added 17.8 mmol of I, 25 mL of H_2O, and 56.2 mmol of NaOH. The mixture was allowed to stir for 3 days under ambient conditions prior to neutralization with 98% H_2SO_4. V, along with NaF and Na_2SO_4 (total weight 5.44 g), was recovered by removing the water under vacuum transfer. The infrared spectrum gave the following absorption bands (cm^{-1}): 3001 (vw), 1312 (m), 1276 (s), 1252 (s), 1230 (s), 1124 (m, with sh at 1140), 1072 (ms), 884 (s), 844 (s), 814 (m), 712 (m), 664 (w), 634 (mw), 594 (mw), 578 (w,sh), 548 (w), 528 (w).

SF_5CFHSO_3H (VI). To a 25-mL Pyrex glass round-bottomed flask equipped with a Teflon stirring bar were added 5.28 g of a mixture of V, NaF, and Na_2SO_4 (4.7 g or 17.9 mmol SF_5CFHSO_3Na) and 42.2 mmol of 100% H_2SO_4. The mixture was slowly distilled under reduced pressure, giving 2.56 (10.7 mmol) of the clear colorless acid, SF_5CFHSO_3H: yield 60%; bp 89–90 °C (0.15 mm). When $Ca(SF_5CHFSO_3)_2$ was reacted in place of SF_5CFHSO_3Na, the acid was obtained in 68% yield. The infrared spectrum gave the following absorption bands (cm^{-1}): 2990 (vw), 1383 (vw), 1313 (mw), 1250 (s, b), 1220 (s), 1113 (m), 1052 (ms), 870 (vs, b), 814 (m), 714 (ms), 660 (mw), 630 (ms), 587 (ms), 550 (mw), 522 (mw), 455 (w), 400 (w).

The ^{19}F NMR spectrum (ϕ) gave the following relative peak areas: SF (1.0), SF_4 (4.1), CF (1.0). In the negative ion mass spectrum, a molecular ion was not observed, but other appropriate negative ions were found. Mass spectrum (*m/e*): 239 $(M - H)^-$, 127 $(SF_5)^-$, 114 $(M + H - SF_5)^-$, 113 $(HFCSO_3H)^-$, 112, $(FCSO_3H)^-$, 108 $(SF_4)^-$, 101 $(SF_3C)^-$, 94 $(HCSO_3H)^-$, 93 $(CSO_3H)^-$, 89 $(SF_3)^-$, 83 $(SF_2CH)^-$, 81 $(SO_3H)^-$, 80 $(SO_3)^-$, 76 $(CSO_2)^-$, 70 $(SF_2)^-$, 64 $(SFCH, SO_2)^-$. Other fragment ions due to an acid dimer were present in small amounts. Anal. Calcd: C, 5.00; H, 0.84; F, 47.47. Found: C, 5.18; H, 0.81; F, 47.7.

III and H_2O. To a 40-mL Kel-F vessel with a Teflon top and Whitey stainless-steel valve were added 1.69 mmol of III and 2.22 mmol of H_2O. The reaction vessel was heated at 55 °C (58 h) and at 90–100 °C (35 h). Under these conditions, no reaction was observed.

$SF_5CF{=}CF_2$ and SO_2F_2. To a 75-mL stainless-steel Hoke vessel equipped with a Whitey high-pressure stainless-steel valve was added 56 mmol of CsF. The CsF was dried under vacuum at ~140 °C. to the dried CsF were added 177 mmol of predried diglyme, 41.2 mmol of $SF_5CF{=}CF_2$, and 40.7 mmol of SO_2F_2. The reaction mixture was heated at ~120 °C (10 h) with frequent shaking. The major products found via their characteristic infrared spectrum were SO_2F_2, diglyme, SF_4, and a fluorocarbon substance. If acetonitrile is used as the solvent, the major products were SO_2F_2, CH_3CN, and SF_5CFHCF_3.

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Synthesis, Structure, and Electronic Features of (μ-Sulfido)bis[(*N*,*N'*-ethylenebis(salicylaldiminato))iron(III)], $[Fe(salen)]_2S$, Containing the Only Authenticated Example of the Fe(III)–S–Fe(III) Single Bridge

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In a continuing investigation of sulfido-bridged iron complexes, the previously reported title compound was prepared by a new method, the reaction of $[Fe(salen)]_2O$ and $(Me_3Si)_2S$ in dry DMF. $[Fe(salen)]_2S$ was obtained as a black solid that crystallizes in triclinic space group $P\bar{1}$ with a = 10.792 (2) Å, b = 11.746 (2) Å, c = 13.215 (3) Å, α = 110.56 (2)°, β = 99.23 (2)°, γ = 72.27 (2)°, and Z = 2. With use of 2720 unique data ($F_o^2 > 3\sigma(F_o^2)$) the structure was refined to R (R_w) = 4.33 (4.48). The molecule is binuclear with two $[Fe(salen)]^+$ half-dimers bridged by a sulfide atom. Ligands in the half-dimers are nonplanar and adopt the umbrella conformation; Fe–O and Fe–N bonds are of normal lengths. The Fe(III) atoms are displaced 0.591 and 0.625 Å from the least-squares N_2O_2 coordination planes toward the μ-S atom, forming pyramidal FeN_2O_2S units. The Fe–S–Fe bridge is unsymmetrical, with bond distances of 2.150 (2) and 2.190 (2) Å. The overall configuration of $[Fe(salen)]_2S$ is similar to that of its congeneric analogue $[Fe(salen)]_2O$ in its solvated and unsolvated crystalline forms. The Fe–S–Fe bridge angle of 121.8 (1)° is substantially smaller than the Fe–O–Fe angle (145°) in $[Fe(salen)]_2O$ and any other binuclear Fe(III) complexes containing an unsupported μ-oxo bridge. Magnetic susceptibility measurements at 22–291 K demonstrate that $[Fe(salen)]_2S$ is antiferromagnetic. Analysis of the data under the Hamiltonian $\mathcal{H} = -JS_1\cdot S_2$ provided an excellent fit with $J = -176$ cm^{-1} and g = 2.016. The most recent value for $[Fe(salen)]_2O$ is -178 cm^{-1}, showing essentially equal magnetic coupling of the two complexes when configured with the indicated bridge angles. A simple MO argument suggests that at equal bridge angles $[Fe(salen)]_2S$ may be the more strongly coupled. Isotropic ^1H NMR shifts are mainly contact in origin, and shift ratios with $[Fe(salen)]_2O$ indicate that hyperfine coupling constants at equivalent positions are different in the two complexes. In DMF solution $[Fe(salen)]_2S$ displays a S → Fe(III) charge-transfer band at 490 nm (ϵ_M 6930), similar to that of sulfide hemerythrin, and one-electron oxidation and reduction at −0.28 and −1.27 V vs. SCE, respectively. The reduction product has an oxidation level equivalent to that of the currently characterized state of sulfide hemerythrin. $[Fe(salen)]_2S$ is the only structurally authenticated example of a molecule with a Fe(III)–S–Fe(III) single bridge.

Introduction

The bridge unit Fe(III)–O–Fe(III) is a frequent constituent of synthetic iron complexes.[2] It has been stabilized at 4-, 5-, and 6-coordinate Fe(III) sites, with prominent examples of the first two types being $[Fe_2OCl_6]^{2-}$[3] and $[Fe(salen)]_2O$[4-9] and other complexes derived from salicylaldiminato ligands.[7,10-13] Complexes with unsupported bridges have varying Fe–O–Fe angles (~140–180°[3-6,10,11,14-16]) and are invariably antiferromagnetic with $-J \cong$ 180–230 cm^{-1}.[2,14,16] This bridge is of biological significance as well. Its presence has been established in several met forms of the invertebrate oxygen-binding protein hemerythrin[17] (Hr) by X-ray diffraction[17a,18] and EXAFS[19] investigations. Excellent models of the met-Hr active site have been prepared in which, as in the protein, the bridge is supported by two μ-RCO_2^- ligands.[20,21]

In contrast to the biological and extensive synthetic occurrence of the Fe_2O unit, the supported or unsupported single-bridge Fe(III)–S–Fe(III) has not been structurally authenticated. This Fe_2S unit poses a number of fundamental questions, including the value of the bridge angle and its variability and the transmission of electronic effects between half-dimers, compared to structurally analogous oxo-bridged complexes. Double bridges of this type have been shown to occur in, e.g., the extensively investigated antiferromagnetic dimers $[Fe_2(\mu\text{-}S)_2L_4]^{2-}$ (L = RS^-, halide).[22] Corresponding oxo-bridged complexes are unknown. An attempt to prepare a singly bridged 4-coordinate dimer from $[Fe_2OCl_6]^{2-}$ and hexamethyldisilathiane, a reagent shown to be useful for O → S ligand substitution,[23] resulted in the formation of known $[Fe_2S_2Cl_4]^{2-}$ in high yield in reaction 1.[23a] The only previously

$$[Fe_2OCl_6]^{2-} + 2(Me_3Si)_2S \xrightarrow{MeCN} [Fe_2S_2Cl_4]^{2-} + (Me_3Si)_2O + 2Me_3SiCl \quad (1)$$

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