to explicitly recognize two different NF_4^+ sites in the analysis. In this case, the actual spectral predictions may be obtained by a procedure that we have detailed elsewhere for the case of disorder.[3] In the latter case, the space group of each alternative ordered lattice is determined, and the spectral predictions are obtained by correlation between them. In the present case, in addition to the S_4 site-only space group for NF_4^+ ($P\bar{4}2m$, D_{2d}^1), we need the corresponding C_{2v} site-only space group, $Pmm2$ (C_{2v}^1), with $Z = 1$. We would expect correlation between D_{2d} and C_{2v} to give the spectral predictions—in particular, to predict a splitting of the degenerate E mode of the former. Such a splitting is reported in the ν(N-F) feature but not in the δ(N-F) feature.

We now turn to the BF_4^- anion. As noted by Christe et al.,[1] these anions are all arranged with one B-F bond parallel to the crystallographic z axis to within experimental error. Such an arrangement has been noted elsewhere, as have its significant spectroscopic consequences.[4] As far as the BF_4^- anion is concerned, then, it has 3-fold rotational symmetry about the local z axis. Surely no less important is that it occupies, to within about 1%, the S_4 site of the $P\bar{4}2m$ NF_4^+ lattice discussed above. That is, the BF_4^- anion is at a site of near-perfect 4-fold cation site symmetry; it is surely this combination of C_3 and C_4 coincident sites, leading to a 12-fold potential energy profile and the consequent low librational barrier, that is responsible for the large temperature coefficients reported for three of the fluorines of the BF_4^-—we have incipient disorder of the BF_4^- anions. Turning now to the vibrational properties of the BF_4^- anion, we note that both its own (C_3) and site (C_4) rotational symmetries preserve x,y degeneracy. To a first approximation, the fact that a C_3 molecule occupies a C_4 site is irrelevant—they are equivalent in that the modes and multipoles of the C_3 molecule have a 1:1 mapping onto the corresponding modes of a similar C_4 molecule—the "missing" modes of the latter are not of relevance. As far as the NF_4^+ is concerned, we could either work in terms of C_3 (or, more conveniently, C_{3v}) or C_4 (or, more conveniently, C_{4v})—the predictions do not differ. Herein lies, we believe, one aspect of the basis of Christe et al.'s choice of C_{3v} as the symmetry explaining the vibrational properties of the BF_4^- anion in $NF_4^+BF_4^-$. Vibrationally, the different orientations of the F_3BF^- group with respect to the crystallographic axes are unimportant. Irrespective of this orientation, for each F_3B unit, vectors parallel to x and y crystal axes exist—this is simply a restatement of the common x,y isotropy of C_3 and C_4. That is, $Z = 1$ not only for the NF_4^+ cations but also for the BF_4^- anions; no factor group effects are predicted and none observed. The second aspect of Christe's choice of C_{3v} symmetry is also explained. The correlation $T_d \rightarrow C_{3v}$ leads to a 2:1 splitting of T_2 modes and a 1:1 splitting of E (T_d) modes. The present example provides an even better example of the consequences of the C_{3v} orientation of a T_d group than does $(NH_4)_2SO_4$.[4]

Conclusion

In the present paper, we have presented an alternative explanation to that of Christe et al.[1] of the vibrational spectra of NF_4BF_4. It has been found possible to dispense with the emphasis placed on the rotational-oscillation motion of the BF_4^- anion by these authors. In so doing, we believe that we have restored physical meaning to those details of their X-ray results that they themselves doubted. In particular, we regard the presence of two crystallographically independent sets of NF_4^+ cations as entirely consistent with the spectroscopic data. The long wavelength of the radiation associated with infrared and Raman spectroscopies (implicitly assumed to be infinite, $k = 0$, when one applies the factor group method) means that vibrationally coupled molecules cannot be distinguished—their relative phases are locked together.

In contrast, diffraction methods involve wavelengths exploring a quite different part of k space, the difference in phase associated with the scattering from each of the vibrationally coupled molecules enabling a distinction between them. The present work underlines the fact that an assumption is involved when a crystallographic space group is taken to be that appropriate for a spectroscopic (and not just vibrational spectroscopic) analysis. In addition, we have suggested a method of analysis appropriate to structures in which one species occupies more than one site. Taken together with earlier work on disorder,[3] the present approach provides hope that disordered structures with multiple site occupancy may be amenable to vibrational analysis.

Acknowledgment. We are indebted to the EEC and NATO for partial financial support.

Registry No. $NF_4^+BF_4^-$, 15640-93-4.

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Preparation, Characterization, and Chemistry of $F_4S{=}\overline{CCF_2OS}O_2$

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Recently, we found a convenient route to synthesize the ketene $F_5SC(SO_2F){=}C{=}O$ (**1**) from the acyl fluoride $F_5SCH(SO_2F)COF$ (**2**) and the base $F_3B{\cdot}N(C_2H_5)_3$ (**3**).[1] In an attempt to prepare ketene **1** directly, the dehydrohalogenation of the sultone $F_5S\overline{CHCF_2OS}O_2$ (**4**) with base **3** was tried. Unlike as was found for the sultone $F_3C\overline{CHCF_2OS}O_2$,[2] where the sole product was the ketene $F_3CC(SO_2F){=}C{=}O$, a mixture of two compounds was obtained, ketene **1** and what has now been shown to be its isomer, $F_4S{=}\overline{CCF_2OS}O_2$ (**5**). Compound **5** is the first cyclic example of a novel class of compounds, the alkylidenesulfur tetrafluorides. We are now studying this compound, because it could serve as an important intermediate in the synthesis of a number of new sultones. Since sultones play an important part in the synthesis of sulfonic acids, esters, and polymers containing the SO_2F group, pathways to novel sultones are of interest.

The first member of the alkylidenesulfur tetrafluorides, methylenesulfur tetrafluoride, $CH_2{=}SF_4$, was obtained by Kleemann and Seppelt.[3-6] This compound undergoes facile addition reactions with the polar agents HF, HCl, HBr, ICl, HgF_2, and AsF_5 and with chlorine.[7] These additions are such that *cis*-SF_4X systems are obtained, in contrast to the *trans*-SF_4X compounds from the fluorination of (fluoroalkyl)sulfenyl chlorides.[8] Additional members of this series include $FC(O)CH{=}SF_4$,[9] $H_3CCH{=}SF_4$,[10] $F_3CCH{=}SF_4$, and $F_3CC(CH_3){=}SF_4$.[11,12]

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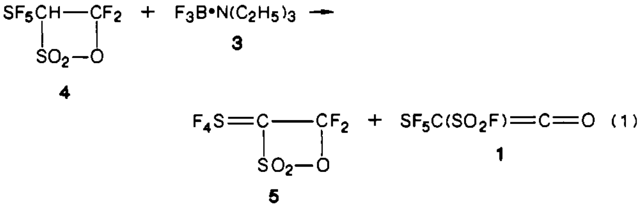
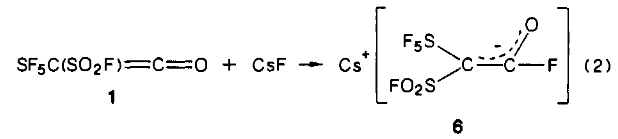
We now find that dehydrohalogenation of sultone **4** with **3** always gives a mixture of **1** and **5**. The ratio of these compounds remains nearly unchanged under a variety of conditions. When sultone **4** is heated with a slight or larger excess (0.1–0.4-fold) of base **3**, heated in the reaction for a longer time, reacted by slow addition of the hot base to its melt, or reacted in chloroform, the reaction produces the mixture of 30–35% **1** and 65–70% **5**:

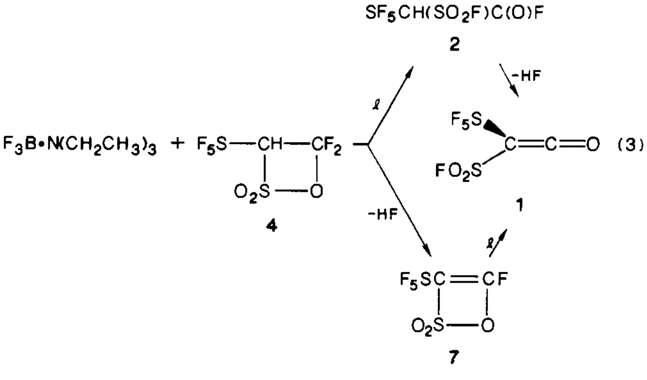


Separation of **1** and **5** is difficult, as their boiling points lie close together. A small quantity of pure **1** may be collected at 92 °C and pure **5** at 94 °C; however, most of the material decomposes during the distillation. Fortunately, we find that ketene **1** forms a stable addition complex, **6**, with CsF:[13]



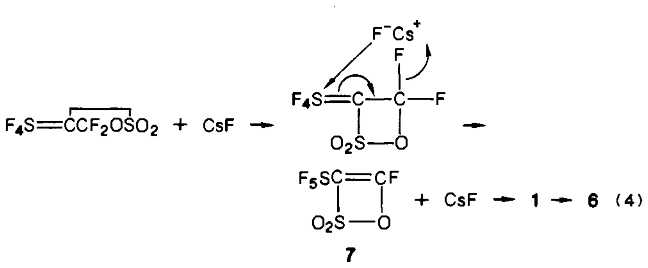
Treatment of the mixture of **1** and **5** with CsF removes **1**, allowing recovery of **5**. It is necessary to use very finely ground and thoroughly dried CsF to obtain a ketene-free product.

In eq 1, ketene **1** could be formed by several pathways. One possibility is the partial rearrangement of **4** to **2** by **3**, with subsequent HF removal. This is the route suggested by Russian investigators to account for the sole formation of ketene $F_3CC(SO_2F){=}C{=}O$ from sultone $F_3\overline{CCHCF_2OSO_2}$ and **3**.[2] Whereas this possibility cannot be excluded for eq 1, it may also be possible that HF is eliminated from **4** to give a ring-unsaturated sultone **7**, which then rearranges to **1**:



An intermediate similar to **7** was proposed in the formation of $t\text{-}C_4F_9C(SO_2F){=}C{=}O$ from $t\text{-}C_4F_9C{\equiv}CF$ and SO_3.[14] Also, **5** did not rearrange detectably to $F_4S{=}C(SO_2F)COF$ (**8**) or **1** in the presence of **3**; even prolonged heating of the reaction mixture did not alter the ratio of **1** and **5**.

When a mixture of **1** and **5** is treated with cesium fluoride, more $Cs^+[F_5SC(SO_2F)COF]^-$ (**6**) is found than can arise from **1**. Formation of **6** from **5** is confirmed in a separate experiment where pure **5** is treated with CsF. Thus, **5** may form an addition compound with CsF which subsequently rearranges to **1**:



Compound **5** is a stable colorless liquid with an unpleasant odor. It can be exposed to air for short times without decomposition. Hydrogen fluoride adds to **5**, giving sultone **4** in high yields:

$$\underset{\mathbf{5}}{F_4S{=}\overline{CCF_2OSO_2}} + HF \rightarrow \underset{\mathbf{4}}{F_5S\overline{CHCF_2OSO_2}} \qquad (5)$$

It is much more difficult to effect addition of HCl to **5**. At room temperature no reaction occurs; only after heating with an excess of gaseous HCl for nearly 100 h (68 °C) is reaction complete without significant byproduct formation:

$$\underset{\mathbf{5}}{F_4S{=}\overline{CCF_2OSO_2}} + HCl \xrightarrow{\Delta} \underset{\mathbf{9}}{ClSF_4\overline{CHCF_2OSO_2}} \qquad (6)$$

This contrasts very strongly with the ease of HCl addition to $H_2C{=}SF_4$.[7] It is assumed that the large sultone ring impedes the attack of HCl at the sulfur and the neighboring carbon atom. Compound **9** is a colorless liquid with a repugnant odor. Its ^{19}F NMR spectrum reveals three types of S–F fluorines in the ratio of 1:2:1, whereas the CF_2 group appears as an AB system with asymmetric coupling to the proton, analogous to sultone **4**.

The cesium salt (**6**), synthesized separately, is characterized by high chemical and thermal stability. In contrast to related compounds,[15] it is air stable: a sample was kept at ≈30 °C in an open container for several weeks without detected change. Its infrared spectrum contains a strong band at 1766 cm^{-1}, corresponding to the C=O stretching band of the COF group; relative to $F_5SCH(SO_2F)C(O)F$,[16] it is shifted 90 cm^{-1} toward lower frequency, as expected for an enolate type anion. The ^{19}F NMR spectrum is peculiar in that the SF_5– and the SO_2F– fluorines are strongly deshielded,[17] whereas the COF resonance appears, as expected, at a strongly shielded position.[15] These chemical shifts suggest that the negative charge is concentrated at the COF group, whereas the SF_5– and the SO_2F– groups seem to exert a +I effect. This compound, **6**, is also characterized by extreme solubility with minor decomposition in either acetone or acetonitrile and by virtual insolubility in methylene chloride. These latter properties may be used for its purification, as it can be precipitated from concentrated acetone solutions by addition of CH_2Cl_2. Compound **6** melts at a low temperature (148–151 °C).

For $F_4S{=}\overline{CCF_2OSO_2}$, as with the other $F_4S{=}C$, compounds, we find that the four fluorine atoms of the SF_4 group are rigidly bound; no evidence of exchange is observed in its ^{19}F NMR spectrum. The ^{19}F NMR spectrum of **5** (Figure 1a) can be described as an AA′BCXX′ system, which may be interpreted to a satisfactory degree with the aid of an NMR simulation program. Each line in the AA′BC spectrum shows an additional triplet splitting of different magnitude in the A, B, and C part of the spectrum. The CF_2 group appears roughly as a pentet, which can be explained by the couplings to the A, B, and C fluorines. The chemical shifts and couplings within the AA′BC system compare favorably with the quantities of the other known

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(13) It should be noted that compound **6** is the intermediate that would normally be expected in the rearrangement of **1** to the acyl fluoride $F_4S{=}C(SO_2F)C(O)F$ (**8**). This type of rearrangement is not observed here but is found in the reaction of CsF with $(F_3C)_2C{=}C{=}O$: England, D. C.; Krespan, C. G. *J. Am. Chem. Soc.* **1966**, *88*, 5582.

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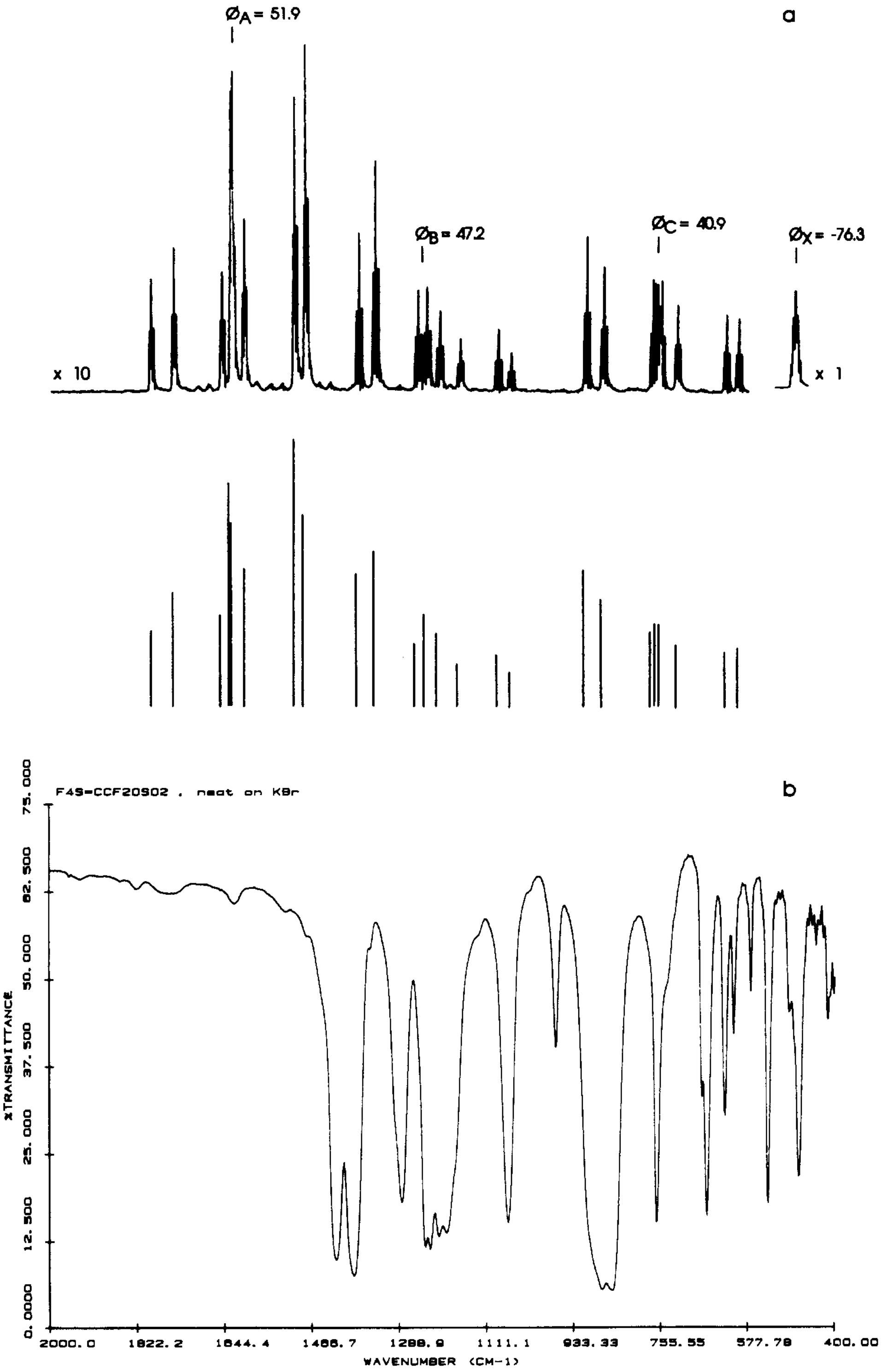
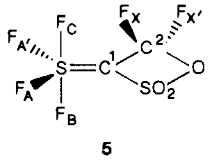


Figure 1. (a) ^{19}F NMR spectrum of **5** and (below) simulated ^{19}F NMR spectrum. In the line spectrum couplings to CF_2 are not included. (b) IR spectrum of **5**.

compounds of this type.[9-12] On this basis we now propose the following structure for **5**:



5

The ^{13}C spectrum of **5** reveals two resonance groups, one at 114.5 ppm and a weaker one at 80.7 ppm. From the intensities and the splitting patterns we assign the one at 80.7 ppm to C^1, as the absence of an attached spin one-half nucleus decreases relaxation, leading to partial saturation. The C^1 resonance appears approximately as a pentet of triplets; it is assumed that the four fluorines have coupling constants of comparable magnitude ($\approx$32 Hz) to C^1 which would account for the pentet splitting, while the triplet coupling (7.8 Hz) would arise from coupling to the fluorines at C^2. The other resonance signal (C^2) is a triplet of doublets. The triplet coupling (282 Hz) is nearly the same as in **4** (293 Hz)[16] and is attributed to the C^2–F couplings, and the smaller doublet coupling (23.2 Hz) is assumed to arise from (trans) C^2–F_B coupling. This latter coupling was unchanged on raising the sample temperature to 40 °C, implying that we are not resolving multiple ring conformations.

The ^{19}F NMR spectrum of **9** shows similarity to the spectrum of the only other known *cis*-ClF_4S compound[7] and is properly described as an ABCDXY system (X, Y = CF_2) with a chiral center. The interpretation of this NMR spectrum is not yet complete. Ring fluorines X, Y appear in the same region as in sultone **4** and exhibit the same pattern of an AB system with large geminal coupling and coupling of only one fluorine to the ring proton. The ^{13}C spectrum of **9** with proton coupling shows a triplet and two multiplets. Proton decoupling leads to the collapse of the two multiplets into one, at 109 ppm. This multiplet consists of nine lines, which show additional splitting and may now be assigned to C^1. The remaining resonances, from C^2, appear as four lines, the middle two of which overlap to produce a distorted triplet centered at 113.4 ppm. Extracted coupling constants are J_{C^1H} = 158 Hz, J_{C^2H} = 3 Hz, and J_{C^2F} = 294 Hz; the carbon-numbering system is analogous to that given for compound **5**.

The infrared spectra of **5** (see Figure 1b) and **9** are in accord with the proposed structures. Vibrational bands for the asymmetric and symmetric stretching modes of the SO_2 group are observed: 1415 and 1192–1235 cm^{-1} for **5** and 1430 and 1214 cm^{-1} for **9**. For the C=S bond a strong band in the 1200-cm^{-1} region is usually found.[6,10,11] This assignment is complicated by the presence of strong carbon–fluorine and SO_2 symmetric vibrational modes. Additional bands in the 800–900-cm^{-1} region (for **5** and **9**) are attributed to the S–F stretching modes of the SF_4 group.

Experimental Section

All manipulations were carried out in oven-dried glassware. Volatile materials were handled in a Pyrex-glass vacuum line, equipped with a mercury manometer and a Televac vacuum gauge. Sultone **4** and base **3** were made according to the literature.[16,18] Cesium fluoride was obtained from PCR. Infrared spectra were obtained from neat samples between KBr or NaCl plates on a Nicolet DX 20 spectrometer. Fluorine NMR spectra were run on a Varian EM-390 spectrometer at 84.67 MHz; ^1H and ^{13}C spectra were obtained on a General Electric QE-300 spectrometer at 300 and 75 MHz, respectively. The mass spectra were obtained on a VG 7070 mass spectrometer at 70 eV. Elemental analyses were carried out by Beller Mikroanalytisches Laboratorium, Göttingen, West Germany.

$F_4S{=}\overline{CCF_2OS}O_2$ (5). In a vacuum compartment consisting of two 50-mL round-bottom flasks connected by a transfer line with an outlet to a vacuum line, 9.63 g (35.7 mmol) of sultone **4** and 6.68 g of $F_3B\cdot N(C_2H_5)_3$ (39.5 mmol); were heated slowly with stirring in one of the 50-mL flasks at atmospheric pressure; the other flask was held at −196 °C. When the oil bath temperature reached 76 °C, the solution bubbled slightly and separated suddenly into two layers. Heating was continued for 2.5 min; the final temperature was 80 °C. The reaction flask was cooled (−196 °C), and the entire vacuum compartment was evacuated. The reaction flask was warmed to 60 °C for 45 min, while in the receiving flask, cooled to −196 °C, 8.45 g of product was collected; the product consisted (^{19}F NMR) of a mixture of two parts of **5** and one part of **1**. Yield of **1** + **5**: 94.8%.

Separation of 1 and 5. The crude material obtained above was transferred to a 30-mL reaction flask equipped with a Kontes Teflon valve containing 10.90 g (71.7 mmol) of comminuted cesium fluoride, shaken and kept at room temperature overnight. A second treatment with 8.58 g of CsF (56.4 mmol) at room temperature for 3 h removed the remaining ketene completely, leaving 4.02 g of almost pure **5**. Yield: 45.1% (with respect to **4**).

The cesium fluoride was rinsed with several small portions of acetone after the reaction, and a total of 4.97 g of $Cs^+[F_5SC(SO_2F)COF]^-$ was obtained; no other compound could be detected. To obtain a sample for analysis, part of the above volatile material was subjected to trap-to-trap distillation, where the traps were held at −10, −63, −110, and −196 °C. The material that was collected in the −63 °C trap (quantitative) was free of one impurity (ϕ = 73 ppm in the ^{19}F NMR spectrum). A second impurity (ϕ = 68 ppm in ^{19}F NMR spectrum, supposedly **5**) could be removed by heating the material recovered from the trap-to-trap distillation with a small amount of $F_3B\cdot N(C_2H_5)_3$ for a short time (0.5 min) followed by vacuum-transferring away **5**. A third impurity (ϕ = 70 ppm, probably $F_5SCH_2SO_2F$) could not be removed, but accounted for only 1%.

^{19}F NMR spectrum (neat sample, CCl_3F external), AA′BCXX′ spectrum: ϕ_A = 51.87, ϕ_B = 47.16, ϕ_C = 40.90, ϕ_X = −76.30 ppm. Integral A:B:C:X = 2.0:1.0:1.0:1.7. $J_{A'B} = J_{AB}$ = 161.8 Hz; $J_{AC} = J_{A'C}$ = 164.9 Hz. J_{BC} = 20.4 Hz; J_{AX} = 4.1 Hz; J_{BX} = 6.0 Hz; J_{CX} = 5.4 Hz.

^{13}C NMR (neat sample; $CDCl_3$ external): δ_1 = 80.7, (approximate p-t, $J_{SF_4C^1}$ = 31.6 Hz, $J_{CF_XC^1}$ = 7.8 Hz), δ_2 = 114.5 ppm (d-t, $J_{C^2F_X}$ = 282.4 Hz, $J_{C^2F_B}$ = 23.2 Hz).

Mass spectrum (electron impact, 70 eV; *m/e*, species, % abundance): 250, M^+ (^{32}S), 4.6; 184, $(M - COF_2)^+$, 1.3; 170, $(M - SO_3)^+$, 21.7; 165, $F_3SCSO_2^+$, 2.4; 151, $(M - SO_3 - F)^+$, 10.0; 145, $C_2F_3S_2^+$, 1.6; 143, $CFO_3S_2^+$, 1.4; 127, SF_5^+, $FSCSO_2^+$, 5.3; 113, $C_2F_3S^+$, 1.6; 105, OSF_3^+, 3.2; 94, $C_2F_2S^+$, 1.5; 91, C_2FOS^+, 4.4; 89, SF_3^+, 100; 83, SO_2F^+, 2.5; 82, CF_2S^+, 1.6; 70, SF_2^+, 10.9; 67, FOS^+, 6.6; 66, CF_2O^+, 1.9; 64, SO_2^+, 8.5; 63, CFS^+, 4.9; 62, $C_2F_2^+$, 1.0; 60, COS^+, 1.2; 51, SF^+, 3.4.

Infrared spectrum (neat, KBr, cm^{-1}): 1415 (s), 1379 (vs), 1282 (m), 1235 (s), 1225 (s), 1207 (s), 1192 (s), 1066 (s), 969 (m), 874 (vs), 857 (vs), 763 (s), 671 (m), 661 (s), 624 (m), 606 (w), 572 (w), 535 (s), 493 (w), 472 (s), 439 (w).

Anal. Calcd for $C_2F_6O_3S_2$: C, 9.60; F, 45.6; S, 25.63. Found: C, 9.23; F, 46.1; S, 25.39.

Reaction of 5 with HF. A 30-mL Kel F vessel was charged via vacuum transfer with 0.04 g of gaseous HF (2 mmol) and then with 0.34 g (1.4 mmol) of **5**. After the vessel was kept at room temperature for 16 h, it was cooled to −78 °C and the excess HF was pumped away through a cold trap (−196 °C). A total of 0.31 g of product was left behind. The ^{19}F NMR spectrum of this material ($CDCl_3$) showed two major products, whose resonances were coincident with those of sultone **4** and the compound $F_5SCH_2SO_2F$. Sultone **4** accounted for 80% of the spectral intensity, while the latter compound accounted for 18%. No **5** was left behind. The infrared spectrum of the neat sample was identical with that reported for **4**.[16]

Reaction of 5 with HCl. Into a 40-mL Carius tube containing 1.08 g of **5** (4.32 mmol) was condensed 19.8 mmol of hydrogen chloride. The vessel was heated to 68 °C (92 h) and chilled (−196 °C). Excess HCl was removed by pumping off volatiles at −78 °C through a cold trap (−196 °C). Finally, the reaction product was collected by vacuum transfer at room temperature with occasional warming. The crude product (0.93 g) contained two impurities that were probably **4** and $F_5SCH_2SO_2F$. They could be removed by trap-to-trap distillation (−30, −75, −100, −196 °C), leaving 0.78 g of **9** in the −30 °C trap. Yield: 63.0%.

Infrared spectrum (heat, KBr, cm^{-1}): 2992 (m), 1477 (vw), 1430 (s), 1317 (m), 1275 (m), 1214 (vs), 1178 (w), 1097 (m), 1076 (s), 958 (w), 886 (w), 853 (s), 835 (vs), 814 (s), 786 (s), 770 (msh), 743 (s), 658 (s), 642 (w), 610 (w), 589 (s), 561 (vw), 549 (w), 527 (m), 516 (m), 492 (vw), 478 (vw), 452 (w), 438 (w).

Mass spectrum (*m/e*, species, % abundance): 269, $(M - O)^-$, 3.0; 179, $(MH - Cl - O - 3F)^-$, 1.6; 177, $(M - HCl - O - 3F)^-$, 2.9; 167, $(M - HCl - SO_2F)^-$ (rearrangement), 13.5; 166, $(MH - HCl - F - COF_2)^-$, 3.9; 165, $(M - HCl - F - COF_2)^-$, 100.0; 161, $(M - HCl - 3F - 2O)^-$, 1.2; 144, $HCFO_3S_2^-$, 2.4; 143, $(M - ClSF_4)^-$, 6.1; 142, $(M - HCl - SF_4)^-$, 43.1; 127, SF_5^-, $FSCSO_2^-$, 17.0; 123, $(M - HCl - 5F - 2O)^-$, 2.0; 120, SF_4C^- 2.1; 108, SF_4^-, 5.5; 105, $C_2HOS_2^-$, 3.7; 101, CSF_3^-, 3.2; 99, HCF_2OS^- 11.3; 96, $CHFS_2^-$, 4.2; 94, $F_2SC_2^-$, 11.8; 89, SF_3^-, 11.4; 85, CF_3O^- (rearrangement), 5.1; 83, SO_2F^-, F_2SCH^-, 100.0; 79, $C_2HF_2O^-$, $CFOS^-$, 1.4; 78, $C_2F_2O^-$, 45.2; 76, C_2HFS^-, CSO_2^-, 12.6; 70, SF_2^-, 2.2.

^{19}F NMR (neat sample, CCl_3F external), ABCDXY system: ϕ_A = 141.7 (quartet, intensity = 1.0), ϕ_{BC} = 120.0 (m, intensity = 2.0), ϕ_D = 67.0 (m, intensity = 1.2), $\phi_{X(Y)}$ = −74.9 (d, intensity = 1.0), $\phi_{Y(X)}$ = −78.9 ppm (d-m, intensity = 1.1, J_{XY} = 100.8 Hz).

^1H NMR (neat sample, $CDCl_3$ external): δ = 7.09 ppm (m).

^{13}C NMR (neat sample, $CDCl_3$ external): ^1H coupled, δ = 113.4 (t, J_{C^2F} = 294 Hz), δ = 108.8 ppm (d-m, J_{C^1H} = 157.5 Hz); ^1H decoupled, δ = 113.4 (t), δ = 108.8 ppm (m). In the ^1H-coupled spectrum the lines of the triplet show further signs of coupling but were not resolved.

Preparation of $Cs^+[F_5SC(SO_2F)COF]^-$. Into a 30-mL Pyrex-glass reaction vessel, with a ground-glass cap and a side arm with a ground-glass stopcock, containing 3.0555 g of dried CsF (20.1 mmol) was added 2.62 g of distilled acetonitrile. Then 6.6535 g of **1** (26.6 mmol) was vacuum-transferred (−196 °C) into the reaction vessel. Upon reaching room temperature most of the CsF dissolved in a vigorous reaction causing the flask to warm. Dissolution slowed with time and was complete after 3.5 h of shaking. A slightly turbid and thick yellowed solution was obtained. Pumping away excess ketene **1** and solvent at room temperature through a cold trap (−196 °C) left 8.0795 g of an off-white solid. This corresponds to a ketene:CsF ratio of 0.9985 and a yield of 99.9%, mp 148–151 °C.

Infrared spectrum (neat, NaCl, cm^{-1}): 1766 (vs), 1395 (m), 1380 (m), 1257 (m), 1203 (s), 1077 (m), 948 (w), 864 (s), 843 (vs), 789 (vs), 747 (m), 726 (m), 705 (m), 666 (m), 616 (s), 584 (s), 569 (s).

^{19}F NMR spectrum, AB_4MX (acetone, CCl_3F external): ϕ_A = 92.3, ϕ_B = 79.5, ϕ_M = 68.5 (d-p, SO_2F), ϕ_X = 16.4 ppm (d-p, COF). Intensity

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A:B:M:X = 1.0:4.4:1.1:1.0. J_{AB} = 148.0 Hz; J_{BM} = 9.7 Hz; J_{BX} = 21.5 Hz; J_{MX} = 7.1 Hz.

Anal. Calcd for $C_2CsF_7O_3S_2$: C, 5.97; Cs, 33.06; F, 33.1; S, 15.95. Found: C, 6.00; Cs, 33.13; F, 33.6; S, 15.95.

Reaction of 5 and CsF. Finely ground cesium fluoride (2.80 g, 18 4 mmol) was dried (3 days, 115 °C, high vacuum) in a 20-mL Pyrex-glass reaction vessel, equipped with a Kontes Teflon valve. Then 0.19 g of **5** (0.76 mmol) was added by vacuum transfer (−196 °C); the vessel was maintained at 40 °C (19 h). The weight gain of the vessel was 0.16 g, after the volatile material had been removed by vacuum transfer. An infrared spectrum of the solid showed vibrational bands that were attributable to the complex $Cs^+[F_5SC(SO_2F)COF]^-$. A ^{19}F NMR spectrum of the acetone extract, which was obtained as described below, was also consistent with only the presence of the cesium compound.

The reaction mixture was rinsed several times with acetone (4 × 3 mL), the acetone extract was filtered, the filter residue was washed with several small portions of acetone, and the solution was brought to dryness, leaving 0.15 g of the cesium salt, **6**. Yield: 49.1%.

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Metal Complexes with Tetrapyrrole Ligands. 53.[1] ^1H NMR Spectrum of Dicerium(III) Tris(octaethylporphyrinate), $Ce_2(OEP)_3$: Evidence for Alkyl Group Steric Interaction

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The synthesis and single-crystal, solid-state structure of a novel dilanthanide tris(porphyrinate), $Ce_2(OEP)_3$, was previously reported.[3] In this triple decker each cerium atom is sandwiched between two octaethylporphyrin rings as illustrated in Figure 1. Two salient structural features are the strong C_{4v} doming of the outer OEP rings and the 24.5° staggering of adjacent OEP rings, both effects undoubtedly to relieve inter-ring alkyl crowding. This paper is concerned with the ^1H NMR spectrum of $Ce_2(OEP)_3$ in CCl_4, the analysis of the isotropic shifts of this paramagnetic binuclear metalloporphyrin, and the structural information that can be deduced regarding the extent of alkyl congestion and doming in solution. We also report the ^1H NMR spectra of the previously described homologues of Pr,[4] Nd,[5] Sm,[5] and Eu.[6]

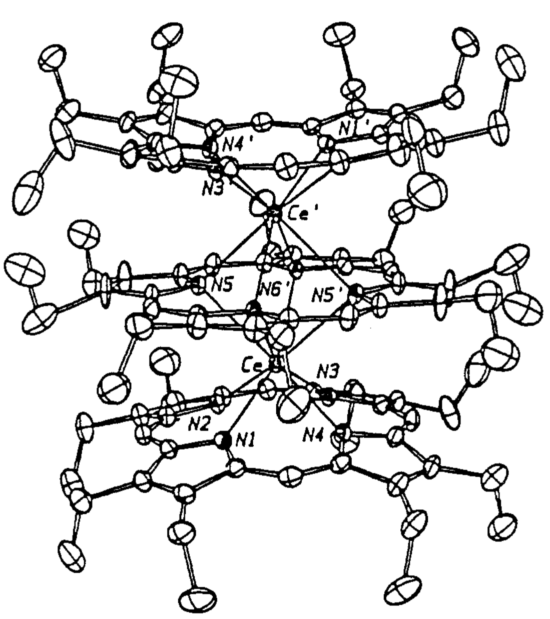

Figure 1. ORTEP plot of $Ce_2(OEP)_3$ (taken from ref 1 with permission).

Table I. $Ln_2(OEP)_3$ ^1H NMR Isotropic Shifts[a]

	CH_3		CH_2		meso	
	outer	inner	outer	inner	outer	inner
Ce	1.19	−7.59	−3.69 −2.82	−9.42	−4.72	−16.25
Pr	0.95	−5.93	−2.76 −2.04	−6.80	−7.28	−12.90
Nd	0.45	−2.79	−1.24 −0.72	−3.01	−3.53	−7.31
Sm	0	−0.63	−0.28 −0.32	−0.89	−0.39	−1.54
Eu	−0.61	2.16	−0.57 1.42	1.48	4.58	5.46

[a] Shifts are in ppm relative to $La_2(OEP)_3$ in CCl_4 at 293 K (see also ref 3).

The ^1H NMR spectrum of $Ce_2(OEP)_3$ was previously described.[3] The isotropic shifts relative to those of diamagnetic $La_2(OEP)_3$ are listed in Table I and are due to the presence of the paramagnetic Ce^{3+} ions. Two sets of OEP proton resonances are observed and attributed to the outer and inner OEP rings, respectively. Since the outer rings do not possess a symmetry plane, the outer ring α-CH_2 protons are diastereotopic and two resonances, separated by 0.87 ppm, result.

The observed isotropic shift ($\Delta H/H$) for any proton is the sum of two components: $\Delta H/H = (\Delta H/H)_{dip} + (\Delta H/H)_{con}$. The contact shift, $(\Delta H/H)_{con}$, is directly related to spin delocalization via covalency, whereas the dipolar shift, $(\Delta H/H)_{dip}$, results from a dipolar, through-space interaction and is a function of the magnetic anisotropy and geometry of the complex.[7] From numerous NMR studies of the interaction of organic substrates with lanthanide(III) chelates, commonly called "lanthanide shift reagents", it is accepted that ^1H NMR lanthanide-induced isotropic shifts are primarily dipolar in origin.[8,9] This seems especially certain for protons four or more bonds removed from the paramagnetic lanthanide ion.[10] We will proceed with this assumption for $Ce_2(OEP)_3$; hence, $\Delta H/H = (\Delta H/H)_{dip}$.

The dipolar shift for nuclei in complexes of axial symmetry is given by eq 1,[11] where $\chi_\parallel$ and $\chi_\perp$ represent the principal com-

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