of 2.45 Å and 2.35 Å are very close to the nearest-neighbor distance in elemental Si (2.34 Å). The intrachain Te–Te distances range from 3.840 (3) to 3.886 (3) Å; these are much longer than the nearest-neighbor Te–Te distance in the element (2.86 Å). The nearest-neighbor Te–Te interchain distances range from 3.815 (3) to 3.830 (5) Å, which are typical for Te–Te van der Waals bonding; interlayer Te–Te distances in the layered compound $TaTe_2$, for example, range from 3.527 (8) to 3.999 (10) Å.[9]

The silicon-centered square-antiprismatic tantalum chain found in Ta_4SiTe_4 is similar to that found in one type of Ta_5Si_3[10] that adopts the W_5Si_3 structure.[11] In this structure, the metal squares stack in a nearly antiprismatic Si-centered chain with additional W and Si atoms bonding between the chains. In comparison, Ta_4SiTe_4 is novel in that the tantalum silicon chains are surrounded by tellurium and are relatively isolated from one another.

It would be interesting to compare this structure with those of other ternary tantalum tellurides. However, the ternary tantalum tellurides have not been extensively investigated—only five have been reported in the literature—Cu_3TaTe_4,[12] Ag_2TaTe_3,[13] Mo_2TaTe_4,[14] $Ta_3Pd_3Te_{14}$,[15] and $TaNiTe_5$.[15] The Ta_4SiTe_4 structure is very different from any of these phases.

It is interesting to compare Ta_4SiTe_4 with other infinite chain structures, including $InMo_3Te_3$ and Ta_2S. The structure of $InMo_3Te_3$[16] consists of infinite chains of triangular Mo_3 monomer, edge-bridged by Te, which are stacked antiprismatically to form a one-dimensional metal atom network. Individual chains are separated by channels occupied by the ternary cation, In. The Ta_2S structure[17] contains infinite chains of a pentagonal Ta_5 monomer stacked antiprismatically. An additional Ta atom sits in the center of the pentagonal antiprism, similar to Si in the Ta_4SiTe_4 structure. The chains in Ta_2S are interconnected via sulfur atoms. The Ta_4SiTe_4 chain structure (antiprismatically stacked squares, Si centered) may be viewed as intermediate between $InMo_3Te_3$ (triangles) and Ta_2S (pentagons, Ta centered).

Since it was found that the new zirconium halide cluster phases could be synthesized with a wide variety of heteroatoms,[1-4] many of which adopt the same structure, we investigated whether other atoms could substitute for Si in the interstitial site. Results from X-ray powder diffraction indicate that Ta_4SiTe_4 is in fact just one member of a class of isostructural compounds with the general formula Ta_4ZTe_4, where Z = Cr, Fe, Co, Ni, Al, and Si. Furthermore, we have found,[18] by powder diffraction, that niobium forms an analogous class, Nb_4ZTe_4, with the same set of interstitial heteroatoms. A detailed study of these new phases will be the subject of a future publication.

In summary, we have synthesized a new material, Ta_4SiTe_4, which is one member of the new class of isostructural low-dimensional compounds, Ta_4ZTe_4. A comparative study of the properties of these phases, where only the stabilizing heteroatom is changing, should be interesting.

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Supplementary Material Available: A table of refined anisotropic thermal parameters for Ta_4SiTe_4 (1 page); tables of observed and calculated structure factors for Ta_4SiTe_4 (5 pages). Ordering information is given on any current masthead page.

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An Open Structure for the Adduct of Fluoride Ion with Oxalyl Fluoride

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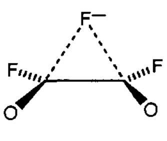
Stable, isolable tris(dimethylamino)sulfonium salts of the perfluoroalkoxides $FC(O)(CF_2)_nCF_2O^-$ (n = 0, 1, 3) and $^-OCF_2(CF_2)_nCF_2O^-$ (n = 1, 3) have been synthesized and characterized. The $C_2F_3O_2^-$ anion generated from oxalyl fluoride has an open ground-state structure $FC(O)CF_2O^-$ and not a bridged-fluoride structure as previously proposed. High-level ab initio calculations on the isomers of $C_2F_3O_2^-$, including vibrational spectra calculations, corroborate the open structure. The bridged structures for $C_2F_3O_2^-$ actually are transition states for intramolecular fluoride transfers.

Introduction

Ault has reported the synthesis of $C_2F_3O_2^-Cs^+$ by codeposition of CsF with oxalyl fluoride in an argon matrix.[1] On the basis of the analysis of the matrix infrared spectrum, the species produced were assigned the unusual symmetrically fluoride-bridged structures *cis*-**1** and *trans*-**1**, rather than the open structure **2**. These bridged anions were reported to rearrange to the trifluoroacetate anion, $CF_3CO_2^-$, upon warming the matrix to room temperature.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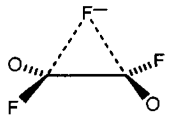
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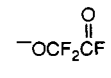
$$^-OCF_2\overset{\overset{O}{\|}}{C}F$$
2

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Ault's report coupled with our finding that tris(dialkylamino)sulfonium cations uniquely produce stable salts of diverse fluorinated anions, including perfluoroalkoxides[2] and fluoride-bridged hypervalent ions,[3] prompted us to investigate the reaction of $(TAS)(CH_3)_3SiF_2^-$ (TAS = tris(dimethylamino)sulfonium $([(CH_3)_2N]_3S^+)$) with oxalyl fluoride and homologous diacid fluorides as a possible way to synthesize isolable salts of $C_2F_3O_2^-$ and related fluoride ion adducts. We also performed high-quality ab initio calculations on the isomeric structures **1** and **2**, including calculations of their infrared spectra. The experimental and complementary theoretical results that substantiate an open structure **2** for the $C_2F_3O_2^-$ anion are described herein.

Experimental Section

Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, NY. ^{19}F NMR spectra were recorded on a Nicolet NT 200 spectrometer at 188.2 MHz, and the chemical shifts are reported in parts per million from $CFCl_3$. Infrared spectra were recorded on a Nicolet Model 60SX spectrophotometer. The IR data reported for the anion salts do not include any bands associated with or masked by the sulfonium counterion in the region of interest. The IR spectra (KBr) of the sulfonium bromides were recorded independently and show the following absorptions in the region of interest: tris(dimethylamino)sulfonium bromide ((TAS)Br),[4] 1475, 1459, 1453 cm^{-1}; tris(piperidino)sulfonium bromide ((TPS)Br), 1470, 1463, 1450, 1440 cm^{-1}.

Solvents with minimum water content are required for preparation and manipulation of the fluoride adducts reported here. Tetrahydrofuran and diethyl ether were distilled from sodium/benzophenone and stored over activated molecular sieves. All reactions were carried out in an atmosphere of dry nitrogen, and manipulations of the salts were performed in a Vacuum Atmospheres drybox. Commercial samples of oxalyl and hexafluoroglutaryl fluorides (PCR, Inc.) were redistilled prior to use. Difluoromalonyl fluoride was prepared by a procedure developed previously in our laboratory.[5]

Tris(dimethylamino)sulfonium Difluorohydroxyacetyl Fluoride(1−) ((TAS)2). A mixture of TAS trimethyldifluorosilicate (13.8 g, 50 mmol) and THF (50 mL) at −30 °C was treated slowly with oxalyl fluoride (3.0 mL). The mixture was allowed to warm to 25 °C, purged with N_2 for 45 min to remove excess oxalyl fluoride, and transferred to the drybox. Ether was added, and the white solid that precipitated was collected by filtration and dried to give 14.0 g (100%) of (TAS) **2**: mp 223 °C dec; ^{19}F NMR (DMF-d_7) δ −7.0 (brd s); ^{19}F NMR (CD_2Cl_2, −90 °C) δ −7.5 (brd s, $w_{1/2}$ = 145 Hz); IR (KBr) 1840, 1520 (brd) cm^{-1}. Anal. Calcd for $C_8H_{18}F_3N_3SO_2$: C, 34.65; H, 6.54; N, 15.15; F, 20.55; S, 11.56. Found: C, 34.63; H, 6.81; N, 15.07; F, 20.80; S, 11.75.

Tris(piperidino)sulfonium Difluorohydroxyacetyl Fluoride(1−) ((TPS)2). A mixture of tris(piperidino)sulfonium trimethyldifluorosilicate (2.20 g, 5.56 mmol) and THF (20 mL) at −20 °C was treated with oxalyl fluoride (0.5 mL, 9 mmol). The mixture was warmed to 25 °C and stirred for 1.0 h. A slow stream of N_2 was passed through the mixture for 1.0 h, and the solution was evaporated to give 2.2 g (100%) of crude product, which was recrystallized from THF/ether to afford 1.65 g of pure (TPS) **2**: mp 191–192 °C; ^{19}F NMR (CD_2Cl_2) δ −13.2 (brd s); IR (KBr) 1843, 1568, 1533, 1511 cm^{-1}. Reflectance IR spectra of the solid showed a C=O absorption at 1845 cm^{-1}. Anal. Calcd for $C_{17}H_{30}F_3N_3O_2S$: C, 51.37; H, 7.61; F, 14.34; N, 10.57; S, 8.07. Found: C, 51.10; H, 8.09; F, 14.24; N, 11.27; S, 8.21.

Crystals of (TPS)**2** were grown for X-ray analysis, but good-quality diffraction data could not be obtained.

Tris(dimethylamino)sulfonium 2,2,3,3-Tetrafluoro-3-hydroxypropanoyl Fluoride(1−) ((TAS)3). A mixture of TAS trimethyldifluorosilicate (11.0 g, 40 mmol) and THF (75 mL) at −30 °C was treated with difluoromalonyl fluoride (5.8 g, 3.5 mL, 40 mmol). The mixture was warmed to 25 °C, stirred for 0.5 h, and evaporated to give 13.1 g (100%) of white solid: mp 123–124 °C; ^{19}F NMR (DMF-d_7) δ −8.4 (brd s, 3 F), −115.8 (s, 2 F); IR (KBr) 1863, 1567, 1530 cm^{-1}. The Raman spectrum also featured a band at 1863 cm^{-1}. Anal. Calcd for $C_9H_{18}F_5N_3O_2S$: C, 33.03; H, 5.54; N, 12.84; F, 29.02; S, 9.80. Found: C, 33.49; H, 5.71; N, 13.20; F, 29.18; S, 9.97.

Bis[tris(dimethylamino)sulfonium] 1,1,2,2,3,3-Hexafluoro-1,3-propanediolate(2−) ($(TAS)_2$5). A solution of (TAS)3 (3.27 g, 10 mmol) in THF (50 mL) was treated with TAS trimethyldifluorosilicate (2.75 g, 10 mmol). The mixture was stirred for 0.5 h, filtered, and evaporated to give 5.05 g of off-white solid. The crude product was triturated with THF, filtered, and dried to give 3.4 g of white solid: mp 90–92 °C; ^{19}F NMR (DMF-d_7) δ −21.4 (brd s, 4 F), −116.8 (s, 2 F), and a small doublet at −148.2 (due to HF_2 anion); IR (KBr) 1570 (brd), 1523 cm^{-1}. A very weak band at 1863 cm^{-1} corresponding to **3** also was present, which apparently arose by reaction of **5** with KBr or adventitious H_2O. The Raman spectrum of the solid **5** showed no C=O stretch.

Tris(dimethylamino)sulfonium 2,2,3,3,4,4,5,5-Octafluoro-5-hydroxypentanoyl Fluoride(1−) ((TAS)4). A solution of perfluoroglutaryl fluoride (6.5 g, 26.6 mmol) in THF (25 mL) was chilled to ca. 0 °C and treated with TAS trimethyldifluorosilicate (6.56 g, 23.9 mmol). After 1.0 h at ambient temperature, the volatiles were removed to provide 9.86 g (97%) of white solid, mp 150–151 °C dec, which was recrystallized from THF/ether to give 5.6 g of product: mp 159–160 °C; ^{19}F NMR (CD_2Cl_2) δ −23.9 (brd s, 3 F), −121.01 (m, 4 F), −129.57 (m, 2 F); IR (KBr) 1868 (C=O), 1170 cm^{-1} (CF_2); IR (Nujol) 1860 cm^{-1}; IR (THF, 5% solution) 1858, 1173 cm^{-1}. The COSY spectrum at 376.46 MHz showed coupling between nuclei at δ −121 and −129, and broadening of signals at δ −23 and −121 was observed at low temperatures, but exchange rates were too fast to produce interpretable spectra. Anal. Calcd for $C_{11}H_{18}N_3F_9O_2S$: C, 30.92; H, 4.25; N, 9.83; F, 40.01; S, 7.50. Found: C, 31.14; H, 4.61; N, 10.13; F, 40.04; S, 7.79.

Bis[tris(dimethylamino)sulfonium] 1,1,2,2,3,3,4,4,5,5-Decafluoro-1,5-pentanediolate(2−) ($(TAS)_2$6). A solution of perfluoroglutaryl fluoride (2.44 g, 10 mmol) in THF (20 mL) was cooled at −20 °C and treated with TAS trimethyldifluorosilicate (5.50 g, 20 mmol). The mixture was stirred for 2.0 h and evaporated to give 5.47 g (90%) of white solid, which was recrystallized from CH_2Cl_2/THF to afford 4.42 g of pure product: mp 174 °C dec; ^{19}F NMR (DMF-d_7) δ −21.5 (s, 4 F), −119.31, −120.00 (singlets, 6 F); IR (KBr) 1550, 1170–1135 cm^{-1}. Anal. Calcd for $C_{17}H_{36}N_6F_{10}S_2O_2$: C, 33.44; H, 5.94; N, 13.76; F, 31.11; S,, 10.50. Found: C, 34.04; H, 6.21; N, 14.01; F, 31.04; S, 10.71.

Calculations. The calculations were done with the program GRADSCF[6] on CRAY-1A and CRAY XMP/24 computers. Geometries were gradient optimized.[7] Force fields were determined by using analytic second-derivative techniques.[8] Correlation corrections were done at the MP-2 level in the valence space.[9] The initial calculations were done with a double-ζ basis set augmented by d polarization functions on carbon and oxygen, as this level has previously been shown to be adequate for calculations of the structures and relative energetics of fluorooxyanions.[2] The basis set is from Dunning and Hay,[10] giving a basis set ($DZD_{C,O}$) of the form (9,5,1/9,5)/[3,2,1/3,2] in the order C,O/F. Subsequent calculations were done by augmenting this basis set with d polarization on the F atom and diffuse p functions[10] on all atoms, giving a basis set (DZD + diff) of the form (9,6,1)/[3,3,1] for all atoms.

Results and Discussion

TAS Perfluoroalkoxide Salts. The general synthesis of TAS perfluoroalkoxides outlined in our previous work[2] was used to prepare the difunctional salts of interest, some of which might exhibit intramolecular fluoride transfer or have bridged-fluoride structures. When treated with 1 or 2 equiv of TAS trimethyldifluorosilicate, α,ω-diacid fluorides readily gave mono- or bisalkoxides (eqs 1 and 2), except for oxalyl fluoride. In this case,

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$$\mathrm{FC(O)(CF_2)_{\mathit{n}}C(O)F} \xrightarrow{\mathrm{TAS^+Me_3SiF_2^-}} \mathrm{FC(O)(CF_2)_{\mathit{n}}CF_2O^-TAS^+} \quad (1)$$

$$\begin{array}{l}(\mathrm{TAS})\mathbf{2}\ (n = 0)\\ (\mathrm{TAS})\mathbf{3}\ (n = 1)\\ (\mathrm{TAS})\mathbf{4}\ (n = 3)\end{array}$$

$$\mathrm{FC(O)(CF_2)_{\mathit{n}}C(O)F} \xrightarrow{\mathrm{2TAS^+Me_3SiF_2^-}} \mathrm{TAS^{+\,-}OCF_2(CF_2)_{\mathit{n}}CF_2O^-TAS^+} \quad (2)$$

$$\begin{array}{l}(\mathrm{TAS})_2\mathbf{5}\ (n = 1)\\ (\mathrm{TAS})_2\mathbf{6}\ (n = 3)\end{array}$$

a 1:1 adduct $TAS^+C_2F_3O_2^-$ was easily produced, but attempts to generate the bisadduct, $TAS^{+\,-}OCF_2CF_2O^-TAS^+$, were unsuccessful. The monoadduct failed to react with additional TAS trimethyldifluorosilicate under all conditions tried.

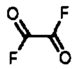
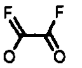
The TAS mono- and bisalkoxides are extremely moisture-sensitive, but they all are isolable and stable up to their melting points in an inert atmosphere. In marked contrast with the unstable cesium salt,[1] $TAS^+C_2F_3O_2^-$ is stable in the solid state up to 223 °C and shows no indication of rearrangement to TAS trifluoroacetate in solution.[11]

The ^{19}F NMR spectra of the monoalkoxides **2**–**4** are characterized by averaged chemical shifts for fluorines on oxygen-bearing carbons. Likewise, only one resonance is observed for the CF_2 groups adjacent to the carbonyl carbon and the CF_2O^- moiety. The rates of fluoride transfer apparently are too fast, even at low temperature (−80 °C), to observe the number and kinds of distinct resonances expected for the static structures **2**–**4**. There was no evidence for disproportionation of the alkoxides ($2FC(O)(CF_2)_nCF_2O^- \rightleftarrows {}^-OCF_2(CF_2)_nCF_2O^- + FC(O)(CF_2)_nC(O)F$) under the conditions studied, however.

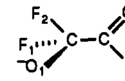
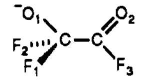
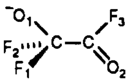
The infrared spectra of the monoalkoxide salts of **3** and **4** in the solid state (Figure 1) and in solution show strong, slightly perturbed acid fluoride C=O stretches. The spectra are given in the region of 2400–1400 cm^{-1}, as the cations contribute too many bands in the region ~1470–400 cm^{-1} to allow reliable assignments to the anion absorptions. We observe variations in the frequencies and/or intensites of the cation absorption bands with variations in the counterion. Thus, simple subtraction of spectra does not give the anion frequencies. The absorptions in **3** and **4** are at 1863 and 1868 cm^{-1} (KBr), respectively, which are red-shifted with respect to the IR absorptions at 1885 and 1876 cm^{-1} for $FC(O)CF_2C(O)F$ and $FC(O)CF_2CF_2CF_2C(O)F$. The monoalkoxide **3**, and bisalkoxides **5** and **6**, also show distinct C–O stretching modes in the 1520–1570-cm^{-1} region, which are near the reported values of 1553 cm^{-1} for $TAS^+CF_3O^-$ (solution)[2] and 1514 cm^{-1} for $Cs^+CF_3O^-$ (solid).[12] (Curiously, the monoalkoxide **4** shows no absorption in the 1500–1570-cm^{-1} region but rather has a broad 1450–1500-cm^{-1} absorption that overlaps with the envelope of absorptions for the TAS^+ cation.)

These infrared data indicate the anions **3** and **4** are simple, open-alkoxide structures with no fluoride bridging, even though they do undergo rapid fluoride exchange on the NMR time scale. The IR spectrum of $TAS^+C_2F_3O_2^-$ similarly shows strong absorptions at 1840 and 1520 cm^{-1} (very broad) (1843 cm^{-1} and a broad band with maxima at 1511, 1533, and 1568 cm^{-1} for the tris(piperidino)sulfonium salt), which strongly suggests an open structure **2** for this anion as well. The red shift in the C=O stretching frequency in **2** from the IR transition[12] in *trans*-(*cis*)-oxalyl fluoride at 1857 cm^{-1} (1897 and 1869 cm^{-1}) is comparable to that observed for the other examples. Due to the difference in our results and those of Ault,[1] we therefore undertook a theoretical study of the $C_2F_3O_2^-$ isomers to corroborate the open structure **2** for the oxalyl fluoride adduct.

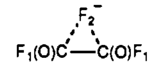
Table I. Geometry Parameters

param	trans ($DZD_{C,O}$)	trans (DZP + diff)	trans (exptl)[a]	cis ($DZD_{C,O}$)	cis (DZP + diff)
r(CO)	1.162	1.164	1.180	1.160	1.162
r(CC)	1.535	1.535	1.536	1.537	1.537
r(CF)	1.307	1.298	1.329	1.311	1.303
θ(FCC)	110.5	110.6	109.8	112.4	112.2
θ(OCC)	125.5	125.2	126.0	123.6	123.7
θ(FCO)	124.0	124.2	124.2	124.0	124.1

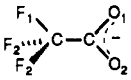




param	**2a** ($DZD_{C,O}$)	**2a** (DZP + diff)	**2b** ($DZD_{C,O}$)	**2b** (DZP + diff)	**2c** (DZP + diff)
$r(CF_1)$	1.421	1.410	1.420	1.408	1.401
$r(CF_2)$	1.398	1.385	1.420	1.408	1.401
$r(CO_1)$	1.227	1.233	1.217	1.223	1.227
r(CC)	1.551	1.553	1.563	1.566	1.572
$r(CF_3)$	1.341	1.329	1.344	1.335	1.326
$r(CO_2)$	1.173	1.175	1.171	1.172	1.175
$\theta(O_1CC)$	114.7	114.5	117.1	117.3	117.8
$\theta(F_1CC)$	103.0	102.8	102.1	102.0	101.8
$\theta(F_2CC)$	104.0	104.4	102.1	102.0	101.8
$\theta(F_1CF_2)$	100.6	100.9	100.5	100.9	100.9
$\theta(F_1CO_1)$	116.0	116.0	116.2	116.1	116.0
$\theta(F_2CO_1)$	116.5	116.3	116.2	116.1	116.0
$\theta(O_2CC)$	130.6	130.2	128.2	128.4	128.9
$\theta(F_3CC)$	110.4	110.7	113.3	112.8	112.2
$\theta(O_2CF_3)$	118.9	119.0	118.5	118.8	118.8



1

param	trans ($DZD_{C,O}$)	trans (DZP + diff)	cis ($DZD_{C,O}$)	cis (DZP + diff)
$r(CF_1)$	1.328	1.315	1.333	1.321
r(CO)	1.178	1.179	1.176	1.176
r(CC)	1.501	1.507	1.508	1.511
$r(CF_2)$	2.002	2.021	1.999	2.018
$\theta(F_1CC)$	110.7	111.0	112.7	112.5
θ(OCC)	127.1	126.7	125.6	125.5
$\theta(F_1CO)$	120.6	120.9	120.4	120.6
$\theta(F_2CC)$	67.9	68.1	67.8	68.0
$\theta(CF_2C)$	44.1	43.8	44.3	44.0



param	$DZD_{C,O}$	DZP + diff	exptl[b]
$r(CF_1)$	1.337	1.327	1.346 (5)[c]
$r(CF_2)$	1.342	1.334	
r(CC)	1.575	1.572	1.542 (9)
$r(CO_1)$	1.222	1.224	1.269 (5)
$r(CO_2)$	1.223	1.225	
$\theta(F_1CC)$	114.8	114.5	111.3 (2)
$\theta(F_2CC)$	112.3	111.8	
$\theta(F_1CF_2)$	105.5	105.9	107.2 (2)
$\theta(F_2CF_2)$	105.8	106.3	
$\theta(O_1CC)$	114.4	114.7	115.5 (2)
$\theta(O_2CC)$	112.0	112.3	
$\theta(O_1CO_2)$	133.7	133.0	128.2 (4)

[a] Reference 14. [b] From the crystal structure of $NH_4^+CF_3CO_2^-$: Cruickshank, D. W. J.; Jones, D. W.; Walker, G. *J. Chem. Soc.* **1964**, 1303. [c] Average values.

Calculations. Geometries and Relative Energies. The optimized geometries with the $DZD_{C,O}$ and DZP + diff basis sets for oxalyl fluoride and the structural isomers of $C_2F_3O_2^-$ (*cis*- and *trans*-**1**, **2** (three conformers), and $CF_3CO_2^-$) are given in Table I. Total energies and relative energies are given in Table II and III, respectively. The $DZD_{C,O}$ and DZP + diff structures for oxalyl fluoride are virtually identical, except that r(C–F) is ca. 0.01 Å

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(11) An authentic sample of $TAS^+CF_3CO_2^-$ has been prepared by treating $CF_3C(O)OSiMe_3$ with 1 equiv of $TAS^+Me_3SiF_2^-$ (E. D. Laganis, unpublished results). The material is a waxy solid: ^{19}F NMR ($CDCl_3$) δ −74.9 (s).

(12) Ault, B. S. *J. Phys. Chem.* **1980**, *84*, 3448.

(13) (a) Durig, J. R.; Brown, S. C.; Hannum, S. E. *J. Chem. Phys.* **1971**, *54*, 4428. (b) Möller, G.; Tinti, D. S. *Mol. Phys.* **1985**, *54*, 541.

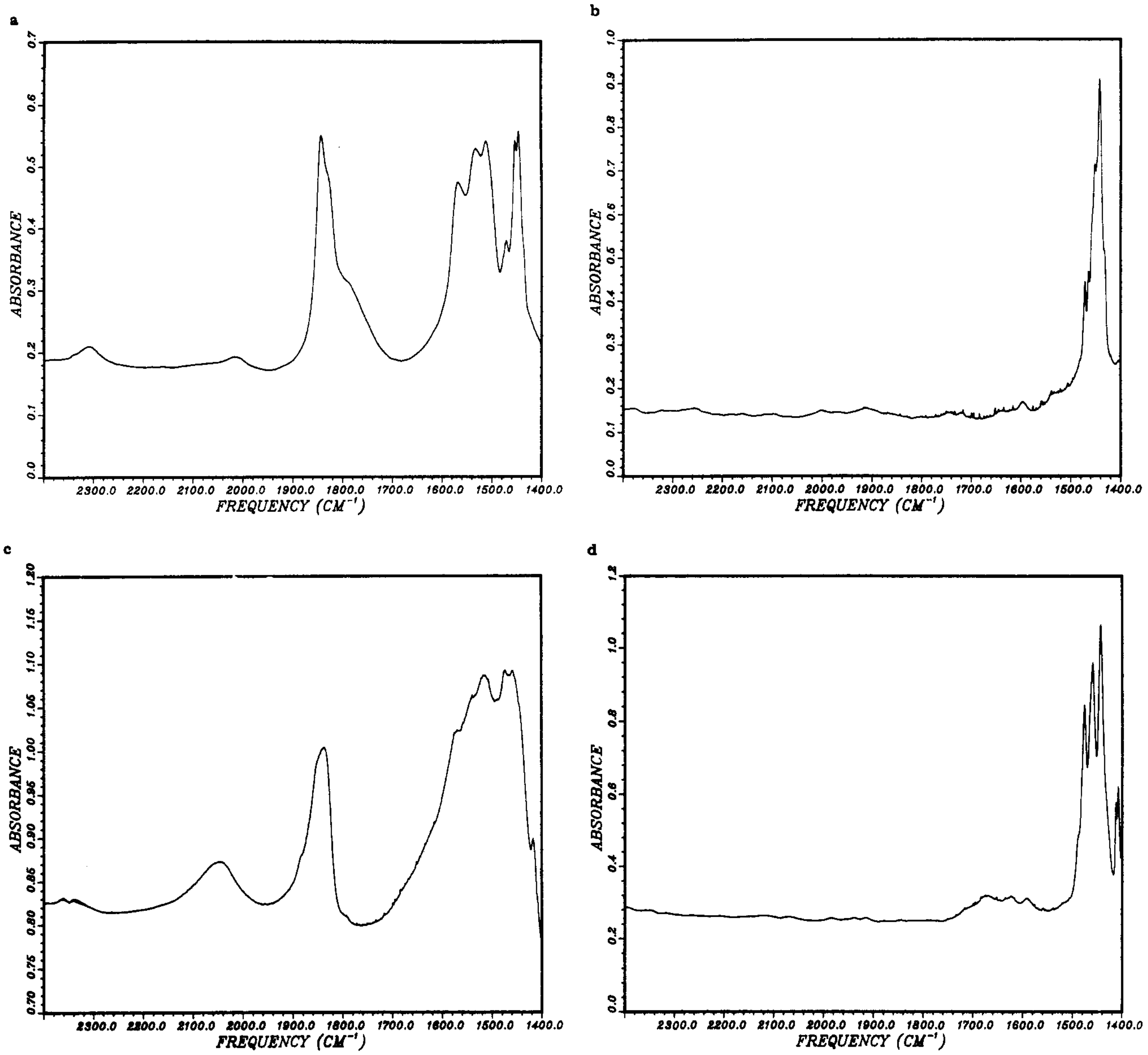

Figure 1. Infrared spectra of $C_2O_2F_3^-$ with the cations TPS^+ and TAS^+ and spectra of the cations with Br^-: (a) $TPS^+C_2O_2F_3^-$; (b) TPS^+Br^-; (c) $TAS^+C_2O_2F_3^-$; (d) TAS^+Br. The spectral region is 2400–1400 cm^{-1}.

Table II. Total Energies (au)

molecule	$DZD_{C,O}$ (SCF)	$DZD_{C,O}$ (MP-2)	DZP + diff (SCF)	DZP + diff (MP-2)
trans-**1**	−523.916990	−524.845974	−523.953313	−525.077174
cis-**1**	−523.915482	−524.845418	−523.951439	−525.076533
2a	−523.937351	−524.859090	−523.974604	−525.089775
2b	−523.935917	−524.858756	−523.972474	−525.088949
2c			−523.970799	−525.086344
$CF_3CO_2^-$	−523.943859	−524.861034	−523.986174	−525.094776
trans-$C_2F_2O_2$	−424.415151	−425.212214	−424.444277	−425.364619
cis-$C_2F_2O_2$	−424.413673	−425.211722	−424.442552	−425.363981
CF_3O^-	−411.188911[a]		−411.223131	−412.044397
$CF_2{=}O$	−311.670165[b]		−311.699611	−312.325317

[a] Reference 2. [b] Reference 16.

shorter with the DZP + diff basis set. The agreement between the calculated and experimental (gas phase)[14] structures for *trans*-oxalyl fluoride is excellent, with the largest errors being somewhat overcontracted theoretical C–O (by 0.016 Å) and C–F (by 0.029 Å) bonds. This shortening at the Hartree–Fock level follows expected trends. The structure of the cis isomer, which is not known experimentally, is predicted to be very similar to the trans structure. The only comparatively small difference is about a 2° larger FCC bond angle and a 2° smaller OCC bond angle in the cis isomer. The θ(FCC) angle probably opens slightly in the cis isomer to relieve C–F bond dipole–dipole repulsions.

The trans isomer is 0.4 kcal/mol lower in energy than the cis isomer at the MP-2 level and about 1 kcal/mol lower at the SCF level (Table III). These results agree with the qualitative experimental observation that both rotamers are present in the gas phase and the trans structure predominates.

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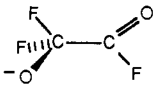
(14) Structure reported by: Möller, G.; Olmstead, M. M.; Tinti, D. S. *J. Am. Chem. Soc.* **1987**, *109*, 95. Structure is from the work of: Hedberg, K.; Friesen, D. T. *Diss. Abstr. Int. B* **1981**, *41*, 3458.

Table III. Relative Energies (kcal/mol)

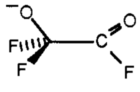
molecule	$DZD_{C,O}$ (SCF)	$DZD_{C,O}$ (MP-2)	DZP + diff (SCF)	DZP + diff (MP-2)
		$C_2O_2F_2$		
trans	0.0	0.0	0.0	0.0
cis	0.9	0.3	1.1	0.4
		$C_2F_3O_2^-$		
$CF_3CO_2^-$	−4.1	−1.2	−7.3	−3.1
2a	0.0	0.0	0.0	0.0
2b	0.9	0.2	1.3	0.5
2c			2.4	2.2
trans-**1**	12.8	8.2	13.3	7.9
cis-**1**	13.7	8.6	14.5	8.3

We have shown previously that the structures of perfluorinated anions, including alkoxides,[2] carbanions,[15] and fluoride-bridged species,[3] can be calculated accurately at the SCF level with polarized double-ζ basis sets, and we expect the results for the $C_2F_3O_2^-$ isomers to be equally reliable.

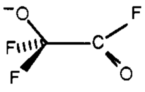
Three conformational isomers of the open structure (**2a–c**) were studied. Structure **2a** (C_1 symmetry) has eclipsing C═O and C–F bonds, **2b** (C_s symmetry) has eclipsing C═O and C–O⁻ bonds, and **2c** has eclipsing acid fluoride C–F and C–O⁻ bonds. Both **2a** and **2b** are minima on the potential energy surface, but **2c** is a transition state.



2a (C_1)



2b (C_s)



2c (C_s)

The CF_2O^- group in **2a** has two very long C–F bonds, comparable in length to those found in CF_3O^- (1.394 Å)[2] or $CF_3CF_2O^-$ (1.414 Å),[2] and a short C–O bond as in CF_3O^- (1.214 Å) or $CF_3CF_2O^-$ (1.222 Å). Small θ(FCF) and θ(FCC) bond angles, and large θ(FCO) and θ(CCO) angles, as compared with tetrahedral values also are evident in the CF_2O^- group. These abnormal geometries are characteristic of β-fluorinated anions and have been attributed to negative anionic hyperconjugation.[2,15] The geometry of the FC═O group in **2a** is similar to that calculated with the DZ + D_C basis set for $CF_3C(O)F$ (r(C–F) = 1.311 Å, r(C═O) = 1.159 Å, θ(FCO) = 124.5°[17] compared to the corresponding values of 1.341 Å, 1.173 Å, and 118.9° in **2a**). Structure **2b** is very similar to **2a** with differences of ~0.01 Å. The exact eclipsing of the oxygens in **2b** is consistent with the increase in r(C–C). Structure **2b** is 0.5 kcal/mol less stable than **2a** at the DZP + diff/MP-2 level and 1.3 kcal/mol at the SCF level.

One other possible open conformer **2c** is a transition state, as shown by force field calculations (vide infra). It lies 2.4 kcal/mol above **2a** at the SCF level and 2.2 kcal/mol at the MP-2 level. Structure **2c** is the transition state for converting **2a** to its mirror image conformer. Rotation about the C–C bond in **2a** to reach **2c** results in lengthening the C–C bond by 0.019 Å, but the FC═O geometry basically remains unchanged. The length of the equivalent geminal C–F bonds in the transition state is essentially the average of the geminal bond lengths in **2a**.

The geometry of the OCCO framework in the fluoride-bridge structures *trans*- and *cis*-**1** is surprisingly similar to that in the neutral oxalyl fluoride. For example, the C–C bond length in *trans*-**1** is only 0.028 Å longer than in *trans*-$C_2F_2O_2$, and the CO and CF bond lengths increase by only about 0.015 Å upon addition of fluoride. The FCO angles decrease by 3–4° as the groups become slightly pyramidal. The distance from C to the bridging F⁻ is 2.0 Å, which is significantly smaller than the sum of the van der Waals radii (3.2 Å).[18] The F⁻ is symmetrically positioned (by symmetry) for *trans*-**1** but is slightly displaced away from the C–C axis toward the fluorines in *cis*-**1**.

Table IV. Vibrational Transitions and Infrared Intensities for *trans*- and *cis*-Oxalyl Fluoride

sym	ν, cm⁻¹ $DZD_{C,O}$	ν, cm⁻¹ DZP + diff	ν, cm⁻¹ obs[a]	scale factor	I, km/mol $DZD_{C,O}$	I, km/mol DZP + diff
			Trans			
a_g	2171	2157	1866	0.865	0	0
	1466	1483	1290	0.870	0	0
	904	914	812	0.888	0	0
	579	581	*513*[b]		0	0
	451	453	420	0.927	0	0
a_u	512	512	461	0.900	79	70
	42	47	54[c]		0.8	1.8
b_g	910	915	*800*[d]		0	0
b_u	2149	2135	1857	0.870	735	740
	1258	1287	1122	0.872	540	536
	744	749	676	0.903	88	84
	270	270	265	0.981	6.5	6.4
			Cis			
a_1	2190	2179	*1897*[e]	0.879	454	456
	1449	1468	*1267*[f]	0.863	463	483
	900	910	799	0.878	25	18
	463	463	415	0.896	1.4	1.4
	274	273			6	4.9
a_2	906	912			0	0
	25	14			0	0
b_1	515	515			78	70
b_2	2138	2127	*1869*[g]	0.879	121	118
	1240	1262			246	234
	742	747	664	0.889	83	81
	560	564	*510*[h]		1.2	0.6

[a] Reference 13, reassigned values in italics. [b] Originally assigned at 595 cm⁻¹. This value is the original b_g assignment. [c] Gas-phase torsion. Solid-phase torsion is 94 cm⁻¹. [d] Reassigned to one of the "factor-group split" transitions at 812 and 799 cm⁻¹. Originally assigned as 513 cm⁻¹. [e] Originally assigned as antisymmetric C═O stretch. [f] Originally assigned as antisymmetric C–F stretch. [g] Originally assigned as symmetric C═O stretch. [h] Assigned to very weak IR transition observed in the gas phase.

The relative energies of *cis*- and *trans*-**1** parallel those found in oxalyl fluoride with *trans*-**1** being 0.3 kcal/mol more stable than *cis*-**1** at the MP-2 level with the DZP + diff basis set and 1.2 kcal/mol at the SCF level. Most significant, however, force field calculations (vide infra) show that *both cis- and trans-1 are transition states rather than energy minimum structures.*

As expected, $CF_3CO_2^-$ is an energy minimum. The structure is unexceptional except perhaps for the rather large OCO bond angle (133°). It also is interesting that theory predicts that the C–O bond lengths in $CF_3CO_2^-$ and the CF_2O^- group of **2a** or **2b** are nearly identical. This again reflects the double-bond character (negative hyperconjugation) of the C–O bond in a CF_2O^- group.

The relative energies of the possible energy-minimum structures for $C_2F_3O_2^-$ increase in the order $CF_3CO_2^-$ < $FC(O)CF_2O^-$ (**2a**) < $FC(O)CF_2O^-$ (**2b**). The global minimum $CF_3CO_2^-$ structure is 3.1 kcal/mol more stable than **2a** at the DZP + diff/MP-2 level. This agrees with the experimental finding for $Cs^+C_2F_3O_2^-$.[1] The purported bridged-fluoride structures **1** for the matrix-isolated $Cs^+C_2F_3O_2^-$ species, however, cannot be correct since they are transition states. In fact, they are transition states for intramolecular fluoride transfer that lie only about 8 kcal/mol in energy above that of **2a** or **2b** at the DZP + diff/MP-2 level.[19,20] This

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(15) Farnham, W. B.; Dixon, D. A.; Calabrese, J. C. *J. Am. Chem. Soc.* **1988**, *110*, 2607.

(16) Dixon, D. A.; Fukunaga, T.; Smart, B. E. *J. Am. Chem. Soc.* **1986**, *108*, 4027.

(17) Experimental values are r(C–F) = 1.32 Å, r(C═O) = 1.16 Å, and θ(FCO) = 121.5 ± 2° from: Ter Brake, J. H. M.; Driessen, R. A.; Renes, G. H.; Lowrey, A. H. *J. Mol. Struct.* **1982**, *81*, 227.

(18) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.

(19) There is a significant correlation correction to the energy of **1** relative to that of **2**. *trans*-**1** is 13.3 kcal/mol higher in energy than **2a** at the SCF level. This stabilization of a bridged structure relative to an open one due to correlation corrections is well-known in other systems: Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley-Interscience: New York, 1986; p 385.

is consistent with the rapid exchange process observed for $TAS^+C_2F_3O_2^-$ in solution on the NMR time scale. Further support for the assignment of the open structure **2** for both the stable $TAS^+(C_2F_3O_2^-$ and matrix-isolated$Cs^+C_2F_3O_2^-$ salts is provided by the computed infrared spectra results, which are presented below.

Vibrational Spectra. In order to determine whether a structure is at a minimum, the matrix of second derivatives is required. These data can be converted to provide information about the vibrational spectra, and the infrared intensity of a fundamental vibrational transition can be calculated. The vibrational spectrum of *trans*-oxalyl fluoride has been measured both in the gas[13] and in the solid,[13,14] and we first compare our calculated spectrum with the experimental one. The calculated values determined at this level (Table IV) are too high because of the neglect of correlation corrections and because the calculated values are harmonic frequencies whereas the experimental values are anharmonic. Scale factors of 0.9 are usually required to bring agreement between the experimental and theoretical values. Most of the scale factors for *trans*-$C_2F_2O_2$ are between 0.87 and 0.90, as would be expected. We disagree only with two assignments[13] that were based on the Raman spectrum, which was difficult to obtain. We reassign the b_g transition at 513 cm^{-1} as ν_4 (a_g), which would then have a scale factor of 0.862. The b_g transition clearly cannot be at 513 cm^{-1}. Rather we assign this transition to be one of the two components of the intense transition near 800 cm^{-1}. These were initially assigned at 812 and 799 cm^{-1} as factor-group splitting of a single transition. We prefer to assign them as two different transitions. Our result is consistent with the observation of two bands at 804 and 774 cm^{-1} in the Raman spectrum of the complex of oxallyl fluoride with dioxane in the crystal.[14] The agreement between the calculated and experimental value of the torsion frequency is good considering the breadth of the observed weak transition.

On the basis of bands observed in the fluid phase but not in the solid,[13] the spectrum of *cis*-$C_2F_2O_2$ has been partially assigned. Three prominent bands were observed in the infrared spectrum at 1897, 1267, and 799 cm^{-1}. The bands were assigned as the b_2 C=O and C–F stretches and the a_1 C–C stretch. Our calculations clearly show that the a_1 C=O and C–F stretches are more intense than the b_2 stretches. Furthermore, the a_1 stretches are at higher frequency than the b_1 stretches. We have thus reversed the assignments in Table IV. The scale factors with the reassigned spectral values are now very similar to those observed in *trans*-$C_2F_2O_2$. On the basis of above results for *trans*-$C_2F_2O_2$, a scale factor of 0.90 would give reasonable values for the unobserved frequencies in the cis isomer. The unobserved transitions, except for the torsion, are near transitions of the trans isomer. The torsional frequency is predicted to be very low at 14 cm^{-1}. Thus, the cis structure is almost a transition state on the C–C torsional surface.

From the above results, we expect our spectral predictions for the frequencies of the fluoride adducts to be quite good after scaling. This is important as it will allow us to better interpret the observed spectra of the adduct. The calculated results for the various isomers are given in Table V. For comparison with experiment, the most important region is that of the CO stretches, and the experimental and theoretical values (scaled) for the CO stretches are given in Table VI. A scale factor of 0.87 was used for the C=O stretches in **1** and **2**. Ault[1] reports that the region between 1500 and 1800 cm^{-1} is free of absorptions in his matrix experiments. He observed two transitions at 1498 and 1457 cm^{-1}, which were assigned to the C=O stretching modes in *cis*- and *trans*-**1**, respectively. Our scaled calculations on *cis*-**1** and *trans*-**1** clearly show that the C=O stretches are at much higher frequencies. The highest CO stretching mode is shifted to the red by about 50 cm^{-1} and the other CO stretching mode is shifted by ~125 cm^{-1} to the red in comparison with the $C_2F_2O_2$ frequencies. Although C=O absorptions from unreacted oxalyl fluoride in the matrix could interefere with observing the higher frequency C=O absorptions predicted for **1**, the strong C=O absorptions at about 1735 cm^{-1} (scaled) should be easily detectable. Neither Ault's spectrum of $Cs^+C_2F_3O_2^-$ nor ours of $TAS^+C_2F_3O_2^-$ has any absorption near this frequency. Ault also observed a pair of absorptions at 376 and 395 cm^{-1}, which were assigned to the stretching modes of the bridging fluorines in *cis*- and *trans*-**1**. Our calculations, however, predict much lower values near 250 cm^{-1} (scaled) for this stretching mode in the respective isomers.

These inconsistencies, coupled with the fact that the bridged structure is calculated to be a transition state, conclusively exclude **1** from being the observed species. In the solid, we observe CO stretches at about 1840 cm^{-1} for $TAS^+C_2F_3O_2^-$. Our corrected values for **2a** and **2b** using a scaling factor of 0.87 gives values of 1805 and 1821 cm^{-1} in reasonable agreement with our experimental value. We thus assign the absorption at 1840 cm^{-1} to the CO stretch in the O=C–F group.

To determine the scaling factor for the CO stretch in the CF_2O^- group, the force field for CF_3O^- was calculated at the DZP + diff level. The calculated CO stretch in CF_3O^- is 1697 cm^{-1} as compared to the experimental matrix value of 1514 cm^{-1} for $Cs^+CF_3O^-$, giving a scaling factor of 0.892. Scaling the CO bond stretch in the CF_2O^- group by 0.892 leads to frequencies of 1466 and 1512 cm^{-1} for **2a** and **2b** in excellent agreement with Ault's observed frequencies of 1457 and 1498 cm^{-1}. These C–O stretches are predicted to be quite intense, and with the small calculated energy difference between **2a** and **2b** of 0.5 kcal/mol, both structures could be observed as an equilibrium mixture in the matrix. We thus confidently assign the absorptions observed by Ault in this region to the C–O stretching modes in the two conformers of the open anion **2**. The transitions observed by Ault at 395 and 376 cm^{-1} can be assigned to the calculated transitions at 456 cm^{-1} for **2a** and 444 cm^{-1} for **2b**, giving scale factors of 0.87 and 0.84, respectively. These bands include significant motion of the oxygens.

The spectrum for $TAS^+C_2F_3O_2^-$ shows a broad C–O absorption at 1520 cm^{-1}, which also agrees with the theoretical value for **2b**. If the experimental[2] solution value of 1553 cm^{-1} for the C–O stretch in $TAS^+CF_3O^-$ is used for calculating the scale factor, a larger value of 0.915 results, and the corrected theoretical values for the stretching modes in **2a** and **2b** become 1504 and 1550 cm^{-1}. These values now agree with both that observed for $TAS^+C_2F_3O_2^-$ and the broad band with maxima at 1511 (or 1533) and 1568 cm^{-1} in the corresponding TPS salt.

Fluoride Affinity. The fluoride affinity of a molecule A is defined as the negative of ΔH of reaction 3. Although absolute

$$A + F^- \rightarrow AF^- \qquad (3)$$

proton affinities can be calculated very accurately,[21] direct calculation of absolute fluoride affinities is complicated by the difficulty in calculating the absolute electron affinity of F. Relative fluoride affinities can be calculated quite accurately, however. We calculate the fluoride affinity of oxalyl fluoride relative to that of carbonyl fluoride (eq 4) since the absolute fluoride affinity

$$CF_2O + {}^-OCF_2CFO \rightarrow COFCOF + CF_3O^- \qquad (4)$$

of COF_2 is well established experimentally as 42.6 kcal.[22] The values of ΔE for reaction 4 at the SCF level with the DZP + diff basis set and at the MP-2 level are 4.3 and 3.8 kcal/mol. (With

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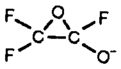
[20] One other possible "bridged-type" structure is the epoxide



2d

Using the coordinates of perfluoroethylene oxide, we obtain an energy for **2d** 57 kcal/mol higher than that of **2a** with the DZ + $D_{C,O}$ basis set at the SCF level. Optimization of **2d** leads to **2a**.

[21] Dixon, D. A.; Lias, S. G. In *Molecular Structures and Energetics*; Ed. Greenberg, A., Leibman, J. F., Eds.; VCH: Deerfield Beach, FL, 1987; Vol. 2, Chapter 7, p 269.

[22] Larson, J. W.; McMahon, T. B. *J. Am. Chem. Soc.* **1985**, *107*, 766.

Table V. Vibrational Spectra and Infrared Intensities for $C_2O_2F_3^-$ Isomers

	ν, cm^{-1}		I, (km/mol)				ν, cm^{-1}		I, (km/mol)	
sym	$\mathrm{DZD_{C,O}}$	DZP + diff	$\mathrm{DZD_{C,O}}$	DZP + diff		sym	$\mathrm{DZD_{C,O}}$	DZP + diff	$\mathrm{DZD_{C,O}}$	DZP + diff
					2a					
a	2079	2075	359	369		a	607	616	14	11
	1689	1644	678	687			539	546	5.0	3.7
	1343	1349	172	188			454	456	3.0	3.0
	1078	1095	629	613			406	406	0.2	0.3
	1002	1014	273	280			262	263	9.3	10
	876	882	11	7.8			250	250	6.2	4.7
	809	823	129	127			60	64	2.4	3.6
	746	755	63	58						
					2b					
a′	2112	2093	374	377		a′	417	415	0.9	0.9
	1739	1695	564	572			255	255	2.9	2.3
	1321	1326	492	526		a″	969	981	248	281
	1039	1047	324	301			796	809	224	201
	834	846	97	87			552	560	1.0	0.3
	746	754	44	45			267	265	9.6	8.0
	607	615	4.3	3.6			53	56	0.5	0.6
	441	444	3.1	2.2						
					2c					
a′		2076		328		a′		398		0.1
		1684		852				274		6.3
		1335		44		a″		1003		294
		1069		596				810		179
		852		17				564		0.1
		766		60				274		7.4
		621		2.0				55*i*		
		457		3.4						
					$CF_3CO_2^-$					
a′	1968	1931	879	977		a′	409	414	0.9	0.2
	1574	1576	63	67			272	273	2.1	1.4
	1353	1351	330	326		a″	1264	1279	374	363
	1303	1321	355	327			898	904	53	50
	888	893	129	109			568	572	11	10
	783	790	46	53			287	288	12	12
	637	643	1.4	1.3			19	18	0.3	0.3
	466	468	0.4	0.1						
					trans-**1**					
a	2100	2079	109	129		b	2009	1994	1081	1062
	1457	1473	1.4	1.0			1203	1237	597	584
	913	925	15	11			776	788	12	5.9
	699	690	219	201			713	726	84	87
	570	560	51	66			324	318	13	12
	457	457	8.6	10			225	223	0.5	0.7
	304	275	55	93			205*i*	176*i*		
	166	163	0.9	0.7						
					cis-**1**					
a′	2117	2103	623	634		a″	2002	1995	311	298
	1445	1459	520	540			1177	1203	282	268
	901	914	59	45			770	782	11	6.5
	676	656	265	260			712	724	75	81
	471	469	17	18			571	575	4.2	2.4
	329	322	11	9.8			163	158	0.2	3.4
	308	279	56	91			206*i*	179*i*		
	227	222	0.8	0.2						

Table VI. Calculated and Experimental Stretching Frequencies (cm^{-1}) in **1** and **2**

	ν(CO)	
structure	calc[a]	exptl
trans-**1**	1809, 1735	
cis-**1**	1830, 1736	
2a	1805, 1466	1457,[b] 1498[b]
2b	1821, 1512	1840,[c] 1520[c]

[a] Scaled values; see text. Scale factor = 0.87 for C=O stretches. [b] Cs^+ salt, ref 1. [c] TAS^+ salt, this work.

the smaller $\mathrm{DZD_{C,O}}$ basis set, ΔE = 2.2 kcal/mol at the SCF level.) Thus, the fluoride affinity of oxalyl fluoride is 3.8 kcal/mol above that of COF_2 at the MP-2 level, which gives an absolute value of 46.4 kcal/mol. This agrees with the experimental value of 45.7 kcal/mol,[22] suggesting that **2** rather than **1** or $CF_3CO_2^-$ is also formed upon addition of fluoride to oxalyl fluoride in the gas phase.

Conclusion. The calculated and experimental results reported here and in previous work[1] are consistent with an open as opposed to a bridged structure for the fluoride adduct of oxalyl fluoride. The isomeric bridged structures, in fact, are transition states for intramolecular fluoride transfer. The frequencies of the C=O stretching modes in the bridged structures are not as strongly perturbed as originally expected when compared to those in oxalyl fluoride. The global minimum on the potential energy surface for the $C_2F_3O_2^-$ structural isomers is $CF_3CO_2^-$, in agreement with the previously reported rearrangement of $Cs^{+}\,{}^{-}OCF_2C(O)F$ to $Cs^{+}\,{}^{-}O_2CCF_3$. The failure to observe this rearrangement with $TAS^{+}\,{}^{-}OCF_2C(O)F$ illustrates how the TAS^+ cation can strongly affect kinetic stability.