Structure of the Fluorosulfite Anion: Rotational Disorder of SO_2F^- in the Alkali Metal Fluorosulfites and Crystal Structures of α- and *β*-$CsSO_2F$

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^{19}F solid-state NMR spectra of the alkali metal fluorosulfites KSO_2F, $RbSO_2F$, α-$CsSO_2F$, and *β*-$CsSO_2F$ show that the fluorosulfite anion is subjected to dynamical disorder at room temperature. This disorder can be modeled by 120° rotational jumps with respect to the C_3-pseudoaxis of the anion. The exchange frequency of this disorder decreases with decreasing temperature. The calculated jump frequencies at room temperature are 5×10^5 Hz for KSO_2F, 2×10^5 Hz for $RbSO_2F$, 1×10^7 Hz for α-$CsSO_2F$, and 5×10^5 Hz for *β*-$CsSO_2F$, respectively. The crystal structures of α- and *β*-$CsSO_2F$ were determined for the first time (α: *Pnma*; $Z = 4$; $a = 790.98(8)$, $b = 666.07(7)$, $c = 798.93(9)$ pm; $T = 293$ K. *β*: *R*3*m*; $Z = 3$; $a = 659.22(6)$, $c = 800.50(4)$ pm; $T = 293$ K). X-ray single-crystal data of KSO_2F, $RbSO_2F$, and α-$CsSO_2F$ taken at various temperatures were refined using the disorder model developed from the NMR results. It is shown that it is impossible to obtain reliable structural parameters of the SO_2F^- ion by refinement of X-ray data as long as rotational disorder persists. The preference of an ordered structure increases with decreasing temperature. The degree of disorder remaining in α-$CsSO_2F$ at 93 K is small. The structural parameters of the fluorosulfite anion as obtained by a routine refinement of this phase (S−F, 169.0(2) pm; S−O, 147.8(1) pm) are the best lower (S−F) and upper (S−O) limits of the "true" bond lengths determined experimentally. They comply with the values obtained from quantum chemical calculations.

Introduction

In a previous paper, we have reported on X-ray single-crystal structure determinations of KSO_2F and $RbSO_2F$.[1] The reliability of the crystallographic results as judged by the generally accepted figures of merit (*R*-values, residual electron densities) and by chemical plausibility (meaningful anisotropic displacement parameters, bond lengths, angles) did not let us doubt the measured structure of the fluorosulfite anion. The key features of this structure were S−F and S−O bond lengths of 159.1 and 152.6 pm, respectively. Our results were in contrast to quantum chemical calculations by Kornath, Neumann, and Ludwig,[2] which resulted in a long S−F bond of 169.8 pm and relatively short S−O bonds of 145.8 pm. Because these calculations were performed on the free gaseous ion, we ascribed the discrepancies to effects due to the positive field generated by the cationic surroundings in the crystal.

Since then, our results have been questioned by Kornath, Blecher, and Ludwig[3] stating that the geometric features of the fluorosulfite anion have "obviously been the consequence of disorder". However, the authors did not give experimental evidence of this postulated disorder. Recently, Mews, Christe, and co-workers[4] addressed the problem of disorder of the fluorosulfite anion by a crystallographic investigation of four fluorosulfite salts [$(Me_2N)_3S^+$ (TAS), $(Me_2N)_3SO^+$ (TAOS), Me_4N^+ (TMA), K^+]. They claim to have found the fluorosulfite anion to be disordered in all four compounds, but the kind of disorder is different. The refinement of the single-crystal data was carried out by introducing mixed occupancies for the O/F atoms. In the TAS, TAOS, and TMA fluorosulfite, they found in each case one "nondisordered" S−O bond of about 147 pm. The supposed dependence of the measured S−F bond length from the refined occupation was extrapolated to full occupancy. This method leads to a value of >170 pm for the nondisordered structure which corresponds to the results of quantum chemical calculations.

Although we agree that the structure of the SO_2F^- anion represents a problem case, we consider the method adopted by Mews, Christe, and co-workers not valid for extracting experimental bond lengths from disordered structures, independent of any apparent quality of its results. Especially, the refinement of obviously wrong bond lengths by introducing mixed occupation of the ligand atoms does not lead to an adequate description of the chemical situation. The following extrapolation of data obtained by this refinement method is dubious and highly dependent on the function chosen to interpret the data. We regard the resulting consistence of the bond lengths with the quantum chemically calculated values as coincidental. This point is strengthened by the fact that the authors do not give "experimental" values for the bond angles and cannot account for the deviations of the measured angles from the calculated ones, partly being on the order of 10° (O−S−F in $TAS^+SO_2F^-$). In addition, it is not possible to determine the nature of any disorder in these fluorosulfite salts by time averaging diffraction methods.

Nevertheless, the results of Mews, Christe, and co-workers concerning the ostensive lengthening of the S−F bond with decreasing temperature encouraged us to reinvestigate the alkali fluorosulfite salts, spending special attention on the presence of disorder. We have addressed this problem by temperature-dependent ^{19}F solid-state NMR investigations on KSO_2F, $RbSO_2F$, α-$CsSO_2F$, and *β*-$CsSO_2F$. In our concomitant single-

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crystal X-ray investigations, we have determined the crystal structures of the two $CsSO_2F$ phases for the first time. Actually, we have found disorder in all four phases, and we have developed a disorder model that allows simulation of the NMR spectra as well as refinement of the X-ray data sets using a split model that accounts for both bond lengths and angles. The results of ^{19}F NMR spectroscopy and refinements of X-ray single-crystal data present a consistent picture not only of the structure of the fluorosulfite anion but also of the nature of its disorder in the alkali salts (that also agrees with the results of quantum chemical calculations).

Experimental Section

All experimental work was carried out under thoroughly dried argon using standard Schlenk techniques or an argon filled glovebox (H_2O < 0.1 ppm). Working with liquid sulfur dioxide and, especially, with pressurized glass ampules is potentially hazardous. Adequate precautions have to be taken.

The alkali metal fluorides (KF, Merck, p.a., min 99%; RbF, Merck, Selectipur, min 99.5%; CsF, Merck, Optipur, min 99.5%) were finely ground and dried in vacuo at 473 K for 2 days prior to use. They were stored in sealed glass ampules under argon.

Sulfur dioxide (Messer Griesheim, 3.8) was dried by conducting the gas through a column filled with SICAPENT (Merck) and condensed into a Schlenk tube equipped with Teflon valves (Young) where it was stored over calcium hydride at room temperature under its own vapor pressure (about 4 bar).

Acetonitrile (Merck, isocratic grade, min 99.8%) was dried by refluxing with phosphorus pentoxide (Merck) for 16 h, distilled into a Schlenk tube, and stored over molecular sieve 300 pm (Merck).

Powder samples of KSO_2F, $RbSO_2F$, and β-$CsSO_2F$ were prepared by condensing about 2 mL of SO_2 on the corresponding alkali metal fluoride in a Schlenk tube, stirring the mixture for 1−4 days at 258 K, cooling to 195 K, and condensing the excess SO_2 into a cooling trap at 77 K. The purity of the samples particularly depends on the particle size and the solubility of the fluoride. α-$CsSO_2F$ was prepared by heating β-$CsSO_2F$ in a sealed glass ampule to 383 K for 2 days.

Single crystals of KSO_2F, $RbSO_2F$, and β-$CsSO_2F$ were grown from acetonitrile solution in a temperature gradient 313/298 K under an SO_2 pressure of about 5 bar. Single crystals of α-$CsSO_2F$ formed at the liquid/gaseous phase boundary at 348 K under an SO_2 pressure of about 8 bar.

All powders were checked for purity by X-ray powder diffraction (STOE StadiP, Cu Kα_1).

X-ray single-crystal data of KSO_2F and $RbSO_2F$ were taken at various temperatures using a STOE Stadi4 equipped with a cryostat ($T_{min} = 123$ K). Data of α-$CsSO_2F$ were taken at various temperatures on a STOE IPDS equipped with a cryostat ($T_{min} = 93$ K). Data of β-$CsSO_2F$ were taken on a Bruker AXS P4 at room temperature. Crystal structure solution and refinements were performed using the programs of the SHELX-97 package.[5] Low temperature powder data were collected on a Guinier-Simon camera in the temperature range 293−123 K.

^{19}F solid state MAS NMR spectra were recorded using a Bruker DSX 400 using a 2.5 mm MAS probe allowing temperature-dependent measurements in the range 200−400 K. Rotational frequencies of 10 or 20 kHz were used. Chemical shifts are referenced relative to $CFCl_3$. The rotors were filled in a drybox.

Results and Discussion

Crystal Structures of KSO_2F, $RbSO_2F$, α-$CsSO_2F$, and β-$CsSO_2F$. KSO_2F and $RbSO_2F$ are isomorphous. They are structurally related to $KClO_3$ ($P2_1/m$, $Z = 2$). The fluorosulfite anion occupies a position of site symmetry *m*; it is surrounded by seven cations forming an irregular polyhedron (Figure 1). The bond lengths and angles of the fluorosulfite anion obtained by a routine refinement assuming no disorder are given in Table 6.

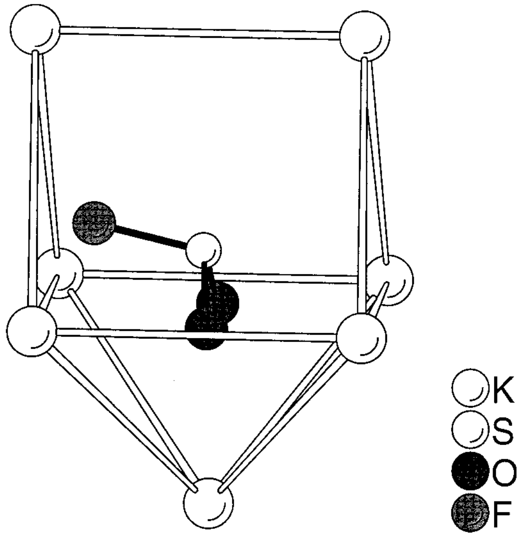

Figure 1. C_s symmetric coordination of the fluorosulfite anion by seven potassium cations in KSO_2F (routine refinement of room temperature data).

Table 1. Crystal Data and Refinement Results of α-$CsSO_2F$ and β-$CsSO_2F$

	α-$CsSO_2F$		β-$CsSO_2F$	
space group (no.)	*Pnma* (62)		*R*3*m* (160)	
a^a [pm]	790.98(8)		659.22(6)	
b^a [pm]	666.07(7)			
c^a [pm]	798.93(9)		800.50(4)	
V^a [10^6 pm^3], *Z*	420.9(1)		301.27(5), 3	
T [K]	293(2)		293(2)	
ρ_{calcd} [g cm^{-3}]	3.431		3.571	
μ (Mo Kα) [mm^{-1}]	9.21		9.588	
R_{int}, R_σ	0.0289, 0.0135		0.0492, 0.0390	
number of reflns	5472		1058	
unique reflns	652		361	
number of reflns $F_o > 4\sigma(F_o)$	576		361	
	routine ref	split ref	routine ref	split ref
param	28	29	19	13
restraints	0	10	1	5
R1 ($F_o > 4\sigma(F_o)$)	0.0156	0.0193	0.0271	0.0306
wR2	0.0356	0.0462	0.0672	0.0761
GOF	1.013	1.042	1.124	1.181
restrained GOF	1.013	1.039	1.122	1.192
Flack's param			−0.07(9)	0.00(9)
e_{max}/e_{min} [$e^-/10^6$ pm^3]	0.42/−0.46	0.75/−0.95	0.54/−2.20	0.60/−2.40

[a] Lattice parameter refinement of powder data (Cu Kα_1; α, 49 single indexed lines, d_{min} = 150.8; β, 34 single indexed lines, d_{min} = 109.2 pm).

$CsSO_2F$ was first described by Seel and Riehl[6] who indexed the powder pattern based on a cubic unit cell. They concluded from the similarity to the pattern of $CsClO_3$ that $CsSO_2F$ also is structurally analogous to the corresponding chlorate. Actually, this phase is rhombohedral β-$CsSO_2F$ ($R3m$, $Z = 3$), which forms below 50 °C. The rhombohedral angle deviates but slightly from 90°. The single-crystal structure analysis (Tables 1, 2) confirms a close relationship to $CsClO_3$. The anions are surrounded by eight cations (Figure 2) and vice versa; the structure can be deduced from the CsCl type by the group−

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Table 2. Atomic Parameters of β-$CsSO_2F$ (293 K) Obtained by Routine Refinement and by Split Refinement

Routine Refinement

atom	Wyckoff	site sym	x	y	z	sof	U_{eq}
Cs	3a	$3m$	0	0	0.0993	0.16667	0.0348(2)
S	3a	$3m$	0	0	0.614(2)	0.16667	0.036(1)
O	9b	m	0.254(4)	0.127(2)	0.695(3)	0.33333	0.043(3)
F	9b	m	−0.109(4)	0.109(4)	0.724(5)	0.16667	0.049(7)

Split Refinement

atom	Wyckoff	site sym	x	y	z	sof	U_{eq}
Cs	3a	$3m$	0	0	0.0988	0.16667	0.0350(2)
S	9b	m	0.0113(5)	−0.0113(5)	0.61536(8)	0.16667	0.0280(9)
O	9b	m	0.2470(7)	0.1235(4)	0.688(1)	0.33333	0.056(3)
F	9b	m	−0.1196(7)	0.1196(7)	0.719(2)	0.16667	0.036(3)

Table 3. Atomic Parameters of α-$CsSO_2F$ (293 K) Obtained by Routine Refinement and by Split Refinement

Routine Refinement

atom	Wyckoff	site sym	x	y	z	sof	U_{eq}
Cs	4c	m	0.86232(2)	$^1/_4$	0.39258(2)	0.5	0.02964(7)
S	4c	m	0.4266(1)	$^1/_4$	0.6176(1)	0.5	0.0371(2)
O	8d	1	0.4032(3)	0.4320(3)	0.7296(3)	1.0	0.0463(5)
F	4c	m	0.2586(4)	$^1/_4$	0.5076(3)	0.5	0.0641(8)

Split Refinement

atom	Wyckoff	site sym	x	y	z	sof	U_{eq}
Cs	4c	m	0.86229(3)	$^1/_4$	0.39262(3)	0.5	0.02975(9)
S1	4c	m	0.4356(1)	$^1/_4$	0.6282(1)	0.236(2)	0.0329(3)
S2	4c	m	0.4183(1)	$^1/_4$	0.60778(8)	0.264(2)	0.0329(3)
O1	8d	1	0.4214(7)	0.4347(4)	0.7279(5)	0.472(4)	0.0347(9)
O2	8d	1	0.2772(5)	0.284(1)	0.4915(6)	0.264(2)	0.0347(9)
O3	8d	1	0.396(1)	0.0688(7)	0.7106(9)	0.264(2)	0.0347(9)
F1	4c	m	0.2480(4)	$^1/_4$	0.5219(6)	0.236(2)	0.035(1)
F2	8d	1	0.3762(6)	0.4317(7)	0.7531(6)	0.264(2)	0.035(1)

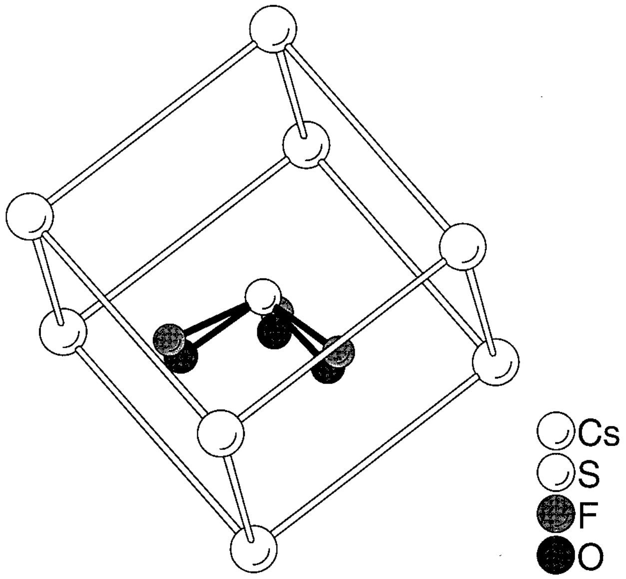

Figure 2. Superposition of three fluorosulfite anions due to site symmetry 3 and nearly cubic coordination by eight cesium cations in β-$CsSO_2F$ (routine refinement of rt data).

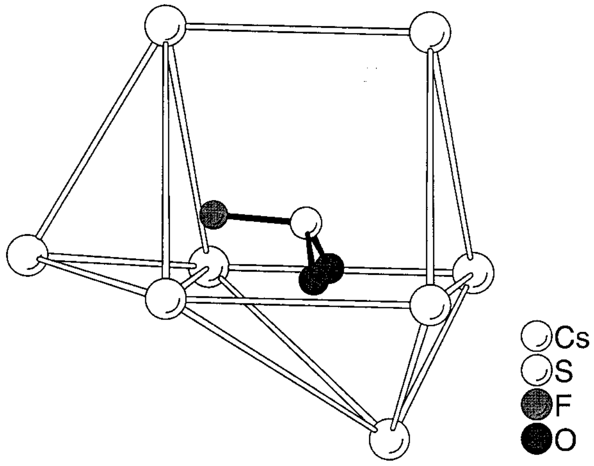

Figure 3. C_s symmetric coordination of the fluorosulfite anion by eight cesium cations in α-$CsSO_2F$ (routine refinement of rt data).

subgroup relations $Pm\bar{3}m \rightarrow R\bar{3}m \rightarrow R3m$. Because the anion occupies a position of site symmetry $3m$, the fluorosulfite anion exhibiting point symmetry C_s must be disordered in this phase. The positions of the fluorine and the oxygen atoms are clearly distinct in this case showing a superposition of three fluorosulfite anions (Figure 2). Nonetheless, in comparison with KSO_2F and $RbSO_2F$, the bond lengths obtained by routine refinement deviate even more from the calculated values (Table 6). This result shows that the refinement method of Mews, Christe, and co-workers is questionable because their extrapolation method will inevitably fail in this case. Instead, it is necessary to refine the sulfur atom on split positions as discussed later.

Above 373 K, β-$CsSO_2F$ slowly transforms to a previously unknown orthorhombic phase, α-$CsSO_2F$ ($Pnma$, $Z = 4$). The crystal structure of α-$CsSO_2F$ (Tables 1, 3) resembles the $BaSO_4$-type, the lone pair of the sulfur(IV) atom substituting one oxygen ligand of the sulfate tetrahedron. As in KSO_2F and $RbSO_2F$, the fluorosulfite anion occupies a position of site symmetry m (Figure 3). The bond lengths and angles as obtained by a routine refinement are quite similar to those obtained from KSO_2F and $RbSO_2F$ (Table 6).

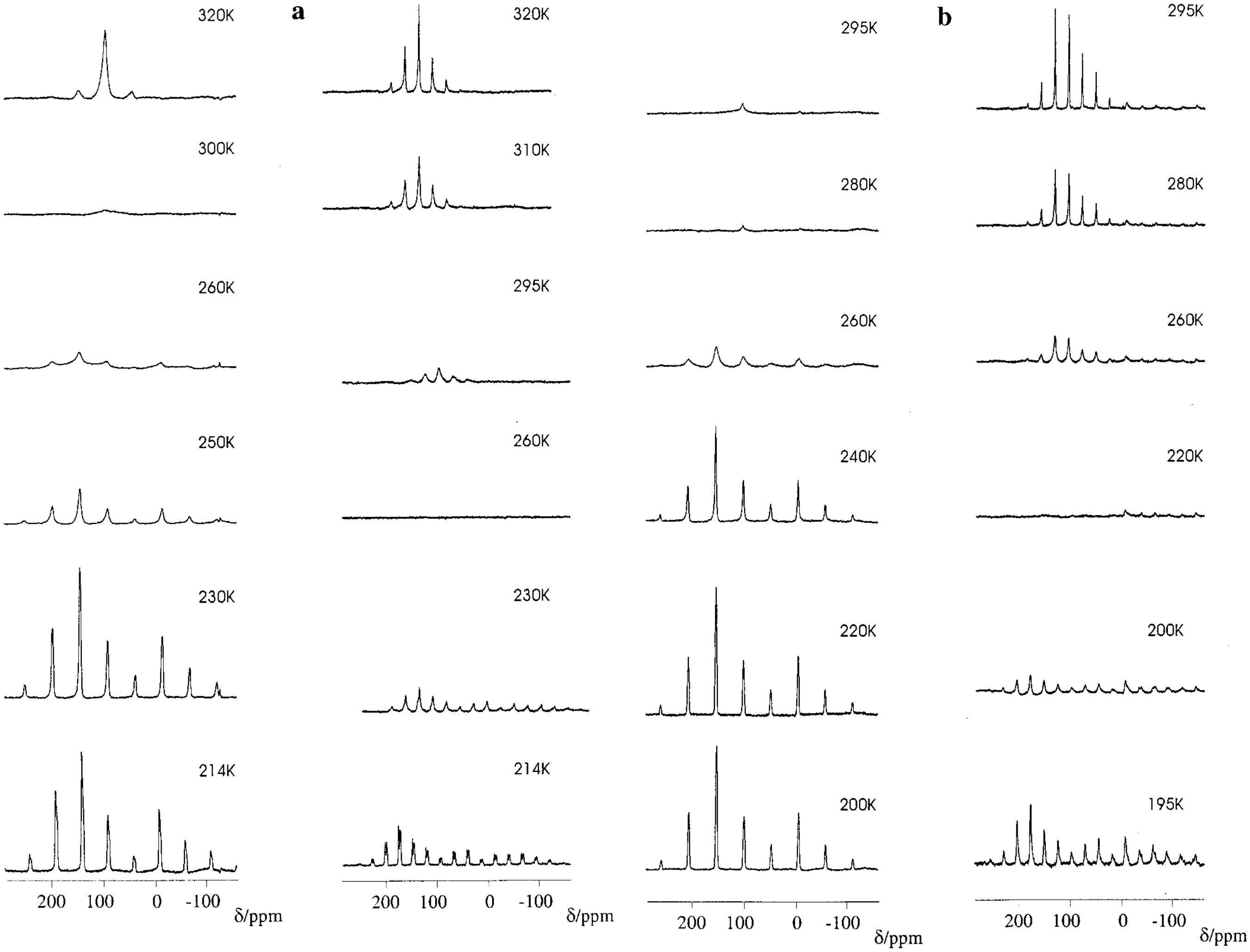

Figure 4. Experimental ^{19}F MAS spectra as a function of the temperature for the studied compounds: (a) left, KSO_2F; right, $RbSO_2F$; (b) left, β-$CsSO_2F$; right, α-$CsSO_2F$.

Table 4. Compilations of the ^{19}F NMR Data for the Studied Alkali Fluorosulfites

sample	δ_{iso}/ppm pos 1	δ_{iso}/ppm pos 2	Δ/ppm pos 1	Δ/ppm pos 2	η pos 1	η pos 2	occupancy $T = 200$ K	occupancy $T = 295$ K
KSO_2F	90	87	−226	−235	0.1	0.0	60:20:20	33:33:33
$RbSO_2F$	95	92	−220	−226	0.15	0.15	44:28:28	46:27:27
α-$CsSO_2F$	98		−233		0.1		*a*	54:23:23
β-$CsSO_2F$	99		−218		0.15		33:33:33	33:33:33

[a] SO_2F^- anion is still rotating at the lowest accessible temperature.

^{19}F Solid-State NMR Spectroscopy. At room temperature, the fluorosulfite anion is subjected to dynamic disorder in all studied phases, as shown by the ^{19}F MAS NMR spectra of KSO_2F, $RbSO_2F$, α-, and β-$CsSO_2F$ in the temperature range 195−320 K (Figure 4, Table 4). On decreasing the temperature, this dynamic is frozen (with respect to the time scale of the NMR experiment), resulting in static disorder. For clarity, we discuss the case of $RbSO_2F$ first.

At 320 K, the ^{19}F signal of $RbSO_2F$ is quite narrow (Figure 4a). The line width of the isotropic signal and the accompanying spinning sidebands is gradually increasing with decreasing temperature. At 260 K, the characteristic frequency of the motional disorder obviously coincides with the MAS frequency, indicated by the observed coalescence. The spectra at temperatures <260 K are indicative of two different fluorine environments, exhibiting slightly differing isotropic chemical shift values but nonetheless similar CSA patterns (CSA = chemical shift anisotropy) (Table 6). The line widths of the two resonances and the respective spinning sidebands decrease with decreasing temperature, indicating a successive decrease in the characteristic frequency of the motional process.

We modeled this dynamic process by the assumption of 120° rotational jumps of the anion with respect to the C_3 pseudoaxis of the fluorosulfite anion, approximately given by the direction of the lone pair. The three possible orientations generated thereby differ in the relative positions of the mirror planes of anion and cationic environment. In the following, the orientation in which the mirror planes of the anion and the crystal structure coincide is called the "crystallographic" orientation. The remaining two orientations in which the S−F bond of the anion is aligned along one of the S−O bonds of the "crystallographic" orientation are crystallographically equivalent. They are called the "disordered" orientations.

Table 5. Exchange Frequencies for the Pseudo-C_3 Jump Rotation

	$RbSO_2F$		KSO_2F		α-$CsSO_2F$		β-$CsSO_2F$	
	T/K	ν_{exch}/Hz	T/K	ν_{exch}/Hz	T/K	ν_{exch}/Hz	T/K	ν_{exch}/Hz
	320	6×10^5	320	6×10^6	295	1×10^7	295	5×10^5
	300	2×10^5	310	9×10^5	280	2×10^6	280	1×10^5
	260	5×10^3	295	5×10^5	260	9×10^5	260	2000
	250	2×10^3	260	1×10^4	220	5×10^4	240	500
	230	500	230	750	200	800	220	100
	214	100	214	1	195	200	200	1
coalesc temp[a]/K	260		280		215		275	

[a] $\nu_{exchange} = \nu_{MAS}$.

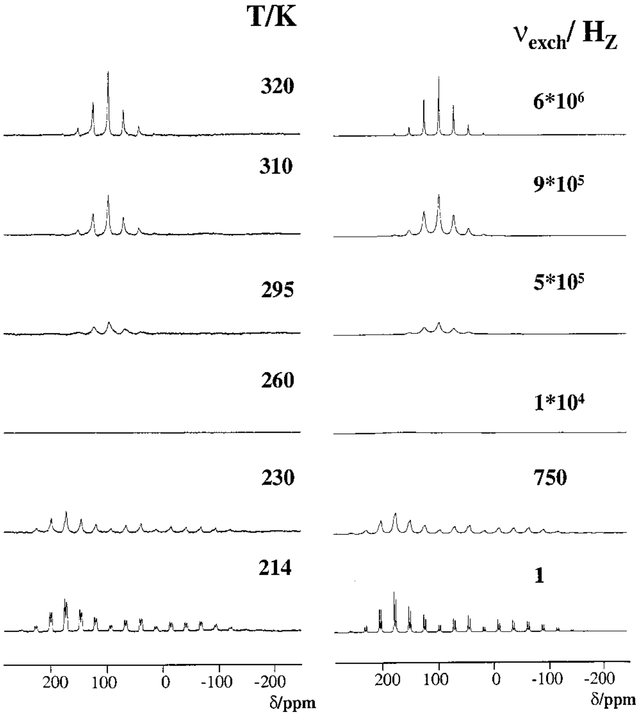

Figure 5. Experimental ^{19}F MAS spectra of $RbSO_2F$ (left) and their simulations (right) using the model discussed in the text. The temperatures and exchange frequencies are indicated.

As shown by the NMR experiment, the exchange between the three orientations is rapid above the coalescence temperature (Table 5); only an averaged ^{19}F signal can be detected. Below the coalescence temperature, the different orientations produce distinct ^{19}F signals. The two disordered orientations show the same signal because they are equivalent. The adaption of the spectrum taken at 214 K gives two signals at isotropic shifts of 257 and 254 ppm. We tentatively assigned the narrow line at 257 ppm to the "crystallographic" fluorine atom. The adaption also shows that the anisotropic tensors are almost identical, and the intensities of the two signals correspond to a distribution of the three orientations of 44:28:28. Assuming the rotational jump model, all spectra can be simulated quite satisfactorily using self-written software employing the standard treatment of the effect of motional processes on the NMR line shape[7,8] taking the exchange frequency and the distribution on the orientations as parameters (Figure 5, Table 5). A simulation of the room-temperature spectrum assuming free rotation around the C_3 pseudoaxis fails.

Unfortunately, these results show that cooling to 214 K does not resolve the disorder of the fluorosulfite anion. Instead, the dynamical disorder is changed into a static disorder.

The ^{19}F NMR spectra of KSO_2F are quite similar to those of $RbSO_2F$ (Figure 4a). The coalescence temperature of 300 K is 40 K higher than that of $RbSO_2F$. This is the consequence of the smaller cation, leading to smaller lattice constants and, consequently, a higher potential for the rotation of the anion.

Here, the two different crystallographic sites are not as clearly resolved in the ^{19}F MAS spectra as in the case of $RbSO_2F$. The simulation of the low temperature spectrum yields relative occupancies of 60:20:20, whereas the spectrum taken at 320 K is in accordance with an equal distribution, assuming an exchange frequency of 8×10^5 Hz, indicating an increasing preference of the crystallographic orientation with decreasing temperature.

The ^{19}F NMR spectra of α-$CsSO_2F$ also resemble those of $RbSO_2F$ (Figure 4b). Because of the bigger cation, the coalescence temperature is lower than that of $RbSO_2F$. At 195 K, the peaks of the signal are still too broad to allow us to decide whether there are one or two signals. The simulation of the spectra is achieved with the same model as above; the distribution at room temperature evaluates to 54:23:23.

β-$CsSO_2F$ unambiguously shows only one signal below the coalescence temperature of 300 K (Figure 4b). Because low temperature Guinier-Simon photographs give no indication of a phase transition to a less symmetric phase in which the site symmetry of the SO_2F^- anion might be reduced, we assume that the fluorosulfite is statically disordered in this phase. As expected, all spectra can be modeled with a 1:1:1 distribution because the three orientations are equivalent.

Single-Crystal X-ray Investigations. Since the NMR experiments have proven the disorder of the SO_2F^- anion in the alkali metal fluorosulfites, we have collected single-crystal X-ray data of KSO_2F, $RbSO_2F$, and α-$CsSO_2F$ at various (low) temperatures. Thereby, we intended to achieve complete ordering at low temperatures in order to obtain unambiguous experimental evidence concerning the structure of the fluorosulfite anion, or at least to monitor the increasing preference of the "crystallographic" orientation of the anion with decreasing temperature.

Routine refinements of these data sets using only the "crystallographic" orientation confirm the virtual increase of the S−F bond length with decreasing temperature in all three compounds (Table 6). Obviously, this effect can be ascribed to an increasing preference of the "crystallographic" orientation as suggested by the NMR results of KSO_2F. Moreover, it turned out that the structural parameters of the fluorosulfite anion in α-$CsSO_2F$ at 93 K (S−F, 169.0(2) pm; S−O, 147.8(1) pm; O−S−F, 100.5(1)°; O−S−O, 109.8(1)°) as determined by this routine refinement come close to the values predicted by Mews, Christe, and co-workers (S−F, 170−176 pm; S−O, 147 pm; O−S−F, 100.5°; O−S−O, 113°) by means of quantum chemical calculations on the free gaseous ion.

With the observed rotational disorder as a physical basis, we used a split model for the refinements that accounts for the three possible orientations of the anion.

Because strong correlation effects prevented a refinement of the geometric parameters of the fluorosulfite anion, they were restrained to the quantum chemically calculated values suggested by Mews, Christe, and co-workers (S−F, 171 pm; S−O, 147 pm; O−S−F, 100.5°; O−S−O, 113°), which are the least prejudiced estimates of the respective parameters. The variation of these parameters (S−F, 169−173 pm; S−O, 145−148 pm; O−S−F, 99−102°; O−S−O, 110−115°) resulted in equally

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Table 6. Results of Routine Refinements (r. r.) of KSO_2F, $RbSO_2F$, α-$CsSO_2F$, and β-$CsSO_2F$ (*R*-Values, Virtual Structural Parameters of the SO_2F^- Anion)

	KSO_2F (r. r.)				$RbSO_2F$ (r. r.)				α-$CsSO_2F$ (r. r.)					β-$CsSO_2F$ (r. r.)
T/K	293	223	173	123	293	223	173	123	293	233	202	143	93	293
R_{int}	0.0272	0.1045	0.0422	0.0505	0.0309	0.0396	0.0587	0.0504	0.0289	0.0266	0.0251	0.0254	0.0239	0.0492
R_σ	0.0312	0.1015	0.0448	0.0520	0.0344	0.0428	0.0604	0.0524	0.0135	0.0122	0.0114	0.0108	0.0088	0.0390
param	28	28	28	28	28	28	28	28	28	28	28	28	28	19 (1 restraint)
R1	0.0381	0.0345	0.0294	0.0281	0.0432	0.0476	0.0527	0.0580	0.0156	0.0146	0.0146	0.0137	0.0117	0.0271
R1 (all)	0.0584	0.0473	0.0378	0.0353	0.0561	0.0600	0.0651	0.0660	0.0203	0.0185	0.0177	0.0153	0.0126	0.0271
wR2	0.1045	0.0992	0.0748	0.0709	0.1255	0.1398	0.1474	0.1709	0.0356	0.0331	0.0322	0.0321	0.0279	0.0672
GOF	1.102	1.156	1.150	1.133	1.171	1.112	1.117	1.080	1.013	1.120	1.112	1.169	1.238	1.124
rest. GOF	1.102	1.156	1.150	1.133	1.171	1.112	1.117	1.080	1.013	1.120	1.112	1.169	1.238	1.122
e_{max}	0.50	0.53	0.73	0.59	1.05	1.58	1.80	3.33	0.42	0.43	0.49	0.59	0.61	0.54
e_{min}	−0.63	−0.69	−0.79	−0.75	−1.12	−1.43	−2.24	−2.27	−0.46	−0.43	−0.44	−0.65	−0.51	−2.20
S−F/pm	159.6(2)	161.3(2)	162.7(1)	162.5(1)	159.1(5)	160.8(4)	163.4(4)	164.4(5)	159.4(3)	160.9(3)	162.2(2)	165.3(2)	169.0(2)	158(4)
S−O/pm	153.0(2)	152.7(1)	152.2(1)	152.4(1)	152.9(4)	152.8(4)	152.6(4)	151.3(5)	151.8(2)	150.9(2)	150.5(2)	149.4(2)	147.8(1)	156(3)
O−S−F/°	102.7(1)	102.2(1)	102.0(1)	102.0(1)	102.3(2)	102.3(2)	102.0(2)	101.5(2)	102.9(1)	102.5(1)	102.1(1)	101.4(1)	100.5(1)	103(2)
O−S−O/°	104.7(1)	105.4(1)	105.8(1)	105.7(1)	105.0(3)	105.6(3)	106.6(3)	107.1(3)	106.0(2)	106.4(2)	107.0(1)	108.3(1)	109.8(1)	106(2)

Table 7. Results of Split Refinements (s. r.) of KSO_2F, $RbSO_2F$, α-$CsSO_2F$, and β-$CsSO_2F$ (*R*-Values, Occupancies)

	KSO_2F (s. r.)				$RbSO_2F$ (s. r.)				α-$CsSO_2F$ (s. r.)					β-$CsSO_2F$ (s. r.)
T	rt	223	173	123	rt	223	173	123	rt	233	202	143	93	293
R_{int}	0.0272	0.1045	0.0422	0.0505	0.0309	0.0396	0.0587	0.0504	0.0289	0.0266	0.0251	0.0254	0.0239	0.0492
R_σ	0.0312	0.1015	0.0448	0.0520	0.0344	0.0428	0.0604	0.0524	0.0135	0.0122	0.0114	0.0108	0.0088	0.0390
param	29	29	29	29	29	29	29	29	29	29	29	29	29	13
restraints	10	10	10	10	10	10	10	10	10	10	10	10	10	5
R1	0.0463	0.0441	0.0350	0.0360	0.0467	0.0497	0.0541	0.0623	0.0193	0.0195	0.0185	0.0173	0.0147	0.0306
R1 (all)	0.0675	0.0576	0.0433	0.0433	0.0598	0.0621	0.0666	0.0704	0.0248	0.0233	0.0214	0.0189	0.0157	0.0306
wR2	0.1115	0.1136	0.0802	0.0832	0.1315	0.1452	0.1434	0.1814	0.0462	0.0446	0.0410	0.0409	0.0355	0.0761
GOF	1.064	1.107	1.113	1.101	1.124	1.098	1.099	1.068	1.042	1.077	1.069	1.094	1.116	1.181
rest. GOF	1.072	1.120	1.135	1.145	1.119	1.092	1.094	1.065	1.039	1.076	1.069	1.095	1.127	1.192
e_{max}	0.84	1.15	1.01	1.04	1.06	1.62	1.81	3.51	0.75	0.74	0.70	0.81	0.85	0.60
e_{min}	−1.15	−1.56	−1.20	−1.42	−1.14	−1.52	−2.23	−2.25	−0.95	−1.30	−1.14	−1.42	−1.36	−2.40
														158(4)
occupancy	50:25	60:20	64:18	60:20	42:29	50:25	58:21	58:21	48:26	50:25	56:22	66:17	82:9	156(3)

good *R*-values/residual electron densities confirming the strong correlation. The isotropic displacement parameters of all oxygen atoms were constrained to the same value. The fluorine and sulfur atoms, respectively, were treated in the same way. The results of these refinements are summarized in Table 7 (further details are given in the Supporting Information). In KSO_2F, $RbSO_2F$, and α-$CsSO_2F$, the population of the "crystallographic" orientation increases with decreasing temperature. In KSO_2F and $RbSO_2F$, the disorder is "frozen" below 173 K at a distribution of about 60:20:20. In α-$CsSO_2F$, depopulation of the "disordered" orientations proceeds down to 93 K, the lowest accessible temperature. These findings are consistent with the NMR results and thus confirm the found rotational disorder.

In general, the split refinements using adequate models for the disorder have yielded low *R*-values/residual electron densities as well as sensible site occupation factors that are in accordance with the NMR results. The fact that the *R*-values and so forth are slightly higher than those in the routine refinements must be attributed to the reduced number of free parameters due to the use of restraints, and the marginal improvement of them when introducing more parameters in the routine refinements shows that the split model contains all information attainable from these data sets. However, it has proven impossible to separate fluorine from oxygen atoms, foiling all efforts to extract the "true" structure of the fluorosulfite anion from a disordered phase, no matter how sophisticated the split refinement method might ever be. Because α-$CsSO_2F$ at 93 K is the least disordered structure known until now, the results of the routine refinement represent a lower limit for the S−F bond length of 169.0(2) pm and an upper limit for the S−O bond length of 147.8(1) pm, differing only slightly from the values predicted by quantum chemical calculations.

The apparent success of the refinement method of Mews, Christe, and co-workers depends on the fact that the base triangle OOF of the fluorosulfite anion is almost equilateral. Therefore, the positions of the ligand atoms of differently oriented anions are virtually identical. This produces strong correlations between positional and displacement parameters of the fluorine and oxygen atoms in our split refinements preventing anisotropic refinement of these atoms.

However, the positions of the sulfur atoms of the "crystallographic" and the "disordered" orientations are different and must be treated correspondingly. It turned out that the positions of the "disordered" sulfur atoms differ too little from the special position of the crystallographic mirror plane so that they are shifted to this special position during refinement, introducing bias to bond lengths and angles. It should be noted that it is not possible to obtain a consistent model for the disorder of the fluorosulfite anion without introducing split positions for the sulfur atom.

Conclusions

(i) At room temperature, the fluorosulfite anion is dynamically disordered in all four phases of alkali metal fluorosulfites examined in this study. The disorder consists of 120° rotational jumps with respect to the C_3 pseudoaxis of the SO_2F^- anion. With the application of this simple model, the simulation of ^{19}F MAS data and the refinement of X-ray single-crystal data succeeds. Moreover, both methods show that the disorder is gradually reduced when decreasing the temperature (except for β-$CsSO_2F$ where the three orientations of the anion are equivalent).

(ii) At low temperatures, the dynamic nature of this disorder changes to static. In KSO_2F and $RbSO_2F$, the fluorosulfite anions are frozen before complete ordering is attained. In α-$CsSO_2F$, the amount of disorder continues to decrease down to 93 K.

(iii) It is impossible to obtain reliable structural parameters of the fluorosulfite ion by the refinement of X-ray data as long as the SO_2F^- ion exhibits rotational disorder.

(iv) The conventional refinement of the data set of α-$CsSO_2F$ taken at 93 K which shows only little disorder yields a lower limit for the true S−F bond length of 169.0(2) pm and an upper limit for the S−O bond length of 147.8(1) pm, verifying the results of quantum chemical calculations.

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Supporting Information Available: Tables concerning the structure determinations, atomic coordinates, anisotropic displacement parameters, bond lengths and angles, and SHELX input files of the split refinements. This material is available free of charge via the Internet at http://pubs.acs.org.

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