The Crystal Structure of Lithium Fluorosulphate LiSO₃F

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$LiSO_3F$ is, monoclinic, space group $C2/m$, $Z = 4$, with $a = 8.54$ (2), $b = 7.62$ (1), $c = 4.98$ (2) Å, $\beta = 90.0$ (3)°; $D_m = 2.20$, $D_c = 2.17$ g cm⁻³. The structure, which was refined to $R = 0.085$ for 332 densitometer intensities, consists of Li^+ and SO_3F^- ions arranged in alternating cationic and anionic layers. The layers are bound into a three-dimensional structure by Li–O bonds. The SO_3F group is tetrahedral with a fixed position for the F atom. The whole group is coordinated by eight Li atoms in a slightly distorted cubic arrangement. Li atoms are coordinated tetrahedrally by four O atoms. Two LiO_4 tetrahedra share a common edge to form Li_2O_6 groups. The important bond lengths are S–O 1.455 and 1.424, S–F 1.555, and Li–O 2.045 and 1.903 Å. The e.s.d.'s are 0.004–0.03 Å for the lengths and 0.2–0.9° for the angles.

Introduction

$LiSO_3F$ was first prepared by Traube, Hoerenz & Wunderlich (1919) by the reaction of LiOH with NH_4SO_3F. After recrystallization from water they obtained $LiSO_3F.3H_2O$. The anhydrous compound was then supposedly obtained by drying the hydrate *in vacuo*.

The structures of fluorosulphates have been studied for some time. Unfortunately, the simple fluorosulphates, KSO_3F and NH_4SO_3F (O'Sullivan, Thompson & Trotter, 1967, 1970), exhibit a certain degree of disorder of the SO_3F anions, which prevents an accurate determination of the S–F length. Far-infrared spectroscopy of alkaline fluorosulphates (Ruoff, Milne, Kaufmann & Leroy, 1970) reflects the disorder of the Na, K, Rb, and Cs salts. However, the sharp and distinct absorption bands in the region of lattice vibrations in the spectrum of $LiSO_3F$ suggest an ordered arrangement of the SO_3F anion.

Therefore we considered it useful to solve the structure of $LiSO_3F$ to obtain the geometry of the SO_3F ion and confirm or refute the suggestion made by Ruoff *et al.* (1970).

Experimental

Single crystals of $LiSO_3F$ were prepared by the reaction of LiCl with excess HSO_3F at 120°C. After the removal of HCl *in vacuo* the solution was slowly cooled and the resultant crystals filtered and washed with liquid SO_2 to remove excess HSO_3F. Since the compound is very hygroscopic, all manipulations were performed in the absence of moisture in Schlenk-type vessels. The purity of the salt and the absence of a hydrate was checked by chemical analysis and by infrared spectroscopy.

$LiSO_3F$ forms well-developed rectangular prisms bounded by (110), (1̄10), and (001), the longest side of the prisms being parallel to c. The crystal used for the structure determination was $0.15 \times 0.22 \times 1.0$ mm and was sealed in a thin-walled quartz capillary. The lattice parameters were obtained from precession photographs and refined from powder data. For the collection of intensities the crystal was mounted on a Nonius Weissenberg goniometer with c as the rotation axis. The reflexions *hk*0–*hk*4 were recorded by a multiple-film equi-inclination integrating Weissenberg technique with Ni-filtered Cu $K\alpha$ radiation. Only reflexions with $h + k = 2n$ were present. Since the crystal is monoclinic, from its diffraction symmetry, the systematic absences indicate space groups $C2$, Cm, or $C2/m$. From these, $C2/m$ was chosen and confirmed by a successful solution.

The intensities were measured photometrically on a Zeiss–Jena densitometer; weak reflexions were estimated visually. Over 1000 measured reflexions were reduced to 332 symmetry-independent data, including 77 unobserveds which were substituted by statistical values (Hamilton, 1955). The independent data were converted to observed structure amplitudes by applying Lorentz and polarization corrections; an absorption correction was applied on the assumption of a cylindrical crystal of diameter 0.18 mm ($\mu = 77.3$ cm⁻¹) (Weber, 1967). Scattering factors of Li^+, F^-, and O^- were those of Cromer & Mann (1968); that for S^{3+} was obtained by interpolation between the values for S^{6+} (Mirkin, 1961) and S^0 (Cromer & Mann, 1968).

Structure determination and refinement

The structure was solved from geometrical considerations. $3m$ (C_{3v}) symmetry for the anion being assumed, four SO_3F groups can only be placed in the special

Table 1. *Final atomic parameters and their estimated standard deviations*

The values have been multiplied by 10^4. The temperature factor is in the form:
$$T_i = \exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)].$$

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
S	2913 (2)	0	2715 (4)	45 (3)	56 (4)	137 (14)	0	−11 (4)	0
F	2744 (7)	0	5827 (12)	123 (8)	162 (11)	275 (31)	0	38 (11)	0
O(1)	1310 (6)	0	1722 (13)	44 (7)	80 (9)	237 (30)	0	−18 (9)	0
O(2)	3726 (4)	1597 (6)	2208 (10)	81 (6)	104 (8)	367 (30)	−39 (5)	−40 (9)	36 (10)
Li	0	1947 (18)	0	88 (18)	79 (22)	340 (85)	0	−32 (30)	0

position with point symmetry *m*, with F and one O lying in the symmetry plane. The coordinates of the S atom thus deduced were (0·250, 0·0, 0·250). Isotropic full-matrix refinement based on this single atom gave $R = 0·33$. Subsequent electron density maps clearly revealed the whole SO_3F group. The O and F atoms could be distinguished by their different distances from the central atom. The correct choice of the position of the F atom was checked by simultaneous least-squares refinement, switching the positions of the O in the symmetry plane and F, and observing the change in R. After refinement R dropped to 0·18. An electron density map then showed the position of the Li atom. At this stage, anisotropic temperature factors were introduced, which reduced R to 0·12. After rescaling the observed structure factors on $\Sigma F_o/\Sigma F_c$ for every recorded level, additional refinement yielded a final R of 0·085; $R_w = 0·11$.* The weighting scheme was derived by plotting $|\Delta F|$ (mean) *versus* $|F_o|$ (mean) for groups of 50–60 reflexions of similar magnitudes. The weight was taken as proportional to $1/|\overline{\Delta F}|^2$ (Stout & Jensen, 1968). R and R_w for the observed data only were 0·073 and 0·094. No extinction correction was made and all independent reflexions were included in the refinement. The maximum shift in positional parameters during the last cycle was $<0·03\sigma$, the average shift was $<0·01\sigma$. The programs used in the refinement were *TLS* and *TLSI* (Novák, 1973), based on *ORFLS* (Busing, Martin & Levy, 1962).

The final atomic parameters are given in Table 1.†

Description and discussion of the structure

The structure of $LiSO_3F$ consists of Li^+ and SO_3F^- ions arranged in distinct, mutually alternating layers parallel to (100). The layers are bound into a three-dimensional network by Li—O bonds.

* $R_w = \left[\sum\limits_i w_i(|F_o| - |F_c|)^2 / \sum\limits_i w_i|F_o|^2\right]^{1/2}.$

† A list of structure factors can be obtained from the authors and has also been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32912 (3 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

The SO_3F group forms a slightly distorted tetrahedron with a fixed position for the F atom and with the S—F direction approximately along **c**. There is no apparent bonding between F and Li atoms, the shortest Li—F distance being 3·464 Å, substantially more than the sum of the van der Waals radii (1·225 + 1·35 Å) (Pauling, 1960). O(1), lying in the symmetry plane, bridges two Li cations, while O(2) and O'(2^i) each coordinate one Li ion (Fig. 1). The bond distances and
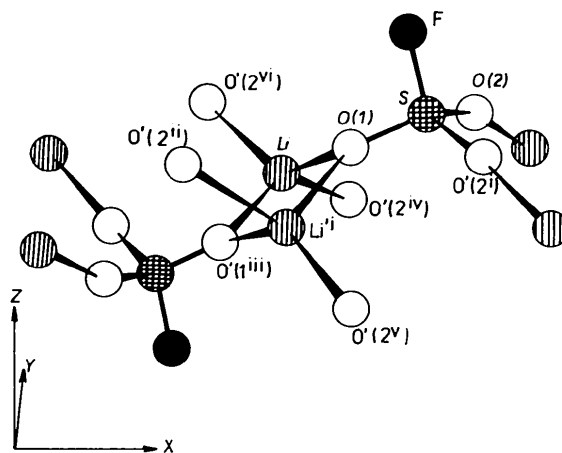

Fig. 1. A perspective view illustrating the bonding in $LiSO_3F$.

Table 2. *Interatomic distances* (Å) *and angles* (°) *in the SO_3F group*

The interatomic distances and bond angles listed in Tables 2, 3 and 4 were computed with *ORFFE* (Busing, Martin & Levy, 1964). They include the cell-parameter errors but averaging over the thermal motion of the atoms was not considered to be appropriate. The equivalent positions used in Tables 2, 3 and 4 and in Fig. 1 are: (i) $x,\bar{y},z$; (ii) $\frac{1}{2} + x, \frac{1}{2} + y, z$; (iii) $\bar{x},y,\bar{z}$; (iv) $\frac{1}{2} - x, \frac{1}{2} - y, \bar{z}$; (v) $\frac{1}{2} - x, \frac{1}{2} + y, \bar{z}$; (vi) $\frac{1}{2} + x, \frac{1}{2} - y, z$. The atoms marked by a prime are from neighbouring unit cells.

S—O(1)	1·455 (6)	O(1)—S—O(2)	113·5 (2)
S—O(2)	1·424 (4)	O(2)—S—O'(2^i)	117·4 (4)
S—F	1·555 (7)	O(1)—S—F	104·5 (5)
F—O(1)	2·380 (10)	O(2)—S—F	102·8 (3)
F—O(2)	2·330 (8)		
O(1)—O(2)	2·407 (6)		
O(2)—O'(2^i)	2·433 (9)		

Table 3. *Interatomic distances* (Å) *and angles* (°) *in the* Li_2O_6 *species*

Li–O(1)	2·045 (10)	O(1)–Li–O'(2^{iv})	110·6 (2)
Li–O'(2^{iv})	1·903 (10)	O'(2^{vi})–Li–O'(2^{iv})	108·7 (7)
O(1)–O'(1^{iii})	2·818 (10)	O(1)–Li–O'(1^{iii})	87·1 (6)
O'(2^{vi})–O'(2^{iv})	3·090 (10)	Li–O(1)–Li'^{i}	92·9 (9)
Li–Li'^{i}	2·965 (30)		

Table 4. *Distances* (Å) *in the* $(SO_3F)Li_8$ *coordination polyhedron*

S–Li	3·195 (10)	F–Li	4·011 (13)
S–Li^{vi}	3·226 (10)	F–Li^{vi}	4·187 (13)
S–Li'	4·640 (14)	F–Li'	3·464 (10)
S–Li'^{vi}	4·661 (12)	F–Li'^{vi}	3·665 (12)

angles in the SO_3F group (Table 2) are as expected, S–O (mean) = 1·434, S–F = 1·555 Å, compared with 1·43 and 1·58 Å for KSO_3F (O'Sullivan *et al.*, 1967), 1·45 and 1·55 Å for NH_4SO_3F (O'Sullivan *et al.*, 1970), and 1·415 and 1·540 Å for $FXeOSO_2F$ (Bartlett, Wechsberg, Jones & Burbank, 1972). The whole group is coordinated by eight Li in a distorted cubic arrangement.

Li cations are coordinated tetrahedrally by O atoms, and two LiO_4 tetrahedra always share a common edge forming isolated Li_2O_6 groups (Fig. 1). It is quite common for LiO_4 tetrahedra to be joined by edges, corners or both into fairly complex Li_xO_y species, *e.g.* in LiH_2PO_3 (Philippot & Lindqvist, 1970), $LiCO_3$ (Zemann, 1957), Li_3PO_4 (Zemann, 1960), β-$LiIO_3$ (Schulz, 1973), β-Li_2SO_4 (Alcock, Evans & Jenkins, 1973; Nord, 1976), and $Li_2Cr_2O_7.2H_2O$ (Datt, Rannev, Balitcheva & Ozerov, 1970; Datt & Ozerov, 1974). In fact, simple isolated tetrahedral LiO_4 or Li_2O_6 species, as found in $LiKPO_3F.H_2O$ (Galigné, Durand & Cot, 1974) and $Li_2NH_4(PO_3)_3$ (Averbuch-Pouchot, Durif & Guitel, 1976) respectively, are rather exceptional.

The skeletal Li_2O_2 group in the Li_2O_6 species is planar with Li–O = 2·045 Å and Li–O–Li = 92·9°. The terminal Li–O distance of 1·903 Å is in the range of the shortest Li–O distances found in other structures (1·82–1·96 Å). The planes of the terminal O atoms and of the Li_2O_2 bridging group make an angle of 82·7°. Interatomic distances and angles for the Li_2O_6 group are listed in Table 3. Distances in the $(SO_3F)Li_8$ coordination polyhedron are in Table 4.

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