741. *Complex Fluorides. Part IX.* The Lattice Constants and Infrared Spectra of the Fluorosulphates.*

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The valencies of the fluorosulphate ion SO_3F^- are directed from the central sulphur atom towards the corners of a tetrahedron. The potassium, ammonium, and rubidium salts are isomorphous with the perchlorates and are ionic, but in other salts there is evidence for distortion of the anion by partial covalent-bond formation. The infrared spectra agree closely with the published Raman spectrum for the fluorosulphate ion. Assignments are made for infrared peaks observed and the differences between the infrared and Raman spectra are discussed. The ammonium salt shows strong evidence for hydrogen bonding.

KETELAAR and WEGERIF[1] showed that the structures of salts AMX_4^{n-} having tetrahedral anions are all closely related. It was not considered necessary that the ligands, X, should all be the same, the fluorochromates $MCrO_3F$ and the osmiamates $MOsO_3N$ forming part of the series. The series is now extended to include the fluorosulphates.

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* Part VIII, *J.*, 1957, **674.**

[1] Ketelaar and Wegerif, *Rec. Trav. chim.*, 1938, **57**, 1269.

Lange [2] showed that, from gross morphology, potassium fluorosulphate appears to be isomorphous with potassium perchlorate and Seifert,[3] from *X*-ray crystallography, that cæsium fluorosulphate has the scheelite structure and is probably isomorphous with cæsium fluorochromate. Since potassium fluorochromate also has a pseudo-scheelite structure,[1] potassium and rubidium fluorosulphates should have either the scheelite structure of the fluorochromates, or the barium sulphate structure of the perchlorates.

Potassium, rubidium, and ammonium fluorosulphates are orthorhombic at room temperature, probably having the space group *Pnma*; they are isomorphous with the corresponding perchlorates. Cell sides were found to be as follows: KSO_3F: $a_0 = 8{\cdot}57 \pm 0{\cdot}03$; $b_0 = 5{\cdot}93 \pm 0{\cdot}05$; $c_0 = 7{\cdot}36 \pm 0{\cdot}03$ Å; $RbSO_3F$: $a_0 = 9{\cdot}21 \pm 0{\cdot}03$; $b_0 = 5{\cdot}80 \pm 0{\cdot}05$; $c_0 = 7{\cdot}67 \pm 0{\cdot}03$ Å; NH_4SO_3F: $a_0 = 8{\cdot}79 \pm 0{\cdot}03$; $b_0 = 6{\cdot}07 \pm 0{\cdot}05$; $c_0 = 7{\cdot}32 \pm 0{\cdot}03$ Å, and the unit cell volumes were 375, 410, and 386 Å^3 for potassium, rubidium, and ammonium fluorosulphates respectively. The unit cells are not completely regular as regards axial ratios, $a : b : c$ being 1·445 : 1 : 1·242 for KSO_3F, 1·585 : 1 : 1·320 for $RbSO_3F$, and 1·449 : 1 : 1·208 for NH_4SO_3F, but this lack of regularity probably only reflects the slightly differing cation sizes in a fairly complex lattice and the presence of hydrogen bonding in the ammonium salt.

The unit-cell volume of the ammonium salt lies closer to that of the potassium salt than of the rubidium salt. For salts of complex fluoro-acids the ammonium salt generally has a rather larger unit-cell volume than the rubidium salt, the complex chloro- and bromo-salts having the reverse relationship.[4] The small unit-cell volume in the present salt is possibly due to hydrogen-bond formation, and this would also account for the non-regularity in axial ratios. Its existence is clearly shown in the infrared spectrum of ammonium fluorosulphate.

Sodium fluorosulphate gives a powder pattern similar to that of anhydrous sodium perchlorate, which has the anhydrite structure,[5] but the pattern could not be indexed and the two salts are probably not isomorphous. The greater polarizing power of the sodium ion would make it the most likely of all the alkali metals examined to distort the fluorosulphate ion. Silver fluorosulphate gives a very different powder pattern from potassium fluorosulphate and there is probably some covalent-bond formation between the silver and the fluorosulphate group. Such covalent-bond formation appears quite general amongst silver salts of oxyanions.[6] The distortion of the fluorosulphate ion inferred from the *X*-ray data for these two salts is confirmed by the infrared spectra; such distortion will lower the symmetry of the anion and give rise to the possibility of many more infrared absorption peaks.

Thus, crystallographic evidence shows that the fluorosulphates are isomorphous with the perchlorates, having tetrahedral symmetry about the central sulphur atom. Such an ion will have the symmetry group C_{3v}, having six fundamental modes of vibration, all of which will be both infrared- and Raman-active. An assignment had already been made to all the infrared bands observed and the assignments were completely confirmed by Siebert's Raman spectra.[7] Complete values for the observed infrared and Raman frequencies are given in the Table, together with the assignments for the various bands. Within the limits of experimental error, the values found for most of the fundamentals are in good agreement when the results of infrared and Raman spectroscopy are compared. The only major disagreement is in the value for the S–F stretching frequency, ν_2. The value for the symmetrical S–F stretching in sulphur hexafluoride [8] is 775 cm.$^{-1}$ and Siebert records 786 cm.$^{-1}$ for the corresponding Raman frequency for an aqueous solution of

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[2] Lange, *Ber.*, 1929, **62**, 786.

[3] Seifert, *Z. Krist.*, 1942, **104**, 385.

[4] Cox and Sharpe, *J.*, 1954, 1798.

[5] Zachariasen, *Z. Krist.*, 1930, **73**, 141.

[6] Sharp and Sharpe, unpublished results.

[7] Siebert, *Z. anorg. Chem.*, 1957, **289**, 15.

[8] Eucken and Ahrens, *Z. phys. Chem.*, 1934, *B*, **26**, 297; Yost, Steffens, and Gross, *J. Chem. Phys.*, 1934, **2**, 311.

sodium fluorosulphate.[7] Siebert comments that this value is surprisingly high as it would be expected that the high "ionic-character" of the bond $O_2S(O^-)$–$F \rightleftharpoons O_2S({:}O) + F^-$ would lower this frequency as in the analogous case of boron trifluoride and the fluoroborate ion [9] (symmetrical B–F stretching frequencies 888 and 771 cm.$^{-1}$ respectively). For both the fluoroborate and the fluorosulphate ions, removal of the fluoride ion leaves a stable, known entity. We have concluded that the difference in S–F stretching frequencies in the solid state and in aqueous solution is due, in the latter case, to some form of hydrogen bonding between the water molecules and the oxygen atoms of the fluorosulphate ion. This would reduce the possible "ionic character" of the S–F bond and its frequency would approach that found in sulphur hexafluoride. Similar distortion is most likely to occur in the solid state with cations of high polarizing power and it is significant that sodium fluorosulphate gives a strong infrared band at 785 cm.$^{-1}$. A similar band is found in silver fluorosulphate, but here the symmetry of the anion has been destroyed and other additional bands occur. Siebert[10] has come to a very similar conclusion on the value of the S–F stretching frequency, and has found that there is a similar result for all the ions XSO_3^- when the values of the S–X frequencies are compared in the solid and in solution. Extra infrared bands are a good criterion for anion–cation interaction and triphenylmethyl fluorosulphate is completely ionic in character.[11]

Infrared and Raman spectra of the fluorosulphates.

$NaSO_3F$	KSO_3F	$RbSO_3F$	$CsSO_3F$	NH_4SO_3F	$AgSO_3F$	$Ph_3C{\cdot}SO_3F$ [a]	$NaSO_3F$ [b]	Assignment	Calc.	Notes
*	—	*	*	*	*	*	409	ν_6 (E_1)	390	(1)
*	565 m	*	*	*	*	*	566	ν_3 (A_1)	—	(2)
	583 s						592	ν_5 (E)	—	(3)
740 m	732 s	729 s	728 s	737 s	767 s	710 m	786	ν_2 (A_1)	—	(4)
785 s	—	—	—	—	785 s	—	—	—	—	
—	970 w	973 w	971 w	970 w	975 w	—	—	$\nu_6 + \nu_3$	955	
								$\nu_6 + \nu_5$	973	
1095 s	1073 s	1072 s	1071 s	1072 s	1057 s	1070 s	1082	ν_1 (A_1)	—	(5)
1275 s	1277 s	1274 s	1258 s	1270 s	1235 s	—	—	$\nu_2 + \nu_5$	1315	
1295 s	1299 s	1294 s	1300 s	1304 s	1282 s	1289 s	1287	ν_4 (E)	—	(6)
—	1656 w	1661 w	1662 w	—	1631 s	1643 w	—	$\nu_1 + \nu_5$	1656	
2370 w	2347 w	2342 w	2353 w	—	2273 w	2320 w	—	$\nu_1 + \nu_4$	2372	

[a] Sharp and Sheppard, ref. 11. [b] Raman spectrum; Siebert, ref. 7. * Not examined below 650 cm.$^{-1}$.

Notes.—(1) Rock. (2) Symmetrical SO_3 deformation. (3) Asymmetrical SO_3 deformation. (4) S–F stretching. (5) Symmetrical S–O stretching. (6) Asymmetrical S–O stretching.

The assignments of the other infrared bands follow simply from the relations between the observed frequencies of the sulphate ion (symmetry group T_d), the fluorosulphate ion (symmetry group C_{3v}), and sulphuryl fluoride (symmetry group C_{2v}). The infrared absorption pattern of the fluorosulphate ion is very similar to that of the isoelectronic perchloryl fluoride.[12] For the fairly strong band at 1277 cm.$^{-1}$ the combination frequency $\nu_2 + \nu_5$ was preferred. This was considered more probable than the alternative of $\nu_2 + \nu_3$, as Fermi resonance will occur between the fundamental ν_4 and the combination frequency to give enhanced intensity to the latter. By comparison with the spectrum of perchloryl fluoride the absorption band corresponding to the vibration ν_6 should lie below 400 cm.$^{-1}$, that is, out of the range of the potassium bromide prism. If the weak absorption peak at 970 cm.$^{-1}$ corresponds to either of the combinations $\nu_3 + \nu_6$ or $\nu_5 + \nu_6$, this would lead to a value of about 390 cm.$^{-1}$ for the vibration ν_6.

The infrared frequencies of the ammonium ion in ammonium fluorosulphate occur at 1410, 1448, 3040, and 3125 cm.$^{-1}$. The position of the N–H vibration at about 1400 cm.$^{-1}$ has been used as diagnostic of the presence of hydrogen bonding [13] and the splitting of this,

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[9] Siebert, *Z. anorg. Chem.*, 1953, **274**, 34.

[10] *Idem*, personal communication.

[11] Sharp and Sheppard, *J.*, 1957, 674.

[12] Lide and Mann, *J. Chem. Phys.*, 1956, **25**, 1128.

[13] Bovey, *ibid.*, 1950, **18**, 1684.

and of the 3100 cm.$^{-1}$ band, in the spectrum of this salt shows the presence of this form of linkage. However, the hydrogen bonding does not seem sufficiently strong to affect the fluorosulphate ion frequencies, although the displacement of the 1400 cm.$^{-1}$ band to 1448 cm.$^{-1}$ is greater than that hitherto recorded for any ammonium salt except ammonium fluoride. The splitting of this band is similar to that observed by Wagner and Hornig [14] for the low-temperature form of ammonium chloride.

EXPERIMENTAL

The fluorosulphates were prepared by Woolf's method [15] and analysed by evaporation with concentrated hydrochloric acid and estimation as barium sulphate. Sodium fluorosulphate was prepared from bromine trifluoride and sodium persulphate (Found: SO_3F^-, 81·1. Calc. for $NaSO_3F$: SO_3F^-, 82·1%), potassium fluorosulphate from bromine trifluoride and potassium persulphate (Found: SO_3F^-, 71·4. Calc. for KSO_3F: SO_3F^-, 71·6%), and rubidium fluorosulphate from bromine trifluoride and an equimolecular mixture of rubidium chloride and nitrosonium pyrosulphate (Found: equiv., 190; SO_3F^-, 52·8. Calc. for $RbSO_3F$: equiv., 185; SO_3F^-, 53·6%). Cæsium fluorosulphate was prepared as an equimolecular mixture with cæsium fluoride from bromine trifluoride and cæsium sulphate, the products being heated to 250° to destroy cæsium bromofluoride. It was identified by means of its *X*-ray powder photograph.[3] Ammonium fluorosulphate was prepared by heating ammonium pyrosulphate with ammonium fluoride followed by extraction of the required salt with ammoniacal methyl alcohol [16] (Found: N, 12·2. Calc. for NH_4SO_3F: N, 12·0%), and silver fluorosulphate from bromine trifluoride and an equimolecular mixture of silver chloride and nitrosonium pyrosulphate (Found: Ag, 52·2. Calc. for $AgSO_3F$: Ag, 52·1%).

X-Ray powder photographs were taken with Cu-$K\alpha$ radiation. The samples were filled into Pyrex capillaries, the " dry-box " technique being used for $NaSO_3F$ and $AgSO_3F$, and the capillaries were sealed with warm picein wax. *X*-Ray powder photographs were indexed by analogy with the known structure of potassium perchlorate.[17]

Infrared spectra were measured in Nujol and hexachlorobutadiene mulls on a Perkin-Elmer Model 21 spectrometer with rock-salt or potassium bromide optics. Where necessary, mulls were prepared in the " dry-box."

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[14] Wagner and Hornig, *ibid.*, 1950, **18**, 296.

[15] Woolf, *J.*, 1950, 1053.

[16] Mellor, " A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longmans, Green and Co., London, 1930, p. 685.

[17] Gottfried and Schusterius, *Z. Krist.*, 1932, **84**, 65.