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SHORT COMMUNICATION

Structure of Tetramethlyammonium Fluorosulfate $N(CH_3)_4SO_3F$(VI)

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Recently the structure of tetramethylammonium salts of IO_4^-, CrO_3F^- and ReO_4^- have been described {1-3}. All these compounds have the $N(CH_3)_4ClO_4$ structure {4}. At room temperature, potassium fluorosulfate is orthorhombic with the space group Pnma. The cesium salt has, however, the sheelite structure. Tetramethylammonium fluorosulfate might have either the orthorhombic or tetragonal structure. The structure of tetramethylammonium fluorosulfate is described for the first time in this communication.

Experimental

Tetramethylammonium fluorosulfate, $N(CH_3)_4SO_3F$ was prepared by adding $N(CH_3)_4F$ to a concentrated solution of HSO_3F. The Ka of HSO_3F is 0.12 at 25°C {5}. The temperature was therefore kept low during the preparation of the compound. The crystals obtained were filtered, washed with cold alcoholic water and analyzed. Approximately 4.5 g of compound was isolated in one batch. Found: N, 7.93; C, 27.57; H, 6.97; S, 18.01. Calculated for $N(CH_3)_4SO_3F$: N, 8.09; C, 27.75; H, 6.94; S, 18.50.**

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** C,H,N analyses performed by Galbraith Laboratories, Knoxville, Tennessee.

The x-ray powder diffraction data of this compound are given in Table I. A Picker x-ray diffractometer was used to take the spectra of the compound and the data were obtained by the least squares refinement of the x-ray powder diffraction data using an IBM 370 computer.

Table I

Powder diffraction data for $N(CH_3)_4SO_3F$

hkl	$d_{obs.}$ (Å)	$d_{calc.}$ (Å)	Intensity
101	4.81	4.81	m.s.
200	4.19	4.20	v.s.
111	4.00	4.17	m.s.
201	3.45	3.41	m.
211	3.16	3.16	s.
220	2.96	2.96	s.
102	2.77	2.77	s.
221	2.65	2.65	m.s.
301	2.53	2.53	m.s.
311	2.42	2.41	m.s.
321	2.19	2.16	w.
302	2.02	2.02	w.
330	1.98	1.98	m.s.
331	1.87	1.87	m.
322	1.82	1.82	w.
421	1.79	1.79	m.
213	1.73	1.73	m.
313	1.57	1.57	m.
440	1.48	1.48	w.
530	1.44	1.44	w.

All the peaks excepting one appearing at 4.62 have been accounted for in the Table. The peak at 4.62 is attributed to the decomposition of $N(CH_3)_4SO_3F$ into $N(CH_3)_4HSO_4$. In Table II the cell dimensions of a series of isostructural compounds of $N(CH_3)_4^+$ are described.

Table II

A comparison of various tetramethylammonium compounds with tetragonal structures.

Salt	a=b(Å)	c(Å)	References
$N(CH_3)_4ClO_4$	8.29	6.01	{4}
$N(CH_3)_4CrO_3F$	8.30	6.01	
$N(CH_3)_4SO_3F$	8.38	5.86	
$N(CH_3)_4ReO_4$	8.47	6.03	{3}

It is of interest to note that of all cations, $N(CH_3)_4^+$ is the only known ion to give a series of isostructural crystals with IO_4^-, SO_3F^- , ReO_4^-, etc. A comparison of the structures of the salts of K^+, NH_4^+ and $N(CH_3)_4^+$ is described in Table III.

Table III

A comparison of the structures of combinations of various cations and anions.

	NH_4^+	K^+	$N(CH_3)_4^+$
SO_3F^-	orthorhombic {6}	orthorhombic {6}	tetragonal
ClO_4^-	orthorhombic {6}	orthorhombic {6}	tetragonal {4}
IO_4^-	tetragonal {6}	tetragonal {6}	tetragonal {1}
CrO_3F^-	orthogonal {6}	tetragonal {6}	tetragonal {2}
ReO_4^-	tetragonal {6}	tetragonal {6}	tetragonal {3}

The infrared and Raman spectra of this compound with the suggested assignm are given in Table IV.

Table IV

Infrared and Raman spectra of tetramethylammonium fluorosulfate

I.R.	Raman	Assignments	Notes
	380s	$\nu_6(E_1)$	{a}
585s		$\nu_5(E)$	{b}
710s 730s	750s	$\nu_2(A_1)$	{c}
955s		$\nu_6 + \nu_3$	
1079s	1062s	$\nu_1 + (A_1)$	{d}
1285s		$\nu_4 + \nu_5$	{e}
2355s		$\nu_1 + \nu_4$	

Notes:--- (a) Rock. (b) Asymmetrical SO_3 deformation. (c) S-F stretching. (d) Symmetrical S-O stretching. (e) Asymmetrical S-O stretching.

These assignments agree with the suggested values given previous workers { The peaks of the tetramethylammonium ion, i.e., C-H, C-N frequencies, are well and so they have not been reported in Table IV for assignments.

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