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SYNTHESIS AND CHARACTERIZATION OF NEW FLUOROSULFINATE: NH_4SO_2F‡

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SUMMARY

Sulfur dioxide reacts with dry ammonium fluoride to give ammonium fluorosulfinate. The infrared and low temperature Raman spectra of the new salt are described.

INTRODUCTION

Tetramethylammonium and group 1 cation fluorosulfinates were first reported by Seel and Riehl [1]. Chemically, fluorosulfinates behave as activated metal fluorides and are used as mild fluorinating agents in halogen-fluorine-exchange reactions [2]. They are formed by the action of sulfur dioxide on the corresponding fluoride:

$$MF + SO_2 \rightarrow MSO_2F \quad (M = Na, K, Rb, Cs, Me_4N) \qquad (1)$$

Fluorosulfinates of lithium or the group 2 elements have not been observed. This has been explained in terms of the greater stability of fluoride lattices containing small cations such as lithium or calcium [1]. A comparison of effective

‡ Dedicated to Professor J. Fuchs, Berlin, on the occasion of his 65th birthday.

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ion radii [3] shows that the radius of the ammonium cation is well within the range of cations of existing fluorosulfinates:

Li^+	106 pm	Na^+	153 pm	NH_4^+	166 pm
Ca^{2+}	114 pm	Cs^+	202 pm	NMe_4^+	215 pm

Here the synthesis and spectroscopic identification of the new salt NH_4SO_2F is reported.

RESULTS AND DISCUSSION

NH_4SO_2F is synthesized by the reaction of sulfur dioxide with dried ammonium fluoride at elevated pressure and room temperature according to equation 1. The progress of the reaction is monitored by observing the increase in weight of the solid product. A typical yield is the absorption of over eighty percent of the theoretically calculated amount of sulfur dioxide.

Ammonium fluorosulfinate decomposes immediately in the presence of water and has to be stored in sealed glass ampoules that were previously flame dried.

The sensitivity of NH_4SO_2F to water precluded a satisfactory characterization by means of infrared spectroscopy. Raman spectra were recorded at temperatures around -100°C; at room temperature the compound decomposed or sublimed in the laser beam. A list of the infrared and Raman active transitions considered as fundamentals is given in Table 1, together with a tentative assignment on the basis of the work of MATHIEU and POULET on NH_4^+ [4] and the work of PAETZOLD and AURICH on KSO_2F [5] and our own spectroscopic data for NH_4F. Although special care is taken to ensure the absence of water in ammonium fluoride (see experimental section) small amounts of HF_2^- could always be detected in the spectra.

EXPERIMENTAL

IR spectra were recorded on a Perkin-Elmer model 883 grating spectrometer. Samples were analyzed as Nujol mulls (between KSR5 plates). Raman Spectra were obtained with a Dilor model RT 30 spectrometer (triple monochromator). An argon ion laser (Spectra Physics model 2000) was employed for excitation using the 514.5 nm line and an interference filter to remove unwanted plasma lines from the laser emission. The sample was illuminated in the 90 ° and 180 ° geometries in a capillary tube of 5 mm inner diameter cooled by a flow of cold nitrogen gas [6].

TABLE 1

The vibrational spectrum of NH_4SO_2F and its assignment in comparison to NH_4^+ and KSO_2F (Observed Frequencies in cm^{-1})

NH_4SO_2F		NH_4^+ [4]		KSO_2F		Assignment in point groups T_d (NH_4^+) and C_s (SO_2F^-)
Raman (-100°C)	IR	Raman	IR	Raman[a]	IR [5]	
2870 (m)[b]		2845				ν_1 (A_1) stretch
2009 (vw)		2006				ν_2 (E) bend
3087 (m,br)		3089	3134			ν_3 (F_2) stretch
1403 (vw)	1399 (vs)	1403	1397			ν_4 (F_2) bend
1098 (s)	1114 (s)			1104 (s)	1105 (s)	ν_1 (A') sym. SO_2 stretch
600 (vw)	580 (w)			590 (w)	595 (s)	ν_2 (A') sym. SO_2F bend
450 (vs,br)[c]	483 (vs)			496 (s)	496 (vs)	ν_3 (A') sym. SF stretch
248 (vs)						ν_4 (A') sym. SO_2F bend
1150 (w)	1167 (s)			1183 (w)	1182 (vs)	ν_5 (A'') asym. SO_2 stretch
370 (w,br)				365 (w,br)		ν_6 (A'') asym. SO_2F bend

[a] Raman spectrum recorded at room temperature. Argon ion laser, excitation line 488 nm.

[b] The following abbreviations have been used: s, strong; m, medium; w, weak; v, very; br, broad.

[c] The half band width of this Raman band is ca. 110 cm^{-1}.

KSO_2F was prepared according to literature methods [1]. NH_4F (MERCK) was purified and dried by three vacuum sublimations at a bath temperature of + 70°C. SO_2 (LINDE) was dried by storage and distillation over CaH_2.

Preparation of Ammonium Fluorosulfinate (NH_4SO_2F)

In the dry box a 350 ccm stainless steel autoclave containing metal steel balls was charged with dried ammonium fluoride (8.8g, 0.24 mol). On a glass vacuum line sulfur dioxide (30g, 0.47 mol) was condensed onto the NH_4F and the autoclave shaken for two days at room temperature. All volatiles were removed in vacuo and the obtained mixture of NH_4F and NH_4SO_2F powdered in the dry box. The autoclave was recharged with the powdered mixture and sulfur dioxide added again. This procedure was repeated twice and 20.5g (85% yield) white product (m.p. 120°C, sealed capillary) obtained.

Analysis: Found: H 4.7; F 24.1; N 15.0 %. H_4FNO_2S requires H 4.0; F 18.7; N 13.9 %.

A sample containing approximately 18 mol% $NH_4^+FHF^-$ requires H 4.5; F 24.1; N 15.0 %.

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