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SHORT COMMUNICATION

Uranium (IV) Fluorosulfate

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The reactions of anhydrous transition metal oxychlorides or chlorides with peroxydisulfuryl difluoride ($S_2O_6F_2$) have provided a route for the preparation of transition metal fluorosulfates and oxyfluorosulfates [1, 2].

We have found that UCl_4 reacts with $S_2O_6F_2$ according to the following equation:

$$UCl_4 + 2S_2O_6F_2 = U(SO_3F)_4 + 2Cl_2 \qquad (1)$$

Uranium (IV) fluorosulfate is a tan crystalline solid that is hydrolytically unstable and is soluble in dimethylsulfoxide (DMSO) and acetonitrile. It begins to decompose in vacuo at around 90° and upon heating to 300° produces UF_4 in 69% yield.

The infrared spectrum of $U(SO_3F)_4$ contains more absorption bands than may be ascribed to any one type of fluorosulfate group. It is known that for either monodentate bound SO_3F groups or bidentate SO_3F groups (either chelating or bridging) nine fundamental infrared bands are expected. For $U(SO_3F)_4$, a monodentate SO_3F group is present as characteristic SO bands [3] are found at 1410, 1290 and 970 cm^{-1} while additional SO bands at 1160 and 1080 cm^{-1} are characteristic of a bidentate SO_3F group [4, 5]. The third S-O stretching mode expected for a bidentate SO_3F group is probably buried under the broad band centered at 1410 cm^{-1}. The presence of more than one type of SO_3F group is further supported by the presence of two bands

in the 800 - 900 cm^{-1} region, where only S-F stretching modes occur in fluorosulfates.

The ^{19}F nuclear magnetic resonance spectrum of $U(SO_3F)_4$ in DMSO consists of a singlet at -39.6 ppm relative to $CFCl_3$ (internal standard). The singlet ^{19}F peak shows that all SO_3F groups are rapidly exchanging with solvent.

While we were preparing this paper the first uranium fluorosulfate, $UF_2(SO_3F)_3$, was reported [6].

EXPERIMENTAL

$S_2O_6F_2$ was obtained as a gift from Professor F. Aubke, Department of Chemistry, University of British Columbia, Vancouver B.C. The infrared spectrum agreed with published values. UCl_4 was purchased as an anhydrous solid (99%) from Research/Inorganic Chemical Company and was used without further purification.

Infrared spectrum was recorded with a Perkin-Elmer model 467 i.r. spectrophotometer. The spectrum of $U(SO_3F)_4$ was obtained neat between AgCl windows. The X-ray pattern was obtained using an XRD-5 General Electric Powder camera. The sample was contained in a 0.5 mm capillary. The fluorine nmr spectrum was obtained with a Varian HA-100 nmr spectrometer.

Preparation of $U(SO_3F)_4$

To 1.850 mmol of UCl_4 in a 50 ml Pyrex-glass vessel equipped with a Kontes Teflon stopcock, 38.77 mmol of $S_2O_6F_2$ was added. In addition to Cl_2, a tan product [1.883 mmol of $U(SO_3F)_4$] was formed at r.t. (8.3 d) in 100% yield (nc); dec. 90°. Calcd. for $U(SO_3F)_4$: F, 12.0; S, 20.2; U, 37.5. Found: F, 12.2 S, 19.7; U, 38.2.

The infrared spectrum showed the following bands (cm^{-1}): 1410 (s, vb), 1290 (s,b), 1160 (s,b), 1080 (s), 970 (m-w), 870 (m) 835 (m), 710 (w), 585 (m), 560 (m). With KRS-5 windows, an additional band at 400 (w) cm^{-1} is observed.

The powder spectrum gave the following d values (in Å) with their respective intensities: 4.37 (s), 4.10 (m), 3.64 (m), 3.22(m), 2.73 (s), 2.12 (m), 1.98 (m), 1.79 (s), 1.73 (m).

Decomposition of $U(SO_3F)_4$

1.308 mmol of $U(SO_3F)_4$ in a 50 ml Pyrex-glass vessel equipped with a Kontes Teflon stopcock was heated from r.t. to 300° for two hours while pumping away volatile materials through a trap cooled to -195°. A white solid and an orange solid condensed in the trap. The material in the -195° trap gave upon hydrolysis a positive test for SO_4 ions. A bright green solid (0.8990 mmol of UF_4, 69% yield) remained in the 50 ml vessel. Calcd. for UF_4: F, 24.2; U, 75.8. Found: F, 24.5; U, 75.6.

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