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DIOXOURANIUM(VI) AND OXOURANIUM(IV) FLUOROSULPHATES AND DOUBLE FLUOROSULPHATES OF URANIUM(IV)

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SUMMARY

$UO_2(SO_3F)_2$, $UO(SO_3F)_2$, $U(SO_3F)_4$ and $MU(SO_3F)_6$, M = Mg, Zn have been prepared by reacting $UO_2(O_2CCH_3)_2$, $U(O_2CCH_3)_4$, $U(O_2CCF_3)_4$ and $MU(O_2CCH_3)_6$ with HSO_3F. The analysis of i.r. spectral data of $UO_2(SO_3F)_2$, $UO(SO_3F)_2$ and $MU(SO_3F)_6$ shows the presence of only one type of SO_3F group with reduced symmetry C_s. In $U(SO_3F)_4$, two SO_3F groups are bidentate, while the other two are monodentate. A sharp band at 925 cm^{-1} in $UO_2(SO_3F)_2$ is diagnostic of UO_2^{2+}. The diffuse reflectance spectra of $UO(SO_3F)_2$, $U(SO_3F)_4$ and $MU(SO_3F)_6$ reveal hexacoordination of U(IV), while the magnetic moments of these compounds support the existence of U(IV). $UO_2(SO_3F)_2$ and $UO(SO_3F)_2$ decompose thermally in a single step with the evolution of SO_2F_2 and formation of their respective sulphates.

INTRODUCTION

Uranium(V) fluorosulphates have been reported by Wilson and Bougon [1,2]. Recently, uranium(IV) fluorosulphate was also reported [3]. However, oxouranium(IV) or dioxouranium(VI) fluorosulphates have not been studied. This paper reports the preparation of the novel fluorosulphates, viz., dioxouranium(VI) fluorosulphate $UO_2(SO_3F)_2$, oxouranium(IV) fluorosulphate $UO(SO_3F)_2$, zinc-uranium(IV) fluorosulphate, $ZnU(SO_3F)_6$ and magnesium-uranium(IV) fluorosulphate $MgU(SO_3F)_6$. A new preparative method for uranium(IV) fluorosulphate is also reported. The compounds have been characterized from their elemental analysis, infrared spectra, diffuse reflectance spectra, magnetic susceptibility measurements and thermal analysis.

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EXPERIMENTAL

Materials: Uranium(IV) trifluoroacetate was prepared by reacting $U(O_2CCH_3)_4$ with trifluoroacetic acid at reflux temperature. Uranium(IV) acetate and its double acetates, $MU(O_2CCH_3)_6$; M = Zn, Mg were prepared as reported [4]. Dioxouranium(VI) acetate was prepared by the action of acetic anhydride on hydrated uranyl nitrate. Fluorosulphuric acid was prepared and purified by double distillation [5]. Sulphuryl chloride (E. Merck) was used as such.

Oxouranium(IV) fluorosulphate. Excess (6-8 fold) of fluorosulphuric acid was distilled onto a known weight of uranium(IV) acetate. The contents were magnetically stirred and heated at reflux temperature for 2 h., under nitrogen. The green solid formed was filtered in an atmosphere of dry N_2, washed repeatedly with fluorosulphuric acid, followed by sulphuryl chloride and finally dried in vacuo.

Dioxouranium(VI) fluorosulphate. Excess (6-8 fold) of fluorosulphuric acid was distilled onto a known weight of dioxouranium(VI) acetate. The contents were magnetically stirred for 7-8 h. at room temperature. The yellow solid formed was filtered, washed and dried as above.

Magnesium-uranium(IV) fluorosulphate and Zinc-uranium(IV) fluorosulphate. Excess of fluorosulphuric acid was distilled onto a known weight of $MgU(O_2CCH_3)_6$. The contents were magnetically stirred at room temperature for about 14 h. The green solid was filtered, washed and dried as above. In case of the preparation of $ZnU(SO_3F)_6$, addition of HSO_3F was made at ∿10°C and the temperature of the reaction vessel was not allowed to rise above 25°C. The reaction was complete in ∿14 h. The compound was filtered, washed and dried as above.

Uranium(IV) fluorosulphate. Excess (4-6 fold) of fluorosulphuric acid was distilled, in an atmosphere of dry nitrogen, onto a known weight of uranium(IV) trifluoroacetate. The contents were magnetically stirred at room temperature in an atmosphere of dry N_2 gas for ∿14 h. The solid formed was filtered, washed and dried as above.

Analytical Methods. Uranium in $UO(SO_3F)_2$, $UO_2(SO_3F)_2$ and $U(SO_3F)_4$ was determined as U_3O_8 [6]. Magnesium, zinc and uranium in $MgU(SO_3F)_6$ and $ZnU(SO_3F)_6$ were determined as reported [4]. Sulphur and fluorine were determined after hydrolysing the products with 10% NaOH solution, sulphur as $BaSO_4$ and fluorine volumetrically by titrating against standard thorium nitrate solution using alizarin-red as an indicator. The analytical data are given in Table I.

Table 1. Analytical Data

Compound	Found*(%) U	S	F	Zn	Mg
$UO(SO_3F)_2$	51.92 (52.65)	14.48 (14.16)	8.04 (8.40)	-	-
$UO_2(SO_3F)_2$	50.50 (50.85)	13.85 (13.67)	8.36 (8.12)	-	-
$U(SO_3F)_4$	36.98 (37.54)	20.32 (20.19)	11.55 (11.98)	-	-
$ZnU(SO_3F)_6$	26.18 (26.52)	21.34 (21.40)	12.48 (12.70)	6.99 (7.28)	-
$MgU(SO_3F)_6$	27.67 (27.80)	22.13 (22.43)	13.48 (13.31)	-	3.06 (2.83)

*Values in parenthesis are required.

Physical Measurements. The i.r. spectra of the compounds were recorded as Nujol or hcb mulls in AgCl and polythene plates, using a Perkin-Elmer 621 spectrophotometer. Diffuse reflectance spectra were recorded by means of an S. P. 700 spectrometer using freshly sublimed MgO as a reflecting reference. Magnetic susceptibilities were determined using a Gouy balance at room temperature. Calibrations were carried out using $HgCo(NCS)_4$[7]. The diamagnetic corrections were obtained from the literature [8]. Thermal analysis was carried out by means of a Stanton thermobalance at a heating rate of 4°/minute. All manipulations were carried out in a dry box filled with dry N_2.

RESULTS and DISCUSSION

Fluorosulphuric acid reacts with $UO_2(O_2CCH_3)_2$, $U(O_2CCF_3)_4$, $ZnU(O_2CCH_3)_6$ and $MgU(O_2CCH_3)_6$ exothermally at room temperature to give $UO_2(SO_3F)_2$ $U(SO_3F)_4$, $ZnU(SO_3F)_6$ and $MgU(SO_3F)_6$ respectively. Fluorosulphuric acid reacts with $U(O_2CCH_3)_4$ at reflux temperature yielding $UO(SO_3F)_2$; at room temperature, a compound of no definite stoichiometry could be isolated. The reaction between HSO_3F and $ZnU(O_2CCH_3)_6$ was carried out at a low temperature in view of the highly exothermic nature of the reaction. All these fluorosulphates are insoluble in usual non-coordinating organic solvents and also in fluorosulfuric acid. The addition of small amounts of $UO_2(SO_3F)_2$ and $UO(SO_3F)_2$ to HSO_3F does not change its conductance. This may be taken as an indication of complete insolubility of these fluorosulphates in HSO_3F. The insolubility may be ascribed to the polymeric nature of these fluorosulphates.

Thermal Analysis: The thermograms of the two fluorosulphates $UO_2(SO_3F)_2$ and $UO(SO_3F)_2$ were recorded up to 650°. $UO_2(SO_3F)_2$ is stable up to 260°, above this temperature it decomposes endothermally in a single step. The observed loss in weight 21.49% (calc. 21.79%) up to 450° corresponds to the evolution of one mole of SO_2F_2. After this it registers a constant weight up to 650°C. The final weight of the yellow residue and its elemental analysis corresponds to UO_2SO_4. The TG curve of $UO(SO_3F)_2$ shows that it decomposes from 210° to 610° in a single step endothermally. The observed loss in weight 22.80% (calc. 22.50%) corresponds to the evolution of a mole of SO_2F_2. The light green residue was analysed to be $UOSO_4$. The evolution of SO_2F_2 during decomposition of these fluorosulphates was confirmed from the infrared spectra of the gaseous products obtaining by heating the compounds separately in an evacuated system.

Infrared spectra. The i.r. spectrum of $UO(SO_3F)_2$, [Table II], reveals the presence of only one type of fluorosulphate group with reduced symmetry, C_s. The bands at 1395, 1140 and 1080 cm^{-1} (characteristic SO bands) correspond to bidentate bridging fluorosulphate groups [9, 10, 11, 12]. Medium intensity bands at 735 and 715 cm^{-1} may be assigned to antisymmetric and symmetric stretching vi-

Table II. Infrared Spectral Data (cm^{-1})

$UO(SO_3F)_2$,	$UO_2(SO_3F)_2$,	$U(SO_3F)_4$,	$ZnU(SO_3F)_6$,	$MgU(SO_3F)_6$,	Assignment*
1395 s	1380 s	1410 s,b	1400 s	1395 s	$\nu_4(E)$
1140 s	1155 s	1290 s,b	1160 s	1150 s	
		1200 w			
		1150 s			
1080 ms	1075 ms	1070 s	1070 ms	1080 ms	$\nu_1(A_1)$
		975 w			
-	925 s	-	-	-	$\nu(U=O)$
848 m	855 m	880 m	865 m	840 m	$\nu_2(A_1)$
	835 vw	850 m			
735 m	-	-	-	-	$\nu(O-U-O)$
715 m					
600 mw	605 mw	590 m	600 mw	600 mw	$\nu_5(E)$
580 m	570 m	565 m	-	560 m	
	-				
555 w	550 w	535 w	545 w	540 w	$\nu_3(A_1)$
500 w					
440 mw	445 mw	450 mw	435 mw	420 mw	$\nu_6(E)$
380 w	380 w	415 w	390 w	-	

*Based on C_{3V} symmetry for SO_3F group.

brations of a unit of O-U-O in a polymeric structure [13], where the U-O bond order is greater than one but less than two [14]. The evidence for a strong multiply bonded, $U{=}O^{2+}$, entity in the compound is absent as no sharp band is observed in the metal-oxygen multiple bond region[13,15].

The various bands in the i.r. spectrum of $U(SO_3F)_4$ are comparable with the reported values [3]. We observe additional weak bands at 1200 and 535 cm^{-1}. From this and also from the diffuse reflectance spectrum and magnetic susceptibility results (discussed later), it may be concluded that two of the fluorosulphate groups are bidentate while the other two are monodentate. This would give hexacoordination of uranium(IV).

On comparing the i.r. spectra of $MgU(SO_3F)_6$ and $ZnU(SO_3F)_6$ with those of $Mg(SO_3F)_2$ and $Zn(SO_3F)_2$ [16], it is evident that $MU(SO_3F)_6$, M=Mg, Zn are not simply mixtures, but are definite novel fluorosulphate species. The various infrared bands in $MU(SO_3F)_6$ reveal the presence of only one type of bridging-bidentate fluorosulphate group.

The various i.r. bands in $UO_2(SO_3F)_2$ also indicate bridging bidentate fluorosulphate groups. A strong band at 925 cm^{-1} confirms the presence of UO_2^{2+} entity. A very weak band at 835 cm^{-1} may be attributed to the symmetric vibrations of the uranyl group [17].

Electronic and Magnetic Properties. The maxima observed in the diffused reflectance spectra in the region 320-1000 n.m., of $UO(SO_3F)_2$, $U(SO_3F)_4$, $MU(SO_3F)_6$ are identical but weak in intensities. The comparison of the electronic spectra has been used to distinguish various geometries of different compounds [18-22]. Six- and eight-coordinate uranium(IV) compounds conform to a 'weak' and a 'strong' spectrum respectively [19]. The weak intensities of various bands in the spectra of these fluorosulphates put them in the 'weak' category. The octahedral uranium(IV) species [23] exhibit weak bands in the regions 400, 590 and 630 n.m. as well as a band at 450 n.m. The latter also appears in the spectra of 8-coordinate uranium(IV) species [24]. It is, therefore, probable that the weak bands observed in these fluorosulphates around 400, 580 and 630 n.m. may be assigned to the transitions of six coordinate uranium(IV).

Magnetic moments of uranium(IV) compounds range from 2.7 B. M. for chloride to 3.7 B. M. for the hydrated oxalate [25,26]. The magnetic moments of various fluorosulphates at room temperature, suggest similar geometry about uranium(IV).

Compound	μ_{eff}(B. M.)
$UO(SO_3F)_2$	2.87
$U(SO_3F)_4$	2.95
$ZnU(SO_3F)_6$	2.92
$MgU(SO_3F)_6$	2.90

Where magnetic measurements on $UO(SO_3F)_2$, $U(SO_3F)_4$, $ZnU(SO_3F)_6$ and $MgU(SO_3F)_6$ confirm the presence of uranium(IV) species, the reflectance spectra emphasize the six coordination around uranium. In $ZnU(SO_3F)_2$ and $MgU(SO_3F)_6$, the SO_3F groups may, therefore, be arranged in such a manner so that hexacooridnation around uranium is satisfied. This is possible only if all the fluorosulphate groups are involved in coordination between Zn and U or Mg and U as the case may be. $ZnU(SO_3F)_6$ and $MgU(SO_3F)_6$ may be regarded as ternary fluorosulphates rather than ionic complexes. Similar formulation has been found in $AgPt(SO_3F)_6$ and Ag $Sn(SO_3F)_6$ [27].

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