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FLUOROSULFATES OF THE NOBLE METALS, PART 7[a]: THE TRIS FLUOROSULFATES OF OSMIUM AND RHODIUM

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SUMMARY

The syntheses of $Os(SO_3F)_3$ and $Rh(SO_3F)_3$ by the oxidation of osmium and rhodium metal powder with bis(fluorosulfuryl) peroxide, $S_2O_6F_2$, are reported. The conditions required for metal oxidation, extremely mild for osmium, and severe for rhodium, and the reaction times represent two extremes in the behaviour of noble metals towards $S_2O_6F_2$. For $Os(SO_3F)_3$ evidence from diffuse reflectance and infrared spectra as well as from bulk magnetic susceptibility measurements suggests polymorphism with a slow conversion occurring at room temperature in an excess of $S_2O_6F_2$.

INTRODUCTION

We have reported previously in this series on the syntheses of binary and ternary fluorosulfates for most of the platinum metals. The principal synthetic route had been metal oxidation by bis(fluorosulfuryl)peroxide, $S_2O_6F_2$, in fluorosulfuric acid, HSO_3F, as reaction medium, according to:

$$M + n/2\ S_2O_6F_2 \xrightarrow[25\ -\ 120°C]{HSO_3F} M(SO_3F)_n,\ n = 2,\ 3 \text{ or } 4;\ M = Pd,\ Pt,\ Ir \text{ or } Ru. \quad (1)$$

In addition to the binary fluorosulfates $Pd(SO_3F)_2$, $Pd^{(II)}[Pd^{(IV)}(SO_3F)_6]$

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[a] For the preceding publication in this series see Ref. 3

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[1], [2], $Pt(SO_3F)_4$ [3], $Ir(SO_3F)_3$ [4], $Ir(SO_3F)_4$ [4], and $Ru(SO_3F)_3$ [5] a number of ternary fluorosulfates, generally of the type $M^I_n[M(SO_3F)_6]$ with M^I an alkali metal and n = 2 or 3, have been obtained for all four metals.

In order to complete the series for the platinum metals and to compare structural features and reactivity patterns, we wish to report on the preparation of the binary fluorosulfates of osmium and rhodium, $Os(SO_3F)_3$ and $Rh(SO_3F)_3$ by metal oxidation with $S_2O_6F_2$.

EXPERIMENTAL

Chemicals

Osmium metal powder -60 mesh of 99.9% purity and rhodium metal powder -60 mesh, again of 99.9% purity were obtained from the Ventron Corporation.

Technical grade fluorosulfuric acid was double distilled at atmospheric pressure as described previously [6]. Bis(fluorosulfuryl)peroxide was synthesized according to a published method [7]. All other chemicals used in this study were obtained from commercial sources in the highest degree of purity available.

Instrumentation and Analysis

Details on our instrumentation and the techniques employed in manipulating volatile and moisture sensitive substances, the recording of ESR, infrared, Raman and electronic spectra, and the calibration of magnetic susceptibility measurements have been published previously [2] [3] [5]. The Gouy apparatus used in this study has been described earlier [8]. Diamagnetic corrections were calculated from Pascal's constants [9]. All reactions were carried out in Pyrex reaction vials of about 40 mL content fitted with Kontes Teflon stem valves and Teflon coated magnetic stirring bars. The course of the reactions was monitored by recording weight changes for the nonvolatile products. Microanalyses were performed by Analytische Laboratorien, Gummersbach, West Germany.

SYNTHETIC REACTIONS AND ELEMENTAL ANALYSES

(I) Osmium tris(fluorosulfate), $Os(SO_3F)_3$

In a typical preparation, excess $S_2O_6F_2$ (~ 3 mL) was distilled in vacuo onto 0.172 g (0.903 mmol) of osmium powder in a one-part Pyrex reactor. The resulting mixture was stirred at a constant temperature of 60°C, and the progress of the reaction was monitored by the disappearance of the metal powder and more accurately by the weight increase of non-volatile solid. After three days, the weight of the homogeneous-looking bright green solid reached a constant value of 0.431 g. The expected yield based on $Os(SO_3F)_3$ was 0.440 g. Elemental analysis: calculated % for $Os(SO_3F)_3$: Os, 39.02; S, 19.74; F, 11.69. Found %: Os, 39.10; S, 19.87; F, 11.85, and 11.88. The material decomposed above 130°C to a black liquid.

On standing in excess $S_2O_6F_2$ at room temperature over a period of several weeks, bright green $Os(SO_3F)_3$ gradually turned into a light green solid. However no change in sample weight was detected. In addition, the elemental analysis (Os, 39.28; S, 19.55; F, 11.89) did not show an appreciable change in composition. This material, tentatively labelled the β-form, decomposed at 140°C to a black liquid.

(II) Rhodium tris(fluorosulfate), $Rh(SO_3F)_3$

In a typical reaction,0.102 g (0.991 mmol) of rhodium was heated in a thick wall Pyrex reactor in approximately 10 mL of a 1:1 mixture (by volume) of HSO_3F and $S_2O_6F_2$ to 130°C before any sign of a reaction, the formation of bright orange flakes, was noted. The reaction mixture was maintained at this temperature for about 3 weeks, until all metal had been consumed. During this period the oxygen formed was intermittently removed and about 2 mL of

$S_2O_6F_2$ were added after two weeks. Removal of all volatiles yielded 0.425 g (1.06 mmol) of bright orange, hygroscopic powder. The weight of the product was obtained after reweighing the badly etched reactor once all product had been completely removed. The orange powder was found to be thermally stable up to 190°, where the formation of black particles indicated the beginning of decomposition. The composition as $Rh(SO_3F)_3$ was established by microanalysis. Calculated % for $Rh(SO_3F)_3$: Rh, 25.72; S, 24,04; F, 14.25. Found: Rh, 25.52; S,24.18; F, 14.21 and S:F ratio 1.009.

RESULTS AND DISCUSSION

(I) Synthesis

As described in the experimental section both osmium and rhodium metal powder are oxidized by bis(fluorosulfuryl) peroxide to the +3 oxidation state. In both instances the corresponding tris(fluorosulfates) $Os(SO_3F)_3$ and $Rh(SO_3F)_3$ form as sole reaction products in an analytically pure form. However reaction conditions and the times required to effect complete oxidation differ rather drastically, and it appears that both metals occupy opposite ends of the reactivity scale noted for reactions of electron rich 4d and 5d black transition metals [1] - [5] inclusive of silver [10] and gold [11] with the oxidizing agent $S_2O_6F_2$.

The oxidation of osmium proceeds with remarkable ease, even in the absence of HSO_3F according to:

$$Os + 3/2\ S_2O_6F_2 \xrightarrow[3d]{60^\circ} Os(SO_3F)_3 \qquad (2)$$

Only $Ag(SO_3F)_2$ forms in a similar direct oxidation of silver, with a longer reaction time (7 days) at a reaction temperature of 70°C [10]. As found in the case of silver, addition of HSO_3F should accelerate the oxidation of osmium, however now, at a reaction temperature of 65°C, a rather inhomogeneous looking viscous brown liquid with some green particles forms. In spite of several attempts, no homogeneous material of constant weight is obtained after removal of all volatiles in vacuo.

Likewise attempts to achieve further oxidation by an excess of $S_2O_6F_2$ and a reaction temperature of 70°C to 100°C lead only to viscous dark green liquids without any appreciable increase in weight. It appears then that $S_2O_6F_2$ alone and a reaction temperature of 60°C are both necessary and sufficient to produce analytically pure $Os(SO_3F)_3$.

Quite in contrast to this smooth metal oxidation, rhodium will not react with a $S_2O_6F_2$ solution in HSO_3F until the temperature is raised to 130°C and prolonged reaction times are required for a complete conversion, according to:

$$Rh + 3/2\ S_2O_6F_2 \xrightarrow[21d,\ HSO_3F]{130^\circ C} Rh(SO_3F)_3 \qquad (3)$$

Resistance towards oxidation by $S_2O_6F_2$ appears to be even more pronounced for rhodium than had been noted for iridium, where complete conversion occurs after 6 days at 140°C [4]. A similar slight difference is found for rhodium and iridium in oxidation reactions at very high temperatures with oxygen and the halogens [12].

However unlike iridium further oxidation to a thermally labile tetrakis-(fluorosulfate) is not noted for rhodium and some of the ensuing complications - a rapid consumption of $S_2O_6F_2$ and formation of O_2 - observed during the thermolysis of $Ir(SO_3F)_4$ at the reaction temperature, appear to be avoided in the case of the rhodium oxidation. All colour changes noted during the reaction point to a single, red-orange species which appears to be somewhat soluble in HSO_3F at 130°C and insoluble at ambient temperature.

Nevertheless the previously noted thermal instability of the $SO_3F\cdot$ radical to produce O_2 and $S_2O_5F_2$ [13] is sufficient to require intermittent pumping to release the pressure inside the reaction vessel and addition of more $S_2O_6F_2$ at least once during the reaction.

The fluorosulfate radical formed in the reversible dissociation reaction

$$S_2O_6F_2 \rightleftharpoons 2\cdot SO_3F \qquad (4)$$

is reported to attack glass at elevated temperatures [13], with HF, formed during high temperature dissociation of fluorosulfuric acid [14]according to:

$$HSO_3F \longrightarrow HF + SO_3 \qquad (5)$$

which also contributes to the extensive damage to the reaction vessel. It is hence surprising that a satisfactory analysis for $Rh(SO_3F)_3$ is obtained with no indication of the formation of SiF_6-derivatives from microanalysis or the I.R. spectrum. Given the lack of reactivity shown by rhodium under the reaction conditions described, it appears unlikely that the use of nickel, stainless steel or monel metal reactors, available to us, would have resulted in a similarly pure product, due to possible metal contamination. The extreme reaction conditions needed, restrict the choice of suitable materials for reactors rather severely.

The bright orange-red colour of $Rh(SO_3F)_3$ is not unexpected for Rh(III), compounds. Both RhF_3 and $RhCl_3$ are reportedly [12] red. Due to the tedious method of synthesis, the small scale of our preparations and the high price of rhodium powder, only small amounts of rhodium tris(fluorosulfate) are obtained, insufficient for a magnetic study using the Gouy method. However the absence of an ESR signal and the rather straightforward infrared spectrum, to be discussed below, suggest that $Rh(SO_3F)_3$ just like $Ir(SO_3F)_3$ [4] is diamagnetic.

A few additional comments concern the preparation of osmium(III) fluorosulfate. As described in the experimental section, allowing freshly prepared bright green $Os(SO_3F)_3$ to remain in contact with excess $S_2O_6F_2$ results in a gradual subtle change in color to a greyish green. While neither the mass of the solid, nor its elemental composition change, some observations as well as slight differences in both the infrared spectra and the magnetic susceptibilities, to be discussed subsequently, suggest a structural change is occurring. The initial product termed α-$Os(SO_3F)_3$ is insoluble in fluorosulfuric acid, and remains bright green in color on cooling. The new or β-form of $Os(SO_3F)_3$ turns grey at liquid nitrogen temperature and appears to be only sparingly soluble in HSO_3F. Labelling of the two different forms introduced here is strictly arbitrary, to allow easy differentiation. The presence of two distinctly different pure polymorphic forms is not implied.

The electronic spectrum of a solution of β-$Os(SO_3F)_3$ in HSO_3F has two bands at $\lambda_{max} \sim 370$ nm ($\varepsilon_{max} = 650\ M^{-1}\ cm^{-1}$) and at 640 nm ($\varepsilon_{max} = 33.5\ M^{-1}cm^{-1}$), slightly shifted from 350 and ~ 590 nm observed in a diffuse reflectance spectrum. A diffuse reflectance spectrum of the α-form shows in addition to similarly shaped bands at 350 and 650 nm respectively an additional shoulder at ~ 400 nm.

There is very little difference in thermal stability between the two materials; both melt between 130 and 140°C under decomposition to black liquids. Dark colours are not uncommon for binary osmium(III) compounds. $OsCl_3$ and $OsBr_3$ are reported to be dark grey while OsI_3 is black [12]. In addition, polymorphism seems to occur for binary Os(III) compounds. Eg., different forms of $OsCl_3$ are said to form depending on the method of preparation [12], although these materials are not as well characterized as the α- and β-polymorphs of $RuCl_3$ [12]. Finally the previously reported $Ru(SO_3F)_3$ [5] exhibits a rather complex magnetic behaviour, which strongly suggests the presence of at least two polymorphic forms.

Attempts to obtain ternary fluorosulfate complexes of osmium by reaction of Os metal in $HSO_3F/S_2O_6F_2$ with $CsSO_3F$, present at mole ratios of $CsSO_3F/Os$ varying from 1 to 3, result in inhomogeneous green-brown solids, similar in appearance to the products obtained from the osmium oxidation by $S_2O_6F_2$ in HSO_3F. In the absence of HSO_3F only mixtures of α-$Os(SO_3F)_3$ and $CsSO_3F$ are present as is evident from the infrared spectra. In contrast ruthenium forms various alkali-metal fluorosulfate complexes with the metal in the +3 and the +4 oxidation state [5].

(II) Infrared Spectra

Vibrational information is restricted primarily to infrared spectra, obtained on thin films pressed between AgCl or AgBr windows, because the reactivity of the compounds precludes the use of mulling agents. Hence bands are usually quite broad, in particular in the SO_3F-stretching region. Both forms of $Os(SO_3F)_2$ are sufficiently light in color to permit recording of Raman spectra, using the green Ar^+ line for excitation, but even here only two bands at 1235 and ~ 1000 cm^{-1} are clearly detectable. Observed band positions and estimated intensities are listed in Table 1.

The spectrum of $Rh(SO_3F)_3$ appears to be rather uncomplicated. Both band positions and their relative intensities compare well with infrared spectra reported for $Fe(SO_3F)_3$ [15], $Ga(SO_3F)_3$ [16] and $Cr(SO_3F)_3$ [17]. In all instances a regular octahedral coordination environment is suggested with bidentate bridging fluorosulfate groups resulting in polymeric substances with very little solubility in HSO_3F. A similar band pattern, complicated by extensive band proliferation, had been found for $Mn(SO_3F)_3$ [18]. Here extensive Jahn-Teller distortion is suggested by the magnetic data. Infrared data for $Ir(SO_3F)_3$ are too fragmentary to allow any comparison [14].

TABLE 1

Infrared Spectra of α-$Os(SO_3F)_3$, β-$Os(SO_3F)_3$, $Ru(SO_3F)_3$ and $Rh(SO_3F)_3$

α-$Os(SO_3F)_3$[a] $\nu[cm^{-1}]$ Int.	β-$Os(SO_3F)_3$[b] $\nu[cm^{-1}]$ Int.	$Ru(SO_3F)_3$[c] $\nu[cm^{-1}]$ Int.	$Rh(SO_3F)_3$ $\nu[cm^{-1}]$ Int.	Approximate Description
1445 vs	1450 s	1430 s,sh	1425 s,sh	νSO_3 mo. or bi.
1410 s	1395 vs	1390 vs	1370 vs	
1225 vs	1230 vs	1220 s		νSO_3 sym mo.
1160 vs,b	1135 s,b	1110 s,sh	1120 m,sh	νSO_3 asym bi.
~ 1070 w,sh	1075 s,b		1050 s,b	νSO_3 sym bi.
1025 s	1015 m sh	1025 vs,b		νSO-M
	1000 w			
950 w	950 w	920 w	920 w	?
890 s	880 s,br			
850 s,sh	840 s,sh	860 s	830 s,b	νSF
800 vs,b	820 vs,b	820 s, sh	815 s	
640 m	660 s	645 m	650 m	νM-O + def.
575 s	585 s	585 m	595 m	δ SO_3 asym
535 s	540 m	550 ms	545 m	δ SO_3 sym
470 vw	470 vw, sh	474 vw, sh		νM-O + def.
450 vw	450 w	450 w	450 w	ρSO_3F
395 vw	385 w	395 w	390 w	

[a] Raman bands at 1027 s and 1235 s.
[b] Raman bands at 999 vs and 1235 s.
[c] Ref. [5].

Abbreviations

s = strong, m = medium, w = weak, v = very, b = broad,
sh = shoulder, ν = stretch, δ = bend, ρ = rock,
sym = symmetric, asym = asymmetric, mo. = monodentate,
bi. = bidentate, def. = deformation mode,
Int. = estimated intensity.

Both forms of $Os(SO_3F)_3$ give rise to more complex band patterns than are found for $Rh(SO_3F)_3$. Spectral differences between both osmium compounds however are small and involve for the most part changes in relative intensity for closely spaced bands e.g., at ~ 1400 and 650 cm^{-1}, and the emergence of a new band at 1075 cm^{-1} in β-$Os(SO_3F)_3$, present only as a weak shoulder in the α-form, as well as slight shifts in band position, in particular in the SO_3F stretching range. A visual comparison of the spectra suggests a strong similarity, and it appears that the infrared spectra reflect different mixtures of two or perhaps more polymorphic forms rather than two distinctly different pure modifications.

The complexity of the spectra for both forms closely parallels observations made previously for $Ru(SO_3F)_3$ [5], where the presence of both mono- and bidentate SO_3F-groups has been suggested. The lack of reliable Raman data for the whole spectral range precludes a more detailed discussion.

(III) Magnetic Properties of $Os(SO_3F)_3$

The magnetic susceptibility data between 77 and 298 K are listed for both forms of $Os(SO_3F)_3$ in Table 2 together with the calculated magnetic moments.

In both instances we are dealing with magnetically concentrated substances and magnetic moments measured fall below 0.55 μ_B, well below the spin only value of 1.73 μ_B, suggesting strong antiferromagnetic coupling. This is not entirely unexpected and is encountered also for $Ru(SO_3F)_3$ [5] and for $Ir(SO_3F)_4$ and complexes containing the $[Ir(SO_3F)_6]^{2-}$ ion [4], where the metal ions have a d^5 electron configuration in common. However the extent of antiferromagnetic coupling in binary fluorosulfates appears to increase in the order of $Ir^{4+} < Ru^{3+} < Os^{3+}$ for the fluorosulfates. This order is apparent from the magnitude of both χ_M^{cor} and μ_{eff} and the observed temperature dependance of both.

TABLE 2

Magnetic Susceptibility Data of $Os(SO_3F)_3$

α-$Os(SO_3F)_3$			β-$Os(SO_3F)_3$		
$\chi_M^{cor}(x10^6)$ [cm^3 mol^{-1}]	μ_{eff} [μ_B]	T [K]	$\chi_M^{cor}(x10^6)$ [cm^3 mol^{-1}]	μ_{eff} [μ_B]	T [K]
107.3	0.483	272	129.7	0.532	273
107.5	0.463	249	135.7	0.519	248
116.7	0.457	224	139.1	0.499	224
120.6	0.438	199	144.5	0.480	199
121.4	0.413	176	152.7	0.463	175
122.6	0.385	151	162.5	0.443	151
126.8	0.359	127	163.9	0.409	128
130.3	0.336	109	179.7	0.394	108
112.4	0.263	77	201.5	0.353	77

Attempts to fit the data to the Curie-Weiss law have suggested Weiss constants of +19 K and -43 K for $Ir(SO_3F)_4$ [4] and $Ru(SO_3F)_3$ [5] respectively. For β-$Os(SO_3F)_3$, which shows reasonably regular magnetic behavior to allow such a plot, a Weiss constant of -260 K is found. For α-$Os(SO_3F)_3$ a Curie-Weiss plot is not possible and trends in χ_M^{cor} and μ_{eff} are somewhat erratic, even though the latter are of the same order of magnitude as those found for β-$Os(SO_3F)_3$.

Wherever identical or nearly identical temperatures allow a comparison between both sets of data, magnetic susceptibilities and hence magnetic moments are consistently higher for β-$Os(SO_3F)_3$, and it appears that the transition on standing in an excess of $S_2O_6F_2$ involves a gradual increase in dilute paramagnetic species or a decrease in antiferromagnetically coupled metal centres.

The presence of an identical origin of the observed paramagnetism for both forms of $Os(SO_3F)_3$ is reflected in their ESR spectra. In both cases broad, single line spectra are obtained, and the g_o values for α-$Os(SO_3F)_3$ are with 1.997 at 295 and 1.993 at 80 K not significantly different from the corresponding values of 2.007 at 295 K and 1.986 at 80 K observed for β-$Os(SO_3F)_3$, with both sets of g_o values rather close to the free electron value.

It appears then that $Os(SO_3F)_3$, just like $Ru(SO_3F)_3$ [5] will have to be viewed as a mixture of two or possibly more phases with distinctly different magnetic properties. Both $OsCl_3$ and more distinctively $RuCl_3$ provide precedents [12]. The only difference between the two fluorosulfates appears to be the observation of a distinct color change of a freshly prepared sample on prolonged standing in an excess of $S_2O_6F_2$, with concomittant subtle changes in the visible and infrared spectra and the magnetic properties. In the case of $Ru(SO_3F)_3$, only the magnetic properties had provided an indication for a phase mixture [5].

Very few relevant magnetic measurements on Os(III) compounds appear to have been reported [9]. Various hexahalide complexes as well as coordination complexes appear to be magnetically dilute with μ_{eff} values close to the spin only value for one unpaired electron [9]. On the other hand $OsCl_3$ is magnetically concentrated with μ_{eff} decreasing from 1.55 μ_B at 295 K to 1.27 μ_B at 77 K [19] and an approximate Weiss constant, calculated from the published data [19], of -40 K. It appears that for β-$Os(SO_3F)_3$ far more extensive antiferromagnetic coupling is encountered than is reported for $OsCl_3$ [9].

CONCLUSIONS

The syntheses of the two binary tris(fluorosulfates) $Rh(SO_3F)_3$ and $Os(SO_3F)_3$ reported here complete the series of noble metal fluorosulfates and their derivatives [1] to [5], [10], [11]. Both present interesting contrasts and extremes for the group, ranging from Ru to Ag in the 4d-, and Os to Au in the 5d series. While all compounds are obtained by metal oxidation with $S_2O_6F_2$, the severe conditions required and the long reaction times needed to obtain $Rh(SO_3F)_3$ represent the limit of usefulness for the synthetic route employed, metal oxidation in HSO_3F. The structure of this compound appears to be simple and polymeric with bidentate bridging fluorosulfate groups with several close precedents among metal tris(fluorosulfates).

Osmium tris(fluorosulfate) on the other hand requires the mildest reaction conditions and the absence of HSO_3F for its preparation, in order to avoid formation of mixed oxidation state products. The molecular and electronic structure of $Os(SO_3F)_3$ is puzzling, starting with visibly and spectroscopically detectable changes on exposure to $S_2O_6F_2$ at room temperature. The role of $S_2O_6F_2$ in this process is not understood, but in its absence, green $Os(SO_3F)_3$ is indefinitely stable. The mixed phase in $Os(SO_3F)_3$ suggested by bulk magnetic susceptibility measurements have contrasting magnetic features resulting in rather weak overall paramagnetism. The antiferromagnetic coupling encountered here is the strongest from among all the noble metal fluorosulfates studied. This in turn is puzzling since the bulky SO_3F groups usually give rise to magnetically dilute system as eg., in the case of palladium(II) fluorosulfates [1][2].

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