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SYNTHESIS AND CHARACTERIZATION OF OSMIUM OXIDE HEXAFLUORIDE, $OsOF_6$

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SUMMARY

Osmium oxide hexafluoride $OsOF_6$ is prepared by fluorination of osmium tetraoxide using krypton difluoride in HF solution. This new Os (VIII) derivative is characterized by elemental analysis, X-ray powder data and vibrational spectroscopy. The fluorination of the ruthenium and osmium tetraoxides is compared and briefly discussed.

INTRODUCTION

Among the expected oxide fluorides of osmium in the formal +8 oxidation state, OsO_2F_4 and $OsOF_6$ are still unknown. During their attempts to prepare OsO_2F_4, Bartlett and his coworkers [1,2] observed that the fluorination of OsO_3F_2 led to a formal reduction of Os(VIII) into Os(VII). However, the reactions were achieved at temperature at which compounds of marginal thermal stability may have been difficult to isolate. A different approach was attempted here, consisting in using the low-temperature fluorination method previously used to fluorinate RuO_4 [3]. This method, which proved to be successful, led to the synthesis of osmium oxide hexafluoride $OsOF_6$ as described in this paper together with the characterization of this new Os (VIII) oxide fluoride.

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EXPERIMENTAL

General procedure, characterization and materials. Volatile materials were manipulated in a Monel Teflon-FEP vacuum manifold. Prior to handling the moisture-sensitive compounds, the system was passivated with chlorine trifluoride. The syntheses were achieved using a device (thereafter referred to as "reaction-tube") made up of a 6 mm o. d. Teflon-FEP U-tube with a side arm, itself made up of a 90° bent 4 mm o.d. Teflon-FEP-U tube sealed to the 6 mm o.d. tube, and two Monel valves attached to the U-tube. This system allowed the transfer of volatile materials into the reaction-tube under dynamic vacuum. Moisture sensitive non-volatile materials were transferred in the dry atmosphere of a glove box. Infrared spectra were recorded in the range 4000-200 cm $^{-1}$ on a Perkin Elmer Model 283 spectrophotometer. Spectra of solids were obtained by using dry powders pressed between AgBr or AgCl windows in an Econo press (Barnes Engineer Co.). Raman spectra were recorded on a Coderg Model T800 spectrophotometer using the 647.1nm excitation of a Kr ion Model 2016 Spectra-Physics laser filtered with a Coderg premonochromator. In order to prevent their decomposition by the laser beam, the solids contained in the side arm of the reaction-tube or in 2 mm o.d. glass capillaries, were immersed in liquid nitrogen. The spectra of the solutions contained in the side-arm of the reaction-tube, were run at room temperature. In the range of observation, the frequency accuracy was estimated to be approximately ± 3 cm $^{-1}$ for the infrared spectra and ± 1 cm $^{-1}$ for the Raman spectra. X-ray powder diffraction patterns of the samples sealed in 0.5 mm o.d. quartz capillaries were obtained by using a Philips camera (diameter 11.46 cm) with Ni-filtered Cu-K_α radiation. The melting point was determined using a silicone oil bath in which the sample, contained in a sealed 2 mm o. d. glass capillary attached to a platinum resistance, was heated at a rate of 8°C / hr. Elemental analyses were performed by Mikroanalytische Laboratories, Elbach, Germany.

Osmium tetraoxide OsO_4, from Merck, was transferred and stored over P_2O_5. The fluorine (from Union Carbide) used for the preparation of krypton difluoride KrF_2 was passed over NaF to remove HF, and krypton (from l'Air liquide) was used without purification. The synthesis of KrF_2 was made as previously described [4].

Commercial HF (from Union Carbide) was dehydrated over bismuth pentafluoride before use [5]

Synthesis of $OsOF_6$. In a typical preparation, 0.295 g (1.160 mmol) of OsO_4 was condensed under dynamic vacuum into the reaction-tube cooled at -78° C. 0.6977 g of HF was condensed onto the OsO_4 cooled at -196° C, and the resulting mixture warmed to room temperature. An amount of 0.559 g of krypton difluoride (4.594 mmol) was then condensed onto the OsO_4 / HF mixture cooled at -196°C. The ternary mixture was slowly warmed to room temperature, periodically cooled to - 196°C in order to remove the volatiles at this temperature, and warmed up again. From the addition of KrF_2, the solution, initially pale orange-yellow, turned brown-red and a deep red solid started to form. After a two- day period at room temperature, the Raman spectra of the solution indicated that there was still some KrF_2 as evidenced by a strong band at 461 cm^{-1} [6], and that all the OsO_4 had reacted. In addition, two weak bands were observed at 690 and 942 cm^{-1}.

After evacuation of the volatiles at -78° C, the solid was pumped at ca. -15°C to ensure complete removal of HF and KrF_2. Unfortunately this pumping was probably achieved at a temperature at which the red solid had already some volatility since a small amount of it was detected in the trap cooled at liquid nitrogen temperature. This loss was confirmed by weighing, since only 0.3634 g of solid was recovered in the reaction-tube, vs. 0.3716 g expected from a conversion of the initial amount of OsO_4 into $OsOF_6$ *(vide infra)*. The attempt, which was made to let decompose the excess of KrF_2 on standing at room temperature in order to avoid its evacuation by pumping, was not successful. The weight of the deep red crystalline corresponded bettter with the $OsOF_6$ formulation than with any other imaginable oxide fluoride. The color of the product (close to that of CrO_3) did not correspond to any of the known fluorides or oxide fluorides of osmium in the higher oxidation states. In the solid state, OsF_6 was reported to be yellow [7], $OsOF_4$ bluish-green [8], OsO_2F_3 yellow -green [8], $OsOF_5$ emerald-green [9], and OsO_3F_2 orange [10]. The heptafluoride, the synthesis of which has, however, not been confirmed, was also reported to be of a different color (pale-yellow) [11]. Elemental analyses were performed on samples resulting from two preparations (I and II). *Anal. calcd. for $OsOF_6$* : Os 59.40, F 35.60, O 4.99 ; *found* : (I) Os 58.65, F 35.37 , O (by difference) 5.99 ; (II) Os 58.90, F 35.36 O (by difference) 5.54.

RESULTS AND DISCUSSION

The reaction of OsO_4 with KrF_2 in HF solution leads to the fluorination of the tetraoxide without any evidence of formal reduction of osmium. Contrary to milder fluorinating agents such as BrF_3 [10] or ClF_3 [12], KrF_2 allows the substitution of three oxygen atoms by fluorine. However, the limit seems to be reached since for a different preparation, even a twofold excess of KrF_2 did not result in additional oxygen-fluorine exchange and concomitant formation of higher fluorides. Furthermore, OsF_6, which was not observed, is stable at the temperature of the reaction and expected to be the most probable decomposition product of these hypothetical higher fluorides. Consequently, neither these fluorides nor OsF_6 seem to be involved in this synthesis.

TABLE I

X-ray Powder Data [a] for $OsOF_6$

d, Å	intensity	d, Å	intensity
4.58	s	2.01	m
4.29	vw	1.94	m
4.10	s	1.84	mw
3.62	s	1.78	mw
3.12	w	1.68	vvw
2.68	m	1.62	w
2.44	mw	1.59	w
2.33	mw	1.58	w
2.31	m	1.57	mw
2.15	mw	1.54	w
2.10	vw	1.47	mw

[a] s=strong, m= medium, w=weak, v= very

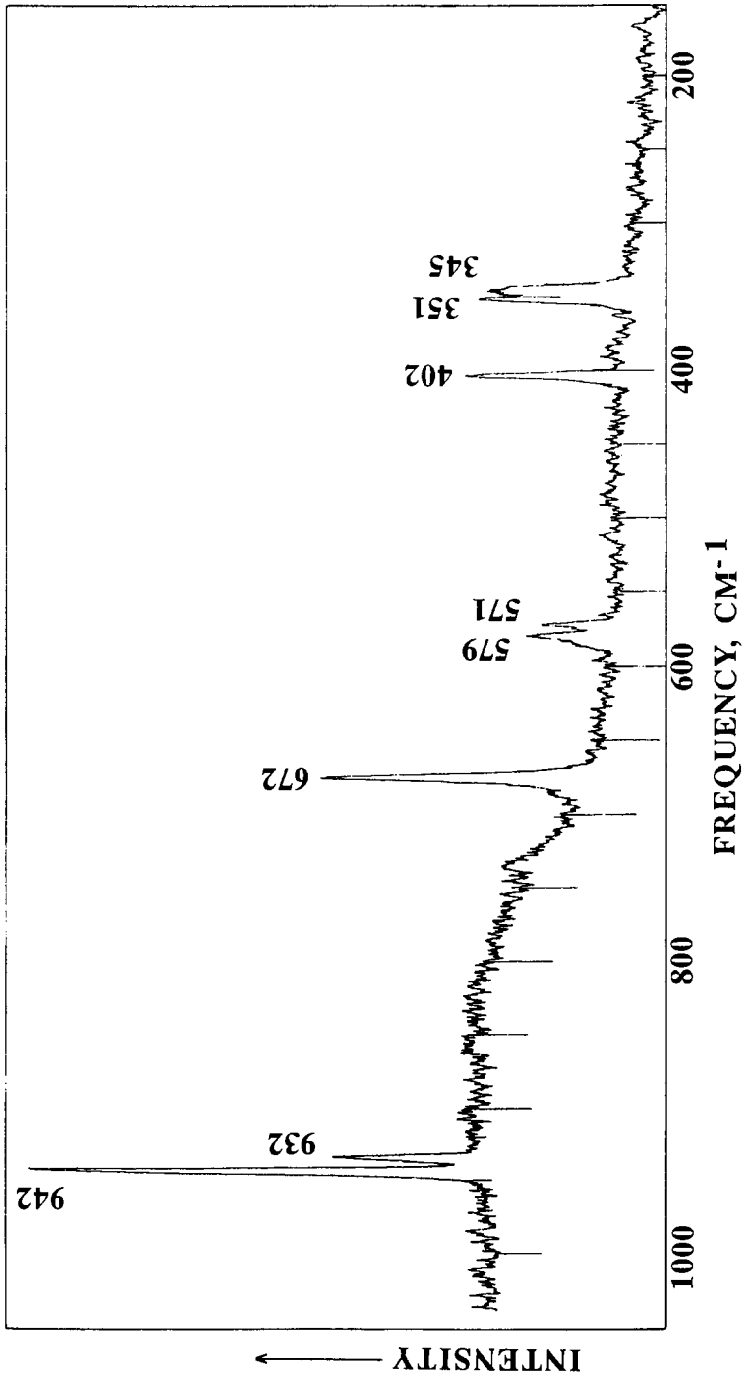

Fig.1. Raman Spectrum of $OsOF_6$.

The X-ray powder data for $OsOF_6$ are listed in Table I, and its Raman spectrum in the solid state is shown in Figure 1. It should be pointed out that from the absence of their characteristic bands [13, 14], no KrF_2 adducts were identified in this spectrum. The presence of a dioxygenyl derivative was also ruled out for the same reason [15]. The simplicity of the spectrum seems to indicate a high symmetry for the molecular unit, as would be the case, for instance, for a pentagonal bipyramid arrangement of the ligands around the osmium atom (symmetry C_{5v}). With this asssumption, the strong band at 942 cm $^{-1}$ was assigned to the Os=O stretching, and the weak band at 932 cm $^{-1}$ was explained as factor group splitting. It is noted that the frequency of this vibration is lower than that of any of the known Os (VIII, VII,) oxide fluorides. The strong band at 672 cm $^{-1}$ was tentatively assigned to the axial Os--F stretching mode and the bands at 579 cm $^{-1}$ and 571 cm $^{-1}$ were assigned to the equatorial symmetrical Os--F stretching mode split by the factor group symmetry. The band at 402 cm $^{-1}$ and the doublet at 351, 345 cm $^{-1}$ were assigned to bending modes. The two weak bands that were observed at 942 and 690 cm $^{-1}$ for the HF solution, are in reasonable correspondence to the strong bands of the solid at 942 and 672 cm $^{-1}$. The weak intensity of these bands for the solution precluded any polarization measurement.

Due to the high reactivity of $OsOF_6$ and the lack of a suitable low-temperature cell, no satisfying infrared spectrum could be obtained with the Ag Br pellets. The spectra displayed several bands of non-reproducible relative intensities with only minor features assignable to $OsOF_6$. Silver chloride pellets were found to be more resistant to the fluorination by $OsOF_6$, and bands located at (940,930) (vs), 675 (s), 588(s) and 570 (sh) cm $^{-1}$ could confidently be assigned to $OsOF_6$. Nevertheless, a few extra bands indicated that $OsOF_6$ had partially reacted with the Ag Cl pellets. The fluorination power of $OsOF_6$ however strong it may be, was found to be insufficient to fluorinate ClF_3 into ClF_5. The red solution obtained by dissolving $OsOF_6$ in ClF_3, displayed, in addition to those of the solvent, two Raman bands of medium intensity at 934 and 687 cm $^{-1}$, which corresponded to those observed for the HF solution. The Raman spectrum of the solid residue obtained after evacuation of the solvent was identical with that of $OsOF_6$.

The melting point of $OsOF_6$ was found to be 89±1°C. Surprisingly, no decomposition was noticed to occur at this temperature. The vapor pressure of $OsOF_6$ is much lower than that of the volatile derivatives $OsOF_5$ [1] , OsF_6, [16] and OsO_4, [17]. Its determination would require appropriate equipment for measurements in the low pressure range.

When exposed to air, $OsOF_6$ instantaneously hydrolysed to give a black residue. However, when the hydrolysis was controlled by slow diffusion of air into the container initially under vacuum, a myriad of small colorless crystals progressively appeared. These volatile crystals were identified as OsO4 from a single crystal X-ray diffraction study [18] and comparison with literature data [19].

CONCLUSION

A new oxide fluoride of osmium in the formal oxidation state +8 has been synthesized and characterized. Unfortunately, due to the suspension of the laboratory's activities, neither ^{19}F nmr spectra nor single crystal X-ray diffraction data could be obtained on this compound. Consequently, the determination of the molecular structure of $OsOF_6$ is postponed till experiments are again possible. It is worth noting that the synthesis was achieved using conditions similar to those used previously for the fluorination of RuO_4 [3]. Unlike OsO_4, the ruthenium oxide had led to the formation of $RuOF_4$, which implied a formal reduction of ruthenium from the oxidation states +8 to +6. By analogy, the present results give support to the assumption, which had been made that an intermediary ruthenium oxide fluoride in the oxidation state +8 or +7 was involved.

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