

Syntheses of Dioxygenyl Salts by Photochemical Reactions in Liquid Anhydrous Hydrogen Fluoride: X-ray Crystal Structures of α - and β - $O_2Sn_2F_9$, $O_2Sn_2F_9 \cdot 0.9HF$, $O_2GeF_5 \cdot HF$, and $O_2[Hg(HF)]_4(SbF_6)_9$

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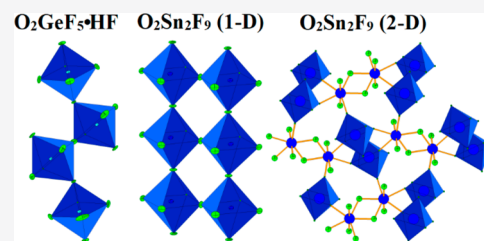


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ABSTRACT: By treating gaseous, liquid, or solid fluorides with UV-photolyzed O_2/F_2 mixtures and by treating solid oxides with UV-photolyzed F_2 (or O_2/F_2 mixtures) in liquid anhydrous HF at ambient temperature, we investigated the possibility of the preparation of $O_2M^{III}F_4$ ($M = B, Fe, Co, Ag$), $O_2M^{IV}F_5$ ($M = Ti, Sn, Pb$), $(O_2)_2M^{IV}F_6$ ($M = Ti, Ge, Sn, Pb, Pd, Ni, Mn$), $O_2M^{IV}_2F_9$ ($M = Sn$), $O_2M^VF_6$ ($M = As, Sb, Au, Pt$), $O_2M^V_2F_{11}$ ($M = Pt$), $O_2M^{VI}F_7$ ($M = Se$), $(O_2)_2M^{VI}F_8$ ($M = Mo, W$), and $O_2M^{VII}F_8$ ($M = I$). The approach has been successful in the case of previously known O_2BF_4 , O_2MF_6 ($M = As, Sb, Au; Pt$), O_2GeF_5 , and $(O_2)_2(Ti_7F_{30})$. Novel compounds $O_2GeF_5 \cdot HF$, α - $O_2Sn_2F_9$ (1-D), and the HF-solvated and nonsolvated forms of β - $O_2Sn_2F_9$ (2-D) were synthesized and their crystal structures determined using single-crystal X-ray diffraction. The crystal structures of all of these materials arise from the condensation of octahedral MF_6 ($M = Ge, Sn$) units. The anion in the crystal structure of $O_2GeF_5 \cdot HF$ is comprised of infinite $[(GeF_5)]^-$ chains of GeF_6 octahedra that share common vertices. The HF molecules and O_2^+ cations are located between the chains. The crystal structure of α - $O_2Sn_2F_9$ (1-D) is constructed from $[O_2]^+$ cations and polymeric $[(Sn_2F_9)]^-$ anions which appear as two parallel infinite chains comprised of SnF_6 units, where each SnF_6 unit of one chain is connected to a SnF_6 unit of the second chain through a shared fluorine vertex. The single-crystal structure determination of $[O_2][Sn_2F_9] \cdot 0.9HF$ reveals that it is comprised of two-dimensional $[(Sn_2F_9)]^-$ grids with $[O_2]^+$ cations and HF molecules located between them. The 2-D grids have a wavelike conformation. The $[(Sn_2F_9)]^-$ layer contains both six- and seven-coordinated Sn(IV) atoms that are interconnected by bridging fluorine atoms. A new, more complex $[O_2]^+$ salt, $O_2[Hg(HF)]_4[SbF_6]_9$, was prepared. In its crystal structure, the Hg atoms bridge to SbF_6 units to form a 3-D framework. The O_2^+ cations are located inside the voids while the HF molecules are bound to Hg atoms through the F atom. Attempts to prepare several chlorine analogues of O_2^+ fluorine salts (i.e., O_2TiCl_5 and O_2MCl_6 ($M = Nb, Sb$)) failed.



INTRODUCTION

Dioxygenyl salts are useful reagents for the oxidation of organic compounds to the corresponding cation radicals.^{1,2} The O_2AsF_6 and O_2SbF_6 are capable of oxidizing C_6F_6 and C_5F_5N to $C_6F_6^+$, yielding $[C_6F_6]^+[MF_6]^-$ ($M = As, Sb$)^{3,4} or $[C_5F_5N]^+[MF_6]^-$ ($M = As$),⁵ respectively. The preparations of substituted and hydrogen-containing fluoroaryl cations (i.e., $[C_6F_5X]^+$, $X = H, CF_3$ or C_6F_5 ; $[1,4-C_6F_4(CF_3)_2]^+$; $[2,3,5,6-C_6F_4X_2]^+$, $X = H$ or CF_3 ; $[2,4,6-C_6H_3F_3]^+$; $[1,2,4,5-C_6H_2Cl_4]^+$) as $[AsF_6]^-$, $[SbF_6]^-$, or $[Sb_2F_{11}]^-$ salts also have been reported.^{6,7} Other examples include the preparation of tertiary amine cation radicals⁸ and the oxidations of N,N,N,N -tetramethyl-*p*-phenylenediamine, 1,4-diazabicyclo[2.2.2]octane, and 1,5-dithiacyclooctane to the corresponding radical cations as shown by EPR spectroscopy.⁹ The reaction of $(CF_3)_2NO$ with O_2SbF_6 produces CF_3 radicals at low temperature.¹⁰ Displacement reactions between O_2MF_6 and suitable amphoteric molecules produce free O_2F radicals which generate atomic fluorine *in situ* upon decomposition.¹¹ A one-step reaction between carbon monoxide and dioxygenyl salts yields oxalyl fluoride $[FC(O)C(O)F]$.¹² The removal of radon

and radioactive noble gas isotopes of xenon from contaminated atmospheres through the use of O_2SbF_6 was also studied.^{13,14} The reactivity of azides toward various dioxygenyl salts was investigated in the scope of research on highly energetic materials.¹⁵

The first dioxygenyl salt, O_2PtF_6 , was reported by Bartlett and Lohmann in 1962.^{16,17} It was initially erroneously identified as $PtOF_4$,¹⁸ which is not surprising given that the $[O_2]^+$ cation as the $[PtF_6]^-$ anion were unknown at that time. It now appears that the dioxygenyl salt, O_2BF_4 , may have been prepared at the same time, although the nature of this material was not elucidated at that time.¹⁹ After more than half a century, the number of known $[O_2]^+$ salts is still limited to approximately 25 examples.^{20,21} Almost two-thirds of them are O_2MF_6 and $O_2M_2F_{11}$ ($M = M^{5+}$) compounds. In addition to

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Table 1. Products Observed Resulting from the Reactions of the Corresponding Fluorides, Oxides, and/or Metals and UV-Irradiated F₂ or F₂/O₂ Mixtures Carried out in aHF at Ambient Temperature

desired product	reactant 1	reactant 2	observed products ^a
O ₂ M ^{III} F ₄	BF ₃	O ₂ /F ₂	O ₂ BF ₄ ^b
O ₂ M ^{III} F ₄	FeF ₃	O ₂ /F ₂	FeF ₃
O ₂ M ^{III} F ₄	CoF ₂	O ₂ /F ₂	CoF ₃
O ₂ M ^{III} F ₄	AgF ₂	O ₂ /F ₂	Ag ₃ F ₈
O ₂ M ^{IV} F ₅	TiO ₂	F ₂	(O ₂) ₂ Ti ₇ F ₃₀
O ₂ M ^{IV} F ₅	SnO ₂	F ₂	O ₂ Sn ₂ F ₉ ·0.9HF, α-O ₂ Sn ₂ F ₉ (1-D) ^c
O ₂ M ^{IV} F ₅	PbO ₂	F ₂	PbF ₄
(O ₂) ₂ M ^{IV} F ₆	TiO ₂	O ₂ /F ₂	(O ₂) ₂ Ti ₇ F ₃₀
(O ₂) ₂ M ^{IV} F ₆	SnO ₂	O ₂ /F ₂	α-O ₂ Sn ₂ F ₉ (1-D), β-O ₂ Sn ₂ F ₉ (2-D), O ₂ Sn ₂ F ₉ ·0.9HF ^c
(O ₂) ₂ M ^{IV} F ₆	PbO ₂	O ₂ /F ₂	PbF ₄
(O ₂) ₂ M ^{IV} F ₆	GeF ₄	O ₂ /F ₂ ^d	O ₂ GeF ₅
(O ₂) ₂ M ^{IV} F ₆	GeF ₄	O ₂ /F ₂	O ₂ GeF ₅ ·HF ^e
(O ₂) ₂ M ^{IV} F ₆	Pd ₂ F ₆	O ₂ /F ₂	O ₂ PdF ₅ /undefined [O ₂ ⁺]-salt ^f
(O ₂) ₂ M ^{IV} F ₆	NiF ₂	O ₂ /F ₂	NiF ₂ /NiF _{2+x}
(O ₂) ₂ M ^{IV} F ₆	MnF ₂	O ₂ /F ₂	undefined [O ₂ ⁺]-salt
O ₂ M ₂ ^{IV} F ₉	SnO ₂ + SnF ₄	F ₂	α-O ₂ Sn ₂ F ₉ (1-D), O ₂ Sn ₂ F ₉ ·0.9HF ^c
O ₂ M ^V F ₆	AsF ₃	O ₂ /F ₂	O ₂ AsF ₆ ^g
O ₂ M ^V F ₆	SbF ₃ /SbF ₅	O ₂ /F ₂	O ₂ SbF ₆ ^g
O ₂ M ^V F ₆	AuF ₃	O ₂ /F ₂	O ₂ AuF ₆ ^g
O ₂ M ^V F ₆	Pt	O ₂ /F ₂	O ₂ PtF ₆ /Pt
O ₂ M ₂ ^V F ₁₁	PtO ₂ , Pt	F ₂	no reaction
O ₂ M ^{VI} F ₇	SeO ₂	F ₂	SeF ₆ (?) ^h
(O ₂) ₂ M ^{VI} F ₈	MoO ₃	O ₂ /F ₂	MoOF ₄
(O ₂) ₂ M ^{VI} F ₈	WO ₃	O ₂ /F ₂	WF ₆ (?) ⁱ
(O ₂) ₂ M ^{VI} F ₈	WF ₆	O ₂ /F ₂ ^c	WF ₆ (?) ⁱ
O ₂ M ^{VII} F ₈	IF ₃	O ₂ /F ₂	IF ₇ (?) ^j
O ₂ M ^{VII} F ₈	IF ₅	O ₂ /F ₂ ^c	IF ₇ (?) ^j

^aProducts were identified by Raman spectroscopy and/or single-crystal X-ray diffraction analysis. There is always a possibility that phases present in minor amounts were overlooked. ^bReference 20. ^cTwo phases with the same empirical chemical formula O₂SnF₉ were obtained. The anion of the first one has a chainlike structure and the second one a layerlike structure. To distinguish between them, the former is designated as 1-D (one-dimensional) and the latter as 2-D (two-dimensional). Additionally, there is a third phase, that is, the HF solvated form of 2-D O₂Sn₂F₉ (i.e., O₂Sn₂F₉·0.9HF). ^dFormed in the absence of aHF solvent. ^eSingle crystals were grown from saturated HF solutions at *T* < −10 °C. ^fThe attempt to grow single crystals from an orange solution at *T* < −5 °C resulted in an orange-red undefined product of very poor crystallinity, whereas the insoluble material corresponded to a mixture of O₂PdF₅ and an undefined [O₂⁺]-salt as shown by Raman spectroscopy. ^gReference 31. ^hWhen isolation was attempted at room temperature (RT), everything pumped away; SeF₆ is a colorless gas at RT. ⁱWhen isolation was attempted at RT, everything pumped away; WF₆ is a colorless liquid at RT. ^jWhen isolation was attempted at RT, everything pumped away; IF₇ is a colorless gas at RT.

O₂MF₆ (M = Sb,²² Au,^{22–25} Rh,²⁵ Ru,^{22,26} Pt^{22,27}), only the crystal structures of O₂BF₄,²⁸ (O₂)₂Ti₇F₃₀,²⁹ O₂Mn₂F₉,³⁰ O₂Ni(AsF₆)₃,²⁰ and O₂(H₃Pd₂F₁₂)²¹ have been reported.

A convenient way to prepare dioxygenyl fluoride salts is by UV photolysis of gaseous, liquid, or solid fluorides with O₂/F₂ and by UV photolysis of oxides with F₂ (or O₂/F₂ mixtures) in liquid anhydrous HF at ambient temperature.³¹ Applying this general method, we systematically investigated the possibility of the preparation of new or already known O₂M^{III}F₄, O₂M^{IV}F₅, (O₂)₂M^{IV}F₆, O₂M^{IV}F₉, O₂M^VF₆, O₂M₂^VF₁₁, O₂M^{VI}F₇, (O₂)₂M^{VI}F₈, and O₂M^{VII}F₈ compounds. We also investigated the possibility of preparing new, more complex [O₂]⁺/metal mixed-cation salts of hexafluoroantimonate(V). The results of this study are described in the present work.

RESULTS AND DISCUSSION

Reactions between the corresponding fluoride, oxides, and/or metals and UV-irradiated F₂ or F₂/O₂ mixtures were carried out in anhydrous hydrogen fluoride (aHF) at ambient temperature (Table 1). Two additional experiments were done in the absence of a solvent. The presence of O₂⁺ in the solid state is easily detected by Raman spectroscopy.^{20,24,47}

Attempted Syntheses of O₂M^{III}F₄ (M = B, Fe, Co, Ag).

The reported syntheses of O₂BF₄ include the reaction between BF₃ and O₂F₂.²⁸ The resulting O₂BF₄ salt decomposes above 0 °C. When the synthesis is done in liquid aHF in a FEP reaction vessel (Table 1), the volatile compounds can be easily pumped away at low temperature and pure O₂BF₄ can be recovered in a quantitative yield (Figure S1, see the Supporting Information).

Attempts to prepare O₂⁺ analogues of KMF₄ (M = Fe, Co)³² failed (Table 1). Only the corresponding trifluorides were recovered after isolation at room temperature.

An attempt to prepare the previously reported O₂AgF₄ salt³³ also failed, although O₂AgF₄ is claimed to have been obtained in some reactions of O₂F₂ with silver compounds in ClF₅ solution. The reaction between AgF₂ and a UV-irradiated mixture of F₂/O₂ (Table 1) resulted in Ag₃F₈ (i.e., the mixed-oxidation-state Ag[AgF₄]₂ fluoride³⁴ (Figure S2, see the Supporting Information).

Attempted Syntheses of O₂M^{IV}F₅ (M = Ti, Sn, Pb). Two examples of O₂M^{IV}F₅ compounds are known from the literature. The first is O₂GeF₅ prepared by UV photolysis of a GeF₄/O₂/F₂ mixture in quartz at −78 °C, which is unstable

at 25 °C.³⁵ The second is O₂PdF₅, isolated from a deep orange solution presumed to contain (O₂)₂PdF₆ dissolved in aHF.³⁶

Since they already contain the required $n(\text{O})/n(\text{M}) = 2:1$ molar ratio as in O₂M^{IV}F₅, the corresponding dioxides MO₂ (M = Ti, Sn, Pb) were used as starting materials (Table 1). The reaction between TiO₂ and F₂ in the presence of UV-light in aHF yielded only the previously known (O₂)₂(Ti₇F₃₀) salt,²⁹ whereas in the case of PbO₂, only PbF₄ was recovered (Table 1 and Figure S3, see the Supporting Information). An attempt to synthesize O₂SnF₅ in a similar manner resulted in two phases of the novel O₂[Sn₂F₉] compound (Figure S3, see Supporting Information).

Attempted Syntheses of (O₂)₂M^{IV}F₆ (M = Ge, Ti, Sn, Pb, Pd, Ni, Mn). Dioxygenyl salts containing doubly charged mononuclear counterions (i.e., [MF₆]²⁻, M = Mn, Ni) were prepared by metathetical reactions between 2O₂SbF₆ and Cs₂MF₆ (M = Mn, Ni) in aHF solution at -45 °C.³⁷ The resulting compounds are marginally stable up to about 10 °C. Addition of a solution of a highly soluble salt A₂PdF₆ (A = K, Cs) in aHF to a solution of O₂AsF₆ in aHF at -30 °C yielded precipitates of AAsF₆ and a deep orange solution presumed to contain (O₂)₂PdF₆.³⁶ Attempts to isolate the latter salt by removal of aHF at -60 °C always resulted in the O₂ and F₂ loss and the recovery of O₂PdF₅. However, further crystallizations at $T < -70$ °C resulted in the growth of single crystals of [O₂][H₃Pd₂F₁₂].²¹ It has been claimed that (O₂)₂SnF₆ was obtained by the reaction of O₂F₂ with SnF₄.³⁸ However, this reaction is of low yield and poor reproducibility.

The products of the reactions between MO₂ (M = Ti, Sn, Pb) and UV-irradiated F₂ in the presence of an excess of O₂ and in aHF solvent were identical to those obtained in attempts to prepare O₂MF₅ compounds where no additional O₂ was used (Table 1). Reactions with TiO₂ gave (O₂)₂(Ti₇F₃₀)²⁹ and reactions with SnO₂ yielded [Sn₂F₉]⁻ salts. In the case of PbO₂, only PbF₄ was recovered.

The reaction between GeF₄ and F₂/O₂ exposed to UV light in the absence of solvent (Table 1) resulted in the previously known O₂GeF₅ salt (Figure S4, see the Supporting Information).³⁵ When the reaction was carried out in liquid HF and single crystals were grown from a saturated HF solution at $T < -10$ °C, the HF solvated form of O₂GeF₅ was obtained (i.e., O₂GeF₅·HF). A similar attempt to grow single crystals from an orange solution prepared by reaction of Pd₂F₆ and a UV-irradiated F₂/O₂ mixture in aHF, and further crystallization at $T < -5$ °C, resulted in an orange-red, poorly crystalline product that was unsuitable for single-crystal X-ray diffraction measurements, and the insoluble material corresponded to O₂PdF₅³⁶ and an undefined [O₂⁺]-salt (Figure S5, see the Supporting Information).

When the NiF₂/F₂/O₂ mixture was irradiated with UV light, aHF-insoluble, pale yellow-green NiF₂ turned black on the surface. This suggests that NiF₂ is partially fluorinated to NiF_{2+x} ($x \leq 1$). The same phenomenon was observed when NiF₂ was exposed to UV-irradiated F₂ in aHF in the absence of O₂.³¹ The Raman spectrum of the product resulting from the reaction of MnF₂ with F₂/O₂ in the presence of a UV source in aHF showed a vibrational band at 1827 cm⁻¹, which could be assigned to O₂⁺ (Figure S6, see the Supporting Information). The $\nu(\text{O}_2^+)$ band occurs at 1805 cm⁻¹ in the Raman spectrum of (O₂)₂MnF₆,³⁷ and that of O₂Mn₂F₉³⁰ at 1838 cm⁻¹. In addition, during the syntheses of MnF₄ by photodissociated F₂ and MnF₂ or MnF₃ in aHF, a broad band at 1834 cm⁻¹ was

sometimes observed.³⁹ This indicates that, in addition to (O₂)₂MnF₆ and O₂Mn₂F₉, at least two more O₂⁺/Mn⁴⁺ fluoride salts must exist, although their compositions remain an open question.

Attempted Syntheses of O₂M^{IV}F₉ (M = Sn). There is only one previously known example of an O₂M^{IV}F₉ salt, i.e., O₂Mn₂F₉, which was first prepared by treating MnO₂ or MnF_x ($x = 2, 3, 4$) with an F₂/O₂ mixture under quite drastic conditions ($p(\text{F}_2)/p(\text{O}_2) \approx 300\text{--}3500$ atm, $T \approx 300\text{--}550$ °C).³⁰

In this work, we were able to prepare an analogue of an O₂M^{IV}F₉ compound with tin by carrying out a chemical reaction between SnO₂, SnF₂ (molar ratio 1:1), and UV-irradiated F₂ in liquid aHF at ambient temperature (Figure S7, see Supporting Information).

Attempted Syntheses of O₂M^VF₆ (M = As, Sb, Au, Pt). Because the O₂M^{VI}F₆ salts are among the most studied O₂⁺ salts,^{17,22–27} we did not place a great deal of emphasis on further examples. The O₂M^{VI}F₆ (M = As, Sb, Au) salts can be conveniently prepared by treating MF₃ (M = As, Sb, Au) or MF₅ (M = As, Sb) with a UV-irradiated F₂/O₂ mixture in aHF (Table 1).³¹ Since AsF₃ is a gas and SbF₃ is a liquid at room temperature, O₂AsF₆ and O₂SbF₆ can be prepared photochemically (even by exposure to daylight⁴⁰) directly from the corresponding binary fluorides, O₂, and F₂ in the absence of HF^{22,41} or by other approaches (using O₂F₂⁴² or high-temperature syntheses^{22,43}). Therefore, the synthetic method is a matter of choice. When the syntheses are done in liquid aHF in FEP reaction vessels, the volatiles can be easily removed at low or ambient temperature and pure O₂MF₆ (M = As, Sb, Au) salts are recovered in quantitative yields. The attempt to prepare O₂PtF₆ by treating Pt metal with a UV-irradiated O₂/F₂ mixture in aHF was only partially successful. The desired compound was formed (Figure S8, see the Supporting Information), but the yield was low. A much more facile synthesis of pure O₂PtF₆ without the demanding synthesis of PtF₆, or the use of high-pressure fluorination, has recently been reported.⁴⁴

Attempted Syntheses of O₂M^VF₁₁ (M = Pt). In addition to O₂M^{VI}F₆, O₂M^VF₁₁ is the second most prevalent group of O₂⁺ salts that is described in the literature.^{41,45–47} Based on vibrational spectroscopic data, their structures consist of O₂⁺ cations and dimeric M₂F₁₁⁻ anions.⁴⁷ The only crystal structure that has been determined from single-crystal X-ray diffraction data for this class of O₂⁺ salts is O₂Pt₂F₁₁, but a complete structure determination has never been published.⁴⁸ Our attempt to prepare O₂Pt₂F₁₁ by reaction between PtO₂/Pt (molar ratio 1:1) and UV-irradiated F₂ in aHF failed (Table 1).

Attempted Syntheses of O₂M^{VI}F₇ (M = Se), (O₂)₂M^{VI}F₈ (M = Mo, W), and O₂M^{VII}F₈ (M = I). There is no indication in the literature for the formation of [SeF₇]⁻, whereas [MF₇]⁻ (M = W, Mo) are well-known.⁴⁹ Tungsten hexafluoride can add two fluoride anions to form [WF₈]²⁻, but [MoF₈]²⁻ has not yet been observed.⁴⁹ The [IF₈]⁻ anion has been observed in the crystal structure of [NO(NO₂)₂][IF₈].⁵⁰ There are reports of the syntheses of NOME₇ (M = Mo, W) and (NO)₂WF₈.⁵¹ A brief mention of analogous O₂⁺ salts is limited to the possible existence of O₂MoF₇ and O₂WF₇,³⁸ although these data have not been confirmed. All of our attempts to synthesize O₂⁺ salts of the [M^{VI}F₇]⁻ (M = Se), [M^{VI}F₈]²⁻ (M = Mo, W) or [M^{VII}F₈]⁻ (M = I) anions failed (Table 1). In each case, nothing remained in the reaction vessels after volatile compounds had been removed under vacuum at room

temperature. It can be assumed that the WF_6 (starting material or formed by fluorination of WO_3) and IF_7 (formed by fluorination of IF_5) were simply pumped off at room temperature. The chemical reaction between MoO_3 and the UV-irradiated F_2/O_2 mixture resulted in a colorless solution from which a colorless material was recovered. Its Raman spectrum was identical to the reported Raman spectrum of solid MoOF_4 , which was obtained by cooling its melt (Figure S9, see the Supporting Information).⁵² A very weak vibrational band at 1850 cm^{-1} was sometimes observed, indicating the presence of an unknown O_2^+ salt.

Attempted Syntheses of $(\text{O}_2)_2\text{Hg}_2\text{F}(\text{SbF}_6)_5$ and $(\text{O}_2)_2\text{Hg}_2(\text{SbF}_6)_6$. In the case of more complex O_2^+ salts, only $\text{O}_2\text{Ni}(\text{AsF}_6)_3$ has been reported thus far.²⁰ Because the synthesis and crystal data of $(\text{O}_2)_2\text{Hg}_2\text{F}(\text{SbF}_6)_5$ have never been published, we were interested in determining if it is possible to prepare this compound in liquid aHF by reaction between O_2SbF_6 , HgF_2 , and SbF_5 (formed *in situ* by fluorination of SbF_3 with elemental F_2) in the required molar ratio, 2:2:3. We also explored the possibility of preparing $(\text{O}_2)_2\text{Hg}_2(\text{SbF}_6)_6$ by using a larger amount of SbF_5 [$n(\text{O}_2\text{SbF}_6)/n(\text{HgF}_2)/n(\text{SbF}_5) = 2:2:4$]. In both cases, the growth of crystals from saturated aHF solutions resulted in single crystals of O_2SbF_6 , $\text{Hg}(\text{HF})(\text{SbF}_6)_2$,⁵⁴ and previously unknown $\text{O}_2\text{SbF}_6 \cdot ([\text{Hg}(\text{HF})][\text{SbF}_6]_2)_4$ (better formulated as $\text{O}_2[\text{Hg}(\text{HF})]_4[\text{SbF}_6]_9$). The pure phase can be obtained when the appropriate starting ratio [$n(\text{O}_2\text{SbF}_6)/n(\text{HgF}_2)/n(\text{SbF}_5) = 1:4:8$] is used (Figure S10, see the Supporting Information).

Attempted Syntheses of $\text{O}_2\text{M}^{\text{IV}}\text{Cl}_6$, $\text{O}_2\text{M}^{\text{IV}}\text{Cl}_5$, and $(\text{O}_2)_2\text{SO}_4$. Since all known O_2^+ salts are based on fluorides, it is clear that nonoxidizable anions are required to stabilize O_2^+ . We were interested in determining what would happen when $\text{SbCl}_5/\text{Cl}_2/\text{O}_2$, $\text{TiCl}_4/\text{Cl}_2/\text{O}_2/\text{HCl}$, and $\text{NbCl}_5/\text{Cl}_2/\text{O}_2/\text{HCl}$ mixtures are exposed to UV-light. Both SbCl_5 and TiCl_4 are liquids, but NbCl_5 is a solid at room temperature. In the cases of TiCl_4 and SbCl_5 , the formation of yellow solids was observed (Figure S11, see the Supporting Information). The absence of vibrational bands in the $1800\text{--}1870\text{ cm}^{-1}$ region of the Raman spectra of the isolated solids showed that no O_2^+ salts were formed. This was also the case when NbCl_5 was used as the starting material. Therefore, the products were not investigated further.

The relative oxidizing strength of O_2^+ has been estimated to be close to that of $\text{Ag}^{2+}_{(\text{soln})}$ (i.e., cationic Ag^{2+} in aHF solution).⁵⁵ A metathetical reaction between K_2SO_4 and $\text{Ag}(\text{SbF}_6)_2$ in aHF yields $\text{Ag}^{\text{II}}\text{SO}_4$.⁵⁶ Our similar attempt to prepare $(\text{O}_2)_2\text{SO}_4$ by a metathetical reaction between K_2SO_4 and $2\text{O}_2\text{SbF}_6$ in aHF also failed. Only KSbF_6 was recovered upon isolation of the solid at $-15\text{ }^\circ\text{C}$.

Crystal Structures of O_2SnF_9 (1-D and 2-D), $\text{O}_2\text{SnF}_9 \cdot 0.9\text{HF}$, $\text{O}_2\text{GeF}_5 \cdot \text{HF}$, and $\text{O}_2[\text{Hg}(\text{HF})]_4(\text{SbF}_6)_9$. The corresponding crystal data and refinement results for α - and β - O_2SnF_9 (1-D and 2-D), $\text{O}_2\text{SnF}_9 \cdot 0.9\text{HF}$, $\text{O}_2\text{GeF}_5 \cdot \text{HF}$, and $\text{O}_2[\text{Hg}(\text{HF})]_4(\text{SbF}_6)_9$ are summarized in Table 2, and the unit cell parameters of O_2GeF_5 are also provided.

Crystal Structures Containing Polymeric $[\text{GeF}_5]^-$ Anions. Besides the well-known octahedral $[\text{GeF}_6]^{2-}$ anion, only two other examples of fluoridogermanate(IV) anions have been described. The first is the polymeric chainlike $([\text{GeF}_5]^-)_\infty$ anion and the second is the $[\text{Ge}_3\text{F}_{16}]^{4-}$ oligomer.⁵⁸ Both are built from GeF_6 octahedra which share common vertices.

Table 2. Summary of Crystal Data and Refinement Results of α - and β - O_2SnF_9 (1-D, 2-D), $\text{O}_2\text{SnF}_9 \cdot 0.9\text{HF}$, $\text{O}_2\text{GeF}_5 \cdot \text{HF}$, and $\text{O}_2[\text{Hg}(\text{HF})]_4(\text{SbF}_6)_9$, Compounds and Unit Cell Data for O_2GeF_5

chemical formula	$\text{O}_2\text{GeF}_5 \cdot \text{HF}^a$	$\text{O}_2\text{SnF}_9 \cdot 0.9\text{HF}$	$\beta\text{-O}_2\text{SnF}_9$ (2-D)
Fw (g/mol)	219.60	460.39	440.42
crystal system	monoclinic	monoclinic	monoclinic
space group	$I2/a$	$P2_1/c$	$P2_1/c$
<i>a</i> (Å)	9.8444(8)	8.9497(5)	9.1318(9)
<i>b</i> (Å)	8.0274(6)	10.5235(5)	9.8027(5)
<i>c</i> (Å)	13.1030(12)	8.7920(4)	8.7741(6)
α (deg)	90	90	90
β (deg)	110.774(10)	94.401(5)	105.334(8)
γ (deg)	90	90	90
<i>V</i> (Å ³)	968.14(15)	825.61(7)	757.46(10)
<i>Z</i>	8	2	4
<i>T</i> (K)	150	150	150
R_1^b	0.0278	0.0351	0.0569
wR_2^c	0.0722	0.0944	0.158
chemical formula	$\alpha\text{-O}_2\text{SnF}_9$ (1-D)	$\text{O}_2[\text{Hg}(\text{HF})]_4(\text{SbF}_6)_9$	
Fw (g/mol)	440.42	3036.14	
crystal system	orthorhombic	monoclinic	
space group	$Immm$	$C2/c$	
<i>a</i> (Å)	4.0473(3)	21.0387(6)	
<i>b</i> (Å)	8.0199(4) Å	10.2412(3)	
<i>c</i> (Å)	11.4491(8)	21.1577(6)	
α (deg)	90	90	
β (deg)	90	99.489(2)	
γ (deg)	90	90	
<i>V</i> (Å ³)	371.63(4)	4496.3(2)	
<i>Z</i>	2	4	
<i>T</i> (K)	200 ^d	150	
R_1^b	0.0152	0.0364	
wR_2^c	0.0362	0.0860	

^aFor nonsolvated O_2GeF_5 , only the unit cell was determined: monoclinic, $P2_1/n$, $a = 6.070(2)\text{ Å}$, $b = 4.993(1)\text{ Å}$, $c = 13.197(4)\text{ Å}$, $\beta = 96.93(3)^\circ$, $V = 397.2\text{ Å}^3$, $Z = 4$, $T = 150\text{ K}$. ^b $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ for $I > 2\sigma(I)$. ^c $wR_2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum w(F_o^2)^2]^{1/2}$. ^dCrystal structure determined at 296 K is the same as at 200 K.

$\text{O}_2\text{GeF}_5 \cdot \text{HF}$. Low-temperature crystallization (Table 1) of the product of the reaction between GeF_4 and a UV-irradiated F_2/O_2 mixture in aHF resulted in the single crystals of $\text{O}_2\text{GeF}_5 \cdot \text{HF}$ (Table 2). The crystal structure consists of infinite polymeric $([\text{GeF}_5]^-)_\infty$ anions, which appear as zigzag single chains of GeF_6 octahedra (Figure 1) linked by *cis*-vertices and O_2^+ cations and HF molecules located between the chains (Figure 2).

The crystal structure of ClO_2GeF_5 also contains infinite polymeric $([\text{GeF}_5]^-)_\infty$ anions appearing as zigzag single chains of GeF_6 octahedra linked by *cis*-vertices.⁵⁷ However, despite the same motif in the GeF_5 chain, the conformations of $([\text{GeF}_5]^-)_\infty$ anions in ClO_2GeF_5 and $\text{O}_2\text{GeF}_5 \cdot \text{HF}$ are different (Figure S12, see the Supporting Information). The geometry of the $([\text{GeF}_5]^-)_\infty$ chains in ClO_2GeF_5 is similar to that observed for $([\text{MnF}_5]^-)_\infty$ in XeF_6MnF_5 ⁵⁹ and $([\text{TiF}_5]^-)_\infty$ in $[\text{C}(\text{NH}_2)_3]_4[\text{H}_3\text{O}][\text{Ti}_4\text{F}_{20}][\text{TiF}_5]_4$,⁶⁰ whereas the geometry of the $([\text{GeF}_5]^-)_\infty$ anion in $\text{O}_2\text{GeF}_5 \cdot \text{HF}$ is closer to that of $([\text{TiF}_5]^-)_\infty$ determined in $\text{A}[\text{TiF}_5]$, $\text{A}[\text{TiF}_5] \cdot \text{HF}$ ($\text{A} = \text{Na}, \text{K}, \text{Rb}, \text{Cs}$)⁶¹ and $[\text{enH}_2]_{0.5}[\text{TiF}_5]$ ($\text{en} = \text{ethylenediamine}$).⁶² In the crystal structure of $\text{O}_2\text{GeF}_5 \cdot \text{HF}$, there is one crystallographically unique germanium atom coordinated by six crystallographically independent fluorine atoms, resulting in

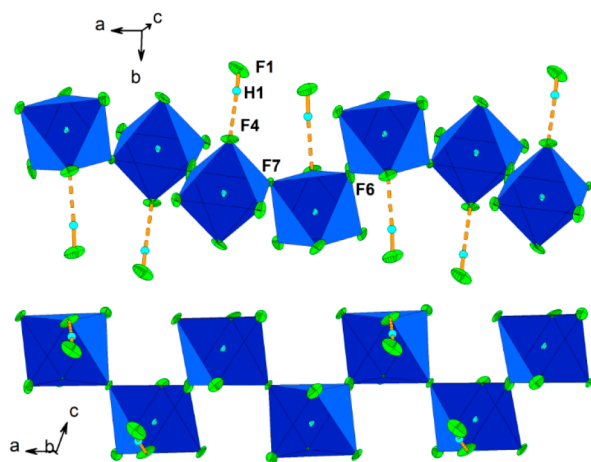


Figure 1. Geometry of $([\text{GeF}_5]^-)_\infty$ anions in $\text{O}_2\text{GeF}_5\cdot\text{HF}$ and hydrogen bonding between HF molecules and the polymeric anions. Thermal ellipsoids are drawn at the 50% probability level.

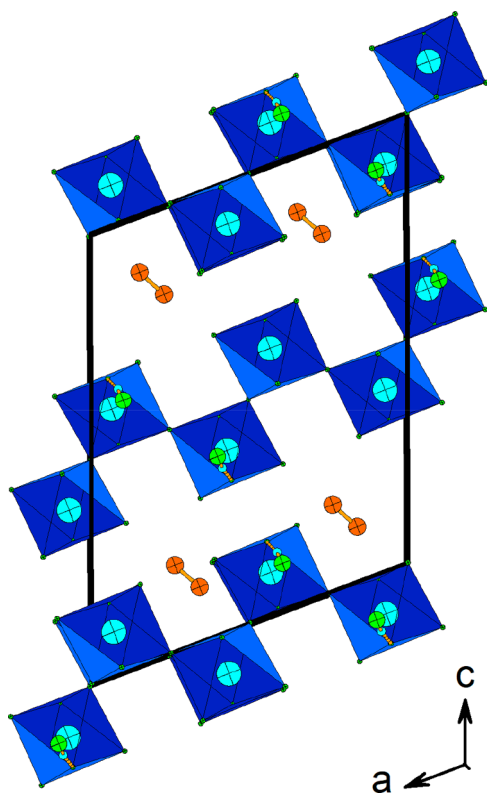


Figure 2. Unit cell and packing of anions, cations, and HF molecules in the crystal structure of $\text{O}_2\text{GeF}_5\cdot\text{HF}$.

slightly distorted GeF_6 octahedra. The $\text{Ge}-\text{F}_t$ bond lengths between germanium atoms (Ge) and terminal fluorine atoms (F_t) range from 1.729(2) Å to 1.7545(19) Å and are shorter than the bonds between Ge and the bridging fluorine atoms (F_b): 1.8817(3) Å for $\text{Ge}-\text{F}_6$ and 1.8934(9) Å for $\text{Ge}-\text{F}_7$. They are comparable to those observed in ClO_2GeF_5 and XeF_5GeF_5 [$\text{Ge}-\text{F}_t = 1.728(3)-1.75(2)$ Å and $\text{Ge}-\text{F}_b = 1.887(1)-1.890(1)$ Å]. The observed $\text{Ge}-\text{F}_6-\text{Ge}$ and $\text{Ge}-\text{F}_7-\text{Ge}$ angles are 180.0° and $140.04(13)^\circ$, respectively. Thus, the zigzag chains of $([\text{GeF}_5]^-)_\infty$ anions in $\text{O}_2\text{GeF}_5\cdot\text{HF}$ are oriented along the *a*-axis (Figure 1). Each GeF_6 octahedron of the $([\text{GeF}_5]^-)_\infty$ chain has one interaction with one HF

molecule by means of a hydrogen bond, where the $(\text{Ge}-)\text{F}_4\cdots(\text{H}-)\text{F}_1$ distance is 2.511 Å.

O_2GeF_5 . The reaction between GeF_4 and F_2/O_2 exposed to UV-light in the absence of solvent (Table 1) resulted in crystalline O_2GeF_5 (Figure S4, see the Supporting Information). Since numerous repeated attempts to obtain good quality X-ray diffraction data were unsuccessful, only the unit cell is reported (Table 2). Preliminary results show that the geometry of the anion is the same as that in the HF-solvated form, $\text{O}_2\text{GeF}_5\cdot\text{HF}$, i.e., both compounds consist of polymeric $([\text{GeF}_5]^-)_\infty$ chainlike anions of the same geometry. It can be concluded that $\text{O}_2\text{GeF}_5\cdot\text{HF}$ prepared at low temperature releases HF at elevated temperature to form O_2GeF_5 . This is in accordance with the formula unit volumes ($V_{\text{F.U.}}$) of both compounds: O_2GeF_5 ; $V_{\text{F.U.}} = 99.3 \text{ \AA}^3$ and $\text{O}_2\text{GeF}_5\cdot\text{HF}$; $V_{\text{F.U.}} = 121.0 \text{ \AA}^3$. The difference of 21.7 \AA^3 can be attributed to the presence of HF in the latter.

Crystal Structures Containing $([\text{Sn}_2\text{F}_9]^-)_\infty$ Double Chainlike and Layerlike $([\text{Sn}_2\text{F}_9]^-)_\infty$ Anions. Raman spectroscopy indicates that the chemical reactions of SnO_2 or a $\text{SnO}_2/\text{SnF}_4$ mixture with a UV-irradiated F_2 or O_2/F_2 mixture in aHF always resulted in two or three phases (Figure S7, see the Supporting Information), which was confirmed by their single-crystal X-ray structures. The crystal structures of three unique O_2^+ salts, all containing polymeric $([\text{Sn}_2\text{F}_9]^-)_\infty$ anions, were determined. Two of them have the same empirical chemical formula, O_2SnF_9 . The anion in the first salt has a chainlike structure, and the second salt has a layerlike structure. To distinguish them, the former is designated as 1-D (one-dimensional) and the latter as 2-D (two-dimensional). The third phase is the HF solvated form of 2-D $\text{O}_2\text{Sn}_2\text{F}_9$ (i.e., 2-D $\text{O}_2\text{Sn}_2\text{F}_9\cdot 0.9\text{HF}$). Bearing in mind that the Rb analogue of NaTi_2F_9 exists as the HF solvated form $\text{RbTi}_2\text{F}_9\cdot\text{HF}$,⁶¹ the existence of a double chain-like 1-D $\text{O}_2\text{Sn}_2\text{F}_9\cdot n\text{HF}$ structure cannot be ruled out.

The layered, polymeric $([\text{Sn}_3\text{F}_{24}]^{4-})_\infty$ anion determined in $[\text{XeF}_5]_4[\text{Sn}_3\text{F}_{24}]$ is the only example of a structurally characterized Sn(IV) fluoride compound that so far does not consist of only $[\text{SnF}_6]^{2-}$ anions.⁶³ Characterizations of other fluoridostannate(IV) anions have been limited to vibrational and NMR spectroscopy (tetrameric $[\text{Sn}_4\text{F}_{20}]^{4-}$ and dimeric $[\text{Sn}_2\text{F}_{10}]^{2-}$ oligomers).^{64,65} Compounds with empirical composition $[\text{N}_2\text{F}][\text{Sn}_2\text{F}_9]$ and $[\text{N}_2\text{F}_3][\text{SnF}_5]$ have also been reported.^{66,67} The former most likely does not have a monomeric structure but is more likely present as an oligomer $[\text{Sn}_4\text{F}_{18}]^{2-}$ or polymeric infinite, double $([\text{Sn}_2\text{F}_9]^-)_\infty$ chain, while the latter most probably has chainlike geometry similar to the $([\text{TiF}_5]^-)_\infty$ anions observed in titanium-based compounds.⁶¹ With 18 different structurally characterized oligomeric and polymeric fluoridotitanate(IV) anions $[\text{Ti}_n\text{F}_{4n+x}]^{x-}$ ($n, x \geq 1$), the chemistry of TiF_4 has been much more extensively investigated⁶⁰⁻⁶² than those of GeF_4 and SnF_4 .

$\alpha\text{-O}_2\text{Sn}_2\text{F}_9$ (1-D). The polymeric $([\text{Sn}_2\text{F}_9]^-)_\infty$ anions in $\alpha\text{-O}_2\text{Sn}_2\text{F}_9$ (1-D) appear as two parallel, infinite zigzag chains comprised of SnF_6 units, where each SnF_6 unit of one chain is connected to a SnF_6 unit of the second chain through a shared fluorine vertex (Figure 3).

The geometries of such polymeric $([\text{M}_2\text{F}_9]^-)_\infty$ anions have been previously observed in various $[\text{Ti}_2\text{F}_9]^-$ salts.^{60,61} However, there is one significant difference. In those compounds, the $\text{Ti}-\text{F}_b-\text{Ti}$ angles within the individual chains, which form double chainlike $([\text{Ti}_2\text{F}_9]^-)_\infty$ anions, are in the

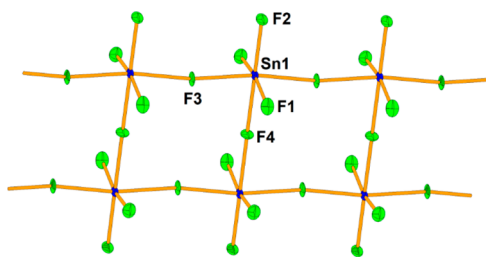


Figure 3. $([\text{Sn}_2\text{F}_9]^-)_\infty$ anion in the crystal structure of $\alpha\text{-O}_2[\text{Sn}_2\text{F}_9]$ (1-D). Thermal ellipsoids are drawn at the 50% probability level.

150–160° range, while the Ti–F_b–Ti angles where the titanium atoms belong to two neighboring chains are in the 140–164° range. The corresponding Sn–F_b–Sn angles in $([\text{Sn}_2\text{F}_9]^-)_\infty$ are more open. The Sn1–F3–Sn1 angles within the individual chains are equal to 170.7(2)°, and the angles, where the Sn atoms belong to two neighboring chains, are linear (Sn1–F4–Sn1 = 180°).

The Sn atom is coordinated by six fluorine atoms. The three Sn–F_b bond lengths between tin and the bridging fluorine atoms are elongated ($2 \times \text{Sn1–F3} = 2.0303(3)$ Å, $\text{Sn1–F4} = 2.0374(4)$ Å) in comparison with the three Sn–F_t bonds between tin and the terminal fluorine atoms ($2 \times \text{Sn1–F1} = 1.898(2)$ Å, $\text{Sn1–F4} = 1.909(4)$ Å).

The negative charge of $([\text{Sn}_2\text{F}_9]^-)_\infty$ anions is compensated by partially disordered O_2^+ cations located between the chains (Figure 4).

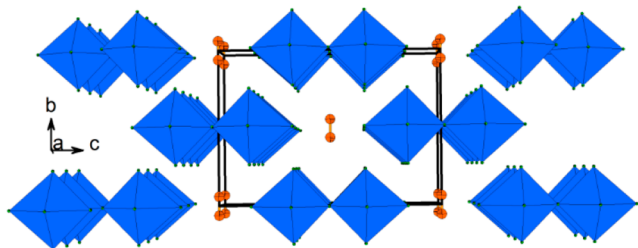


Figure 4. Unit cell and packing of anions, cations, and HF molecules in the crystal structure of $\alpha\text{-O}_2\text{Sn}_2\text{F}_9$ (1-D).

$\text{O}_2[\text{Sn}_2\text{F}_9] \cdot 0.9\text{HF}$. Dioxygenyl nonafluoridodistannate(IV) also crystallized from saturated HF solution as the solvate, $\text{O}_2[\text{Sn}_2\text{F}_9] \cdot 0.9\text{HF}$. The single-crystal structure determination of $\text{O}_2[\text{Sn}_2\text{F}_9] \cdot 0.9\text{HF}$ reveals that its structure is different from that of $\text{O}_2[\text{Sn}_2\text{F}_9]$ (1-D). The anions resemble that determined in $[\text{XeF}_5]_4[\text{Sn}_3\text{F}_{24}]^{4-}$.⁶³ In both compounds (1) the anions consist of two-dimensional (2-D) grids, i.e., $([\text{Sn}_3\text{F}_{24}]^{4-})_\infty$ and $([\text{Sn}_2\text{F}_9]^-)_\infty$, respectively (Figure S13, see Supporting Information), and the $[\text{XeF}_5]^+$ or O_2^+ cations and HF molecules, respectively, are located between the grids (Figure 5). (2) Both types of 2-D grids have wavelike conformations (Figure S13, see Supporting Information), (3) Both the $([\text{Sn}_3\text{F}_{24}]^{4-})_\infty$ and $([\text{Sn}_2\text{F}_9]^-)_\infty$ layers contain six- and seven-coordinated Sn(IV) interconnected by bridging fluorine atoms, and (4) SnF_7 polyhedra in both cases share one edge forming dimer (Figure 6 and Figure S14, see Supporting Information).

The Sn–F bond lengths in $\text{O}_2\text{Sn}_2\text{F}_9 \cdot 0.9\text{HF}$ (2-D), $\alpha\text{-O}_2\text{Sn}_2\text{F}_9$ (1-D), and $[\text{XeF}_5]_4[\text{Sn}_3\text{F}_{24}]^{4-}$ ⁶³ can be divided into several groups (Table 3, Figure 7). The Sn–F_b(–Sn) bonds (F_b = fluorine atoms that bridge two Sn atoms) are longer in seven-coordinated (2.057(4)–2.1120(5) Å) than in six-

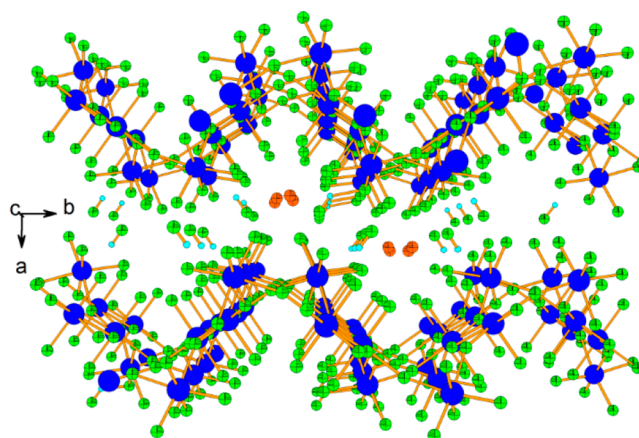


Figure 5. Two-dimensional $([\text{Sn}_2\text{F}_9]^-)_\infty$ grids with a wavelike conformation with the O_2^+ cations and HF molecules located between them in the crystal structure of $\text{O}_2[\text{Sn}_2\text{F}_9] \cdot 0.9\text{HF}$.

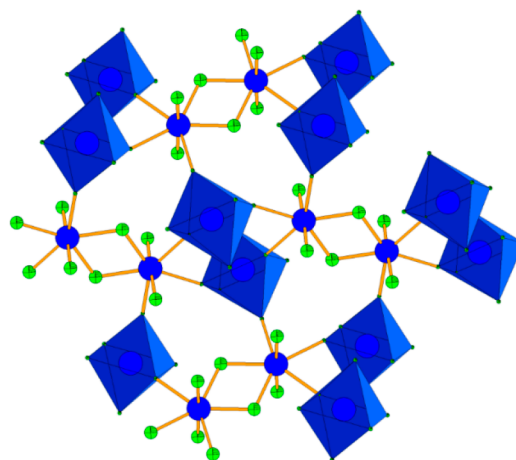


Figure 6. $([\text{Sn}_2\text{F}_9]^-)_\infty$ layer in the crystal structure of $\text{O}_2[\text{Sn}_2\text{F}_9] \cdot 0.9\text{HF}$ contains both six- and seven-coordinated Sn(IV) interconnected by bridging fluorine atoms (view perpendicular to the layer, along the *a*-axis).

coordinated Sn(IV) (1.992(6)–2.0374(4) Å). The Sn–F_b(...Xe) bonds, where F is involved in secondary bonding interactions with $[\text{XeF}_5]^+$ cations or in hydrogen bonding with HF molecules, are shorter (1.919(5)–1.963(6) Å) but longer than the Sn–F_t bonds (F_t = terminal fluorine atoms) of the seven- (1.879(6)–1.883(6) Å) and six-coordinated Sn atoms (1.898(2)–1.909(4) Å).

HF molecules are bound to 2-D grids through F–H...F hydrogen bonds (H...F 1.84 Å, F...F 2.552(7) Å, F...H–F angle 140°). The position of the HF molecule is partially filled, which is likely due to the relative weakness of the above-mentioned hydrogen bonding.

$\beta\text{-O}_2[\text{Sn}_2\text{F}_9]$ (2-D). The third product that resulted from the reaction between SnO_2 or $\text{SnO}_2/\text{SnF}_4$ mixture and a UV irradiated F_2 or O_2/F_2 mixture in aHF is HF-free $\text{O}_2[\text{Sn}_2\text{F}_9]$ which is denoted by $\beta\text{-O}_2[\text{Sn}_2\text{F}_9]$ (2-D). Unfortunately, the same problems as those encountered in the case of unsolvated O_2GeF_5 were observed, i.e., attempts to obtain good quality X-ray diffraction data failed (Table 2). The geometry of the anion is the same as that of solvated $\text{O}_2\text{Sn}_2\text{F}_9 \cdot 0.9\text{HF}$ (2-D), i.e., a layerlike $([\text{Sn}_2\text{F}_9]^-)_\infty$ anion that is present in both compounds. The formula unit volume of $\text{O}_2\text{Sn}_2\text{F}_9$ (1-D) is

Table 3. Geometrical Parameters of Layerlike (2-D) $([\text{Sn}_2\text{F}_9]^-)_\infty$ and the Chainlike (1-D) Anions in the Crystal Structures of $\text{O}_2[\text{Sn}_2\text{F}_9] \cdot 0.9\text{HF}$ (2-D) and $\text{O}_2[\text{Sn}_2\text{F}_9]$ (1-D) and Literature Data for $([\text{Sn}_3\text{F}_{24}]^{4-})_\infty$ Observed in $[\text{XeF}_5]_4[\text{Sn}_3\text{F}_{24}]$

C.N.	bond/Å	$[\text{XeF}_5]_4[\text{Sn}_3\text{F}_{24}]^a$	$\text{O}_2\text{Sn}_2\text{F}_9 \cdot 0.9\text{HF}$ (2-D)	$\alpha\text{-O}_2\text{Sn}_2\text{F}_9$ (1-D)
7	Sn–F _t	1.879(6)/1.883(6)	1.880(4)/1.887(4)	
6	Sn–F _t		1.907(4)/1.909(4)	1.898(2)–1.909(4)
6	Sn–F _b ⋯(H–F)		1.933(4)	
6	Sn–F _b ⋯(XeF ₅)	1.919(5)–1.963(6)		
6	Sn–F _b (–Sn)	1.992(6)/2.002(5)	1.999(4)–2.010(4)	2.0303(3)–2.0374(4)
7	Sn–F _b (–Sn)	2.068(6)–2.120(5)	2.057(4)–2.095(4)	

^aReference 63.

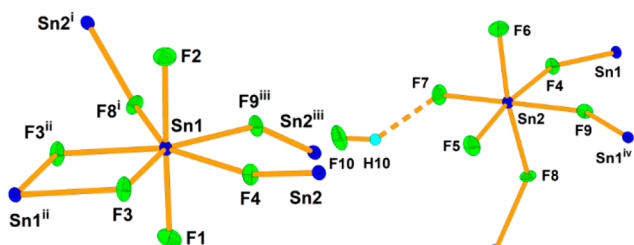


Figure 7. Coordination of two crystallographically unique Sn(IV) atoms and the secondary bonding interactions between SnF_6 octahedra and HF molecules in the crystal structure of $\text{O}_2\text{Sn}_2\text{F}_9 \cdot 0.9\text{HF}$ (2-D). Thermal ellipsoids are drawn at the 50% probability level. Symmetry operations are (i) $2 - x, -1/2 + y, 3/2 - z$; (ii) $2 - x, -y, 1 - z$; (iii) $x, 1/2 - y, 1/2 + z$; and (iv) $x, 1/2 - y, -1/2 + z$.

smaller than that of $\text{O}_2\text{Sn}_2\text{F}_9$ (2-D). For the former, $V_{\text{F.U.}} = 185.82 \text{ \AA}^3$ at 200 K, and for the latter, $V_{\text{F.U.}} = 189.37 \text{ \AA}^3$ at 150 K (Table 2). Because of better packing, $\text{O}_2\text{Sn}_2\text{F}_9$ (1-D) should be a more thermodynamically stable product.

Crystal Structure of $\text{O}_2[\text{Hg}(\text{HF})_4(\text{SbF}_6)_9$. The crystal structure of $\text{O}_2[\text{Hg}(\text{HF})_4(\text{SbF}_6)_9$ is isotopic with that of $\text{H}_3\text{O}[\text{Cd}(\text{HF})_4(\text{SbF}_6)_9$.⁶⁸ It exhibits a complex three-dimensional structure consisting of two crystallographically unique Hg atoms, five crystallographically independent SbF_6 groups, and one HF molecule bound to Hg atoms through its F atom. They form a complex framework with O_2^+ cations located inside the voids (Figure 8).

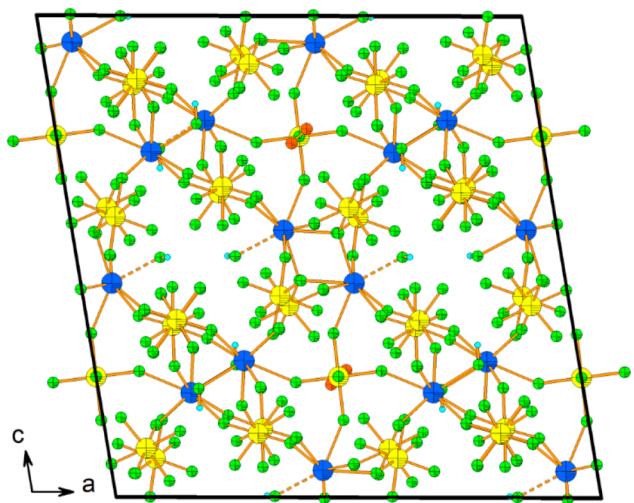


Figure 8. Unit cell and packing of anions, cations, and HF molecules in the crystal structure of $\text{O}_2[\text{Hg}(\text{HF})_4(\text{SbF}_6)_9$.

The Hg1 and Hg2 atoms both possess a square antiprismatic spheres comprised of seven fluorine atoms belonging to seven SbF_6 units and the F atom of the HF molecule. The Hg1–F bond lengths lie in a narrow range, 2.386(5)–2.370(5) Å. The coordination sphere of Hg2 is noticeably distorted; its shape deviates significantly from an ideal square antiprism, and the Hg2–F distances are 2.367(5)–2.451(5) Å.

Four SbF_6^- anions play a role in μ_3 -bridging, being bound to three Hg cations in a *mer*-arrangement, and a SbF_6^- moiety built up around the Sb5 atom displays a μ_4 -bridge (Figure 9).

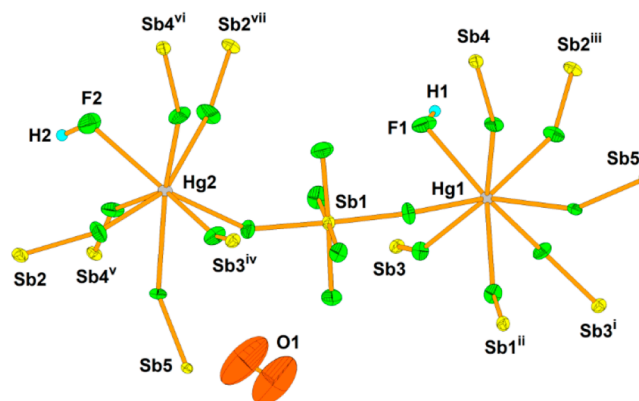


Figure 9. Part of the crystal structure of $\text{O}_2[\text{Hg}(\text{HF})_4(\text{SbF}_6)_9$, showing the environments of both Hg centers and the O_2^+ cation. Fluorine atoms around Sb (with the exception of Sb1) atoms are omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level. Symmetry operations are (i) $-x, 2 - y, 1 - z$; (ii) $1 - x, 1 - y, 1 - z$; (iii) $x, 1 - y, 1/2 + z$; (iv) $x, -1 + y, z$; (v) $x, 1 - y, -1/2 + z$; (vi) $1/2 - x, 1/2 - y, 1 - z$; and (vii) $1/2 - x, 1/2 + y, 1/2 - z$.

The lengths of the terminal Sb–F bonds of the Sb1 to Sb4 polyhedra vary from 1.838(5) to 1.859(6) Å. Notable elongations of Sb3–F33 (1.862(5) Å) and especially Sb4–F43 and Sb1–F13 bonds to 1.868(5) and 1.870(5) Å, respectively, may be attributed to the influence of F–H⋯F(– SbF_5) bond formation (F33⋯H2, 2.13 Å; F43⋯H1, 1.99 Å; F13⋯H2, 2.04 Å). The lengths of bridging Sb–F bonds are 1.891(5)–1.912(5) Å. In the case of the Sb6 coordinating sphere, the two terminal Sb–F bonds, 1.840(8) and 1.862(7) Å, and the bridging Sb–F contacts vary from 1.881(5) to 1.895(5) Å. Each of two HF molecules are bound to the corresponding metal center with Hg–F distances of 2.367(5) and 2.386(5) Å forming rather strong F–H⋯F hydrogen bonds as noted above. The large increased thermal ellipsoids of oxygen atoms and the short O⋯O distance of 0.89(2) Å are a consequence of significant orientational disorder of the O_2^+ cation.

O₂⁺ Bond Lengths. A list of the O–O bond lengths determined in various O₂⁺ salts (including this work) is given in Table 4.

Table 4. O–O Distances (Å) in O₂⁺ Salts Determined by Single Crystal X-Ray Diffraction Data (O₂PtF₆ Was Studied Also Using Neutron-Diffraction Data from a Polycrystalline Sample)

O ₂ ⁺ salt	O–O (Å)	T/K	ref
O ₂ [Hg(HF)] ₄ (SbF ₆) ₉	0.89(2)	150	this work
O ₂ SbF ₆	0.95	RT	22
(O ₂) ₂ Ti ₇ F ₃₀	0.96	153	29
O ₂ GeF ₅ ·HF	1.013(4)	150	this work
O ₂ H ₃ Pd ₂ F ₁₂	1.014(4)	140	21
O ₂ Ni(AsF ₆) ₃	1.018(12)	173	20
O ₂ Sn ₂ F ₉ ·0.9HF	1.046(9)	150	this work
α-O ₂ Sn ₂ F ₉ (1-D)	1.062(14)	200	this work
O ₂ Mn ₂ F ₉	1.10	123	30
	0.96	293	30
O ₂ RhF ₆ ^a	1.1107(16)	133	25
β-O ₂ AuF ₆	0.97	RT	22
α-O ₂ AuF ₆ ^a	1.079(27)	104	23
	1.068(30)	151	24
	1.1091(28)	133	25
O ₂ RuF ₆	1.00	RT	22
	1.125(17)	146	26
	1.12(4)	298	26
O ₂ PtF ₆	0.91(3)/1.21(17)/1.40 ^b	RT	27
	0.96	RT	22
free O ₂ ⁺	1.1227		69

^aRare examples of O₂⁺ salts with ordered O₂⁺ cations. ^bFrom a neutron diffraction study. Various models were tested in an attempt to interpret the experimental data resulting in O–O distances ranging from 0.91 to 1.4 Å. A definitive value for the O–O bond length was not determined, but according to the authors, the model yielding a value of 1.21(17) Å represents the most satisfactory value for the structure of O₂PtF₆.

The reported O–O bond lengths of O₂⁺ span the absurdly short value of 0.89(2) Å to values close to that observed for the gas-phase O₂⁺ cation (1.1227 Å). Their comparison can be difficult due to the large uncertainty of their values. The determination of O–O bond lengths of O₂⁺ is often problematic because of the partial or complete disorder of the O₂⁺ cation in the crystal structures of O₂⁺ salts. For example, the first reported value for O–O bond length in O₂RuF₆ was 1.00 Å (at RT).²² A 3-fold disordering of O₂⁺ yielded a more realistic value of 1.12(4) Å (at 298 K).²⁶ Closer inspection of thermal ellipsoids of oxygen atoms in O₂[Hg(HF)]₄(SbF₆)₉ (Figure 9) reveals unusual enlarged and elongated thermal ellipsoids consistent with oxygen atoms that exhibit static or dynamic disorders. A similar situation occurs in the cases of O₂GeF₅·HF, α-O₂Sn₂F₉ (1-D), and O₂Sn₂F₉·0.9HF. Applying of libration corrections did not result in significant elongation of O–O bonds. More fruitful was an attempt to split oxygen atom positions in α-O₂Sn₂F₉ (1-D) salt. The resulting O–O distance appears to be more adequate, i.e., 1.06(1) Å instead of 0.97(1) Å, for a model without O₂⁺ disordering.

CONCLUSIONS

Photochemical reactions of UV-irradiated O₂/F₂ mixtures with solid, liquid, or gaseous fluorides, and oxides with UV-irradiated F₂ (or O₂/F₂ mixtures) in anhydrous HF are a convenient way to synthesize O₂⁺ salts (Table 5).

Table 5. List of Reported of O₂⁺ Salts (Including This Work) Together with ν(O₂⁺) Values Recorded by Raman Spectroscopy

O ₂ ⁺ salt	ν(O ₂ ⁺) ^a	crystal structure	ref
molecular O ₂	1580		70
(O ₂) ₂ NiF ₆	1801		37
(O ₂) ₂ MnF ₆	1805		37
O ₂ PdF ₅	1820		36, this work
O ₂ RhF ₆	1825	y	23, 25, 26, 47
β-O ₂ AuF ₆	1835 ^b	y	24, 47, this work
α-O ₂ AuF ₆	1838 ^c	y	24
O ₂ Mn ₂ F ₉	1838	y	30
O ₂ RuF ₆	1838	y	22, 26, 47
O ₂ PtF ₆	1838	y	16, 17, 22, 27, 44, 47, this work
O ₂ V ₂ F ₁₁	1839		71
O ₂ BiF ₆	1849		43, 47
O ₂ GeF ₅	1849	y ^d	35, this work
α-O ₂ Sn ₂ F ₉ (1-D)	1849	y	this work
O ₂ Bi ₂ F ₁₁	1853		43
O ₂ NbF ₆	1853		43
(O ₂) ₂ Ti ₇ F ₃₀	1857	y	29, This work
O ₂ AsF ₆	1858		41, 42, 47, 55, this work
O ₂ Nb ₂ F ₁₁	1858		43, 47
O ₂ Ta ₂ F ₁₁	1858		43, 47
O ₂ BF ₄	1860	y	28, this work
O ₂ SbF ₆	1861	y	22, 45, 47, this work
O ₂ [Hg(HF)] ₄ (SbF ₆) ₉	1861	y	this work
(O ₂) ₂ Hg ₂ F(SbF ₆) ₅	1863	y	53
O ₂ Sb ₂ F ₁₁	1864		45, 47
O ₂ Ni(AsF ₆) ₃	1866	y	20
gaseous O ₂ ⁺	1876.4		69
O ₂ Pt ₂ F ₁₁		y ^d	48
[O ₂][H ₃ Pd ₂ F ₁₂]		y	21
O ₂ AgF ₄		y ^d	33
O ₂ GeF ₅ ·HF		y	this work

^aThe values of O₂⁺ stretch are strongly dependent on the nature of counteranions. For more detailed discussion about this topic, see the literature.^{24,72} ^bRecorded at 25 °C ^cRecorded at –163 °C. ^dComplete structure data are not available.

In addition to those given in Table 5, a few others have been mentioned in the literature. The addition of a solution of highly soluble salts A₂PdF₆ (A = K, Cs) in aHF to a solutions of O₂AsF₆ in aHF at –30 °C yield precipitates of AAsF₆ and deep orange solutions presumed to contain (O₂)₂PdF₆.³⁶ Attempts to isolate these salts by removal of aHF at –60 °C always resulted in the loss of O₂ and F₂ and recovery of O₂PdF₅.³⁶ However, further crystallizations at T < –70 °C resulted in the growth of single crystals of [O₂][H₃Pd₂F₁₂].²¹ The (O₂)₂SnF₆, O₂MoF₇ and O₂WF₇ salts have been reported for the reactions between O₂F₂ and SnF₄ and WF₆ or MoF₆, respectively.³⁸ However, these reactions are of low yield and poor reproducibility. The compound, O₂PF₆, slowly decom-

poses at $-80\text{ }^{\circ}\text{C}$ and rapidly at room temperature, giving O_2 , F_2 and PF_5 .^{42,73} The existence of O_2VF_6 , O_2CrF_6 , $\text{O}_2\text{Ru}_2\text{F}_{11}$, and $\text{O}_2\text{M}_3\text{F}_{16}$ ($\text{M} = \text{Sb, Nb, Ta}$) still await confirmation.^{46,71,74} Reported formulation, O_2PdF_6 ,⁷⁵ is most probably O_2PdF_5 ,³⁶ whereas $\text{O}_2[\text{CrF}_4\text{Sb}_2\text{F}_{11}]$,⁷⁶ which was claimed to be prepared by oxidation of O_2 with $\text{CrF}_5 \cdot 2\text{SbF}_5$, is in reality a mixture of $\text{O}_2\text{Sb}_2\text{F}_{11}$ and CrF_4 .⁷⁷

Determination of the single-crystal X-ray structure of $\text{O}_2\text{GeF}_5 \cdot \text{HF}$ showed that its structure consists of infinite polymeric $([\text{GeF}_5]^-)_{\infty}$ anions, which appear as zigzag single chains of GeF_6 octahedra linked by *cis*-vertices and O_2^+ cations and HF molecules located between the chains. The $([\text{GeF}_5]^-)_{\infty}$ anion of O_2GeF_5 appears to have the same structural motif as that of $\text{O}_2\text{GeF}_5 \cdot \text{HF}$.

Three different O_2^+ salts, all containing polymeric $([\text{Sn}_2\text{F}_9]^-)_{\infty}$ anions, were isolated and their structure determined. Two of them have the same empirical chemical formula as $\text{O}_2\text{Sn}_2\text{F}_9$. The anion in $\alpha\text{-O}_2\text{Sn}_2\text{F}_9$ (1-D) has a chainlike structure, and the anion in $\beta\text{-O}_2\text{Sn}_2\text{F}_9$ (2-D) has a layerlike structure. The third phase is the HF solvated form of 2-D $\text{O}_2\text{Sn}_2\text{F}_9$ (i.e., $\text{O}_2\text{Sn}_2\text{F}_9 \cdot 0.9\text{HF}$). Besides the layered polymeric $([\text{Sn}_5\text{F}_{24}]^{4-})_{\infty}$ anion determined in $[\text{XeF}_5]_4[\text{Sn}_5\text{F}_{24}]$,⁶³ these salts provide new examples of structurally characterized Sn(IV) fluoride compounds which do not only consist of $[\text{SnF}_6]^{2-}$ anions.

The complex O_2^+ salt $\text{O}_2[\text{Hg}(\text{HF})_4][\text{SbF}_6]_9$ was prepared by reaction between O_2SbF_6 , HgF_2 , and SbF_5 in anhydrous aHF. Its crystal structure is isotopic to that of $(\text{H}_3\text{O})[\text{Cd}(\text{HF})_4(\text{SbF}_6)_9]$.⁶⁸

EXPERIMENTAL SECTION

Caution! Anhydrous HF and some fluorides are highly toxic and must be handled in a well-ventilated hood, and protective clothing must be worn at all the times.

Materials and Methods. Reagents. Commercially available reagents BF_3 (Union Carbide Austria GmbH, 99.5%), FeF_3 (Alfa Aesar, 97% min), CoF_2 (Johnson Matthey GmbH, 99%), TiO_2 (Koch-Light Laboratories Ltd., 99.5%), SnO_2 (E. Merck AG, Darmstadt, pure), PbO_2 (Riedel de Haën), GeF_4 (Cerac, Incorporated, 99.99%), NiF_2 (Alfa Products, 99.5%), MnF_2 (Alfa Aesar, 99%), SnF_4 (Alfa Aesar, 99%), SbF_3 (Merck KGaA, $\geq 99\%$), Pt (Aldrich, $\geq 99.9\%$), PtO_2 (Aldrich), SeO_2 (Fluka AG, Buchs SG, $> 98\%$), WO_3 (Merck), MoO_3 (Merck, 99.5%), WF_6 (ABCR, 99%), SbCl_5 (Merck, $> 99\%$), TiCl_4 (Acros Organics, 99.9%), NbCl_5 (Alfa Aesar, 99.95%), HCl , and Cl_2 were used as supplied. AgF_2 , AuF_3 , and Pd_2F_6 were synthesized by the reaction of AgNO_3 (Fisher Chemical), AuCl_3 (Alfa Aesar, 99.99%), and Pd sponge (Aldrich 99.9%), respectively, with elemental fluorine F_2 (Solvay Fluor and Derivate GmbH, 99.98%) in aHF (Linde AG, Pullach, Germany, 99.995%) at ambient temperature.³¹ Arsenic pentafluoride was prepared as described previously,⁷⁸ and IF_5 was from our stock. HgF_2 was obtained by high temperature ($230\text{ }^{\circ}\text{C}$) static fluorination of HgCl_2 (Alfa Aesar, 99.5%) in a 100 mL nickel autoclave.

Synthetic Apparatus. All manipulations were carried out under anhydrous conditions. Nonvolatile materials were handled in a M. Braun glovebox in an argon atmosphere, where the quantity of water did not exceed 0.5 ppm. Gaseous F_2 , O_2 , and AsF_5 and volatile compounds, such as aHF and WF_6 , were handled on a vacuum line constructed from nickel and PTFE (polytetrafluoroethylene).

Vessels used for syntheses and single-crystal growth were manufactured from tetrafluoroethylene-hexafluoropropylene block-copolymer (FEP; Polytetra GmbH, Germany) tubes. The reaction vessel was comprised of a tube (i.d. 16 mm, o.d. 19 mm) that was heat-sealed on one end and equipped with a PTFE valve on the other flared end. The crystallization vessel consisted of two FEP tubes: one 16 mm i.d. \times 19 mm o.d. and the other 4 mm i.d. \times 6 mm o.d. Each

tube was heat-sealed on one end and attached *via* linear PTFE connectors to a connecting PTFE T-part at 90° . The PTFE valve was attached to the T-part at 180° to the 19 mm o.d. tube. All PTFE portions of valve were enclosed in brass with threads that prevented deformation of the PTFE portions of the valve and simplified their connection to reaction vessels and to the vacuum system. Magnetic stirring bars, clad in PTFE, were placed inside the reaction vessels. The temperature gradient between the two arms of the crystallization vessels was maintained by cooling a wider arm of a vessel in Huber Ministat 230 (to $-33\text{ }^{\circ}\text{C}$) and Thermo Fisher Scientific EK 90 (to $-60\text{ }^{\circ}\text{C}$) cryostats.

Prior to use, all reaction and crystallization vessels were dried under dynamic vacuum and passivated with elemental fluorine F_2 (Solvay Fluor and Derivate GmbH, 99.98%) at 1 bar for 2 h. Anhydrous HF (Linde AG, 99.995%) was treated with K_2NiF_6 (Advance Research Chemicals Inc., 99.9%) for several hours before use and was usually kept in FEP vessels above K_2NiF_6 .

Synthesis and Crystal Growth. Various amounts (50–200 mg) of solid starting reagents were loaded into reaction vessels inside a drybox (Table S1 in the Supporting Information). Gaseous and liquid reagents were added on a vacuum line. Solvent (HF, 5–10 mL) was condensed onto the reactant at 77 K, and the reaction mixture was warmed to ambient temperature. Fluorine was slowly added to the reaction vessel at ambient temperature until a pressure of 6 bar was attained. A medium-pressure mercury lamp (Hg arc lamp, 450 W, Ace Glass, USA) was used as the UV source.³¹ The reaction mixture was allowed to stir for 1–5 days at ambient temperature. All volatiles were slowly pumped off at ambient temperature. After characterization, the powdered product was transferred to a crystallization vessel where aHF (6–10 mL) was condensed onto the product at 77 K. The solvent and product were warmed to ambient temperature and the resulting clear solution was decanted into the 6 mm o.d. side arm. Evaporation of the solvent from this side arm was carried out by maintaining a temperature gradient of $\sim 10\text{--}20\text{ }^{\circ}\text{C}$ between both tubes for several weeks. Slow distillation of aHF from the 6 mm o.d. tube into the 19 mm o.d. tube resulted in crystal growth inside the 6 mm o.d. tube. Several solutions of dissolved products were allowed to crystallize without prior isolation and characterization.

Crystals were treated in different ways. Some crystals were immersed in perfluorodecalin (melting point 263 K) inside a drybox, selected under a microscope, and mounted on the goniometer head of the diffractometer in a cold nitrogen stream. Others were sealed in quartz capillaries used for the structure determination at room temperature and recording of Raman spectra at several random positions. A special method was applied in order to isolate crystals of $\text{O}_2\text{GeF}_5 \cdot \text{HF}$ that are not stable at ambient temperature. For this, a small portion (1–2 mL) of cold perfluorinated oil (perfluorodecaline $\text{C}_{10}\text{F}_{18}$) was injected inside the narrower FEP tube to cover the crystals. After that, crystals covered with cold oil were selected under a microscope and mounted on the goniometer head of the diffractometer in a cold nitrogen stream.

Characterization Methods. Raman Spectroscopy. Raman spectra with a resolution of 0.5 cm^{-1} were recorded at room temperature on a Horiba Jobin Yvon LabRam-HR spectrometer equipped with an Olympus BXFM-ILHS microscope. Samples were excited by the 632.8 nm emission line of a He–Ne laser with a regulated power in the range $20\text{--}0.0020\text{ mW}$, which gave $17\text{--}0.0017\text{ mW}$ focused on a $1\text{ }\mu\text{m}$ spot through a $50\times$ microscope objective on the top surface of the sample. Single crystals or powdered material were mounted in the glovebox in previously vacuum-dried quartz capillaries, which were initially sealed with Halocarbon 25-5S grease (Halocarbon Corp.) inside the glovebox and later heat-sealed in an oxygen–hydrogen flame outside the glovebox.

Single Crystal X-ray Diffraction Analysis. Single-crystal X-ray data for $\text{O}_2\text{Sn}_2\text{F}_9$ (1-D and 2-D), $\text{O}_2\text{Sn}_2\text{F}_9 \cdot 0.9\text{HF}$, $\text{O}_2\text{GeF}_5 \cdot \text{HF}$, O_2GeF_5 , and $\text{O}_2[\text{Hg}(\text{HF})_4][\text{SbF}_6]_9$ were collected on a Gemini A diffractometer equipped with an Atlas CCD detector, using graphite monochromated $\text{MoK}\alpha$ radiation. The data were treated using the CrysAlisPro software suite program package.⁷⁹ Analytical absorption corrections were applied to all data sets. The structure of $\text{O}_2\text{Sn}_2\text{F}_9$ (1-

D) was solved using the SHELXS program.⁸⁰ All other structures were solved using the dual-space algorithm of the SHELXT⁸¹ program implemented in the Olex crystallographic software.⁸² Structure refinement was performed with SHELXL-2014 software.⁸³ The figures were prepared using DIAMOND 4.6 software.⁸⁴ Hydrogen atoms in the structures of O₂Sn₂F₉·0.9HF, O₂GeF₅·HF, and O₂[Hg(HF)]₄(SbF₆)₉, were placed on ideal positions and refined as the riding atoms with relative isotropic displacement parameters. The common occupancy of atoms belonging to the HF molecule in the O₂Sn₂F₉·0.9HF structure was refined using a free variable.

Crystals of O₂GeF₅ and O₂Sn₂F₉ (2-D) compounds were of extremely poor quality. In the case of O₂Sn₂F₉ (2-D), the crystal structure was completely solved and refined to a reasonable R-factor value. However, the structure suffers from residual electron densities having peaks that are too high. Only the structural motif was identified in the case of O₂GeF₅ salt with a very high R-value (~20%) for the completed model.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.inorgchem.9b03518>.

Raman spectra of the products obtained by photochemical reactions of UV-irradiated F₂ (or O₂/F₂ mixture) with solid, liquid, or gaseous fluorides or oxides in anhydrous HF; photos of the yellow solids formed after SbCl₅/Cl₂/O₂ and TiCl₄/Cl₂/O₂/HCl mixtures were irradiated by UV-light; geometries of the ([GeF₅]⁻)_∞ anions determined in the crystal structures of O₂GeF₅·HF and [ClO₂][GeF₅]; two-dimensional ([Sn₂F₉]⁻)_∞ and ([Sn₃F₂₄]⁴⁻)_∞ grids with a wavelike conformation found in O₂[Sn₂F₉]·0.9HF and [XeF₅]₄[Sn₅F₂₄] (PDF)

Accession Codes

CCDC 1964935–1964938 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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