# **Inorganic Chemistry**

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# Syntheses of Dioxygenyl Salts by Photochemical Reactions in Liquid Anhydrous Hydrogen Fluoride: X-ray Crystal Structures of $\alpha$ - and $\beta$ -O<sub>2</sub>Sn<sub>2</sub>F<sub>9</sub>, O<sub>2</sub>Sn<sub>2</sub>F<sub>9</sub>·0.9HF, O<sub>2</sub>GeF<sub>5</sub>·HF, and O<sub>2</sub>[Hg(HF)]<sub>4</sub>(SbF<sub>6</sub>)<sub>9</sub>

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ABSTRACT: By	treating gaseous liquid or so	lid fluorides with	IW-photolyzed 02G	eF5•HF	$O_2Sn_2F_9$ (1-D) $O_2Sn_2F_9$ (2-D)

**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),  $O_2M^{IV}F_7$  (M = Sn),  $O_2M^{V}F_6$  (M = As, Sb, Au, Pt),  $O_2M^{V}F_1$  (M = Pt),  $O_2M^{VI}F_7$  (M = Se),  $(O_2)_2M^{VI}F_8$  (M = Mo, W), and  $O_2M^{VI}F_8$  (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  $O_2GeF_5$ ·HF,  $\alpha$ - $O_2Sn_2F_9$  (1-D),

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  $O_2GeF_5$ ·HF,  $\alpha$ - $O_2Sn_2F_9$  (1-D), and the HF-solvated and nonsolvated forms of  $\beta$ - $O_2Sn_2F_9$  (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<sub>6</sub> (M = Ge, Sn) units. The anion in the crystal structure of  $O_2GeF_5$ ·HF is comprised of infinite ( $[GeF_5]^-)_{\infty}$  chains of GeF<sub>6</sub> octahedra that share common vertices. The HF molecules and  $O_2^+$  cations are located between the chains. The crystal structure of  $\alpha$ - $O_2SnF_9$  (1-D) is constructed from  $[O_2]^+$  cations and polymeric ( $[Sn_2F_9]^-)_{\infty}$  anions which appear as two parallel infinite chains comprised of SnF<sub>6</sub> units, where each SnF<sub>6</sub> unit of one chain is connected to a SnF<sub>6</sub> unit of the second chain through a shared fluorine vertex. The singlecrystal structure determination of  $[O_2][Sn_2F_9]^{-}0.9$ HF reveals that it is comprised of two-dimensional ( $[Sn_2F_9]^-)_{\infty}$  grids with  $[O_2]^+$ cations and HF molecules located between them. The 2-D grids have a wavelike conformation. The ( $[Sn_2F_9]^-)_{\infty}$  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<sub>6</sub> 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.<sup>1,2</sup> The O<sub>2</sub>AsF<sub>6</sub> and O<sub>2</sub>SbF<sub>6</sub> are capable of oxidizing C<sub>6</sub>F<sub>6</sub> and  $C_5F_5N$  to  $C_6F_6^+$ , yielding  $[C_6F_6]^+[MF_6]^-$  (M = As, Sb)<sup>3,4</sup> or  $[C_6F_5N]^+[MF_6]^-$  (M = As),<sup>5</sup> respectively. The preparations of substituted and hydrogen-containing fluoroaryl cations (i.e.,  $[C_6F_5X]^+$ , X = H, CF<sub>3</sub> or C<sub>6</sub>F<sub>5</sub>;  $[1,4-C_6F_4(CF_3)_2]^+$ ;  $[2,3,5,6-C_6F_5X]^+$  $C_6F_4X_2$ ]<sup>+</sup>, X = H or CF<sub>3</sub>; [2,4,6- $C_6H_3F_3$ ]<sup>+</sup>; [1,2,4,5- $C_6H_2Cl_4$ ]<sup>+</sup>) as  $[AsF_6]^-$ ,  $[SbF_6]^-$ , or  $[Sb_2F_{11}]^-$  salts also have been reported.<sup>6,7</sup> Other examples include the preparation of tertiary amine cation radicals<sup>8</sup> and the oxidations of  $N_i N_i N_i$ . 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.<sup>10</sup> Displacement reactions between O<sub>2</sub>MF<sub>6</sub> and suitable amphoteric molecules produce free O<sub>2</sub>F radicals which generate atomic fluorine in situ upon decomposition.<sup>11</sup> A onestep reaction between carbon monoxide and dioxygenyl salts yields oxalyl fluoride [FC(O)C(O)F].<sup>12</sup> The removal of radon

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

The first dioxygenyl salt,  $O_2PtF_{6}$ , was reported by Bartlett and Lohmann in 1962.<sup>16,17</sup> It was initially erroneously identified as  $PtOF_4$ ,<sup>18</sup> 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.<sup>19</sup> After more than half a century, the number of known  $[O_2]^+$  salts is still limited to approximately 25 examples.<sup>20,21</sup> Almost two-thirds of them are  $O_2MF_6$  and  $O_2M_2F_{11}$  (M = M<sup>5+</sup>) compounds. In addition to



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desired product	reactant 1	reactant 2	observed products <sup>a</sup>
$O_2 M^{III} F_4$	BF <sub>3</sub>	$O_2/F_2$	$O_2BF_4^b$
$O_2 M^{III} F_4$	FeF <sub>3</sub>	$O_2/F_2$	FeF <sub>3</sub>
$O_2 M^{III} F_4$	CoF <sub>2</sub>	$O_2/F_2$	CoF <sub>3</sub>
$O_2 M^{III} F_4$	$AgF_2$	$O_2/F_2$	$Ag_3F_8$
$O_2 M^{IV} F_5$	$TiO_2$	F <sub>2</sub>	$(O_2)_2 Ti_7 F_{30}$
$O_2 M^{IV} F_5$	SnO <sub>2</sub>	F <sub>2</sub>	$O_2Sn_2F_9 \cdot 0.9HF$ , $\alpha - O_2Sn_2F_9 (1-D)^c$
$O_2 M^{IV} F_5$	PbO <sub>2</sub>	F <sub>2</sub>	$PbF_4$
$(O_2)_2 M^{IV} F_6$	$TiO_2$	$O_2/F_2$	$(O_2)_2 Ti_7 F_{30}$
$(O_2)_2 M^{IV} F_6$	SnO <sub>2</sub>	$O_2/F_2$	$\alpha$ -O <sub>2</sub> Sn <sub>2</sub> F <sub>9</sub> (1-D), $\beta$ -O <sub>2</sub> Sn <sub>2</sub> F <sub>9</sub> (2-D), O <sub>2</sub> Sn <sub>2</sub> F <sub>9</sub> ·0.9HF <sup>c</sup>
$(O_2)_2 M^{IV} F_6$	PbO <sub>2</sub>	$O_2/F_2$	$PbF_4$
$(O_2)_2 M^{IV} F_6$	GeF <sub>4</sub>	$O_2/F_2^d$	$O_2GeF_5$
$(O_2)_2 M^{IV} F_6$	$GeF_4$	$O_2/F_2$	$O_2GeF_5 \cdot HF^e$
$(O_2)_2 M^{IV} F_6$	$Pd_2F_6$	$O_2/F_2$	$O_2PdF_5$ /undefined $[O_2^+]$ -salt <sup>f</sup>
$(O_2)_2 M^{IV} F_6$	NiF <sub>2</sub>	$O_2/F_2$	$NiF_2/NiF_{2+x}$
$(O_2)_2 M^{IV} F_6$	$MnF_2$	$O_2/F_2$	undefined [O <sub>2</sub> <sup>+</sup> ]-salt
$O_2 M_2^{IV} F_9$	$SnO_2 + SnF_4$	F <sub>2</sub>	$\alpha$ -O <sub>2</sub> Sn <sub>2</sub> F <sub>9</sub> (1-D), O <sub>2</sub> Sn <sub>2</sub> F <sub>9</sub> ·0.9HF <sup>c</sup>
$O_2 M^V F_6$	AsF <sub>5</sub>	$O_2/F_2$	$O_2AsF_6^g$
$O_2 M^V F_6$	SbF <sub>3</sub> /SbF <sub>5</sub>	$O_2/F_2$	$O_2SbF_6^g$
$O_2 M^V F_6$	AuF <sub>3</sub>	$O_2/F_2$	$O_2AuF_6^g$
$O_2 M^V F_6$	Pt	$O_2/F_2$	$O_2 PtF_6/Pt$
$O_2 M_2^{V} F_{11}$	PtO <sub>2</sub> , Pt	F <sub>2</sub>	no reaction
$O_2 M^{VI} F_7$	SeO <sub>2</sub>	F <sub>2</sub>	$SeF_6$ (?) <sup>h</sup>
$(O_2)_2 M^{VI} F_8$	$MoO_3$	$O_2/F_2$	MoOF <sub>4</sub>
$(O_2)_2 M^{VI} F_8$	WO <sub>3</sub>	$O_2/F_2$	$WF_6$ (?) <sup>i</sup>
$(O_2)_2 M^{VI} F_8$	WF <sub>6</sub>	$O_2/F_2^c$	$WF_6$ (?) <sup>i</sup>
$O_2 M^{VII} F_8$	IF <sub>5</sub>	$O_2/F_2$	$\operatorname{IF}_{7}(?)^{j}$
$O_2 M^{VII} F_8$	IF <sub>5</sub>	$O_2/F_2^c$	$IF_7(?)^j$

Table 1. Products Observed Resulting from the Reactions of the Corresponding Fluorides, Oxides, and/or Metals and UV-Irradiated  $F_2$  or  $F_2/O_2$  Mixtures Carried out in aHF at Ambient Temperature

<sup>*a*</sup>Products 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. <sup>*b*</sup>Reference 20. <sup>*c*</sup>Two phases with the same empirical chemical formula  $O_2SnF_9$  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  $O_2Sn_2F_9$  (i.e.,  $O_2Sn_2F_9 \cdot 0.9HF$ ). <sup>*d*</sup>Formed in the absence of aHF solvent. <sup>*e*</sup>Single crystals were grown from saturated HF solutions at  $T < -10 \, ^\circ\text{C}$ . <sup>*f*</sup>The attempt to grow single crystals from an orange solution at  $T < -5 \, ^\circ\text{C}$  resulted in an orange-red undefined product of very poor crystallinity, whereas the insoluble material corresponded to a mixture of  $O_2PdF_5$  and an undefined  $[O_2^+]$ -salt as shown by Raman spectroscopy. <sup>*g*</sup>Reference 31. <sup>*h*</sup>When isolation was attempted at room temperature (RT), everything pumped away; SeF<sub>6</sub> is a colorless gas at RT. <sup>*i*</sup>When isolation was attempted at RT, everything pumped away; IF<sub>7</sub> is a colorless gas at RT.

 $O_2MF_6$  (M = Sb,<sup>22</sup> Au,<sup>22-25</sup> Rh,<sup>25</sup> Ru,<sup>22,26</sup> Pt<sup>22,27</sup>), only the crystal structures of  $O_2BF_4$ ,<sup>28</sup> ( $O_2$ )<sub>2</sub>Ti<sub>7</sub>F<sub>30</sub>,<sup>29</sup>  $O_2Mn_2F_9$ ,<sup>30</sup>  $O_2Ni(AsF_6)_3$ ,<sup>20</sup> and  $O_2(H_3Pd_2F_{12})^{21}$  have been reported.

A convenient way to prepare dioxygenyl fluoride salts is by UV photolysis of gaseous, liquid, or solid fluorides with  $O_2/F_2$  and by UV photolysis of oxides with  $F_2$  (or  $O_2/F_2$  mixtures) in liquid anhydrous HF at ambient temperature.<sup>31</sup> Applying this general method, we systematically investigated the possibility of the preparation of new or already known  $O_2M^{II}F_4$ ,  $O_2M^{IV}F_5$ ,  $(O_2)_2M^{IV}F_6$ ,  $O_2M^{IV}_2F_9$ ,  $O_2M^VF_6$ ,  $O_2M_2^VF_{11}$ ,  $O_2M^{VI}F_7$ ,  $(O_2)_2M^{VI}F_8$ , and  $O_2M^{VII}F_8$  compounds. We also investigated the possibility of preparing new, more complex  $[O_2]^+/metal$  mixed-cation salts of hexafluoridoantimonate(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  $F_2$  or  $F_2/O_2$  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  $O_2^+$  in the solid state is easily detected by Raman spectroscopy.<sup>20,24,47</sup>

Attempted Syntheses of  $O_2 M^{III}F_4$  (M = B, Fe, Co, Ag).

The reported syntheses of  $O_2BF_4$  include the reaction between  $BF_3$  and  $O_2F_2$ .<sup>28</sup> The resulting  $O_2BF_4$  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  $O_2BF_4$  can be recovered in a quantitative yield (Figure S1, see the Supporting Information).

Attempts to prepare  $O_2^+$  analogues of KMF<sub>4</sub> (M = Fe, Co)<sup>32</sup> failed (Table 1). Only the corresponding trifluorides were recovered after isolation at room temperature.

An attempt to prepare the previously reported  $O_2AgF_4$  salt<sup>33</sup> also failed, although  $O_2AgF_4$  is claimed to have been obtained in some reactions of  $O_2F_2$  with silver compounds in  $ClF_5$  solution. The reaction between  $AgF_2$  and a UV-irradiated mixture of  $F_2/O_2$  (Table 1) resulted in  $Ag_3F_8$  (i.e., the mixed-oxidation-state  $Ag[AgF_4]_2$  fluoride<sup>34</sup> (Figure S2, see the Supporting Information).

Attempted Syntheses of  $O_2 M^{IV} F_5$  (M = Ti, Sn, Pb). Two examples of  $O_2 M^{IV} F_5$  compounds are known from the literature. The first is  $O_2 GeF_5$  prepared by UV photolysis of a GeF<sub>4</sub>/O<sub>2</sub>/F<sub>2</sub> mixture in quartz at -78 °C, which is unstable at 25 °C.<sup>35</sup> The second is  $O_2PdF_5$ , isolated from a deep orange solution presumed to contain  $(O_2)_2PdF_6$  dissolved in aHF.<sup>36</sup>

Since they already contain the required n(O)/n(M) = 2:1molar ratio as in  $O_2M^{IV}F_5$ , the corresponding dioxides  $MO_2$ (M = Ti, Sn, Pb) were used as starting materials (Table 1). The reaction between  $TiO_2$  and  $F_2$  in the presence of UV-light in aHF yielded only the previously known  $(O_2)_2(Ti_7F_{30})$  salt,<sup>29</sup> whereas in the case of PbO<sub>2</sub>, only PbF<sub>4</sub> was recovered (Table 1 and Figure S3, see the Supporting Information). An attempt to synthesize  $O_2SnF_5$  in a similar manner resulted in two phases of the novel  $O_2[Sn_2F_9]$  compound (Figure S3, see Supporting Information).

Attempted Syntheses of  $(O_2)_2 M^{IV} F_6$  (M = Ge, Ti, Sn, Pb, Pd, Ni, Mn). Dioxygenyl salts containing doubly charged mononuclear counterions (i.e.,  $[MF_6]^{2-}$ , M = Mn, Ni) were prepared by metathetical reactions between 2O<sub>2</sub>SbF<sub>6</sub> and Cs<sub>2</sub>MF<sub>6</sub> (M = Mn, Ni) in aHF solution at -45 °C.<sup>37</sup> The resulting compounds are marginally stable up to about 10 °C. Addition of a solution of a highly soluble salt A<sub>2</sub>PdF<sub>6</sub> (A = K, Cs) in aHF to a solution of O<sub>2</sub>AsF<sub>6</sub> in aHF at -30 °C yielded precipitates of AAsF<sub>6</sub> and a deep orange solution presumed to contain  $(O_2)_2$ PdF<sub>6</sub>.<sup>36</sup> Attempts to isolate the latter salt by removal of aHF at -60 °C always resulted in the O<sub>2</sub> and F<sub>2</sub> loss and the recovery of O<sub>2</sub>PdF<sub>5</sub>. However, further crystallizations at T < -70 °C resulted in the growth of single crystals of  $[O_2][H_3Pd_2F_{12}].^{21}$  It has been claimed that  $(O_2)_2$ SnF<sub>6</sub> was obtained by the reaction of O<sub>2</sub>F<sub>2</sub> with SnF<sub>4</sub>.<sup>38</sup> However, this reaction is of low yield and poor reproducibility.

The products of the reactions between  $MO_2$  (M = Ti, Sn, Pb) and UV-irradiated  $F_2$  in the presence of an excess of  $O_2$  and in aHF solvent were identical to those obtained in attempts to prepare  $O_2MF_5$  compounds where no additional  $O_2$  was used (Table 1). Reactions with TiO<sub>2</sub> gave  $(O_2)_2(Ti_7F_{30})^{29}$  and reactions with SnO<sub>2</sub> yielded [Sn<sub>2</sub>F<sub>9</sub>]<sup>-</sup> salts. In the case of PbO<sub>2</sub>, only PbF<sub>4</sub> was recovered.

The reaction between GeF<sub>4</sub> and F<sub>2</sub>/O<sub>2</sub> exposed to UV light in the absence of solvent (Table 1) resulted in the previously known O<sub>2</sub>GeF<sub>5</sub> salt (Figure S4, see the Supporting Information).<sup>35</sup> 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 O<sub>2</sub>GeF<sub>5</sub> was obtained (i.e., O<sub>2</sub>GeF<sub>5</sub>·HF). A similar attempt to grow single crystals from an orange solution prepared by reaction of Pd<sub>2</sub>F<sub>6</sub> and a UV-irradiated F<sub>2</sub>/O<sub>2</sub> 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 O<sub>2</sub>PdF<sub>5</sub><sup>36</sup> and an undefined  $[O_2^+]$ -salt (Figure S5, see the Supporting Information).

When the NiF<sub>2</sub>/F<sub>2</sub>/O<sub>2</sub> mixture was irradiated with UV light, aHF-insoluble, pale yellow-green NiF<sub>2</sub> turned black on the surface. This suggests that NiF<sub>2</sub> is partially fluorinated to NiF<sub>2+x</sub> ( $x \le 1$ ). The same phenomenon was observed when NiF<sub>2</sub> was exposed to UV-irradiated F<sub>2</sub> in aHF in the absence of O<sub>2</sub>.<sup>31</sup> The Raman spectrum of the product resulting from the reaction of MnF<sub>2</sub> with F<sub>2</sub>/O<sub>2</sub> in the presence of a UV source in aHF showed a vibrational band at 1827 cm<sup>-1</sup>, which could be assigned to O<sub>2</sub><sup>+</sup> (Figure S6, see the Supporting Information). The  $\nu$ (O<sub>2</sub><sup>+</sup>) band occurs at 1805 cm<sup>-1</sup> in the Raman spectrum of (O<sub>2</sub>)<sub>2</sub>MnF<sub>6</sub>,<sup>37</sup> and that of O<sub>2</sub>Mn<sub>2</sub>F<sub>9</sub><sup>30</sup> at 1838 cm<sup>-1</sup>. In addition, during the syntheses of MnF<sub>4</sub> by photodissociated F<sub>2</sub> and MnF<sub>2</sub> or MnF<sub>3</sub> in aHF, a broad band at 1834 cm<sup>-1</sup> was sometimes observed.<sup>39</sup> This indicates that, in addition to  $(O_2)_2MnF_6$  and  $O_2Mn_2F_9$ , at least two more  $O_2^+/Mn^{4+}$  fluoride salts must exist, although their compositions remain an open question.

Attempted Syntheses of  $O_2 M^{V_2} F_9$  (M = Sn). There is only one previously known example of an  $O_2 M^{V_2} F_9$  salt, i.e.,  $O_2 Mn_2 F_9$ , which was first prepared by treating  $MnO_2$  or  $MnF_x$ (x = 2, 3, 4) with an  $F_2/O_2$  mixture under quite drastic conditions ( $p(F_2)/p(O_2) \approx 300-3500$  atm,  $T \approx 300-550$ °C).<sup>30</sup>

In this work, we were able to prepare an analogue of an  $O_2M^{IV}{}_2F_9$  compound with tin by carrying out a chemical reaction between SnO<sub>2</sub>, SnF<sub>2</sub> (molar ratio 1:1), and UV-irradiated F<sub>2</sub> in liquid aHF at ambient temperature (Figure S7, see Supporting Information).

Attempted Syntheses of  $O_2 M^V F_6$  (M = As, Sb, Au, Pt). Because the  $O_2M^{\rm VI}F_6$  salts are among the most studied  $O_2^{\,+}$  salts,  $^{17,22-27}$  we did not place a great deal of emphasis on further examples. The  $O_2 M^{VI}F_6$  (M = As, Sb, Au) salts can be conveniently prepared by treating  $MF_3$  (M = As, Sb, Au) or MF<sub>5</sub> (M = As, Sb) with a UV-irradiated  $F_2/O_2$  mixture in aHF (Table 1).<sup>31</sup> Since AsF<sub>5</sub> is a gas and SbF<sub>5</sub> is a liquid at room temperature, O<sub>2</sub>AsF<sub>6</sub> and O<sub>2</sub>SbF<sub>6</sub> can be prepared photochemically (even by exposure to daylight<sup>40</sup>) directly from the corresponding binary fluorides, O2, and F2 in the absence of  $HF^{22,41}$  or by other approaches (using  $O_2F_2^{42}$  or high-temperature syntheses<sup>22,43</sup>). 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  $O_2MF_6$  (M = As, Sb, Au) salts are recovered in quantitative yields. The attempt to prepare O<sub>2</sub>PtF<sub>6</sub> by treating Pt metal with a UV-irradiated O<sub>2</sub>/ F<sub>2</sub> 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  $O_2PtF_6$  without the demanding synthesis of  $PtF_{6}$ , or the use of high-pressure fluorination, has recently been reported.44

Attempted Syntheses of  $O_2M_2^VF_{11}$  (M = Pt). In addition to  $O_2M_F^{VI}F_6$ ,  $O_2M_2^VF_{11}$  is the second most prevalent group of  $O_2^+$  salts that is described in the literature.<sup>41,45-47</sup> Based on vibrational spectroscopic data, their structures consist of  $O_2^+$ cations and dimeric  $M_2F_{11}^-$  anions.<sup>47</sup> The only crystal structure that has been determined from single-crystal X-ray diffraction data for this class of  $O_2^+$  salts is  $O_2Pt_2F_{11}$ , but a complete structure determination has never been published.<sup>48</sup> Our attempt to prepare  $O_2Pt_2F_{11}$  by reaction between PtO<sub>2</sub>/Pt (molar ratio 1:1) and UV-irradiated  $F_2$  in aHF failed (Table 1).

Attempted Syntheses of  $O_2M^{VI}F_7$  (M = Se),  $(O_2)_2M^{VI}F_8$ (M = Mo, W), and  $O_2M^{VII}F_8$  (M = I). There is no indication in the literature for the formation of  $[SeF_7]^-$ , whereas  $[MF_7]^-$  (M = W, Mo) are well-known.<sup>49</sup> Tungsten hexafluoride can add two fluoride anions to form  $[WF_8]^{2-}$ , but  $[MoF_8]^{2-}$  has not yet been observed.<sup>49</sup> The  $[IF_8]^-$  anion has been observed in the crystal structure of  $[NO(NOF)_2][IF_8]$ .<sup>50</sup> There are reports of the syntheses of NOMF<sub>7</sub> (M = Mo, W) and  $(NO)_2WF_8$ .<sup>51</sup> A brief mention of analogous  $O_2^+$  salts is limited to the possible existence of  $O_2MoF_7$  and  $O_2WF_7$ ,<sup>38</sup> although these data have not been confirmed. All of our attempts to synthesize  $O_2^+$  salts of the  $[M^{VI}F_7]^-$  (M = Se),  $[M^{VI}F_8]^{2-}$  (M = Mo, W) or  $[M^{VII}F_8]^-$  (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<sub>6</sub> (starting material or formed by fluorination of WO<sub>3</sub>) and IF<sub>7</sub> (formed by fluorination of IF<sub>5</sub>) were simply pumped off at room temperature. The chemical reaction between MoO<sub>3</sub> 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<sub>4</sub>, which was obtained by cooling its melt (Figure S9, see the Supporting Information).<sup>52</sup> A very weak vibrational band at 1850 cm<sup>-1</sup> was sometimes observed, indicating the presence of an unknown O<sub>2</sub><sup>+</sup> salt.

Attempted Syntheses of (O<sub>2</sub>)<sub>2</sub>Hg<sub>2</sub>F(SbF<sub>6</sub>)<sub>5</sub> and  $(O_2)_2Hg_2(SbF_6)_6$ . In the case of more complex  $O_2^+$  salts, only  $O_2Ni(AsF_6)_3$  has been reported thus far.<sup>20</sup> Because the synthesis and crystal data of  $(O_2)_2Hg_2F(SbF_6)_5^{53}$  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  $(O_2)_2Hg_2(SbF_6)_6$  by using a larger amount of  $SbF_5$  $[n(O_2SbF_6)/n(HgF_2)/n(SbF_5) = 2:2:4]$ . In both cases, the growth of crystals from saturated aHF solutions resulted in single crystals of  $O_2SbF_{61}$  Hg(HF)(SbF<sub>6</sub>)<sub>21</sub><sup>54</sup> and previously unknown  $O_2SbF_6 \cdot ([Hg(HF)][SbF_6]_2)_4$  (better formulated as  $O_2[Hg(HF)]_4[SbF_6]_9)$ . The pure phase can be obtained when the appropriate starting ratio  $[n(O_2SbF_6)/n(HgF_2)/n(SbF_5) =$ 1:4:8] is used (Figure S10, see the Supporting Information).

Attempted Syntheses of  $O_2M^VCI_6$ ,  $O_2M^{IV}CI_5$ , and  $(O_2)_2SO_4$ . 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  $SbCI_5/CI_2/O_2$ ,  $TiCI_4/CI_2/O_2/HCI$ , and  $NbCI_5/CI_2/O_2/HCI$  mixtures are exposed to UV-light. Both  $SbCI_5$  and  $TiCI_4$  are liquids, but  $NbCI_5$  is a solid at room temperature. In the cases of  $TiCI_4$  and  $SbCI_5$ , the formation of yellow solids was observed (Figure S11, see the Supporting Information). The absence of vibrational bands in the 1800–1870 cm<sup>-1</sup> region of the Raman spectra of the isolated solids showed that no  $O_2^+$  salts were formed. This was also the case when  $NbCI_5$  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  $Ag^{2+}_{(solv)}$  (i.e., cationic  $Ag^{2+}$  in aHF solution).<sup>55</sup> A metathetical reaction between  $K_2SO_4$  and  $Ag(SbF_6)_2$  in aHF yields  $Ag^{II}SO_4$ .<sup>56</sup> Our similar attempt to prepare  $(O_2)_2SO_4$  by a metathetical reaction between  $K_2SO_4$ and  $2O_2SbF_6$  in aHF also failed. Only  $KSbF_6$  was recovered upon isolation of the solid at -15 °C.

Crystal Structures of  $O_2SnF_9$  (1-D and 2-D),  $O_2SnF_9$ 0.9HF,  $O_2GeF_5$ ·HF, and  $O_2[Hg(HF)]_4(SbF_6)_9$ . The corresponding crystal data and refinement results for  $\alpha$ - and  $\beta$ - $O_2SnF_9$  (1-D and 2-D),  $O_2SnF_9$ ·0.9HF,  $O_2GeF_5$ ·HF, and  $O_2[Hg(HF)]_4(SbF_6)_9$  are summarized in Table 2, and the unit cell parameters of  $O_2GeF_5$  are also provided.

**Crystal Structures Containing Polymeric [GeF<sub>5</sub>]**<sup>-</sup> **Anions.** Besides the well-known octahedral  $[GeF_6]^{2-}$  anion, only two other examples of fluoridogermanate(IV) anions have been described. The first is the polymeric chainlike  $([GeF_5]^-)_{\infty}^{57}$  anion and the second is the  $[Ge_3F_{16}]^{4-}$ oligomer.<sup>58</sup> Both are built from GeF<sub>6</sub> octahedra which share common vertices. Table 2. Summary of Crystal Data and Refinement Results of  $\alpha$ - and  $\beta$ -O<sub>2</sub>SnF<sub>9</sub> (1-D, 2-D), O<sub>2</sub>SnF<sub>9</sub>·0.9HF, O<sub>2</sub>GeF<sub>5</sub>·HF, and O<sub>2</sub>[Hg(HF)]<sub>4</sub>(SbF<sub>6</sub>)<sub>9</sub> Compounds and Unit Cell Data for O<sub>2</sub>GeF<sub>5</sub>

chemical formula	O2GeF5·HF <sup>a</sup>	$O_2Sn_2F_9$ ·0.9HF		$\beta$ -O <sub>2</sub> Sn <sub>2</sub> F <sub>9</sub> (2-D)	
Fw (g/mol)	219.60	460.39		440.42	
crystal system	monoclinic	monoclinic		monoclinic	
space group	I2/a	$P2_1/c$		$P2_{1}/c$	
a (Å)	9.8444(8)	8.9497(5)		9.1318(9)	
b (Å)	8.0274(6)	10.5235(5)		9.8027(5)	
c (Å)	13.1030(12)	8.7920(4)		8.7741(6)	
$\alpha$ (deg)	90	90		90	
$\beta$ (deg)	110.774(10)	94.401(5)		105.334(8)	
γ (deg)	90	90		90	
V (Å <sup>3</sup> )	968.14(15)	825.61(7)		757.46(10)	
Ζ	8	2		4	
T (K)	150	150		150	
$R_1^{b}$	0.0278	0.0351		0.0569	
$wR_2^c$	0.0722	0.0944		0.158	
chemical formula	$\alpha$ -O <sub>2</sub> Sn <sub>2</sub> F <sub>9</sub>	(1-D)	$O_2[H$	lg(HF)] <sub>4</sub> (SbF <sub>6</sub> ) <sub>9</sub>	
Fw (g/mol)	440.42	3036		.14	
crystal system	orthorhom	bic mone		oclinic	
space group	Immm	C2/c			
a (Å)	4.0473(3)		21.0387(6)		
b (Å)	8.0199(4) Å		10.2412(3)		
c (Å)	11.4491(8)	)	21.1577(6)		
$\alpha$ (deg)	90	90			
$\beta$ (deg)	90	99.48		9(2)	
γ (deg)	90		90		
$V(Å^3)$	371.63(4)	371.63(4)		4496.3(2)	
Ζ	2	2		4	
T (K)	200 <sup>d</sup>	200 <sup>d</sup>		150	
$R_1^{b}$	0.0152	0.0152		0.0364	
$wR_2^c$	0.0362	0.0362		0.0860	

<sup>*a*</sup>For nonsolvated O<sub>2</sub>GeF<sub>5</sub>, only the unit cell was determined: monoclinic, P2<sub>1</sub>/n, a = 6.070(2) Å, b = 4.993(1) Å, c = 13.197(4) Å,  $\beta$  = 96.93(3)°, V = 397.2 Å<sup>3</sup>, Z = 4, T = 150 K. <sup>*b*</sup>R<sub>1</sub> =  $\Sigma ||F_0| - |F_c||/$  $\Sigma |F_0|$  for  $I > 2\sigma(I)$ . <sup>*c*</sup>wR<sub>2</sub> =  $[\Sigma [w(F_0^2 - F_c^2)^2]/\Sigma w(F_0^2)^2]^{1/2}$ . <sup>*d*</sup>Crystal structure determined at 296 K is the same as at 200 K.

 $O_2GeF_5$ ·HF. Low-temperature crystallization (Table 1) of the product of the reaction between GeF<sub>4</sub> and a UV-irradiated  $F_2/O_2$  mixture in aHF resulted in the single crystals of  $O_2GeF_5$ ·HF (Table 2). The crystal structure consists of infinite polymeric ([GeF<sub>5</sub>]<sup>-</sup>)<sub>∞</sub> anions, which appear as zigzag single chains of GeF<sub>6</sub> 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  $([GeF_5]^-)_{\infty}$  anions appearing as zigzag single chains of GeF<sub>6</sub> octahedra linked by *cis*-vertices.<sup>57</sup> However, despite the same motif in the GeF<sub>5</sub> chain, the conformations of  $([GeF_5]^-)_{\infty}$  anions in  $ClO_2GeF_5$  and  $O_2GeF_5$ ·HF are different (Figure S12, see the Supporting Information). The geometry of the  $([GeF_5]^-)_{\infty}$  chains in  $ClO_2GeF_5$  is similar to that observed for  $([MnF_5]^-)_{\infty}$  in  $XeF_5MnF_5^{59}$  and  $([TiF_5]^-)_{\infty}$  in  $[C(NH_2)_3]_4[H_3O]_4[Ti_4F_{20}][TiF_5]_4$ ,<sup>60</sup> whereas the geometry of the  $([GeF_5]^-)_{\infty}$  anion in  $O_2GeF_5$ ·HF is closer to that of  $([TiF_5]^-)_{\infty}$  determined in  $A[TiF_5]$ ,  $A[TiF_5]$ ·HF (A = Na, K, Rb, Cs)<sup>61</sup> and  $[enH_2]_{0.5}[TiF_5]$  (en = ethylenediamine).<sup>62</sup> In the crystal structure of  $O_2GeF_5$ ·HF, there is one crystallographically unique germanium atom coordinated by six crystallographically independent fluorine atoms, resulting in



**Figure 1.** Geometry of  $([GeF_5]^-)_{\infty}$  anions in  $O_2GeF_5$ ·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  $O_2GeF_5$ ·HF.

slightly distorted GeF<sub>6</sub> octahedra. The Ge-F<sub>t</sub> bond lengths between germanium atoms (Ge) and terminal fluorine atoms (F<sub>t</sub>) 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<sub>b</sub>): 1.8817(3) Å for Ge-F6 and 1.8934(9) Å for Ge-F7. They are comparable to those observed in ClO<sub>2</sub>GeF<sub>5</sub> and XeF<sub>5</sub>GeF<sub>5</sub> [Ge-F<sub>t</sub> = 1.728(3)-1.75(2) Å and Ge-F<sub>b</sub> = 1.887(1)-1.890(1) Å]. The observed Ge-F6-Ge and Ge-F7-Ge angles are 180.0° and 140.04(13)°, respectively. Thus, the zigzag chains of ([GeF<sub>5</sub>]<sup>-</sup>)<sub>∞</sub> anions in O<sub>2</sub>GeF<sub>5</sub>·HF are oriented along the *a*-axis (Figure 1). Each GeF<sub>6</sub> octahedron of the ([GeF<sub>5</sub>]<sup>-</sup>)<sub>∞</sub> chain has one interaction with one HF molecule by means of a hydrogen bond, where the  $(Ge-)F4\cdots$  (H-)F1 distance is 2.511 Å.

 $O_2GeF_5$ . The reaction between GeF<sub>4</sub> and F<sub>2</sub>/O<sub>2</sub> exposed to UV-light in the absence of solvent (Table 1) resulted in crystalline O<sub>2</sub>GeF<sub>5</sub> (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, O<sub>2</sub>GeF<sub>5</sub>·HF, i.e., both compounds consist of polymeric ([GeF<sub>5</sub>]<sup>-</sup>)<sub>∞</sub> chainlike anions of the same geometry. It can be concluded that O<sub>2</sub>GeF<sub>5</sub>·HF prepared at low temperature releases HF at elevated temperature to form O<sub>2</sub>GeF<sub>5</sub>. This is in accordance with the formula unit volumes ( $V_{F.U}$ ) of both compounds: O<sub>2</sub>GeF<sub>5</sub>;  $V_{F.U} = 99.3$  Å<sup>3</sup> and O<sub>2</sub>GeF<sub>5</sub>·HF;  $V_{F.U} = 121.0$  Å<sup>3</sup>. The difference of 21.7 Å<sup>3</sup> can be attributed to the presence of HF in the latter.

Crystal Structures Containing  $([Sn_2F_9]^-)_{\infty}$  Double **Chainlike and Layerlike** ([Sn<sub>2</sub>F<sub>9</sub>]<sup>-</sup>)<sub>∞</sub> Anions. Raman spectroscopy indicates that the chemical reactions of SnO<sub>2</sub> or a  $SnO_2/SnF_4$  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  $([Sn_2F_9]^-)_{\infty}$ anions, were determined. Two of them have the same empirical chemical formula, O<sub>2</sub>SnF<sub>9</sub>. 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  $O_2Sn_2F_9$  (i.e., 2-D  $O_2Sn_2F_9$ ·0.9HF). Bearing in mind that the Rb analogue of NaTi<sub>2</sub>F<sub>9</sub> exists as the HF solvated form RbTi<sub>2</sub>F<sub>9</sub>·HF,<sup>61</sup> the existence of a double chain-like 1-D O<sub>2</sub>Sn<sub>2</sub>F<sub>9</sub>·nHF structure cannot be ruled out.

The layered, polymeric  $([\mathrm{Sn}_{5}\mathrm{F}_{24}]^{4-})_{\infty}$  anion determined in  $[\mathrm{XeF}_{5}]_{4}[\mathrm{Sn}_{5}\mathrm{F}_{24}]$  is the only example of a structurally characterized Sn(IV) fluoride compound that so far does not consist of only  $[\mathrm{SnF}_{6}]^{2-}$  anions.<sup>63</sup> Characterizations of other fluoridostannate(IV) anions have been limited to vibrational and NMR spectroscopy (tetrameric  $[\mathrm{Sn}_{4}\mathrm{F}_{20}]^{4-}$  and dimeric  $[\mathrm{Sn}_{2}\mathrm{F}_{10}]^{2-}$  oligomers).<sup>64,65</sup> Compounds with empirical composition  $[\mathrm{N}_{2}\mathrm{F}][\mathrm{Sn}_{2}\mathrm{F}_{9}]$  and  $[\mathrm{N}_{2}\mathrm{F}_{3}][\mathrm{SnF}_{5}]$  have also been reported.<sup>66,67</sup> The former most likely does not have a monomeric structure but is more likely present as an oligomer  $[\mathrm{Sn}_{4}\mathrm{F}_{18}]^{2-}$  or polymeric infinite, double  $([\mathrm{Sn}_{2}\mathrm{F}_{9}]^{-})_{\infty}$  chain, while the latter most probably has chainlike geometry similar to the  $([\mathrm{TiF}_{5}]^{-})_{\infty}$  anions observed in titanium-based compounds.<sup>61</sup> With 18 different structurally characterized oligomeric and polymeric fluoridotitanate(IV) anions  $[\mathrm{Ti}_{4}\mathrm{F}_{4n+x}]^{x-}$   $(n, \ x \ge 1)$ , the chemistry of  $\mathrm{TiF}_{4}$  has been much more extensively investigated<sup>60-62</sup> than those of GeF\_4 and SnF\_4.

 $\alpha$ - $O_2Sn_2F_9$  (1-D). The polymeric  $([Sn_2F_9]^-)_{\infty}$  anions in  $\alpha$ - $O_2Sn_2F_9$  (1-D) appear as two parallel, infinite zigzag chains comprised of SnF<sub>6</sub> units, where each SnF<sub>6</sub> unit of one chain is connected to a SnF<sub>6</sub> unit of the second chain through a shared fluorine vertex (Figure 3).

The geometries of such polymeric  $([M_2F_9]^-)_{\infty}$  anions have been previously observed in various  $[Ti_2F_9]^-$  salts.<sup>60,61</sup> However, there is one significant difference. In those compounds, the Ti- $F_b$ -Ti angles within the individual chains, which form double chainlike  $([Ti_2F_9]^-)_{\infty}$  anions, are in the



**Figure 3.**  $([Sn_2F_9]^-)_{\infty}$  anion in the crystal structure of  $\alpha$ -O<sub>2</sub> $[Sn_2F_9]$  (1-D). Thermal ellipsoids are drawn at the 50% probability level.

 $150-160^\circ$  range, while the Ti– $F_b$ –Ti angles where the titanium atoms belong to two neighboring chains are in the  $140-164^\circ$  range. The corresponding Sn– $F_b$ –Sn angles in  $([Sn_2F_9]^-)_\infty$  are more open. The Sn1–F3–Sn1 angles within the individual chains are equal to  $170.7(2)^\circ)$ , and the angles, where the Sn atoms belong to two neighboring chains, are linear (Sn1–F4–Sn1 =  $180^\circ$ ).

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

The negative charge of  $([Sn_2F_9]^-)_{\infty}$  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  $\alpha$ -O<sub>2</sub>Sn<sub>2</sub>F<sub>9</sub> (1-D).

 $O_2[Sn_2F_9]\cdot 0.9HF$ . Dioxygenyl nonafluoridodistannate(IV) also crystallized from saturated HF solution as the solvate,  $O_2[Sn_2F_9]\cdot 0.9HF$ . The single-crystal structure determination of  $O_2[Sn_2F_9]\cdot 0.9HF$  reveals that its structure is different from that of  $O_2[Sn_2F_9]$  (1-D). The anions resemble that determined in  $[XeF_5]_4[Sn_5F_{24}]^{.63}$  In both compounds (1) the anions consist of two-dimensional (2-D) grids, i.e.,  $([Sn_5F_{24}]^{4-})_{\infty}$  and  $([Sn_2F_9]^-)_{\infty}$ , respectively (Figure S13, see Supporting Information), and the  $[XeF_5]^+$  or  $O_2^+$  cations and HF molecules, respectively, are located between the grids (Figure S13, see Supporting Information), (3) Both the  $([Sn_5F_{24}]^{4-})_{\infty}$  and  $([Sn_2F_9]^-)_{\infty}$ ) layers contain six- and seven-coordinated Sn(IV) interconnected by bridging fluorine atoms, and (4) SnF<sub>7</sub> polyhedra in both cases share one edge forming dimer (Figure 6 and Figure S14, see Supporting Information).

The Sn-F bond lengths in O<sub>2</sub>Sn<sub>2</sub>F<sub>9</sub>·0.9HF (2-D),  $\alpha$ -O<sub>2</sub>Sn<sub>2</sub>F<sub>9</sub> (1-D), and [XeF<sub>5</sub>]<sub>4</sub>[Sn<sub>5</sub>F<sub>24</sub>]<sup>63</sup> can be divided into several groups (Table 3, Figure 7). The Sn-F<sub>b</sub>(-Sn) bonds (F<sub>b</sub> = 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  $([Sn_2F_9]^-)_{\infty}$  grids with a wavelike conformation with the  $O_2^+$  cations and HF molecules located between them in the crystal structure of  $O_2[Sn_2F_9]$ -0.9HF.



**Figure 6.**  $([Sn_2F_9]^-)_{\infty})$  layer in the crystal structure of  $O_2[Sn_2F_9]^-$  0.9HF 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– $F_b$ ( $\cdots$  Xe) bonds, where F is involved in secondary bonding interactions with  $[XeF_5]^+$  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  $F-H\cdots F$  hydrogen bonds ( $H\cdots F$  1.84 Å,  $F\cdots F$  2.552(7) Å,  $F\cdots H-F$  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.

 $\beta$ - $O_2[Sn_2F_9]$  (2-D). The third product that resulted from the reaction between SnO<sub>2</sub> or SnO<sub>2</sub>/SnF<sub>4</sub> mixture and a UV irradiated F<sub>2</sub> or O<sub>2</sub>/F<sub>2</sub> mixture in aHF is HF-free O<sub>2</sub>[Sn<sub>2</sub>F<sub>9</sub>] which is denoted by  $\beta$ -O<sub>2</sub>[Sn<sub>2</sub>F<sub>9</sub>] (2-D). Unfortunately, the same problems as those encountered in the case of unsolvated O<sub>2</sub>GeF<sub>5</sub> 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 O<sub>2</sub>Sn<sub>2</sub>F<sub>9</sub>·0.9HF (2-D), i.e., a layerlike ([Sn<sub>2</sub>F<sub>9</sub>]<sup>-</sup>)<sub>∞</sub>) anion that is present in both compounds. The formula unit volume of O<sub>2</sub>Sn<sub>2</sub>F<sub>9</sub> (1-D) is

Table 3. Geometrical Parameters of Layerlike (2-D)  $([Sn_2F_9]^-)_{\infty}$  and the Chainlike (1-D) Anions in the Crystal Structures of  $O_2[Sn_2F_9] \cdot 0.9$ HF (2-D) and  $O_2[Sn_2F_9]$  (1-D) and Literature Data for  $([Sn_5F_{24}]^{4-})_{\infty}$  Observed in  $[XeF_5]_4[Sn_5F_{24}]$ 

	. , 22 2 ,2			5 5516 5 215
C.N.	bond/Å	$[XeF_5]_4[Sn_5F_{24}]^a$	$O_2Sn_2F_9.0.9HF$ (2-D)	$\alpha$ -O <sub>2</sub> Sn <sub>2</sub> F <sub>9</sub> (1-D)
7	Sn-F <sub>t</sub>	1.879(6)/1.883(6)	1.880(4)/1.887(4)	
6	Sn-F <sub>t</sub>		1.907(4)/1.909(4)	1.898(2)-1.909(4)
6	$Sn-F_b\cdots(H-F)$		1.933(4)	
6	$Sn-F_b\cdots(XeF_5)$	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)	
<sup>a</sup> Roforonco 63				

<sup>&</sup>quot;Reference 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  $O_2Sn_2F_9$ . 0.9HF (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  $O_2Sn_2F_9$  (2-D). For the former,  $V_{F.U.} = 185.82 \text{ Å}^3$  at 200 K, and for the latter,  $V_{F.U.} = 189.37 \text{ Å}^3$  at 150 K (Table 2). Because of better packing,  $O_2Sn_2F_9$  (1-D) should be a more thermodynamically stable product.

**Crystal Structure of**  $O_2[Hg(HF)]_4(SbF_6)_9$ . The crystal structure of  $O_2[Hg(HF)]_4(SbF_6)_9$  is isotypic with that of  $H_3O[Cd(HF)]_4(SbF_6)_9$ .<sup>68</sup> It exhibits a complex three-dimensional structure consisting of two crystallographically unique Hg atoms, five crystallographically independent SbF<sub>6</sub> 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  $O_{2}[Hg(HF)]_{4}(SbF_{6})_{9}$ .

The Hg1 and Hg2 atoms both possess a square antiprismatic spheres comprised of seven fluorine atoms belonging to seven SbF<sub>6</sub> 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<sub>6</sub><sup>-</sup> anions play a role in  $\mu_3$ -bridging, being bound to three Hg cations in a *mer*-arrangement, and a SbF<sub>6</sub><sup>-</sup> moiety built up around the SbS atom displays a  $\mu_4$ -bridge (Figure 9).



**Figure 9.** Part of the crystal structure of  $O_2[Hg(HF)]_4(SbF_6)_9$ 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<sub>5</sub>) 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  $O \cdots O$  distance of 0.89(2) Å are a consequence of significant orientational disorder of the O2<sup>+</sup> cation.

 $O_2^+$  Bond Lengths. A list of the O–O bond lengths determined in various  $O_2^+$  salts (including this work) is given in Table 4.

Table 4. O–O Distances (Å) in  $O_2^+$  Salts Determined by Single Crystal X-Ray Diffraction Data ( $O_2PtF_6$  Was Studied Also Using Neutron-Diffraction Data from a Polycrystalline Sample)

O2 <sup>+</sup> salt	0-0 (Å)	T/K	ref
$O_2[Hg(HF)]_4(SbF_6)_9$	0.89(2)	150	this work
O <sub>2</sub> SbF <sub>6</sub>	0.95	RT	22
$(O_2)_2 Ti_7 F_{30}$	0.96	153	29
O <sub>2</sub> GeF <sub>5</sub> ·HF	1.013(4)	150	this work
$O_2H_3Pd_2F_{12}$	1.014(4)	140	21
$O_2Ni(AsF_6)_3$	1.018(12)	173	20
$O_2Sn_2F_9$ ·0.9HF	1.046(9)	150	this work
$\alpha$ -O <sub>2</sub> Sn <sub>2</sub> F <sub>9</sub> (1-D)	1.062(14)	200	this work
$O_2Mn_2F_9$	1.10	123	30
	0.96	293	30
$O_2 Rh F_6^{a}$	1.1107(16)	133	25
$\beta$ -O <sub>2</sub> AuF <sub>6</sub>	0.97	RT	22
$\alpha$ -O <sub>2</sub> AuF <sub>6</sub> <sup><i>a</i></sup>	1.079(27)	104	23
	1.068(30)	151	24
	1.1091(28)	133	25
O <sub>2</sub> RuF <sub>6</sub>	1.00	RT	22
	1.125(17)	146	26
	1.12(4)	298	26
O <sub>2</sub> PtF <sub>6</sub>	$0.91(3)/1.21(17)/1.40^{b}$	RT	27
	0.96	RT	22
free O2 <sup>+</sup>	1.1227		69

"Rare examples of  $O_2^+$  salts with ordered  $O_2^+$  cations. <sup>b</sup>From 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  $O_2 PtF_{6}$ .

The reported O–O bond lengths of  $O_2^+$  span the absurdly short value of 0.89(2) Å to values close to that observed for the gas-phase  $O_2^+$  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  $O_2^+$  is often problematic because of the partial or complete disorder of the  $O_2^+$  cation in the crystal structures of  $O_2^+$  salts. For example, the first reported value for O-O bond length in  $O_2 RuF_6$  was 1.00 Å (at RT).<sup>22</sup> A 3-fold disordering of  $O_2^+$ yielded a more realistic value of 1.12(4) Å (at 298 K).<sup>26</sup> Closer inspection of thermal ellipsoids of oxygen atoms in O<sub>2</sub>[Hg- $(HF)]_4(SbF_6)_9$  (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  $O_2GeF_5$ ·HF,  $\alpha$ - $O_2Sn_2F_9$  (1-D), and  $O_2Sn_2F_9$ ·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  $\alpha$ -O<sub>2</sub>Sn<sub>2</sub>F<sub>9</sub> (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  $O_2^+$ disordering.

#### CONCLUSIONS

Photochemical reactions of UV-irradiated  $O_2/F_2$  mixtures with solid, liquid, or gaseous fluorides, and oxides with UV-irradiated  $F_2$  (or  $O_2/F_2$  mixtures) in anhydrous HF are a convenient way to synthesize  $O_2^+$  salts (Table 5).

Table 5. List of Reported of O <sub>2</sub> <sup>+</sup> Salts (Including This	
Work) Together with $\nu(O_2^+)$ Values Recorded by Rama	n
Spectroscopy	

O2 <sup>+</sup> salt	$\nu(O_2^+)^a$	crystal structure	ref
molecular O <sub>2</sub>	1580		70
$(O_2)_2 NiF_6$	1801		37
$(O_2)_2 MnF_6$	1805		37
O <sub>2</sub> PdF <sub>5</sub>	1820		36, this work
O <sub>2</sub> RhF <sub>6</sub>	1825	у	23, 25, 26, 47
$\beta$ -O <sub>2</sub> AuF <sub>6</sub>	1835 <sup>b</sup>	у	24, 47, this work
$\alpha$ -O <sub>2</sub> AuF <sub>6</sub>	1838 <sup>c</sup>	у	24
$O_2Mn_2F_9$	1838	у	30
$O_2RuF_6$	1838	у	22, 26, 47
$O_2PtF_6$	1838	У	16, 17, 22, 27, 44, 47, this work
$O_2 V_2 F_{11}$	1839		71
O <sub>2</sub> BiF <sub>6</sub>	1849		43, 47
O <sub>2</sub> GeF <sub>5</sub>	1849	y <sup>d</sup>	35, this work
$\alpha$ -O <sub>2</sub> Sn <sub>2</sub> F <sub>9</sub> (1-D)	1849	у	this work
$O_2Bi_2F_{11} \\$	1853		43
O <sub>2</sub> NbF <sub>6</sub>	1853		43
$(O_{2)2}Ti_7F_{30}$	1857	у	29, This work
O <sub>2</sub> AsF <sub>6</sub>	1858		41, 42, 47, 55, this work
$O_2Nb_2F_{11}$	1858		43, 47
$O_2Ta_2F_{11}$	1858		43, 47
$O_2BF_4$	1860	у	28, this work
O <sub>2</sub> SbF <sub>6</sub>	1861	у	22, 45, 47, this work
$O_2[Hg(HF)]_4(SbF_6)_9$	1861	у	this work
$(O_2)_2Hg_2F(SbF_6)_5$	1863	у	53
$O_2Sb_2F_{11}$	1864		45, 47
$O_2Ni(AsF_6)_3$	1866	у	20
gaseous O <sub>2</sub> <sup>+</sup>	1876.4		69
$O_2Pt_2F_{11}$		y <sup>d</sup>	48
$[O_2][H_3Pd_2F_{12}]$		У	21
$O_2AgF_4$		yd	33
O <sub>2</sub> GeF <sub>5</sub> ·HF		у	this work

<sup>*a*</sup>The values of O<sub>2</sub><sup>+</sup> stretch are strongly dependent on the nature of counteranions. For more detailed discussion about this topic, see the literature.<sup>24,72</sup> <sup>*b*</sup>Recorded at 25 °C <sup>*c*</sup>Recorded at -163 °C. <sup>*d*</sup>Complete 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  $A_2PdF_6$  (A = K, Cs) in aHF to a solutions of  $O_2AsF_6$  in aHF at -30 °C yield precipitates of AAsF<sub>6</sub> and deep orange solutions presumed to contain  $(O_2)_2PdF_6$ .<sup>36</sup> Attempts to isolate these salts by removal of aHF at -60 °C always resulted in the loss of  $O_2$  and  $F_2$  and recovery of  $O_2PdF_5$ .<sup>36</sup> However, further crystallizations at T < -70 °C resulted in the growth of single crystals of  $[O_2][H_3Pd_2F_{12}]$ .<sup>21</sup> The  $(O_2)_2SnF_6$ ,  $O_2MoF_7$  and  $O_2WF_7$  salts have been reported for the reactions between  $O_2F_2$  and  $SnF_4$  and  $WF_6$  or  $MoF_6$ , respectively.<sup>38</sup> However, these reactions are of low yield and poor reproducibility. The compound,  $O_2PF_6$ , slowly decom-

Determination of the single-crystal X-ray structure of  $O_2GeF_5$ ·HF showed that its structure consists of infinite polymeric ( $[GeF_5]^-$ )<sub> $\infty$ </sub> anions, which appear as zigzag single chains of GeF<sub>6</sub> octahedra linked by *cis*-vertices and O<sub>2</sub><sup>+</sup> cations and HF molecules located between the chains. The ( $[GeF_5]^-$ )<sub> $\infty$ </sub> anion of O<sub>2</sub>GeF<sub>5</sub> appears to have the same structural motif as that of O<sub>2</sub>GeF<sub>5</sub>·HF.

Three different  $O_2^+$  salts, all containing polymeric  $([Sn_2F_9]^-)_{\infty}$  anions, were isolated and their structured determined. Two of them have the same empirical chemical formula as  $O_2Sn_2F_9$ . The anion in  $\alpha$ - $O_2Sn_2F_9$  (1-D) has a chainlike structure, and the anion in  $\beta$ - $O_2Sn_2F_9$  (2-D) has a layerlike structure. The third phase is the HF solvated form of 2-D  $O_2Sn_2F_9$  (i.e.,  $O_2Sn_2F_9 \cdot 0.9HF$ ). Besides the layered polymeric ( $[Sn_5F_{24}]^{4-})_{\infty}$  anion determined in  $[XeF_5]_4[Sn_5F_{24}]^{,63}$  these salts provide new examples of structurally characterized Sn(IV) fluoride compounds which do not only consist of  $[Sn_F_6]^{2-}$  anions.

The complex  $O_2^+$  salt  $O_2[Hg(HF)]_4[SbF_6]_9$  was prepared by reaction between  $O_2SbF_6$ ,  $HgF_2$ , and  $SbF_5$  in anhydrous aHF. Its crystal structure is isotypic to that of  $(H_3O)[Cd-(HF)]_4(SbF_6)_9$ .<sup>68</sup>

#### 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<sub>3</sub> (Union Carbide Austria GmbH, 99.5%), FeF<sub>3</sub> (Alfa Aesar, 97% min), CoF<sub>2</sub> (Johnson Matthey GmbH, 99%), TiO<sub>2</sub> (Koch-Light Laboratories Ltd., 99.5%), SnO<sub>2</sub> (E. Merck AG, Darmstadt, pure), PbO2 (Riedel de Haën), GeF4 (Cerac, Incorporated, 99.99%), NiF<sub>2</sub> (Alfa Products, 99.5%), MnF<sub>2</sub> (Alfa Aesar, 99%),  $SnF_4$  (Alfa Aesar, 99%),  $SbF_3$  (Merck KGaA,  $\geq$ 99%), Pt (Aldrich,  $\geq$ 99.9%), PtO<sub>2</sub> (Aldrich), SeO<sub>2</sub> (Fluka AG, Buchs SG, >98%), WO<sub>3</sub> (Merck), MoO<sub>3</sub> (Merck, 99.5%), WF<sub>6</sub> (ABCR, 99%), SbCl<sub>5</sub> (Merck, >99%), TiCl<sub>4</sub> (Acros Organics, 99.9%), NbCl<sub>5</sub> (Alfa Aesar, 99.95%), HCl, and Cl<sub>2</sub> were used as supplied. AgF<sub>2</sub>, AuF<sub>3</sub>, and Pd<sub>2</sub>F<sub>6</sub> were synthesized by the reaction of AgNO<sub>3</sub> (Fisher Chemical), AuCl<sub>3</sub> (Alfa Aesar, 99.99%), and Pd sponge (Aldrich 99.9%), respectively, with elemental fluorine F2 (Solvay Fluor and Derivate GmbH, 99.98%) in aHF (Linde AG, Pullach, Germany, 99.995%) at ambient temperature.<sup>31</sup> Arsenic pentafluoride was prepared as described previously,<sup>7</sup> and IF<sub>5</sub> was from our stock. HgF<sub>2</sub> was obtained by high temperature (230 °C) static fluorination of HgCl<sub>2</sub> (Alfa Aessar, 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<sub>6</sub>, 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 °C) and Thermo Fisher Scientific EK 90 (to -60 °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.<sup>31</sup> 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 ~10-20 °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  $O_2GeF_5$ ·HF that are not stable at ambient temperature. For this, a small portion (1–2 mL) of cold perfluorinated oil (perfluorodecaline  $C_{10}F_{18}$ ) 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<sup>-1</sup> 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 20–0.0020 mW, which gave 17–0.0017 mW focused on a 1  $\mu$ m spot through a 50× 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-SS 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  $O_2Sn_2F_9$  (1-D and 2-D),  $O_2Sn_2F_9 \cdot 0.9HF$ ,  $O_2GeF_5 \cdot HF$ ,  $O_2GeF_5$ , and  $O_2[Hg(HF)]_4(SbF_6)_9$  were collected on a Gemini A diffractometer equipped with an Atlas CCD detector, using graphite monochromated MoK $\alpha$  radiation. The data were treated using the CrysAlisPro software suite program package.<sup>79</sup> Analytical absorption corrections were applied to all data sets. The structure of  $O_2Sn_2F_9$  (1D) was solved using the SHELXS program.<sup>80</sup> All other structures were solved using the dual-space algorithm of the SHELXT<sup>81</sup> program implemented in the Olex crystallographic software.<sup>82</sup> Structure refinement was performed with SHELXL-2014 software.<sup>83</sup> The figures were prepared using DIAMOND 4.6 software.<sup>84</sup> Hydrogen atoms in the structures of  $O_2Sn_2F_9$ ·0.9HF,  $O_2GeF_5$ ·HF, and  $O_2[Hg(HF)]_4(SbF_6)_9$  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  $O_2Sn_2F_9$ ·0.9HF structure was refined using a free variable.

Crystals of  $O_2GeF_5$  and  $O_2Sn_2F_9$  (2-D) compounds were of extremely poor quality. In the case of  $O_2Sn_2F_9$  (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  $O_2GeF_5$  salt with a very high *R*-value (~20%) for the completed model.

#### ASSOCIATED CONTENT

#### **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  $F_2$  (or  $O_2/F_2$  mixture) with solid, liquid, or gaseous fluorides or oxides in anhydrous HF; photos of the yellow solids formed after  $\rm SbCl_5/Cl_2/O_2$  and  $\rm TiCl_4/Cl_2/O_2/HCl$  mixtures were irradiated by UV-light; geometries of the ([GeF\_5]<sup>-</sup>)\_{\infty} anions determined in the crystal structures of  $O_2GeF_5\cdot HF$  and [ClO\_2][GeF\_5]; two-dimensional ([Sn\_2F\_9]<sup>-</sup>)\_{\infty} and ([Sn\_5F\_{24}]^{4-})\_{\infty} grids with a wavelike conformation found in  $O_2[Sn_2F_9]\cdot 0.9HF$  and [XeF\_5]\_4[Sn\_5F\_{24}] (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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