Inorg. Chem. **1998,** *37,* 3829−3834

Facile Routes to NiF_6^{2-}, AgF_4^-, AuF_6^-, and PtF_6^- Salts Using O_2^+ as a Source of O_2F in Anhydrous HF

G. M. Lucier, C. Shen, S. H. Elder, and N. Bartlett*

Chemical Sciences Division, Lawrence Berkeley National Laboratory, and Chemistry Department,
University of California at Berkeley, Berkeley, California 94720

Received December 29, 1997

O_2^+ salts dissolved in liquid anhydrous hydrogen fluoride (aHF) at 20 °C or below oxidize aHF solutions of PtF_6^{2-} to PtF_6^-. The parent base of O_2^+ salts in aHF ($O_2F_{(solv)}$) generated with alkali fluoride is long-lived below −50 °C. An aHF solution of $O_2F_{(solv)}$ oxidizes Au(III) to Au(V) below −50 °C ($2O_2F_{(solv)} + AuF_4^-{}_{(solv)} \rightarrow AuF_6^-{}_{(solv)} + 2O_{2(g)}$). In situ generation of $O_2F_{(solv)}$ ($O_2^+{}_{(solv)} + F^-{}_{(solv)} \rightarrow O_2F_{(solv)}$) with AgF_2 or NiF_2 in suspension in the aHF made basic with alkali fluoride gives AgF_4^- and NiF_6^{2-}salts. Low solubility of $AAsF_6$(A = Cs, K) in aHF provides for the metathetical preparation of $(O_2)_2PdF_6$ solutions in aHF. Removal of aHF, even at −60 °C, results in some O_2 and F_2 loss, to a composition approaching $(O_2)PdF_5$.

Introduction

The high electron affinity[1] of O_2^+ (12.13 eV in $O_2^+{}_{(g)}$) gives O_2^+ salts their remarkable one-electron oxidizing properties, which have been previously exploited by Stein and co-workers to oxidize xenon[2] and radon,[3] by Christe and co-workers[4] to oxidize $(CF_3)_2NO$, and in these laboratories to prepare[5] salts of $C_6F_6^+$. The O_2^+ salts also have the capability, via their parent base, O_2F, of serving as powerful fluorinating agents.

In principle, the interaction of O_2^+ salts with alkali fluorides can release the parent base, O_2F, which has long been known and characterized from matrix isolation studies.[6−8] However, the facile conversion[9,10] of O_2F to O_2 and O_2F_2, and the thermodynamic instability of both O_2F and O_2F_2 toward O_2 and F_2,[11−14] require that the O_2F be released from the O_2^+ salts at low temperatures if it is to be obtained in high yield or used effectively as a fluorinating and oxidizing agent. Kinetic[13] and spectrokinetic studies[11,12] of the $O_2 + F$ reaction have indicated that the O−F bond energy in the gas-phase O_2F species is approximately 13 kcal mol^{-1}, a value lower than the mean thermochemical O−F bond energy in O_2F_2, which is[14] ≈16.5 kcal mol^{-1}. Thermodynamically, each of these dioxygen fluorides is a more potent F atom source than F_2 itself, since[15] $\Delta_f H^\circ_{298.15}(F_{(g)}) \approx 18.9$ kcal mol^{-1}. O_2F_2 is known to be a powerful oxidizing and fluorinating agent with e.g., the capability of oxidizing Pu to PuF_6;[16] hence, O_2F was anticipated to be of at least similar potency.

In 1977, Christe announced[17] his discovery that $O_2^+SbF_6^-$ forms stable solutions in aHF, but early work in our laboratories[18] had indicated that $O_2^+AsF_6^-$ (which is easier to prepare[19] than the antimony salt[20]) was not stable in aHF. Later, however, Shen in this group demonstrated[21] that O_2AsF_6 could be recovered nearly quantitatively from room-temperature solutions in either anhydrous hydrogen fluoride (aHF) or bromine pentafluoride. This indicated that these solvents could be utilized for the liberation of the O_2F and as a vehicle for its chemistry. Because it is low melting (−83.6 °C) and is an excellent ionizing solvent,[22] aHF has been the preferred solvent for the work on which this paper is based.

Experimental Section

CAUTION: Fluorine and anhydrous HF can cause severe burns. Before undertaking work of the kind reported here, the experimentalist must become familiar with these reagents. Fresh tubes of calcium gluconate gel should always be on hand for the fast treatment[23] of skin exposed to these reagents.

Materials. O_2AsF_6 was prepared according to the method of Shamir and Binenboym,[19] and the AuF_4^-, PtF_6^{2-}, PdF_6^{2-} salts were prepared according to the method recently described.[24] F_2, AgF_2, and aHF were obtained and used as given previously,[25] and PdF_4 was obtained[26] from

---

(1) *Ionization Potential and Appearance Potential Measurements, 1971−81*; Levin, R. D., Lias, S. G., Eds.; NSRDS−NBS 71; U.S. Department of Commerce: Washington, DC, October 1982.

(2) Stein, L. *Science* **1972**, *175*, 1363.

(3) Hohorst, F. A.; Stein, L.; Gebert, E. *Inorg. Chem.* **1975**, *14*, 2233.

(4) Christe, K. O.; Schack, C. J.; Wilson, R. D.; Philipovich, D. *J. Fluorine Chem.* **1974**, *4*, 423.

(5) Bartlett, N. H.; Richardson, T. J. *J. Chem. Soc., Chem. Commun.* **1974**, 427. Richardson, T. J.; Tanzella, F. L.; Bartlett, N. *J. Am. Chem. Soc.* **1986**, *108*, 4937.

(6) Arkell, A. *J. Am. Chem. Soc*. **1965**, *87*, 4057.

(7) Spratley, R. D.; Turner, J. J.; Pimentel, G. B. *J. Chem. Phys*. **1966**, *44*, 2063.

(8) Noble, P. N.; Pimentel, G. B. *J. Chem. Phys*. **1966**, *44*, 3641.

(9) Campbell, G. M. *J. Fluorine Chem.* **1989**, *189*, 301.

(10) Abney, K. O.; Eller, P. G.; Eastman, M. P.; Pace, C. F.; Kinkead, S. A.; Kissane, R. J.; Woodruff, W. H. *J. Fluorine Chem.* **1995**, *73*, 137.

(11) Pagsberg, P.; Ratajczak, E.; Sillesan, A.; Jodowski, J. T. *Chem. Phys. Lett.* **1987**, *141*, 88.

(12) Campuzano-Jost, P.; Crocec, A. E.; Hippler, H.; Siefke, M.; Troe, J. *J. Chem. Phys*. **1995**, *102*, 5317.

(13) Lyman, J. L.; Holland, R. *J. Phys. Chem*. **1988**, 92, 7232.

(14) Lyman, J. L. *J. Phys. Chem. Ref. Data*, **1989**, *18* (2), 799.

(15) *JANAF Tables*; Dow Chemical Co.: Midland, MI, 1977.

(16) Malm, J. G.; Eller, P. G.; Asprey, L. B. *J. Am. Chem. Soc.* **1985**, *106*, 2726.

(17) Christe, K. O. *Inorg. Chem.* **1977**, *16,* 2238.

(18) Richardson, T. J. Ph.D. Thesis (LBL Report 3183), University of California at Berkeley, 1974; p 59.

(19) Shamir, J.; Binenboym, J. *Inorg. Chim. Acta* **1968**, *2*, 37.

(20) McKee, D. E.; Bartlett, N. *Inorg. Chem*. **1973**, *12*, 2738.

(21) Shen, C. Ph.D. Thesis, University of California at Berkeley, November 1992, pp 136−7.

(22) Gillespie, R. J.; Humphreys, D. A. *J. Chem. Soc., A* **1966**, 1170.

(23) For treatment of HF injuries, see: Finkel, A. In *Advances in Fluorine Chemistry*; Tatlow, J. C., Peacock, R. D., Hyman, H. H., Eds.; Butterworth and Co. Ltd.: London, 1973; Vol. 7, pp 199−203.

(24) Lucier, G.; Elder, S. H.; Hollander, F. J.; Bartlett, N. *Eur. J. Solid State Inorg. Chem.* **1996**, *33*, 809.

(25) Zemva, B.; Hagiwara, R.; Casteel, W. J., Jr.; Lutar, K.; Jesih, A.; Bartlett, N. *J. Am. Chem. Soc.* **1990**, *112*, 4846.

S0020-1669(97)01603-0 CCC: $15.00

PdF_6^{2-}. NiF_2 (Ozark-Mahoning Pennwalt, Tulsa, OK) was fluorinated (F_2 pressure ~2000 Torr) at ~250 °C to destroy water or hydroxide contamination. The alkali fluorides (Allied Chemical, B&A quality, Morristown, NJ), dried at ~150 °C under dynamic vacuum (10^{-6} Torr), were stored and transferred (as were all other solids) in the dry atmosphere of a Vacuum Atmosphere Corp. DRILAB.

X-ray and Raman samples were prepared in thin-walled quartz capillaries as previously described.[27]

Magnetic measurements were carried out using a SQUID magnetometer as previously outlined.[28]

Preparative Apparatus and Technique. Most operations were carried out with apparatus and techniques as previously described,[25] except for the preparation and manipulation of $O_2F_{(solv)}$.

Generation of $O_2F_{(solv)}$. A reactor was constructed having the general shape of the Greek letter ω, with a side tube extending from a Swagelok tee connected to one end of the ω. Teflon valves were located at both ends of the ω in order to permit passage of volatile material in to or out of either dip in the reactor without disturbing the contents in the other dip. Alkali fluoride (AF) was loaded into the side tube. O_2AsF_6 (in slight molar excess of the AF) was placed into the dip closest to the side tube, and the material to be oxidized and fluorinated by the $O_2F_{(solv)}$ was put into the other dip. The O_2AsF_6-containing dip was cooled to −196 °C as the AF was shaken onto it. Then aHF was condensed onto this mixture. With this still frozen, the other valve of the reactor was opened, and aHF condensed at −196 °C onto the substance to be oxidized. Both dips and the loop between them were then submerged in a cold bath at −50 °C, and the $O_2F_{(solv)}$ generated in the first dip was decanted onto the material in the second.

Oxidation of Pt(IV) to Pt(V) by O_2AsF_6. K_2PtF_6 (86.6 mg, 0.224 mmol) and O_2AsF_6 (52.9 mg, 0.239 mmol) were loaded into separate tubes of an FEP T-reactor, and aHF (~1.1 mL) was condensed onto each of the reagents at −196 °C. Both solid reagents dissolved to their respective solutions on warming to ~20 °C. As the O_2AsF_6 solution was slowly poured onto the K_2PtF_6 solution, vigorous gas evolution occurred, and the resulting solution became yellow-orange. After 10 min, all effervescence had ceased, yet no precipitate had formed. The solution was cooled to −196 °C and the residual gas measured (50 Torr in 85 cm^3, i.e., 0.23 mmol). On warming to ~0 °C, a yellow precipitate remained in a yellow solution. The solution was decanted, and volatiles were removed in a dynamic vacuum to yield an orange solid. An XRDP of this solid showed a rhombohedral pattern, the lines of which lay between those of comparison photographs of $KPtF_6$[29] and $KAsF_6$.[30] This pattern was fully indexed on a unit cell with $a_0 = 4.941(2)$ Å; $\alpha = 97.63(3)°$, $V = 117.1(2)$ Å^3. The volume of this unit cell is not significantly different from the arithmetic mean of the unit cell volumes for $KPtF_6$[29] ($a_0 = 4.960(5)$, $\alpha = 97.4(1)°$, $V = 118.7(5)$ Å^3) and $KAsF_6$[30] ($a_0 = 4.907(1)$ Å, $\alpha = 97.48(1)$, $V = 114.8(1)$ Å^3), which is 116.8(5) Å^3. The total mass expected for a 1:1 $KPtF_6/KAsF_6$ mixture, plus the slight O_2AsF_6 excess, was 132.6 mg; 128.9 mg was found. The K_2PtF_6 pattern was not observable in long-exposure XRDP of the product.

Oxidation of Au(III) to Au(V) with in situ O_2F. An FEP T-reactor was loaded with O_2AsF_6 (564.2 mg, 2.554 mmol) in one tube and $KAuF_4$ (365.1 mg, 1.170 mmol) and KF (171.9 mg, 2.959 mmol) in the other, aHF (3 mL) was condensed (−196 °C) into each tube, and then both were warmed to room temperature. The $KF/KAuF_4$ dissolved to give a yellow solution, whereas the other tube contained O_2AsF_6 beneath its solution. The O_2AsF_6 slurry was poured into the $KF/KAuF_4$, with accompanying vigorous effervescence and the formation of a light yellow precipitate. Some of the aHF was condensed back into the tube that had contained the O_2AsF_6 reagent to rinse any residual of it into the reaction mixture. With the solid product settled and the mixture cooled to 0 °C, the yellow solution was decanted. Removal of volatiles left a yellow powder in each tube. The precipitate weighed 916.2 mg; quantitative production of $KAuF_6$ (1.17 mmol, 409.6 mg) and $KAsF_6$ (2.554 mmol, 582.3 mg) requires 991.9 mg. An XRDP of this product showed a single rhombohedral phase with $a_0 = 4.924(2)$ Å, $\alpha = 97.65(3)°$, $V = 115.9(2)$ Å^3, the line pattern lying between those of $KAsF_6$-30 (loc. cit.) and $KAuF_6$, for which[31] $a_0 = 4.946(3)$ Å, $\alpha = 97.96(5)°$, $V = 117.1(4)$ Å^3. The solid product from the decanted solution (102.7 mg) showed a trace of the $KAsF_6/KAuF_6$ pattern, but the dominant ones were those of, respectively,[32,33] $KAuF_4$ and K_2SiF_6 (the latter from KH_2F_3 interaction with the quartz of the X-ray capillary).

Oxidation of Au(III) to Au(V) with Added $O_2F_{(solv)}$. In an ω reactor, CsF (145.2 mg, 0.9559 mmol) with O_2AsF_6 (238.3 mg,1.079 mmol) generated $O_2F_{(solv)}$ for oxidation of $KAuF_4$ (55.7 mg, 0.178 mmol). With aHF (~3.0 mL) condensed (at −196 °C) onto the O_2AsF_6−CsF mixture and this still frozen, aHF(1.5 mL) was similarly transferred to the $KAuF_4$. Both dips and connecting loop were submerged in a cold bath at −50 °C. The $KAuF_4$ dissolved completely to give a yellow solution; the O_2AsF_6 and CsF rapidly generated O_2F (and precipitated $CsAsF_6$), to give a deep orange solution (this strong color probably arising from higher local temperature, as a result of the exothermic interaction of the CsF with the aHF). Decantation of the O_2F solution into the $KAuF_4$ solution produced an immediate lightening of the solution color, and a yellow precipitate formed. After 5 min, all volatile species were removed at −35 °C or below. An XRDP of the yellow product showed predominantly the pattern[31] of $KAuF_6$, with only faint lines attributable[32] to $KAuF_4$.

Oxidation of Ag(II) to Ag(III) with in situ O_2F. With AgF_2 (72.2 mg, 0.495 mmol), KF (60.9 mg, 1.05 mmol), and a Teflon-coated magnetic stirrer in one tube of an FEP T-reactor, the other containing O_2AsF_6 (122.7 mg, 0.5554 mmol), aHF (2 mL) was condensed into the two tubes at −196 °C, and both tubes were then warmed to ~20 °C. The KF/aHF colorless solution, containing suspended reddish-brown AgF_2, was stirred as the O_2AsF_6 solution was gradually added. There was vigorous effervescence, and the solution turned yellow. Stirring was continued for 30 min, unoxidized AgF_2 was allowed to settle, and the yellow solution was decanted into the other reactor tube. Back-distillation of the aHF (to −196 °C) provided for repeated washing of the remaining AgF_2, until the supernatant was no longer yellow. All volatiles were removed under dynamic vacuum. XRDPs of the resulting yellow product showed the patterns[30,34] of both $KAgF_4$ and $KAsF_6$, and those of the reddish-brown powder showed only the pattern of the starting material, AgF_2. Based on the weight of unreacted AgF_2 (42.2 mg, 0.289 mmol), the yield of $KAgF_4$ was 41.6%.

Oxidation of Ni(II) to Ni(IV) with in situ O_2F. Quantities for two oxidations are given in Table 1. With NiF_2, CsF, and a Teflon-coated magnetic stirrer in one tube of a FEP T-reactor and O_2AsF_6 in the other, aHF(~5.5 mL, in each case) was condensed onto the NiF_2/CsF mixture at −196 °C. This was warmed and maintained at ≤−30 °C. Small portions of the solid O_2AsF_6 were shaken into the solution, which was stirred vigorously over 3 h. A nearly constant, slow effervescence was observed over this time period, with the solution color slowly darkening and a colorless precipitate accumulating. Ultimately, the solution was of the raspberry-red color characteristic of a dilute solution of NiF_6^{2-} ion. Two small aliquots of aHF were successively condensed from this reaction tube into the other tube of the reactor at −196 °C and were used to rinse residual O_2AsF_6 into the bulk solution. The reaction mixture was left undisturbed in a cold bath, maintained at −20 °C, until all solids had settled, and then the cooled solution was decanted from this tube (A) to the other tube (B). The residue in A was washed twice with aHF at −20 °C, the last wash having no color. All volatiles were removed under dynamic vacuum, to yield a pink solid in B; a light yellow solid remained in A. Because

---

(26) Zemva, B.; Lutar, K.; Jesih, A.; Casteel, W. J., Jr.; Bartlett, N. *J. Chem. Soc., Chem. Commun*. **1989**, 346.

(27) Zemva, B.; Lutar, K.; Jesih, A.; Casteel, W. J., Jr.; Wilkinson, A. P.; Cox, D. E.; Von Dreele, R. B.; Borrmann, H.; Bartlett, N. *J. Am. Chem. Soc*. **1991**, *113*, 4192.

(28) Casteel, W. J., Jr.; Lucier, G.; Hagiwara, R.; Borrmann, H.; Bartlett, N. *J. Solid State Chem*. **1992**, *96*, 84.

(29) Bartlett, N.; Lohmann, D. *J. Chem. Soc*. **1964**, 619.

(30) NBS Monogr. (U. S.) **1980**, *25*, 1757.

(31) Bartlett, N.; Leary, K. *Rev. Chim. Miner*. **1976**, *13*, 82.

(32) Hoppe, R.; Klemm, W. *Z. Anorg. Allg. Chem*. **1952**, *26*, 365.

(33) KH_2F_3 interacts with the quartz capillary to form K_2SiF_6 [for the unit cell, see ref. 30, (5, 50)], but gravimetry has established that, under our vacuum conditions (10^{-5} Torr), this is the product from KF in aHF.

(34) Hoppe, R.; Homann, R. *Z. Anorg. Allg. Chem*. **1970**, *379*, 193.

Table 1. Gravimetry for the Interaction of O_2AsF_6 and CsF in AHF with NiF_2 To Form Cs_2NiF_6[a]

weights of reactants, mg (mmol)			weights of products						
			aHF-insoluble at −20 °C, mg (mmol)			aHF soluble at −20 °C, mg (mmol)			
CsF	NiF_2	O_2AsF_6	$CsAsF_6$	NiF_2	Σ_{obs}	Cs_2NiF_6	Cs_2SiF_6	Σ_{calc}	Σ_{obs}
603.6 (3.974)	**73.1** (0.756)	**467.0** (2.114)	680.3 (2.114)	56.4 (0.583)	**736.7**	75.8 (0.173)	308.8 (0.757)	384.6	**380.4**
559.4 (3.683)	**74.3** (0.768)	**483.5** (2.189)	704.5 (2.189)	61.4 (0.635)	**765.9**	58.2 (0.1330)	250.4 (0.614)	308.6	**304.6**

[a] It was assumed that the $CsAsF_6$ was insoluble in the aHF at −20 °C and equal in moles to the starting O_2AsF_6. Remaining CsF was available for the formation of Cs_2NiF_6 and Cs_2SiF_6, the combined weight of which was observed. The quantity of NiF_2 converted to NiF_6^{2-} was derived from the observed weight of remaining NiF_2 and $CsAsF_6$. Weights in bold were directly measured.

Table 2. Formula Weight (per Pd) of the $(O_2)_2PdF_6$ Decompostion Product from Gravimetry[a]

expt no.	reactants, mg (mmol)		total prod, mg	products, mg (mmol)			formula weight/Pd
				expected	excess	decomp.	
1	Cs_2PdF_6 **238.4** (0.4903)	O_2AsF_6 **111.3** (0.5038)	**334.1**	$CsAsF_6$ 162.1 (0.5038)	Cs_2PdF_6 115.9 (0.2384)	$(O_2)_2PdF_6$ 56.1 (0.2519)	223
2	Cs_2PdF_6 **138.6** (0.2851)	O_2AsF_6 **147.5** (0.6677)	**273.8**	CsAsF6 183.5 (0.5701)	O_2AsF_6 21.6 (0.0976)	$(O_2)_2PdF_6$ 68.7 (0.2851)	241
3	K_2PdF_6 **270.4** (0.9055)	O_2AsF_6 **407.4** (1.8440)	**654.6**	$KAsF_6$ 412.9 (1.8110)	O_2AsF_6 7.3 (0.0330)	$(O_2)_2PdF_6$ 234.4 (0.9055)	259
4	K_2PdF_6 **139.6** (0.4675)	O_2AsF_6 **217.6** (0.9850)	**339.1**	$KAsF_6$ 213.2 (0.9350)	O_2AsF_6 11.1 (0.0500)	$(O_2)_2PdF_6$ 114.8 (0.4675)	246

expt no.	reactants (KF), mg (mmol)	total prod, mg	expected products, mg (mmol)			total prod expected, mg
			$KAsF_6$	KH_2F_3	K_2PdF_6	
4+	**0.0605** (1.0400)	**369.3**	224.6 (0.9850)	5.4 (0.0550)	139.6 (0.4675)	369.6

[a] Bold quantities are from weights, nonbold deduced from them; calculated formula weights/Pd are $(O_2)_2PdF_6$, 284.4; O_2PdF_5, 233.4.

CsF forms vacuum-stable hydrofluorides, the composition of which depends on the vacuum conditions and ambient temperature, reliable gravimetry for the excess CsF was achieved by converting it to Cs_2SiF_6. For this, SiF_4 (maintained at 600 Torr) was used. As the pink solid (in B), containing cesium hydrofluorides, interacted with the SiF_4, it became warm. Initially, as HF was released from the cesium hydrofluoride, it became wet (as remaining hydrofluoride dissolved in the HF), but as the conversion to Cs_2SiF_6 progressed, the solid became more friable. All volatiles were removed under dynamic vacuum, and the solids were dried for 1 h before another treatment with SiF_4 (no heating or visible change was observed). An XRDP of the light yellow residue, from A, showed only the pattern of $CsAsF_6$, the color surely resulting from poorly crystallized NiF_2. An XRDP of the light pink product from B gave only the pattern[35] of Cs_2SiF_6; the color, however, indicated the presence of Cs_2NiF_6, this also being supported by the gravimetry (Table 1).

Attempted Oxidation of PdF_6^{2-} with O_2F. With CsF (139.6 mg, 0.9190 mmol) in the side tube of an ω reactor, O_2AsF_6 (207.3 mg, 0.9384 mmol) in the reactor dip closest to it, and Cs_2PdF_6 (118.3 mg, 0.2433 mmol) in the other dip, aHF (3.5 mL) was condensed onto the O_2AsF_6, which was then warmed to −50 °C. The orange solution of $O_2F_{(solv)}$ was decanted at that temperature onto the Cs_2PdF_6, giving a yellow-orange solution. The reaction mixture was permitted to slowly warm to room temperature. The color became yellow. Volatiles were removed under dynamic vacuum, to leave a yellow solid, XRDP of which showed only the hexagonal[35,36] pattern of Cs_2PdF_6.

Formation of $(O_2)_2PdF_6$ Solution. A passivated FEP T-reactor was loaded with K_2PdF_6 (270.4 mg, 0.9055 mmol) in one tube and O_2AsF_6 (407.4 mg, 1.844 mmol) and a magnetic stirrer in the other. Immediately after condensing aHF(4.0 mL) onto the K_2PdF_6 at −196 °C, the solid O_2AsF_6 and magnetic stirrer were poured onto the solid plug of aHF. Warming this tube to −20 °C with vigorous mixing for 1.5 h produced an orange-red solution above an apparently colorless precipitate. Cooling to −196 °C produced a copious crystalline yellow precipitate just prior to solidification of the aHF (∼−80 °C), the solution then being very pale orange. A pressure measurement at this point showed that there was no gaseous product. On warming the solution back to −20 °C, the orange-red solution was restored.

Attempted Isolation of $(O_2)_2PdF_6$ from aHF Solution. The presumed solution of $(O_2)_2PdF_6$ described above appeared deep red at 0 °C. This solution was decanted from one tube of the FEP T-reactor (through the ∼20 °C T-junction) into the other. Immediately afterward, the decantate was cooled to −196 °C. A pressure reading (45 Torr in 75 cm^3) indicated 0.18 mmol of gas. The solution was warmed back to −60 °C, producing a light orange solution with a crystalline yellow precipitate below it. As the volatile species were slowly removed between −60 and −48 °C via dynamic vacuum, the yellow solid approached dryness and darkened to a deep orange-red. Continued vacuum-drying of the material as it warmed to room temperature eventually gave a friable maroon solid. Material prepared in this manner consistently gave no XRDP pattern, except for the faint rhombohedral pattern[30] associated with $KAsF_6$ impurity. Reliable gravimetric analysis of the separated products was not possible, due to the incompleteness of the separation, but the total product weights provided valuable compositional information and are given in Table 2.

Interaction of the Decomposition Product of $(O_2)_2PdF_6$ with aHF, and aHF Containing KF. The dark red product obtained at 20 °C on removal of aHF from the $(O_2)_2PdF_6$ product (O_2 and F_2 were both evolved) did not noticeably dissolve in fresh aHF, although the slight yellow coloring of the solution indicated some $PdF_6^{2-}{}_{(solv)}$ to be present. On addition of a solution of KF in aHF to this mixture, there was, however, a rapid effervescence of O_2, and a clear deep yellow solution

---

(35) Babel, D. *Struct. Bonding* **1967**, *3*, 1.

(36) Cubic Cs_2PdF_6 (a = 9.03(1) Å) and hexagonal K_2PdF_6 (a = 5.777(2) and c = 9.367(2) Å) are the usual products of these compositions from aHF, but the trigonal form of the latter (see ref 32) is also occasionally observed, indicating that, in this material, the two forms have very similar energies.

Table 3. Magnetic Moment Values (in Bohr Magnetons) for O_2PdF_5 Preparations and O_2AsF_6 (Experiment Number Refers to Table 2 Preparations)[a]

	O_2PdF_5	O_2PdF_5	O_2PdF_5	O_2AsF_6
expt no.	3	2	1	na
sample wt (mg)	59.4	88.1	128.4	52.5
μ(5 kG)	1.30	1.58	1.63	1.70
μ(40 kG)	1.32	1.53	1.64	1.70

[a] Sample 1 was prepared with excess Cs_2PdF_6 and had less $CsAsF_6$ impurity, since in this case it had lowered solubility because of the common ion effect of the highly soluble Cs_2PdF_6. Sample 3 is least reliable because it contains $KAsF_6$ (seen in XRDP) and was small. In each case, the magnetic susceptibility obeyed the Curie law (Weiss constant ≈ 0 K).

quickly formed. Removal of aHF left a yellow solid, identified from XRDP as the hexagonal form[36] of K_2PdF_6. See Table 2 for the gravimetry of such a reaction.

Magnetic Susceptibility Data for the Decomposition Product of $(O_2)_2PdF_6$. Findings for the various $(O_2)_{2-x}PdF_{6-x}$ products are in Table 3.

Preparation of PdF_4 was according to the method of Casteel.[37] In one limb of an FEP T-reactor, K_2PdF_6 (204.5 mg, 0.6848 mmol) was dissolved to an orange-yellow solution in aHF (3.5 mL), and AsF_5 gas was slowly added, to a final total pressure, at 20 °C, of 1200 Torr. The initial dark brown precipitate (possibly $KPdF_5$) was transformed over 15 h at 20 °C to the brick-red solid characteristic[38] of PdF_4. Volatiles were removed, and fresh aHF (6 mL) was used to wash the insoluble PdF_4 free of the slightly soluble $KAsF_6$ (with three decantations and back distillations), to give (from the decanted solution and washings) nearly colorless $KAsF_6$ (306.7 mg, 1.345 mmol; theoretical yield 1.370 mmol). The insoluble residue was brick-red PdF_4 (123.1 mg, 0.6749 mmol; theoretical yield 0.6848 mmol). XRDP proved the nature of the solids.

PdF_4 with added O_2F in aHF. An ω reactor was charged with an $O_2F_{(solv)}$-generating mixture (CsF, 167.3 mg, 1.101 mmol; O_2AsF_6, 251.4 mg, 1.138 mmol) in the usual manner, and PdF_4(35.8 mg, 0.196 mmol) was placed in the second dip. $O_2F_{(solv)}$ was made at −50 °C, decanted cold onto the PdF_4, and left to warm slowly with agitation over several hours. No gas evolution was observed up to ∼−30 °C, but the orange coloration associated with $O_2F_{(solv)}$ faded above that temperature, and the 20 °C solution was finally colorless. The residue was PdF_4 (36.5 mg, XRDP showing only PdF_4). Tensimetry, on completion of the reaction, indicated that the gaseous product (≈1.5 mmol) at −196 °C (O_2 and F_2) was consistent with total dissociation of the 1.1 mmol of O_2F to O_2 and $^1/_2F_2$ by the end of the reaction.

Results and Discussion

The long-term stability of aHF solutions of $O_2^+MF_6^-$ salts (M = As, Sb, Bi) at ambient temperatures or below provides for the convenient application of these powerful one-electron oxidizers in an excellent ionizing solvent. A dramatic example is the fast quantitative conversion of Pt(IV) to Pt(V):

$$O_2{}^+{}_{(solv)} + PtF_6{}^{2-}{}_{(solv)} \rightarrow O_{2(g)} + PtF_6{}^-{}_{(solv)} \qquad (1)$$

Unfortunately, the MF_6^- anions that stabilize O_2^+ salts[39] are similar in size to their noble metal relatives and, with alkali cations, give solid solutions, in this case a 1:1 mix of PtF_6^- and AsF_6^-. A clean synthesis is possible, however, if an aHF solution of O_2F is used in place of the O_2^+ salt.

Addition of alkali fluoride in solution in aHF to an O_2AsF_6 salt solution at or below −50 °C usually produced a precipitate of the alkali salt ($AAsF_6$). The supernatant was pale yellow, but there was no evolution of gas, there being no noncondensables at −196 °C. Evidently, the overall reaction involves the alkali fluoride base displacing the parent base of the O_2^+ salt (each base probably being solvated by the aHF):

$$A^+{}_{(solv)} + F^-{}_{(solv)} + O_2{}^+{}_{(solv)} + AsF_6{}^-{}_{(solv)} \rightarrow AAsF_{6(c)} + O_2F_{(solv)}(\leftrightarrow O_2{}^+{}_{(solv)} + F^-{}_{(solv)}) \qquad (2)$$

Here, $F^-{}_{(solv)}$ represents the possible hydrofluorides, $F(HF)^-{}_n$, where n can have values of 1−4. As the temperature rose toward −30 °C, the aHF solution became yellow and then orange, and oxygen and fluorine evolved, this becoming easily observable above −30 °C. It is probable that the color is associated with undissociated O_2F, but O_2F_2 could also be present at these higher temperatures.[9,10]

An instance of the extraordinary oxidizing capability of the $O_2F_{(solv)}$ is the interaction at −50 °C with Au(III) solution to give Au(V) (n.b., F_2 with $Au_{(c)}$ in basic aHF gives,[24] in the absence of exciting radiation, only Au(III); it is necessary[40] to dissociate the F_2 to F in order to generate Au(V)):

$$2O_2F_{(solv)} + AuF_4{}^-{}_{(solv)} \rightarrow 2O_{2(g)} + AuF_6{}^-{}_{(solv)} \qquad (3)$$

Precipitation of the Au(V) salt occurs as the solutions mix. It is not always necessary to maintain such low temperatures, however, especially if the $O_2F_{(solv)}$ can be generated in situ. If, e.g., 2 equiv of alkali fluoride is present in the aHF solution with $AuF_4{}^-{}_{(solv)}$ and an O_2^+ salt is added (even at room temperature), a fast oxidation to $AuF_6{}^-{}_{(solv)}$ occurs, but, as already mentioned for AsF_6^- with PtF_6^-, this results in a solid−solution AsF_6^-/AuF_6^- salt. This oxidation clearly demonstrates that $O_2F_{(solv)}$ is a more potent oxidizer than F_2 and more akin to F atom or[41] KrF_2. Although there is likely to be some stabilization of the O_2F by solvation, this is unlikely to be large, and $\Delta_fH_{298.15}(O_2F_{(solv)})$ is therefore unlikely to be very different from the value for $\Delta_fH_{298.15}(O_2F_{(g)}) = 6.1 \pm 0.5$ kcal mol^{-1}, assessed by Chase[42] from the spectrokinetic studies of Pagsberg et al.[11] and Campuzano-Jost et al.[12] For the gaseous species, this implies a thermochemical O−F bond energy of nearly 13 kcal mol^{-1}, and that of the solvated species can, at best, be only marginally higher. Thermochemically, therefore, $O_2F_{(solv)}$ is not much inferior as a F atom source to KrF_2, in which the mean thermochemical bond energy[43] is 11.5 kcal mol^{-1}.

A particularly useful application of $O_2F_{(solv)}$ is in the oxidation of fluorides that are, themselves, insoluble in aHF, the desired product being itself soluble; examples are the oxidations of AgF_2 and NiF_2. In each case, the AgF_2 or NiF_2 was mixed with alkali fluoride in molar excess of that required, and the solution of the O_2^+ salt was added slowly, and with efficient mixing, to a slurry of the metal fluoride in the basic aHF:

$$2O_2F_{(solv)} + NiF_{2(c)} + 2F^-{}_{(solv)} \rightarrow 2O_{2(g)} + NiF_6{}^{2-}{}_{(solv)} \qquad (4)$$

It is probable that the reaction proceeds with formation first of a higher fluoride, in this case NiF_3, which, being more acidic than NiF_2, interacts with the base:[44]

---

(37) Casteel, W. J., Jr. Ph.D. Thesis, University of California at Berkeley, September 1992; p 58.

(38) Bartlett, N.; Rao, P. R. *Proc. Chem. Soc.* **1964**, 393.

(39) Edwards, A. J.; Falconer, W. E.; Griffiths, J. E.; Sunder, W. A.; Vasile, J. *J. Chem. Soc., Dalton Trans.* **1974**, 1129.

(40) Lucier, G. M.; Graudejus, O.; Elder, S. H.; Whalen, J. M.; Bartlett, N. To be published.

(41) Lutar, K.; Jesih, A.; Lebau, I.; Zemva, B.; Bartlett, N. *Inorg. Chem.* **1989**, *20*, 3467.

(42) Chase, M. W. *J. Phys. Chem. Ref. Data.* **1996**, *25* (2), 551.

(43) Gunn, S. R. *J. Phys. Chem.* **1967**, *71*, 2934.

(44) Zemva, B.; Lutar, K.; Chacon, L.; Fele-Beuermann, M.; Allman, J.; Shen, C.; Bartlett, N. *J. Am. Chem. Soc.* **1995**, *117*, 10025.

$$2NiF_{3(c)} + 2F^-_{(solv)} \rightarrow NiF_{2(c)} + NiF_6{}^{2-}{}_{(solv)} \quad (5)$$

This would explain the poor crystallinity of the NiF_2 remaining after the reaction, at the outset it having been highly microcrystalline.

In the case of AgF_2, when there is a deficiency of base (e.g., when alkali fluoride is gradually *added to* a mixture of AgF_2 and O_2^+ salt), the low-solubility mixed oxidation-state material $(AgF^+)_2AgF_4^-MF_6^-$ is formed.[21,45] When the oxidizing conditions are highly basic throughout the preparation, as in eq 4, AgF_4^- is formed at room temperature in ~41.6% yield, F_2 also being released.

In such preparations, the high solubility of the alkali Ni(IV) and Ag(III) salts provides for the removal of the bulk of the excess alkali fluoride. This was done for the Ag(III) case[46] by adding PF_5 gas until the first red precipitate (AgF_3) appeared, at which point all excess alkali fluoride had been neutralized as APF_6. The APF_6 salts are of low solubility in aHF, and the solutions of the Ag(III) salts can be decanted cleanly from them, since the aHF solutions are usually of low surface tension. In contrast, it should be noted that, in the purification of the AMF_6 salts, e.g., M = Au or Pt, because of their *low* solubility, alkali fluoride impurity was diminished by concentrating the solution to precipitate most of the AMF_6 salt. The highly soluble alkali hydrofluorides remain in solution and are removed from the AMF_6 salt by decantation of the aHF solution to the other arm of a T-reactor.

These high-oxidation-state preparations using $O_2F_{(solv)}$ confirm that this reagent (that can be so readily generated from the easily stored O_2^+ salts) is comparable to KrF_2 in oxidizing potency, yet much simpler to prepare. If, however, elemental fluorine is available to the synthesizer, the Ag(III), Au(V), Ni (IV), and Pt(V) salts are most efficiently prepared using atomic fluorine from the photodissociation[40,46,47] of F_2. For low-temperature synthesis, however, the $O_2F_{(solv)}$ reagent derived from O_2^+ salts is especially convenient. Since there was a possibility that our attempt[40] to prepare PdF_6^- salts photochemically had failed because of their low thermal stability, efforts were made to obtain them at −50 °C or lower, via the $O_2F_{(solv)}$ reagent.

Addition of $O_2F_{(solv)}$ reagent to a solution of PdF_6^{2-} salt at −50 °C did not give any precipitate, nor did it evolve O_2. Warming the mixture merely led to decomposition of the $O_2F_{(solv)}$ reagent. A generation ago, Falconer and co-workers reported[48] the preparation of $O_2^+PdF_6^-$, prepared under 60 000 psi of F_2/O_2 mix at 320 °C. They were unable to obtain crystallographic information (similarity[49] to $O_2^+PtF_6^-$ was anticipated but not found); however, they did provide persuasive vibrational evidence for their conclusion. To check the possibility that the Falconer salt was not merely a Pd(IV) material, such as $(O_2)_2PdF_6$, and to investigate the thermal stability of such a salt, its preparation was undertaken. Dissolution of PdF_4 with O_2F did not occur, but addition of A_2PdF_6 salts (A = K or Cs), which are highly soluble in aHF, to O_2AsF_6 in aHF (both solutions below −30 °C and in 1:2 molar ratio) produced precipitates of $AAsF_6$ and a deep orange solution. Cooling of this solution to -50 °C produced yellow crystals. *There was no O_2 evolution, neither on mixing nor on warming to −20 °C.* The deep orange-yellow solution (presumed to hold $(O_2)_2PdF_6$), separated from the $AAsF_6$ by decantation, became deep red as it warmed to room temperature, but even here gas evolution was slight. The overall reaction (based on weights of $AAsF_6$ formed) can be expressed as

$$2A^+_{(solv)} + PdF_6{}^{2-}{}_{(solv)} + 2O_2{}^+{}_{(solv)} + 2AsF_6{}^-{}_{(solv)} \rightarrow 2AAsF_{6(c)} + 2O_2{}^+{}_{(solv)} + PdF_6{}^{2-}{}_{(solv)} \quad (6)$$

Attempts were made to isolate $(O_2)_2PdF_6$ by removing the aHF at −60 °C. As the solutions became concentrated, there was always loss of O_2 and F_2 (the latter indicated by I_2 liberation from I^-). The composition of the solid, from gravimetry, was always between $(O_2)_2PdF_6$ and O_2PdF_5 and approached that expected for O_2PdF_5 (see Table 2). This is consistent with extensive release of the base, O_2F, when stabilization by solvation was no longer available. The decomposition proceeded as

$$(O_2)_2PdF_{6(c)} \rightarrow (O_2)PdF_{5(c)} + \text{either } O_2F_{(g)} \text{ or } O_{2(g)} + F_{2(g)} \quad (7)$$

Certainly, $(O_2)_2PdF_{6(c)}$ is no more stable than the first bis O_2^+ salts prepared similarly by Bougon et al.[50] more than 12 years ago. Evidently, O_2^+ effectively withdraws F^- even from anions that are of high thermodynamic and kinetic stability. In the preparation (see Table 2) in which Cs_2PdF_6 was present as the aHF was removed, even more O_2F was lost, in this instance the decomposition product composition approaching O_2PdF_5 more closely than in the O_2AsF_6-rich preparations. This may be a consequence of the extra PdF_6^{2-} enhancing the donation of F^- to O_2^+ as the solvating HF was stripped from the latter. Since this decomposition perhaps freed the powerful fluorinator O_2F, the possibility existed that some oxidation of Pd(IV) to Pd(V) could have occurred then. The products of $(O_2)_2PdF_{6(c)}$ decomposition were therefore examined for evidence of even partial formation of Pd(V).

Raman spectroscopy of the dark red solid from the decomposition of $(O_2)_2PdF_6$ gave $\nu(O_2^+) = 1820 \pm 3$ cm^{-1}, a value not significantly different from that obtained by Falconer and co-workers[48] for "O_2PdF_6" (1819 cm^{-1}). Samples made by removing the HF below −60 °C were closest to that composition and gave faint XRDPs which showed similarities to the XRDP of the highly disordered pattern obtained by Jha and co-workers[51] for impure $(NO)_2PtF_6$ made from NO and PtF_6. XRDPs of ordered hexagonal $(NO)_2PtF_6$ are nearly indistinguishable from those of $(NO)_2PdF_6$, prepared by Rao[52] from the interaction of ONF with PdF_4. A plausible impurity in Jha's disordered material was $NOPtF_6$; therefore, the possibility existed that some O_2PdF_6 could have formed as the $(O_2)_2PdF_6$ decomposed. In addition, the $AAsF_6$ precipitates were often yellow; therefore, inclusion of some $APdF_6$ in the $AAsF_6$ could have occurred, although only to a small extent, since the XRDPs showed that the unit cell dimensions of such yellow solids were indistinguishable from those of their colorless, high-purity $AAsF_6$ relatives. A solid solution of PdF_6^- with AsF_6^- should have shown a detectable line shift from the XRDP of $AAsF_6$. It is, therefore, possible that the yellow coloration was due to a low-crystallinity polymeric anion salt of Pd(IV). Despite these

---

(45) Shen, C.; Lucier, G. M.; Bartlett, N. To be published.

(46) Lucier, G. M.; Whalen, J. M.; Bartlett, N. *J. Fluorine Chem.* **1998**, *89*, 101.

(47) Whalen, J. M.; Lucier, G. M.; Chacon, L.; Bartlett, N. *J. Fluorine Chem.* **1998**, *88*, 107.

(48) Falconer, W. E.; DiSalvo, F. J.; Edwards, A. J.; Griffiths, J. E.; Sunder, W. A.; Vasile, M. J. *J. Inorg. Nucl. Chem.* Suppl. **1976**, 59.

(49) Bartlett, N.; Lohmann, D. H. *J. Chem. Soc.* **1962**, 5253.

(50) Bougon, R. A.; Christe, K. O.; Wilson, W. W. *J. Fluorine Chem.* **1985**, *30*, 237.

(51) Bartlett, N.; Beaton, S. P.; Jha, N. K. *Chem. Commun.* **1966**, 168.

(52) P. R. Rao (unpublished) found a unit cell similar for $(NO)_2PdF_6$ to that of $(NO)_2PtF_6$, with $a = 10.00$ and $c = 3.53$ Å.

indications of the possible presence of Pd(V), however, the hard evidence failed to provide the necessary support.

Our deep red solids from $(O_2)_2PdF_6$ (which were of very slight solubility in aHF and, therefore, possibly contained a polymeric anion such as $(PdF_5)_n^{n-}$), did dissolve rapidly, with O_2 evolution, when alkali fluoride was present in the aHF. The product of such reactions, however, was always a PdF_6^{2-} salt. Moreover, addition of a solution of KF in aHF to the dark red, partially decomposed $(O_2)_2PdF_6$ gave the correct mass (see Table 2) for the required mixture of K_2PdF_6 and $KAsF_6$ that the XRDP showed to be present. Unfortunately, the ever-present AsF_6^- salts (even though there in small concentration), as a feature of their high crystallinity,[53] gave strong Raman bands. This, combined with the poor quality of the Raman data from the dark red solids, meant that useful vibrational information for the fluoropalladate species was not obtained. However, the magnetic data on samples from a variety of syntheses showed simple Curie law behavior (i.e., Weiss constant = 0) and always a magnetic moment less than, or approximately equal to, that expected (see Table 3) for the spin-only values from the O_2^+ species alone. Since RhF_6^{2-} salts are[54] one-unpaired-spin paramagnets, isoelectronic with PdF_6^- salts, the latter should be magnetically similar. The Pd anions, whatever their nature, must be diamagnetic, or nearly so. There is, therefore, no firm evidence that $O_2F_{(solv)}$ can generate Pd(V). In that, it is like the photochemical approach[40] with F atom in aHF, which also failed to make Pd(V).

The instability of $(O_2)_2PdF_6$ with respect to easy loss of O_2 and F_2 is in marked contrast to the stability of $(NO)_2PdF_6$. The latter was found by Rao[52] to be stable at 320 °C. Since the O_2^+ and NO^+ are similar in size,[49] the lattice energies of structurally related salts must be close.

Electron capture by O_2^+, and approximately simultaneous loss of F from the PdF_6^- generated by that process, could account for this difference, since the electron affinity of O_2^+ much exceeds that of NO^+ (280 versus 214 kcal mol^{-1}).[55] But the decomposition could also occur by F^- capture from the PdF_6^{2-} by the O_2^+, since O_2F is a weak base, whereas ONF is a strong one.[56] The inability of $O_2F_{(solv)}$ to dissolve any PdF_4 contrasts with the dissolution of the latter in alkali hydrofluoride solutions or its ready interaction[52] with ONF to make $(NO)_2PdF_6$. The enthalpy of ionization of ONF is[56]

$$\Delta H^\circ_{298.15}(\mathrm{ONF}_{(g)} \rightarrow \mathrm{NO}^+_{(g)} + \mathrm{F}^-_{(g)}) = 188\ \mathrm{kcal\ mol^{-1}} \quad (8)$$

This is close to the lattice energy of $KF_{(c)}$ (192 kcal mol^{-1}).[57] Since NO^+ salts are nearly isodimensional with K^+ salts[49] and their solubilities in aHF are comparable, it is probable that $NO^+_{(g)}$ and $K^+_{(g)}$ have similar solvation enthalpies and entropies. The ONF should, therefore, have about the same base strength in aHF as KF.

From the measured[11,12,42] $\Delta_fH^\circ_{298.15}(O_2F_{(g)}) = 6.1 \pm 0.5$ kcal mol^{-1}, $\Delta_fH^\circ_{298.15}(F_{(g)})$[15] = 18.86 kcal mol^{-1}, the electron affinity[58] for F = 81 kcal mol^{-1}, and that for $I(O_2) = 280$ kcal mol^{-1},

$$\Delta H^\circ_{298.15}(\mathrm{O_2F}_{(g)} \rightarrow \mathrm{O_2}^+_{(g)} + \mathrm{F}^-_{(g)}) = 212\ \mathrm{kcal\ mol^{-1}} \quad (9)$$

$NOMF_6$ and O_2MF_6 salts have nearly the same solubility in aHF, and since these lattice energies must be similar,[49,59] this implies (solvation and other entropy terms being comparable) that the solvation energies for O_2^+ and NO^+ in aHF are also akin. Therefore, the differences in the $\Delta H^\circ_{298.15}$ values of eqs 8 and 9 may well express the difference in $\Delta G^\circ_{298.15}$ of ionization for the two molecules (ONF and O_2F) in aHF. If so, O_2F must be much less ionized in aHF than ONF.

Conclusions

This work has shown that, with alkali fluoride in aHF, at −50 °C or below, O_2^+ salts generate stable solutions of dissolved O_2F. Its solutions oxidize Ag(II) to Ag(III), Au(III) to Au(V), and Ni(II) to Ni(IV). The interaction of Pt(IV) salts with O_2^+ in aHF gives Pt(V). Attempts to oxidize Pd(IV) to Pd(V) did not succeed. The salt $(O_2^+)_2PdF_6^{2-}$, prepared metathetically, is highly soluble and long-lived in solution in aHF, even at 0 °C, but loses O_2 and F_2 as the solvent is removed. Solutions of O_2F in aHF have proved to be only weakly basic.

Acknowledgment. The authors gratefully acknowledge the support of this work by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract No. DE-AC-03-76SF00098. This material is also based on work supported by the National Science Foundation under Grant CHE-9302414 awarded to S.H.E.

IC971603N

---

(53) It has been a common experience in these laboratories that small-particle solids which give poor XRDP also give weak and broad-line Raman spectra.

(54) Nyholm, R. S.; Sharpe, A. G. *J. Chem. Soc.* **1952**, 3579.

(55) Levin, R. D.; Lias, S. G. *Ionization Potential and Appearance Potential Measurements, 1971−1981*; NSRDS−NBS 71; U.S. Department of Commerce: Washington, DC, 1982.

(56) Bartlett, N.; Yeh, S.; Kourtakis, K.; Mallouk, T. *J. Fluorine Chem.* **1984**, *26*, 97.

(57) Waddington, T. C. *Adv. Inorg. Chem. Radiochem.* **1959**, *1*, 157.

(58) Sharpe, A. G. In *Halogen Chemistry*; Gutmann, V., Ed.; Academic Press: London, 1967; Vol. 1, pp 1−40.

(59) Mallouk, T. E.; Rosenthal, Y. L.; Müller, Y.; Brusasco, R.; Bartlett, N. *Inorg. Chem.* **1984**, *23*, 3167.