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The Hexafluorochlorine(VII) Cation, ClF_6^+. Synthesis and Vibrational Spectrum

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The ClF_6^+ cation was prepared in the form of its PtF_6^- salt from the reactions of PtF_6 with either $FClO_2$ or ClF_5. A displacement reaction between $ClF_6^+PtF_6^-$ and FNO at −78° yielded only ClF_5 and F_2, indicating that ClF_7 cannot exist under the given reaction conditions. Attempts were unsuccessful to prepare $ClF_6^+BF_4^-$ by low-temperature glow discharge of a ClF_5-F_2-BF_3 mixture, to prepare ClF_6^+ salts from ClF_5, F_2, and the Lewis acid SbF_5, AsF_5, or BF_3 at elevated temperatures and pressures, or to prepare ClF_4O^+ salts either from ClF_3O and PtF_6 or from ClF_3O, F_2, and SbF_5. Iridium hexafluoride was found to be too weak an oxidizer to produce any heptavalent, chlorine-containing cations from $FClO_2$. Vibrational spectra were recorded for PtF_6^- salts of ClF_6^+, ClF_4^+, ClF_2^+, $ClF_2O_2^+$, ClF_2O^+, and ClO_2^+ and for $ClO_2^+IrF_6^-$. Modified valence force fields were computed for the ClF_6^+, PtF_6^-, and IrF_6^- ions.

Introduction

Two preliminary notes on the synthesis of $ClF_6^+PtF_6^-$ from PtF_6 and chlorine fluorides or oxyfluorides have recently been published,[1,2] and the identity of ClF_6^+ was established beyond doubt by ^{19}F nmr spectroscopy.[2,3] The ClF_6^+ cation is of particular interest for two reasons: (1) except for the recently discovered $ClO_2F_2^+$ cation,[4] it is the only known heptavalent chlorine cation and (2) in addition to the NF_4^+ salts,[5-9] it is the only known example of the synthesis of a fluoro cation derived from hitherto unknown compounds (*i.e.*, NF_5 and ClF_7, respectively). In this paper, we give a full account of the synthesis, vibrational spectrum, and force constants of the ClF_6^+ cation.

Experimental Section

Apparatus and Materials. The materials used in this work were manipulated in a well-passivated (with ClF_3) 304 stainless steel vacuum line equipped with Teflon FEP U traps and 316 stainless steel bellow-seal valves (Hoke, Inc., 425 1F4Y). Pressures were measured with a Heise Bourdon tube type gauge (0–1500 mm ± 0.1%). Because of the rapid hydrolytic interaction with moisture, all materials were handled outside of the vacuum system in the dry nitrogen atmosphere of a glove box.

The infrared spectra were recorded on Perkin-Elmer Models 337 and 457 spectrophotometers in the range 4000–250 cm^{-1}. The spectra of gases were obtained using 304 stainless steel cells of 5-cm path length fitted with AgCl windows. The spectra of solids were obtained by pressing two small single-crystal platelets of either AgCl or AgBr to a disk in a Wilks minipellet press. The powdered sample was placed between the platelets before starting the pressing operation.

The Raman spectra were recorded on either a Cary Model 82 or 83 spectrophotometer using the 4880- and 6471-Å exciting lines, respectively. Glass melting point capillaries or clear thin-walled Kel-F tubes were used as sample containers in the transverse-viewing-transverse-excitation technique.

Mass spectra were recorded on a Quad 300 (Electronic Associates Inc.) quadrupole mass spectrometer using a passivated all stainless steel inlet system.

Platinum hexafluoride was either purchased (from Ozark Mahoning Co.) or freshly prepared by burning Pt wire in an F_2 atmosphere at −196°, according to the method of Weinstock and his coworkers.[10] Iridium hexafluoride was obtained from Ozark Mahoning Co. Prior to use, both IrF_6 and PtF_6 were purified by fractional condensation at −78° in a dynamic vacuum. Arsenic pentafluoride (Ozark Mahoning Co.) was purified by fractional condensation and SbF_5 (Ozark Mahoning Co.) by distillation. Chlorine pentafluoride (Rocketdyne) was stored over dry CsF to remove any ClF_3 and purified by fractional condensation through traps kept at −112 and −126° with the material retained at −126° being used. Fluorine (Rocketdyne) was passed over NaF to remove HF. Chloryl fluoride was prepared from $KClO_3$ and ClF_3,[11] ClF_3O by fluorination of $ClONO_2$,[12] and FNO from NO and F_2 at −196°. The purity of the volatile starting materials was determined by measurements of their vapor pressures and infrared spectra.

The $FClO_2$–PtF_6 System. Platinum hexafluoride (17.0 mmol) and $FClO_2$ (46.1 mmol) were combined at −196° in a passivated (with ClF_3) 75-ml stainless steel cylinder. The mixture was allowed to warm up slowly to 25° and was kept at this temperature for 3 days. The cylinder was cooled to −196° and 3.75 mmol of material volatile at this temperature was removed and identified as F_2 by its vapor pressure and mass spectrum. The products volatile at 25° were separated by fractional condensation through traps kept at −78, −126, and −196°. The −126° fraction consisted of $FClO_2$ (28.7 mmol) and the −196° one of $FClO_2$ (0.3 mmol), ClF_5 (0.1 mmol), and a small amount of $FClO_3$. The cylinder contained a stable canary yellow solid (6.618 g), which was identified by infrared spectroscopy as a mixture of $ClO_2^+PtF_6^-$ and $ClO_2F_2^+PtF_6^-$. Hence, PtF_6 (17.0 mmol) had reacted with $FClO_2$ (17.1 mmol) in a 1:1 mole ratio yielding F_2 (3.75 mmol), $ClO_2^+PtF_6^-$ (12.2 mmol = 4.594 g), and $ClO_2F_2^+PtF_6^-$ (4.8 mmol = 2.000 g) as the main products.

Platinum hexafluoride (2.04 mmol) and $FClO_2$ (3.08 mmol) were combined at −196° in a passivated sapphire reaction tube (Varian, Model CS-4250-3). The reactor was rapidly warmed from −196 to −78° and kept at −78° for 48 hr. At the end of this time period, the brown PtF_6 color had completely disappeared and a canary yellow solid had formed. The reactor was cooled to −196° and noncondensable material (0.33 mmol of O_2) was removed. The product volatile at 25° consisted of $FClO_2$ (1.03 mmol). The yellow, solid residue weighed 800 mg and was shown by infrared, Raman, and ^{19}F nmr spectroscopy to be a mixture of $ClF_6^+PtF_6^-$ and $ClO_2^+PtF_6^-$ (weight calculated for a mixture of 1.70 mmol of $ClO_2^+PtF_6^-$ and 0.34 mmol of $ClF_6^+PtF_6^-$ = 796 mg). Hence, PtF_6 (2.04 mmol) had reacted with $FClO_2$ (2.05 mmol) in a 1:1 mole ratio producing O_2 (0.33 mmol) and a 1:5 mole ratio mixture of $ClF_6^+PtF_6^-$ and $ClO_2^+PtF_6^-$.

The ClF_5-PtF_6 System. Platinum hexafluoride (2.70 mmol) and ClF_5 (3.90 mmol) were combined at −196° in a passivated sapphire reactor. The mixture was kept at 25° for 24 hr. Since the brown PtF_6 color was still very intense, the tube was exposed to unfiltered uv radiation from a Hanovia Model 616A high-pressure quartz mercury vapor arc. After 24 hr of uv irradiation, the dark brown PtF_6 color

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had disappeared and a yellow to brown solid had formed. The product was kept for 12 hr at −20° without irradiation and its color changed to yellow-orange. The reactor was cooled to −196° and noncondensables (2.58 mmol of F_2) were removed. The reactor was warmed up to 25° and the volatile products were separated by fractional condensation. They consisted of ClF_5 (1.08 mmol) and ClF_3 (0.12 mmol). The yellow solid residue weighed 1.096 g (weight calculated for a mixture of 0.84 mmol of $ClF_6^+PtF_6^-$ and 1.86 mmol of $ClF_2^+PtF_6^-$ is 1.097 g). The identity of this solid as $ClF_2^+PtF_6^-$ and $ClF_6^+PtF_6^-$ was verified by ^{19}F nmr, infrared, and Raman spectroscopy. Hence, PtF_6 (2.70 mmol) had reacted with ClF_5 (2.70 mmol) producing $ClF_6^+PtF_6^-$ (0.84 mmol), $ClF_2^+PtF_6^-$ (1.86 mmol), and F_2 (2.46 mmol). In addition, some of the ClF_5 (0.12 mmol), which had been used in excess, had decomposed to ClF_3 and F_2.

In a second experiment, PtF_6 (5.26 mmol) and ClF_5 (8.02 mmol) were combined at −196° in a sapphire reactor. The mixture was exposed at ambient temperature to uv radiation from a Hanovia Model 616A high-pressure Hg arc using a Pyrex-water filter. After 14 days of irradiation, the PtF_6 color had disappeared and a yellow to orange solid had formed. The volatile products consisted of F_2 (0.23 mmol), ClF_5 (3.23 mmol), and a trace of ClF_3. The solid residue weighed 2.245 g and was, according to its infrared spectrum, a mixture of $ClF_6^+PtF_6^-$ and $ClF_4^+PtF_6^-$. It appears that owing to the long reaction time and uv irradiation, some PtF_6 (0.46 mmol as indicated by the F_2 evolution and by the weight of the solid reaction product) had reacted with the container walls. Hence, PtF_6 (4.80 mmol) had reacted with ClF_5 (4.79 mmol) producing $ClF_4^+PtF_6^-$ (2.40 mmol) and $ClF_6^+PtF_6^-$ (2.40 mmol). The observed weight of the solid product (2.245 g) agreed well with that calculated (2.252 g) for the above reactions.

Displacement Reaction between FNO and $ClF_6^+PtF_6^-$. To a mixture (0.390 g) of $ClF_6^+PtF_6^-$ (0.30 mmol) and $ClF_2^+PtF_6^-$ (0.66 mmol) in a passivated Teflon-FEP ampoule, FNO (6.75 mmol) was added at −196°. The contents of the ampoule were kept at −78° for 12 hr. The ampoule was cooled to −196° and F_2 (0.28 mmol) was removed. The products volatile at ambient temperature were separated by fractional condensation and consisted of FNO (5.76 mmol), ClF_3 (0.64 mmol), and ClF_5 (0.27 mmol). The yellow, solid residue weighed 0.329 g (calculated weight for 0.96 mmol of $NO^+PtF_6^-$ is 0.326 g) and was identified by its infrared spectrum as $NO^+PtF_6^-$.

Reaction between ClF_3O and PtF_6. Platinum hexafluoride (1.87 mmol) and ClF_3O (4.71 mmol) were combined at −196° in a sapphire reaction tube. When the mixture was allowed to warm to 25°, a rapid reaction with gas evolution occurred and the characteristic PtF_6 color disappeared within a few minutes. The mixture was kept at 25° for several hours and was then cooled to −196°. Fluorine (0.78 mmol) was removed at −196° and ClF_3O (2.05 mmol), ClF_5 (0.14 mmol), and $FClO_2$ (0.48 mmol) were removed at 25°. The canary yellow residue weighed 0.749 g (weight calculated for 1.87 mmol of $ClF_2O^+PtF_6^-$ is 0.746 g) and was identified as $ClF_2O^+PtF_6^-$ by its infrared, Raman, and ^{19}F nmr spectrum.

In another experiment, PtF_6 (2.12 mmol) and ClF_3O (5.51 mmol) were allowed to interact at −45° for 12 hr. The volatile products consisted of F_2 (1.60 mmol), ClF_3O (3.35 mmol), $FClO_2$ (0.07 mmol), and a small amount of ClF_5 and PtF_6. The yellow solid residue weighed 0.837 g (weight calculated for 2.12 mmol of $ClF_2O^+PtF_6^-$ is 0.845 g). The infrared spectrum of the solid showed it to be mainly $ClF_2O^+PtF_6^-$ but also revealed the presence of smaller amounts of $ClO_2F_2^+$ and ClF_6^+ salts.

Reaction between $FClO_2$ and IrF_6. Chloryl fluoride (2.57 mmol) and IrF_6 (1.96 mmol) were combined at −196° in a sapphire reactor. The mixture was kept at −78° for 48 hr and then cooled to −196°. All products were condensed at this temperature. At 25°, almost all of the starting materials were recovered unchanged except for 0.011 g of a yellowish solid which was identified by its infrared spectrum as $ClO_2^+IrF_6^-$. The unreacted starting materials were condensed back into the reactor and kept at 25° for 11 days. After this period, the product still showed the original brown color but had partially solidified. The mixture was cooled to −196° at which temperature 0.03 mmol of noncondensable material was removed. The material volatile at 25° consisted of IrF_6 (1.12 mmol), $FClO_2$ (1.88 mmol), and ClF_5 (0.21 mmol). The yellow crystalline solid weighed 0.147 g (0.39 mmol) and was identified by infrared and Raman spectroscopy as $ClO_2^+IrF_6^-$.

Attempted Syntheses of $ClF_6^+SbF_6^-$, $ClF_6^+AsF_6^-$, $ClF_6^+BF_4^-$, and $ClF_4O^+SbF_6^-$. When mixtures of ClF_5, F_2, and AsF_5 in different mole ratios were heated in Monel cylinders for 5–10 days at 125–145° under autogenous pressures of 500–1000 psi, only unreacted starting materials were recovered in addition to very small amounts of metal AsF_6^- salts. Heating the mixture to 160° resulted in partial breakdown of ClF_5 to ClF_3 and F_2.

Heating a BF_3, F_2, and ClF_5 mixture (mole ratio 1:2.7:2) for 8 days to 95° under an autogenous pressure of 450 psi did not result in the formation of a solid product.

Mixtures of ClF_5, F_2, and SbF_5 (mole ratio 1:5:3) were heated for 3–40 days in Monel cylinders at 140–225° under autogenous pressures of ~1000 psi. At 140° and 3 days' reaction time, no F_2 consumption was observed. At 160° and 25 days' reaction time, 6.5% of the F_2 used was consumed due to attack on the cylinder. The solid product was a mixture of ClF_2^+, ClF_4^+, Ni^{2+}, and Cu^{2+} salts of $SbF_6^- \cdot xSbF_5$. Controlled vacuum pyrolysis of this solid resulted in the evolution of ClF_5 at lower and of ClF_3 at higher temperatures. The composition of the solid residues of this stepwise pyrolysis was monitored by infrared and Raman spectroscopy. It was shown that the more stable component having strong absorptions in the infrared and Raman spectra at 825 and 836 cm^{-1} generated only ClF_3 when heated in the presence of CsF. When the reaction between ClF_5, F_2, and SbF_5 was carried out at 225°, $ClF_2^+SbF_6^-$ was formed with F_2 evolution.

Glow discharge of a BF_3, F_2, and ClF_5 mixture (mole ratio 1:1.42:1) at −78° in a Pyrex apparatus at pressures ranging from 20 to 50 mm produced only $ClF_2^+BF_4^-$ and no ClF_6^+ salt.

Heating a mixture of ClF_3O, F_2, and SbF_5 (mole ratio 1:10:5) in a Monel cylinder to 135° for 6 days under an autogenous pressure of 600 psi produced exclusively $ClF_2O^+SbF_6^- \cdot xSbF_5$.

Results and Discussion

Synthesis of ClF_6^+ Salts. Complex fluoro cations of the type XF_{y-1}^+ are generally prepared through fluorine abstraction from the parent compound XF_y by means of a strong Lewis acid. This was first demonstrated in 1949 by Woolf and Emeleus[13] for BrF_3

$$BrF_3 + SbF_5 \rightarrow BrF_2^+SbF_6^- \tag{1}$$

The synthesis of a fluoro cation from a lower fluoride, according to

$$XF + F^+ \rightarrow XF_2^+ \tag{2}$$

is preempted by the fact that fluorine is the most electronegative element. Hence, F^+ should be extremely difficult if not impossible to prepare by chemical means. The first and only known synthesis of a fluoro cation derived from a nonexisting parent compound was achieved[5,9] in 1966, according to

$$NF_3 + F_2 + AsF_5 \rightarrow NF_4^+AsF_6^- \tag{3}$$

This synthesis involved either glow discharge[5] or elevated temperature and pressure.[9] Since tetrahedral and octahedral species exhibit outstanding stability, as demonstrated by CF_4 and SF_6, the successful synthesis of NF_4^+ suggested the feasibility of synthesizing ClF_6^+ salts.

The application of glow discharge to the synthesis of ClF_6^+ salts is limited to the ClF_5-F_2-BF_3 system. Stronger Lewis acids, such as AsF_5, form adducts with ClF_5,[14] thus preventing the use of the low-temperature glow-discharge technique. In the case of BF_3, we did not successfully prepare $ClF_6^+BF_4^-$, owing to rapid breakdown of ClF_5 to ClF_3 and F_2, followed by removal of the ClF_3 from the gas phase by complex formation with BF_3.[15] The possible utility of the second technique, involving elevated temperature and pressure, for the synthesis of ClF_6^+ salts was also examined with BF_3, AsF_5, or SbF_5 as Lewis acids. At lower temperatures, no fluorination of ClF_5 occurred, whereas at higher temperatures, breakdown of ClF_5 to ClF_3 and F_2 was observed. Since ClF_2^+ salts are thermally more stable than the corresponding ClF_4^+ salts, ClF_3 was continuously removed from the $ClF_5 \rightleftarrows ClF_3 + F_2$ equilibrium by complexing until essentially all the ClF_5 was converted to ClF_2^+ and F_2.

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Since the techniques which had successfully been used for the synthesis of NF_4^+ salts did not result in ClF_6^+, other fluorinating agents were investigated. Of particular interest were the third transition series hexafluorides which exhibit an astonishing oxidizing power.[16] It was found[17] that PtF_6 and $FClO_2$, when combined at −196° and allowed to warm up slowly to 25°, interacted according to

$$2FClO_2 + 2PtF_6 \rightarrow ClO_2F_2^+PtF_6^- + ClO_2^+PtF_6^- \qquad (4)$$

The yield of $ClO_2F_2^+$ was not 50% as expected from the above equation, but generally about 25% owing to the competing reaction

$$2FClO_2 + 2PtF_6 \rightarrow 2ClO_2^+PtF_6^- + F_2 \qquad (5)$$

In some of the experiments, small amounts of $ClF_6^+PtF_6^-$ (see below) or ClF_5 and $FClO_3$ were observed, depending on the exact reaction conditions. The formation of some $FClO_3$ is not surprising since it is known that $FClO_2$ readily interacts with nascent oxygen to yield $FClO_3$.[18,19]

Attempts to suppress the competing reaction (eq 5) by changing the reaction conditions (rapid warm-up from −196 to −78° and completion of the reaction at −78°) resulted on one occasion in an entirely different course for the reaction

$$6FClO_2 + 6PtF_6 \rightarrow 5ClO_2^+PtF_6^- + ClF_6^+PtF_6^- + O_2 \qquad (6)$$

The observed material balance was in excellent agreement with eq 6 and the identity of ClF_6^+ was unequivocally established by ^{19}F nmr spectroscopy.[3] Further modification of the reaction conditions (rapid warm-up of the $FClO_2$-PtF_6 mixture from −196 to either −78 or 25° and completion of the reaction at 25°) did not produce detectable amounts of either $ClO_2F_2^+$ or $ClF_6^+PtF_6^-$, but only $ClO_2^+PtF_6^-$ and ClF_5, F_2, and O_2. This indicates that the nature of the reaction products is more influenced by the warm-up rate of the starting materials from −196 to about −78° than by the final reaction temperature. Slow warm-up favors the formation of $ClO_2F_2^+$, whereas rapid warm-up yields ClF_6^+ or ClF_5 and F_2. The above results for the $FClO_2$-PtF_6 system indicated that ClF_5 might be an important intermediate in the formation of ClF_6^+. In order to prove the correctness of this assumption and in order possibly to increase the yield of ClF_6^+, which according to eq 6 can be at best one-sixth based on PtF_6, we have studied also the ClF_5-PtF_6 system. For the latter system, Roberto reported[1] the formation of a ClF_6^+ salt. Owing to the slow reaction rates in the ClF_5-PtF_6 system, we have used uv radiation. Two reactions were carried out at 25°. When unfiltered uv radiation was used, the reaction was complete in several hours, according to

$$2ClF_5 + 2PtF_6 \xrightarrow[\text{uv}]{\text{unfiltered}} ClF_2^+PtF_6^- + ClF_6^+PtF_6^- + F_2 \qquad (7)$$

and

$$2ClF_5 + 2PtF_6 \rightarrow 2ClF_2^+PtF_6^- + 3F_2 \qquad (8)$$

The relative contributions from (7) and (8) were 62 and 38%, respectively. In addition, some of the ClF_5, which had been used in excess, was recovered in the form of ClF_3 and F_2.

Using a Pyrex-water filter, a reaction time of 2 weeks was required with the products being

$$2ClF_5 + 2PtF_6 \xrightarrow[\text{uv}]{\text{Pyrex filter}} ClF_4^+PtF_6^- + ClF_6^+PtF_6^- \qquad (9)$$

Since unfiltered uv light can decompose ClF_5 into ClF_3 + F_2[20] and since ClF_2^+ salts are more stable than ClF_4^+ salts,[14] the displacement of ClF_4^+ by ClF_3, observed for (7), is not surprising. The identity of the ClF_6^+ salt obtained from the $FClO_2$-PtF_6 system with that from the ClF_5-PtF_6 system was established by infrared, Raman, and ^{19}F nmr spectroscopy. The unusual nature of these reactions and products ask for a possible rationalization. In spite of the complexity of the $FClO_2$-PtF_6 system, the following assumptions appear plausible.

(a) An initial electron transfer from $FClO_2$ to PtF_6 may take place according to

$$FClO_2 + PtF_6 \rightarrow FClO_2{\cdot}^+PtF_6^- \qquad (10)$$

(b) The resulting $FClO_2{\cdot}^+$ radical cation could either stabilize by generating an active fluorine radical, according to

$$FClO_2{\cdot}^+PtF_6^- \rightarrow ClO_2^+PtF_6^- + F{\cdot} \qquad (11)$$

or act itself as the active fluorinating agent, depending upon the relative lifetimes of these two radicals.[21]

(c) In both cases ($F{\cdot}$ or $ClO_2F{\cdot}^+$), the radical might react either with PtF_6 with F_2 evolution

$$F{\cdot} + PtF_6 \rightarrow F_2 + PtF_5 \qquad (12)$$

followed by

$$PtF_5 + FClO_2 \rightarrow ClO_2^+PtF_6^- \qquad (13)$$

or with $FClO_2$

$$FClO_2 + F{\cdot} \rightarrow F_2ClO_2{\cdot} \qquad (14)$$

(d) The resulting $F_2ClO_2{\cdot}$ radical could readily stabilize by transfer of an electron to PtF_6

$$F_2ClO_2{\cdot} + PtF_6 \rightarrow ClO_2F_2^+PtF_6^- \qquad (15)$$

This sequence would account for the formation of $ClO_2F_2^+$ and for the competitive F_2 evolution reaction. Similarly, the formation of ClF_6^+ from ClF_5 and PtF_6 might involve an intermediate $ClF_5{\cdot}^+$ radical cation and suggests a search for radical cations in these systems. The formation of ClF_6^+ from $FClO_2$ might involve either an intermediate ClF_5 molecule or the direct fluorination of $ClO_2F_2^+$ to ClF_6^+. A definitive answer to these interesting questions concerning the most important intermediates is beyond the scope of the present study.

Properties of ClF_6^+ Salts. The $ClF_6^+PtF_6^-$ salts are canary yellow solids. They were stored at 25° in Teflon-FEP containers for several months without noticeable decomposition and formed stable HF solutions. They are very powerful oxidizers and react explosively with organic materials or water. Contrary to a previous statement,[1] no evidence was found during our investigation that the ClF_6^+ salts themselves can be explosive.

The Question of the Existence of ClF_7. A displacement reaction between $ClF_6^+PtF_6^-$ and FNO was carried out under conditions similar to those which had successfully been used for the synthesis of ClF_3O_2 from $ClO_2F_2^+PtF_6^-$ and FNO.[4] Since $ClF_6^+PtF_6^-$ can be considered as a Lewis acid adduct between ClF_7 and PtF_5, the products from the

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(21) When the reaction between $FClO_2$ and PtF_6 was carried out at low temperature in an inert solvent such as BrF_5 or $FClO_3$, no detectable amounts of $ClO_2F_2^+$ were formed with the only products being $ClO_2^+PtF_6^-$ and F_2. One might expect a fluorine radical to have a comparable lifetime in either excess $FClO_2$ or the solvents $FClO_3$ or BrF_5, whereas a $FClO_2{\cdot}^+$ radical could stabilize itself by rapid intermolecular exchange with $FClO_2$ only. Therefore, the lack of $ClO_2F_2^+$ formation in $FClO_3$ or BrF_5 solution strongly suggests that the $FClO_2{\cdot}^+$ cation is the active fluorination agent.

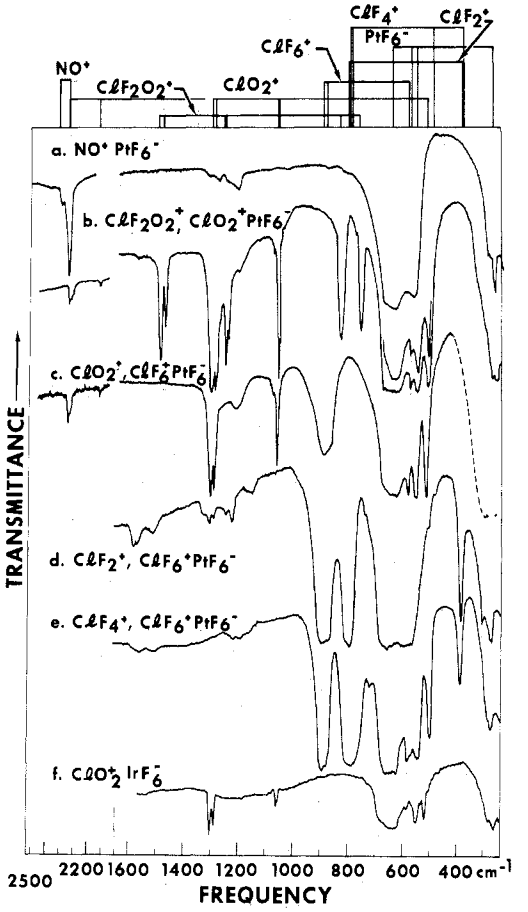

Figure 1. Infrared spectra of the solid products obtained from the following reactions: trace a, displacement reaction between FNO and a mixture of $ClF_2^+PtF_6^-$ and $ClF_6^+PtF_6^-$; traces b and c, $FClO_2 + PtF_6$ at 25 and −78°, respectively; traces d and e, ClF_5 and PtF_6 using unfiltered and filtered uv radiation, respectively; trace f, $FClO_2 + IrF_6$ at 25°. All spectra were recorded as pressed AgBr disks, except for trace c for which a AgCl disk was used.

FNO displacement reaction allow some conclusions concerning the stability of the hypothetical compound ClF_7. The following results were obtained for the displacement reaction

$$ClF_6^+PtF_6^- + FNO \xrightarrow{-78°} NO^+PtF_6^- + ClF_5 + F_2 \qquad (16)$$

This indicates that ClF_7 under the given reaction conditions (−78°) cannot exist.

Iridium Hexafluoride Reactions. Replacement of PtF_6 by IrF_6 in the $FClO_2$ reaction did not result in an oxidative fluorination of Cl(+V) to Cl(+VII). At 25° and long reaction times, only $ClO_2^+IrF_6^-$ and ClF_5 were formed in moderate yields. This demonstrates that IrF_6 is a weaker fluorinating oxidizer than PtF_6 as has previously been demonstrated by Bartlett.[16]

Attempted Synthesis of ClF_4O^+ Salts. The successful syntheses[1,2,4] of the $ClO_2F_2^+$ and the ClF_6^+ cation suggested the possible synthesis of the intermediate ClF_4O^+ cation from ClF_3O and PtF_6. At 25°, the main reaction was

$$2ClF_3O + 2PtF_6 \xrightarrow{25°} 2ClF_2O^+PtF_6^- + F_2 \qquad (17)$$

In addition, small amounts of $FClO_2$ and ClF_5 were observed among the volatile reaction products. When the reaction temperature was lowered to −45°, the main products were again $ClF_2O^+PtF_6^-$ and F_2. However, small amounts of $ClO_2F_2^+$ and $ClF_6^+PtF_6^-$ had also formed. No evidence for the presence of any ClF_4O^+ could be obtained. This suggests that tetrahedral $ClF_2O_2^+$ and octahedral ClF_6^+ are more favorable products than the pseudo trigonal-bipyramidal ClF_4O^+. The formation of small amounts of $ClO_2F_2^+$ and ClF_6^+ (or $FClO_2$ and ClF_5) might be due either to the decomposition of an unstable intermediate, such as ClF_4O^+, into $ClO_2F_2^+$ and ClF_6^+, or at least partially to the formation of some $FClO_2$ from the difficult to handle ClF_3O.[12] Attempts to synthesize $ClF_4O^+SbF_6^-$ from ClF_3O-F_2-SbF_5 at elevated temperature and pressure produced exclusively $ClF_2O^+SbF_6^-\cdot xSbF_5$.[21a]

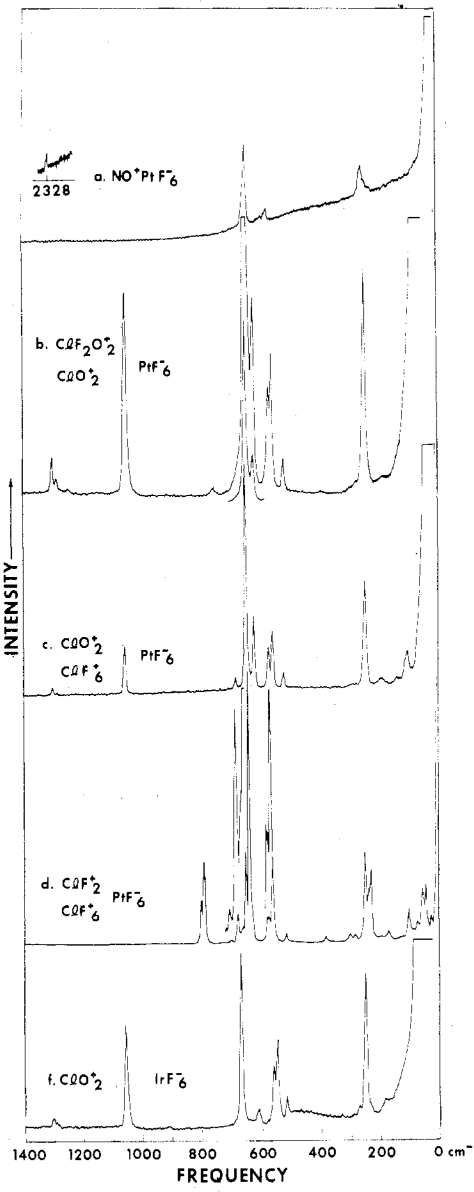

Figure 2. Raman spectra of some of the solid products shown in Figure 1 using the same notations. All spectra were recorded for dry powders in glass melting point capillaries, using the 6471-Å exciting line on a Cary Model 82.

Vibrational Spectra. The infrared and Raman spectra of the solid reaction products are shown by Figures 1 and 2, respectively. The spectrum of $ClF_2O^+PtF_6^-$ was identical with that previously reported[22] and, hence, is not depicted.

(21a) Note Added in Proof. The ClF_3O-PtF_6 reaction was also studied at low temperature in either $FClO_3$ or BrF_5 solution. Furthermore the interaction between $Cs^+ClF_4O^-$ and PtF_6 was investigated either in the absence of a solvent or in $FClO_3$ solution. In all cases the solid reaction product was $ClF_2O^+PtF_6^-$.

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Table I. Vibrational Spectra[a] of Several $\mathrm{PtF_6^-}$ Salts and of $\mathrm{ClO_2^+IrF_6^-}$ and Their Assignment

$\mathrm{NO^+PtF_6^-}$

Obsd freq, $\mathrm{cm^{-1}}$		Assignment for $\mathrm{PtF_6^-}$ in O_h
Ir	Raman	
2385 mw		$\nu(\mathrm{NO})$
2329 ms	2328 (0+)	
1280 w, br		$\nu_1 + \nu_3\ (\mathrm{F_{1}u})\ \mathrm{PtF_6^-}$
1212 w, br		$\nu_2 + \nu_3\ (\mathrm{F_{1}u + F_{2}u})\ \mathrm{PtF_6^-}$
880 vw, br		$\nu_3 + \nu_5\ (\mathrm{A_{2}u + Eu + F_{1}u + F_{2}u})\ \mathrm{PtF_6^-}$
830 vw, br		$\nu_2 + \nu_4\ (\mathrm{F_{1}u + F_{2}u})\ \mathrm{PtF_6^-}$
640 vs, br		$\nu_3\ (\mathrm{F_{1}u})\ \mathrm{PtF_6^-}$
	644 (10)	$\nu_1\ (\mathrm{A_{1}g})\ \mathrm{PtF_6^-}$
	589 (0+)	$\nu_2\ (\mathrm{Eg})\ \mathrm{PtF_6^-}$
570 s	570 (2)	
295 mw		$\nu_4\ (\mathrm{F_{1}u})\ \mathrm{PtF_6^-}$
269 ms		
	249 (4)	$\nu_5\ (\mathrm{F_{2}g})\ \mathrm{PtF_6^-}$
	235 sh	

$\mathrm{ClO_2^+, ClF_2O_2^+PtF_6^-}$

Obsd freq, $\mathrm{cm^{-1}}$		Assignment for $\mathrm{ClO_2^+}$ and $\mathrm{ClF_2O_2^+}$ in C_{2v}, for $\mathrm{PtF_6^-}$ in O_h
Ir	Raman	
2340 2320 w		$\nu_1 + \nu_3\ (\mathrm{B_1})\ \mathrm{ClO_2^+}$
2115 vw		$2\nu_1\ (\mathrm{A_1})\ \mathrm{ClO_2^+}$
1486 1470 s		$\nu_6\ (\mathrm{B_1})\ \mathrm{ClF_2O_2^+}$
1297 vs	1299 (0.5)	$\nu_3\ (\mathrm{B_1})\ \mathrm{ClO_2^+}$
1283 s	1285 (0.17)	
1245 1237 s	1246 (0+)	$\nu_1\ (\mathrm{A_1})\ \mathrm{ClF_2O_2^+}$
1210 w		$\nu_2 + \nu_3\ (\mathrm{F_{1}u + F_{2}u})\ \mathrm{PtF_6^-}$
1052 s	1051 (2.7)	$\nu_1\ (\mathrm{A_1})\ \mathrm{ClO_2^+}$
1047 m		
827 s		$\nu_8\ (\mathrm{B_2})\ \mathrm{ClF_2O_2^+}$
756 s	754 (0.1)	$\nu_2\ (\mathrm{A_1})\ \mathrm{ClF_2O_2^+}$
640 vs	617 (2.5)	$\nu_3\ (\mathrm{F_{1}u})\ \mathrm{PtF_6^-}$
	642 (10)	$\nu_1\ (\mathrm{A_{1}g})\ \mathrm{PtF_6^-}$
580 w	564 (1.3)	$\nu_2\ (\mathrm{Eg})\ \mathrm{PtF_6^-}$
552 s	552 (1.8)	
530 sh		$\nu_3\ (\mathrm{A_1}),\ \nu_7\ (\mathrm{B_1}),\ \nu_9\ (\mathrm{B_2})\ \mathrm{ClF_2O_2^+}$
	514 (0.4)	
514 s		$\nu_2\ (\mathrm{A_1})\ \mathrm{ClO_2^+}$
284 m		$\nu_4\ (\mathrm{F_{1}u})\ \mathrm{PtF_6^-}$
265 s		
	239 (2.9)	$\nu_5\ (\mathrm{F_{2}g})\ \mathrm{PtF_6^-}$
	180 (0+)	$\nu_6\ (\mathrm{F_{2}u})\ \mathrm{PtF_6^-}$

$\mathrm{ClO_2^+, ClF_6^+PtF_6^-}$

Obsd freq, $\mathrm{cm^{-1}}$		Assignment for $\mathrm{ClO_2^+}$ in C_{2v}, for $\mathrm{ClF_6^+}$ and $\mathrm{PtF_6^-}$ in O_h
Ir	Raman	
2340 2320 w		$\nu_1 + \nu_3\ (\mathrm{B_1})\ \mathrm{ClO_2^+}$
1297 vs	1299 (0.3)	$\nu_3\ (\mathrm{B_1})\ \mathrm{ClO_2^+}$
1283 s	1285 (0.1)	
1210 w		$\nu_2 + \nu_3\ (\mathrm{F_{1}u + F_{2}u})\ \mathrm{PtF_6^-}$
1053 s	1054 (2.0)	$\nu_1\ (\mathrm{A_1})\ \mathrm{ClO_2^+}$
1049 m		
890 s		$\nu_3\ (\mathrm{F_{1}u})\ \mathrm{ClF_6^+}$
	679 (0.5)	$\nu_1\ (\mathrm{A_{1}g})\ \mathrm{ClF_6^+}$
640 620 vs	618 (3.1)	$\nu_3\ (\mathrm{F_{1}u})\ \mathrm{PtF_6^-}$
	644 (10)	$\nu_1\ (\mathrm{A_{1}g})\ \mathrm{PtF_6^-}$
580 ms	569 (1.8)	$\nu_2\ (\mathrm{Eg})\ \mathrm{PtF_6^-}$
552 s	554 (2.5)	
516 s	518 (0.6)	$\nu_2\ (\mathrm{A_1})\ \mathrm{ClO_2^+},\ \nu_5\ (\mathrm{F_{2}g})\ \mathrm{ClF_6^+}$
	240 (4.5)	$\nu_5\ (\mathrm{F_{2}g})\ \mathrm{PtF_6^-}$
	185 (0.2)	$\nu_6\ (\mathrm{F_{2}u})\ \mathrm{PtF_6^-}$
	130 (0.1)	Lattice vib
	98 (1.0)	

$\mathrm{ClF_2^+, ClF_6^+PtF_6^-}$

Obsd freq, $\mathrm{cm^{-1}}$		Assignment for $\mathrm{ClF_2^+}$ in C_{2v}, for $\mathrm{ClF_6^+}$ and $\mathrm{PtF_6^-}$ in O_h
Ir	Raman	
1576 w		$\nu_1 + \nu_3\ (\mathrm{B_1})\ \mathrm{ClF_2^+}$
1564 w		$\nu_1 + \nu_3\ (\mathrm{F_{1}u})\ \mathrm{ClF_6^+}$
1510 w		$\nu_2 + \nu_3\ (\mathrm{F_{1}u + F_{2}u})\ \mathrm{ClF_6^+}$
1298 w		$\nu_3\ (\mathrm{B_1})\ \mathrm{ClO_2^+}$
1284		$\nu_1 + \nu_3\ (\mathrm{F_{1}u})\ \mathrm{PtF_6^-}$
1240 w		$\nu_2 + \nu_3\ (\mathrm{F_{1}u + F_{2}u})\ \mathrm{PtF_6^-}$
1216		$\nu_2 + \nu_4\ (\mathrm{F_{1}u + F_{2}u})\ \mathrm{ClF_6^+}$
1160 vw		$\nu_1 + \nu_2\ (\mathrm{A_1})\ \mathrm{ClF_2^+}$
890 vs		$\nu_3\ (\mathrm{F_{1}u})\ \mathrm{ClF_6^+}$
799 vs	799 (1.3)	$\nu_3\ (\mathrm{B_1})\ \mathrm{ClF_2^+}$
789 vs	788 (3.0)	$\nu_1\ (\mathrm{A_1})\ \mathrm{ClF_2^+}$
	784 (1)	
733 vw		$\nu_2 + \nu_6\ (\mathrm{F_{1}u + F_{2}u})\ \mathrm{PtF_6^-}$
	704 (0+)	
	679 (1.0)	$\nu_1\ (\mathrm{A_{1}g})\ \mathrm{ClF_6^+}$
655 vs, br	661 (0+)	$\nu_3\ (\mathrm{F_{1}u})\ \mathrm{PtF_6^-}$
	651 (2.5)	
	639 (10)	$\nu_1\ (\mathrm{A_{1}g})\ \mathrm{PtF_6^-}$
	630 sh	$\nu_2\ (\mathrm{Eg})\ \mathrm{ClF_6^+}$
585 s, br	582 576 (0.8)	$\nu_2\ (\mathrm{Eg})\ \mathrm{PtF_6^-}$
	561 (3.1)	
510 w, sh	513 (0.3)	$\nu_5\ (\mathrm{F_{2}g})\ \mathrm{ClF_6^+}$
478 w, sh		
381 s	381 (0.2)	$\nu_2\ (\mathrm{A_1})\ \mathrm{ClF_2^+}$
376 sh		
304 m	300 (0.3)	$\nu_4\ (\mathrm{F_{1}u})\ \mathrm{PtF_6^-}$
265 s	282 (0.2)	
	249 (3.2)	$\nu_5\ (\mathrm{F_{2}g})\ \mathrm{PtF_6^-}$
	236 sh	
	229 (2.5)	
	170 (0.3)	$\nu_6\ (\mathrm{F_{2}u})\ \mathrm{PtF_6^-}$
	101 (0.9)	Lattice vib
	72 (0.3)	
	54 (1.5)	
	42 (1.6)	
	26 (0.4)	

$\mathrm{ClF_2O^+PtF_6^-}$

Obsd freq, $\mathrm{cm^{-1}}$		Assignment for $\mathrm{ClF_2O^+}$ in C_s, for $\mathrm{PtF_6^-}$ in O_h
Ir	Raman	
1326 ms	1324 (0.6)	$\nu_1\ (\mathrm{A'})\ \mathrm{ClF_2O^+}$
1313 mw	1311 (0.2)	
737 s	737 (2.7)	$\nu_2\ (\mathrm{A'})\ \mathrm{ClF_2O^+}$
705 s	705 (0.8)	$\nu_5\ (\mathrm{A''})\ \mathrm{ClF_2O^+}$
643 vs	658 (4.2)	$\nu_3\ (\mathrm{F_{1}u})\ \mathrm{PtF_6^-}$
630 sh	630 (10)	$\nu_1\ (\mathrm{A_{1}g})\ \mathrm{PtF_6^-}$
564 s	575 sh	$\nu_2\ (\mathrm{Eg})\ \mathrm{PtF_6^-}$
	564 (2.9)	
508 s	506 (0.5)	$\nu_3\ (\mathrm{A'})\ \mathrm{ClF_2O^+}$
401 ms	401 (0.7)	$\nu_6\ (\mathrm{A''})\ \mathrm{ClF_2O^+}$
386 ms	386 (0.2)	$\nu_4\ (\mathrm{A'})\ \mathrm{ClF_2O^+}$
	280 (0.3)	$\nu_4\ (\mathrm{F_{1}u})\ \mathrm{PtF_6^-}$
	239 (7.9)	$\nu_5\ (\mathrm{F_{2}g})\ \mathrm{PtF_6^-}$
	140 (0.3)	Lattice vib
	115 (0.2)	
	58 (1.0)	

$\mathrm{ClF_4^+, ClF_6^+PtF_6^-}$

Obsd freq, $\mathrm{cm^{-1}}$	Assignment for $\mathrm{ClF_4^+}$ in C_{2v}, for $\mathrm{ClF_6^+}$ and $\mathrm{PtF_6^-}$ in O_h
Ir	
1560 w	$\nu_1 + \nu_3\ (\mathrm{F_{1}u})\ \mathrm{ClF_6^+}$
1515 w	$\nu_2 + \nu_3\ (\mathrm{F_{1}u + F_{2}u})\ \mathrm{ClF_6^+}$
1200 w, br	$\nu_2 + \nu_3\ (\mathrm{F_{1}u + F_{2}u})\ \mathrm{PtF_6^-}$
890 vs	$\nu_3\ (\mathrm{F_{1}u})\ \mathrm{ClF_6^+}$
878 sh	
785 vs	$\nu_8\ (\mathrm{B_2}),\ \nu_1\ (\mathrm{A_1}),\ \nu_6\ (\mathrm{B_1})\ \mathrm{ClF_4^+}$
720 vw	$\nu_2 + \nu_6\ (\mathrm{F_{1}u + F_{2}u})\ \mathrm{PtF_6^-}$
670 620 vs	$\nu_3\ (\mathrm{F_{1}u})\ \mathrm{PtF_6^-}$
580 ms	$\nu_2\ (\mathrm{Eg})\ \mathrm{PtF_6^-}$ $\nu_2\ (\mathrm{A_1})\ \mathrm{ClF_4^+}$ $\nu_7\ (\mathrm{B_1})\ \mathrm{ClF_4^+}$
572 mw	
551 sh	
545 s	
500 s	$\nu_3\ (\mathrm{A_1})\ \mathrm{ClF_4^+}$
383 s	$\nu_9\ (\mathrm{B_2})\ \mathrm{ClF_4^+}$
281 sh	$\nu_4\ (\mathrm{F_{1}u})\ \mathrm{PtF_6^-}$
271 s	

$\mathrm{ClO_2^+IrF_6^-}$

Obsd freq, $\mathrm{cm^{-1}}$		Assignment for $\mathrm{ClO_2^+}$ in C_{2v}, for $\mathrm{IrF_6^-}$ in O_h
Ir	Raman	
1300 vs	1301 (0.6)	$\nu_3\ (\mathrm{B_1})\ \mathrm{ClO_2^+}$
1286 s	1287 (0.2)	
1057 s	1057 (6.1)	$\nu_1\ (\mathrm{A_1})\ \mathrm{ClO_2^+}$
	670 (10)	$\nu_1\ (\mathrm{A_{1}g})\ \mathrm{IrF_6^-}$
640 vs, br	613 (0.9)	$\nu_3\ (\mathrm{F_{1}u})\ \mathrm{IrF_6^-}$
580 w	561 (2.5)	$\nu_2\ (\mathrm{E_g})\ \mathrm{IrF_6^-}$
548 s	549 (4.8)	
518 s	519 (1.1)	$\nu_2\ (\mathrm{A_1})\ \mathrm{ClO_2^+}$
279 m		$\nu_4\ (\mathrm{F_{1}u})\ \mathrm{IrF_6^-}$
258 s		
	248 (8.5)	$\nu_5\ (\mathrm{F_{2}g})\ \mathrm{IrF_6^-}$
	185 (0.3)	$\nu_6\ (\mathrm{F_{2}u})\ \mathrm{IrF_6^-}$

[a] Raman intensities are uncorrected.

Attempts to record the Raman spectrum of the $ClF_4^+PtF_6^-$-$ClF_6^+PtF_6^-$ mixture were unsuccessful owing to rapid sample decomposition by the laser beam. From a large number of experiments, those spectra and products were selected which showed the least amounts of by-products. Depending upon the exact reaction conditions, however, the products sometimes were more complex mixtures of ClO_2^+, $ClO_2F_2^+$, and ClF_6^+ or of ClF_2^+, ClF_4^+, and ClF_6^+. The observed frequencies are listed in Table I.

Since most products contain the PtF_6^- anion, its spectrum will be discussed first. The simplest spectrum is that of $NO^+PtF_6^-$. Our observed spectrum is in good agreement with that previously reported[16,23,24] for this compound. In addition to the reported bands, we have observed an infrared band at 268 cm^{-1}. The crystal structure of $O_2^+PtF_6^-$ (which is isomorphous with $NO^+PtF_6^-$ [16]) has been determined.[25] It was shown that PtF_6^- is approximately octahedral;[25] however, its site symmetry[26] is lower than O_h. This site symmetry lowering can cause splitting of most of the bands and violations of the selection rules expected for symmetry O_h. Since the crystal structures and, hence, the actual site symmetries of PtF_6^- in the other chlorine fluoride salts are unknown and since the observed splittings are relatively small, the assignments for PtF_6^- in Table I were made based on the group symmetry O_h. In addition to the previously assigned bands,[16,23,24] the antisymmetric deformation, ν_4 (F_{1u}), and the normally inactive ν_6 (F_{2u}) mode were observed at about 265 and 180 cm^{-1}, respectively. The spectrum observed for IrF_6^- is in good agreement with that of PtF_6^-. In addition to the previously reported[23] bands, the ν_4 and ν_6 modes were also observed for IrF_6^-.

The vibrational spectra of ClO_2^+,[27] $ClF_2O_2^+$,[4,28] ClF_2^+,[29,30] ClF_2O^+,[22,31,32] and ClF_4^+ [33] have been reported elsewhere. The assignments given in Table I are in excellent agreement with those previously given for these ions and, hence, require no further discussion. Assignments for ClF_6^+, whose identity and octahedral structure have been established beyond doubt by ^{19}F nmr spectroscopy,[3] were made on the basis of the following arguments. For octahedral ClF_6^+, we would expect ideally six normal modes of vibration which are classified as $A_{1g} + E_g + 2\ F_{1u} + F_{2g} + F_{2u}$. Of these, only the two F_{1u} modes will be infrared active, while only the A_{1g}, E_g, and F_{2g} modes will be Raman active, assuming no other solid-state effects such as site symmetry lowering or slight distortion of the octahedron. Three different salts containing $ClF_6^+PtF_6^-$ have been studied. In addition to ClF_6^+, they contain the ClO_2^+ or the ClF_2^+ or the ClF_4^+ cation. All three salts show a strong infrared absorption at 890 cm^{-1}. The frequency of this band is higher than that of any known ClF fundamental vibration and is assigned to the antisymmetric stretching vibration, ν_3 (F_{1u}) of ClF_6^+. This assignment is supported by the following observation. In all three salts, the 890-cm^{-1} band shows a pronounced shoulder at 877 cm^{-1}. The observed frequency difference of about 13 cm^{-1} is in good agreement with the ^{35}Cl-^{37}Cl isotopic shift value of 12.5 cm^{-1} computed for octahedral ClF_6^+, assuming 100% characteristic modes. Of the remaining unassigned bands, the second highest frequency belongs to a relatively intense Raman line at 679 cm^{-1}. Clearly, this line must be due to the totally symmetric stretching mode, ν_1 (A_{1g}). The Raman spectrum of ClF_2^+, $ClF_6^+PtF_6^-$ (trace d, Figure 2) shows a band at 513 cm^{-1}. It has the same frequency as the ClO_2^+ deformation mode but cannot be due to ClO_2^+ since there is no evidence for its more intense ν_1 (A_1) mode at about 1050 cm^{-1}. The 513-cm^{-1} band might be assigned to either ν_2 (E_g) or ν_5 (F_{2g}) of ClF_6^+.

Table II. Fundamental Vibrations of ClF_6^+ Compared to Those of Isoelectronic SF_6

ClF_6^+	SF_6 [a]	Assignment in point group O_h
679	769.4	ν_1 (A_{1g})
630	639.5	ν_2 (E_g)
890	947.9	ν_3 (F_{1u})
582	614.5	ν_4 (F_{1u})
513	522	ν_5 (F_{2g})

[a] Data from ref 35 and 36.

It has previously been shown that the vibrational spectra of ClO_2^+,[27] ClF_2O^+,[31] $ClF_2O_2^+$,[4,28] ClF_5,[34] and ClF_4^+ [33] closely resemble those of isoelectronic SO_2, SF_2O, SF_2O_2, SF_5^-, and SF_4, respectively. A similar relationship might be expected for the isoelectronic pair ClF_6^+-SF_6 (see Table II). Comparison with the vibrational spectrum of SF_6 [35,36] suggests that the 513-cm^{-1} band is due to ν_5 (F_{2g}). This is further supported by the absence of another band below 513 cm^{-1}, which might be assigned to this mode and by the observed combination bands in the infrared spectrum. Generally, octahedral species exhibit two relatively intense combination bands in the infrared spectrum due to $\nu_1 + \nu_3$ and $\nu_2 + \nu_3$. For ClF_6^+, two bands were observed at about 1560 and 1515 cm^{-1}, respectively. The 1560-cm^{-1} band represents $\nu_1 + \nu_3$ (computed frequency 1569 cm^{-1}). Assuming the 1515-cm^{-1} band to be due to $\nu_2 + \nu_3$, a value of 625 cm^{-1} can be assigned to ν_2. Inspection of trace d of Figure 2 reveals a shoulder at 630 cm^{-1}, which is assigned to ν_2 (E_g) of ClF_6^+. Since there is no indication in the infrared spectrum for a combination band at about 1400 cm^{-1} ($890 + 513 = 1403$ cm^{-1}), the 513-cm^{-1} Raman band is assigned to ν_5 (F_{2g}).

An alternate, although less probable, assignment is possible for ν_2 (E_g) of ClF_6^+. Trace d of Figure 2 exhibits two bands at 582 and 576 cm^{-1}, respectively. We prefer, however, to attribute both of them to ν_2 (E_g) of PtF_6^- since the ν_5 (F_{2g}) PtF_6^- bands also show additional splitting and since again no evidence for the corresponding $\nu_2 + \nu_3$ combination band can be found in the infrared spectrum at about 1470 cm^{-1}. Thus all the expected active modes have been assigned for ClF_6^+ except for the antisymmetric deformation, ν_4 (F_{1u}).

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This mode should be infrared active and, by comparison with SF_6, occur in the range 550-610 cm^{-1}. A frequency of 582 cm^{-1} is tentatively assigned to ν_4 on the basis of traces c, d, and e of Figure 1 and by comparison with the infrared spectrum of $ClF_2O^+PtF_6^-$.[22]

Force Constants. A modified valence force field was computed for ClF_6^+ in order to obtain a more quantitative understanding of its relative bond strength. Except for the F_{1u} block, all the symmetry force constants are unique. The F_{1u} block is underdetermined since only two frequency values are available for the determination of three force constants. A third frequency value for the F_{1u} block might be obtained from the ^{35}Cl-^{37}Cl isotopic shifts which would allow the computation of a general valence force field. Unfortunately, the isotopic shift for ν_3 could not be determined with sufficient accuracy. Consequently, the usefulness of mathematical constraints, such as minimizing or maximizing the value of one of the symmetry force constants, was tested for isoelectronic SF_6, for which a general valence force field has been reported.[37] It was found that the condition F_{44} = minimum[38] is the best approximation to the general valence force field, though it yields too high a value for F_{34}, due to appreciable coupling of the bonds.[39] It also results in a rather large negative value (−0.269 mdyn/Å) for the stretch-stretch interaction constant, f_{rr}', which is difficult to rationalize. Using the same condition for computing the force field of ClF_6^+, a comparable negative value (−0.297 mdyn/Å) was obtained for f_{rr}' of ClF_6^+. Since for SF_6 the GVFF value of f_{rr}' is essentially zero, we prefer for ClF_6^+ the condition $f_{rr}' = 0$. The resulting force field is listed in Table III and compared to the GVFF values of SF_6.[37] The force constant of greatest interest is the stretching force constant f_r. Its value is 4.7 mdyn/Å with a conservative uncertainty estimate of ±0.2 mdyn/Å considering the uncertainties in the frequency of ν_4 (F_{1u}) and in the approximating method used for the force constant computation. This value is comparable to those of ClF_2^+ (4.74 mdyn/Å[40]) and of the equatorial Cl-F bonds in ClF_4^+ (4.59 mdyn/Å[33]) but significantly higher than those of the remaining known chlorine fluorides. The high value of f_r in ClF_6^+ can be explained to some extent by the formal positive charge which generally increases the stretching force constant values. It also suggests strong covalent contributions to the bonding. The high f_r value is entirely consistent with the high stability observed for the ClF_6^+ salts and parallels the findings for the NF_4^+ salts.[6-9] In both cases, comparison with the isoelectronic molecules SF_6 and CF_4, respectively, suggested unusual stability, although it proved difficult actually to synthesize these salts. In particular, it appears that the synthesis of ClF_6^+ requires an unusually powerful oxidative fluorinating agent such as PtF_6.

Since ν_4 (F_{1u}) and ν_6 (F_{2u}) have been observed for both PtF_6^- and IrF_6^-, a modified valence force field was also computed for these two anions assuming octahedral symmetry and F_{44} = minimum. For PtF_6^- and IrF_6^-, this extremal condition is expected to give a force field close to that of a GVFF owing to the large mass of the central atoms and the resulting weak coupling. The frequencies used for the computation are listed in Table IV, together with the resulting force constants. The value of f_r of PtF_6^- (3.89 mdyn/Å) is intermediate between those of PtF_6 (4.46 mdyn/Å[41]) and PtF_6^{2-} (3.42 mdyn/Å[41]) as expected on the basis of the increasing formal negative charge.

Table III. Symmetry and Internal Force Constants (mdyn/Å) of ClF_6^+ Computed for a Modified Valence Force Field Assuming $f_{rr}' = 0$ and Using the Frequency Values of Table II[a]

	ClF_6^+	SF_6
F_{11}	5.161	6.626
F_{22}	4.443	4.578
F_{33}	4.682	5.256
F_{34}	0.726	0.885
F_{44}	0.955	1.035
F_{55}	0.736	0.763
f_r	4.682	5.258
f_{rr}	0.120	0.341
f_{rr}'	0	0.002
$f_{r\alpha} - f_{r\alpha}''$	0.363	0.443

[a] For comparison the GVFF values of SF_6 are also listed.

Table IV. Symmetry and Internal Force Constants (mdyn/Å) of PtF_6^- and IrF_6^- Computed for a Modified Valence Force Field Assuming F_{44} = Minimum

	PtF_6^- [a]	IrF_6^- [b]
F_{11}	4.613	5.025
F_{22}	3.573	3.510
F_{33}	3.870	3.861
F_{34}	0.100	0.101
F_{44}	0.308	0.307
F_{55}	0.161	0.172
F_{66}	0.181	0.192
f_r	3.894	3.940
f_{rr}	0.173	0.255
f_{rr}'	0.024	0.079
$f_{r\alpha} - f_{r\alpha}''$	0.050	0.051
$f_\alpha - f_{\alpha\alpha} - f_{\alpha\alpha}' + f_{\alpha\alpha}''$	0.171	0.182
$f_{\alpha\alpha} - f_{\alpha\alpha}' - f_{\alpha\alpha}'' + f_{\alpha\alpha}'''$	−0.010	−0.010

[a] Frequencies used: ν_1 642, ν_2 565, ν_3 640, ν_4 270, ν_5 240, ν_6 180 cm^{-1}. [b] Frequencies used: ν_1 670, ν_2 560, ν_3 640, ν_4 270, ν_5 248, ν_6 185 cm^{-1}.

Table V. Summary of Existing Binary Chlorine Fluorides (Nonexisting Species in Parentheses)

Cl_2F^+ [a]	ClF [b]	ClF_2^- [c]
ClF_2^+ [d]	ClF_3 [e]	ClF_4^- [f]
ClF_4^+ [g]	ClF_5 [h]	(ClF_6^-)[g]
ClF_6^+ [i]	(ClF_7)[i]	(ClF_8^-)

[a] K. O. Christe and W. Sawodny, *Inorg. Chem.*, 8, 212 (1969). [b] O. Ruff, E. Ascher, J. Fischer, and F. Laass, *Z. Anorg. Allg. Chem.*, **176**, 258 (1928). [c] K. O. Christe and J. P. Guertin, *Inorg. Chem.*, 4, 905 (1965). [d] J. W. Dale and D. A. MacLeod, private communication, 1950. [e] O. Ruff and H. Krug, *Z. Anorg. Allg. Chem.*, **190**, 270 (1930). [f] L. B. Asprey, J. L. Margrave, and M. E. Silverthorn, *J. Amer. Chem. Soc.*, 83, 2955 (1961). [g] K. O. Christe and D. Pilipovich, *Inorg. Chem.*, 8, 391 (1969). [h] W. Maya and H. F. Bauer, U. S. Patent 3,354,646 (1967). [i] F. Q. Roberto, *Inorg. Nucl. Chem. Lett.*, 8, 737 (1972); K. O. Christe, *ibid.*, 8, 741 (1972).

Summary. The successful synthesis of ClF_6^+ and the evidence for the nonexistence of a stable ClF_7 molecule and ClF_6^- anion[14] complete the series of possible binary chlorine fluoride molecules and ions. Table V summarizes the presently known species. The existence of ClF_6^+ suggests the possibility of preparing ClF_5O and efforts to synthesize this new oxyfluoride will be continued.

Registry No. PtF_6, 13693-05-5; $FClO_2$, 13637-83-7; ClF_5,

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13637-63-3; FNO, 7789-25-5; ClF_3O, 30708-80-6; IrF_6, 7783-75-7; $ClO_2^+PtF_6^-$, 38123-66-9; $ClO_2F_2^+PtF_6^-$, 36609-92-4; $ClF_6^+PtF_6^-$, 36609-91-3; $ClF_2^+PtF_6^-$, 38123-68-1; $ClF_4^+PtF_6^-$, 38123-69-2; $NO^+PtF_6^-$, 17250-51-0; $ClF_2O^+PtF_6^-$, 36544-28-2; $ClO_2^+IrF_6^-$, 38194-37-5; ClF_6^+, 38217-33-3; PtF_6^-, 38123-72-7; IrF_6^-, 22587-75-3.

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Halide-Ion Catalysis of the Bromate-Iodide Reaction in Dimethyl Sulfoxide-Water Solvents. Solvent Enhancement of Nucleophilicity

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The kinetics of the reaction $BrO_3^- + 9I^- + 6H^+ \rightarrow Br^- + 3I_3^- + 3H_2O$ have been measured spectrophotometrically in dimethyl sulfoxide (DMSO)-water solvents. The reaction is catalyzed by added chloride, bromide, and thiocyanate ions, leading to the observed rate law $d[I_3^-]/dt = [BrO_3^-][H^+]^2(k_I[I^-] + k_{Nu}[Nu])$. The mechanism proposed involves prior protonation of BrO_3^- followed by rate-determining attack by the nucleophilic anion on the $H_2BrO_3^+$ species. In 0.700-1.00 mole fraction of DMSO, the order of nucleophilic reactivity is $Cl^- > Br^- > I^-$ which represents an inversion in the order reported in water $I^- > Br^- > Cl^-$. The solvent influence is interpreted to suggest that nucleophilic substitution on $H_2BrO_3^+$ occurs at the harder bromine atom center, rather than at the softer, protonated-oxygen center.

The kinetics of the bromate-iodide reaction

$$BrO_3^- + 9I^- + 6H^+ \rightarrow Br^- + 3I_3^- + 3H_2O \quad (1)$$

and the accompanying ionic strength effects, have been studied thoroughly in aqueous solution.[1-4] Although several bromine intermediates must arise in the course of this reaction, they are apparently much more reactive than is bromate, thus permitting attention to be focused on the rate-determining step. Edwards[1] has made a significant contribution to the understanding of this reaction that has resulted in the mechanistic sketch shown in eq 2-5. Intermediates similar

$$BrO_3^- + 2H^+ \rightleftarrows H_2BrO_3^+ \quad (2)$$

$$I^- + H_2BrO_3^+ \rightarrow I\text{-}BrO_2 + H_2O \quad \text{(rate determining)} \quad (3)$$

$$I^- + H_2BrO_3^+ \rightarrow HOI + HBrO_2 \quad \text{(rate determining)} \quad (4)$$

$$I\text{-}BrO_2 + I^- \rightarrow I_2 + Br^{III} \quad \text{(fast)} \quad (5)$$

to $I\text{-}BrO_2$, with a halogen-halogen bond or a pseudo halogen-halogen bond, have been postulated by others.[5] However, other structures for the intermediate formed in the rate-determining step are possible. In their paper concerning carboxylate catalysis of the bromate-iodide reaction, Barton and Wright[3] have presented a thorough discussion of alternate structures for the transition state and intermediate involved in the rate-determining step.

The site of attack by iodide on the $H_2BrO_3^+$ species is an unresolved question. Attack on either the bromine atom or on a protonated oxygen is consistent with the rate law. Of these two acid centers, bromine would be regarded as the harder center and partially positive oxygen as the softer acid center.[6a] According to the HSAB principle,[6b] hard-base nucleophiles would prefer to react at the bromine center and soft-base nucleophiles at the oxygen center. Chloride and bromide are also oxidized by bromate and the relative rates of reaction for the three halide bases, *in water*, are $I^- > Br^- > Cl^-$. It has been suggested that this order of nucleophilicity may indicate attack on the softer oxygen center since iodide is the preferred nucleophile.[7]

The goal of the present study was to examine the rate of the bromate-iodide reaction in dimethyl sulfoxide (DMSO)-water solvents. In particular, since we had observed that this reaction is catalyzed by bromide and chloride ions,[8] our objective was to determine the order of halide ion nucleophilicity in DMSO-water and, thereby, to obtain information that bears on the question of attack at bromine *vs.* oxygen.

Experimental Section

Solvent and Reagents. All solutions were prepared from commercial grade DMSO (Van Waters and Rogers) and redistilled water as described earlier.[9] To minimize air oxidation of iodide, the pure solvents and the resulting mixtures were swept with prepurified nitrogen before use. B & A reagent grade potassium bromate, recrystallized from water and dried for 3 hr at 180°, was found to be 99.9% pure by iodometric analysis. B & A 60% reagent grade perchloric acid, diluted to 1 *M*, was used as the source of acid. Reagent grade potassium salts were used as received. Potassium perchlorate was used to maintain ionic strength at 0.121 *M*.

Stoichiometry. The stoichiometry of reaction 1 was verified in 0.500 mole fraction of DMSO. Spectrophotometric analysis indicated that 2.9 ± 0.1 mol of triiodide ion was produced per mole of bromate reacting. The amount of hydrogen ion consumed was deter-

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