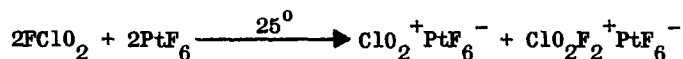


# THE HEXAFLUOROCHLORINE (VII) CATION, $\text{ClF}_6^+$

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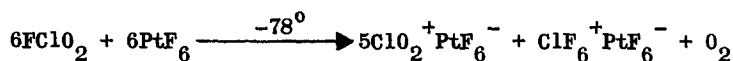
It was recently shown (1) by Christe that  $\text{PtF}_6$  can oxidatively fluorinate  $\text{FClO}_2$  to form the novel  $\text{ClO}_2\text{F}_2^+$  cation according to:



The infrared spectrum of the solid reaction product exhibited, in addition to the bands characteristic of the  $\text{ClO}_2\text{F}_2^+$ ,  $\text{ClO}_2^+$ , and  $\text{PtF}_6^-$  ions, a new band of medium intensity at  $890\text{ cm}^{-1}$ . This band could not be assigned to any known species. The yield of  $\text{ClO}_2\text{F}_2^+$  obtained from the  $\text{PtF}_6$  fluorination reaction at  $25^\circ$  was relatively low, owing to the following competing reaction:



In order to suppress this competing reaction, we have studied the  $\text{FClO}_2\text{-PtF}_6$  system at  $-78^\circ$ . When  $\text{PtF}_6$  was exposed for 48 hours to an excess of  $\text{FClO}_2$  at  $-78^\circ$ , the following unexpected reaction occurred:



The observed  $\text{FClO}_2\text{-PtF}_6$  combining ratio, weight gain, and  $\text{O}_2$  evolution deviated by less than 3% from those calculated for the above equation. The infrared spectrum of the solid reaction product showed  $\text{ClO}_2^+\text{PtF}_6^-$  as the

main product, a trace of  $\text{ClO}_2\text{F}_2^+$ , and a strong  $890\text{ cm}^{-1}$  absorption. The identity of the novel, stable species having an  $890\text{ cm}^{-1}$  infrared absorption as  $\text{ClF}_6^+$  was unambiguously established by  $^{19}\text{F}$  nmr and vibrational spectroscopy, and its reaction chemistry. The  $^{19}\text{F}$  nmr spectrum of the product dissolved in HF contains two sets of quadruplets at  $-391\text{ ppm}$  relative to  $\text{CFCl}_3$  (external standard). The observed splitting is due to chlorine-fluorine spin spin coupling and the two naturally occurring Cl isotopes. The coupling constants are  $J^{35}\text{ClF} = 337$  and  $J^{37}\text{ClF} = 281\text{ cps}$  and are the first reported examples of well resolved chlorine-fluorine spin spin coupling. The pronounced down-field shift and the ineffectiveness of chlorine quadrupole relaxation are convincing evidence for the presence of an octahedral  $\text{ClF}_6^+$  cation.

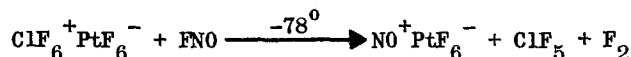
The vibrational spectrum of  $\text{ClF}_6^+$  is given in Table I and is compared to that of isoelectronic  $\text{SF}_6$  (2,3).

TABLE I  
Vibrational Spectrum of  $\text{ClF}_6^+$  and its Assignment

Frequency ( $\text{cm}^{-1}$ ), intensity				Assignment for
$\text{ClF}_6^+$		$\text{SF}_6$		Point Group $O_h$
IR	RA	IR	RA	
	679 vs		769 vs	$\nu_1 (\text{A}_{1g})$
	580 m		640 m	$\nu_2 (\text{E}_g)$
890 vs		948 vs		$\nu_3 (\text{F}_{1u})$
582 m		615 m		$\nu_4 (\text{F}_{1u})$
	513 m		522 m	$\nu_5 (\text{F}_{2g})$

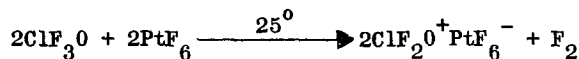
As can be seen, the observed spectrum closely resembles that of  $\text{SF}_6$  and confirms the octahedral structure of  $\text{ClF}_6^+$ . The  $890\text{ cm}^{-1}$  infrared band shows a  $^{35}\text{Cl}$ - $^{37}\text{Cl}$  isotopic splitting. The observed value of about  $13\text{ cm}^{-1}$  is in excellent agreement with the value of  $12.5\text{ cm}^{-1}$  computed for octahedral  $\text{ClF}_6^+$ , assuming 100% characteristic modes.

A displacement reaction between  $\text{ClF}_6^+ \text{PtF}_6^-$  and  $\text{FNO}$  was carried out under conditions similar to those which had successfully been used for the synthesis of  $\text{ClF}_3\text{O}_2$  from  $\text{ClO}_2\text{F}_2^+ \text{PtF}_6^-$  and  $\text{FNO}$  (4). Since  $\text{ClF}_6^+$  can be considered as a Lewis acid adduct of  $\text{ClF}_7$ , the products from the  $\text{FNO}$  displacement reaction should allow some conclusions concerning the stability of the hypothetical compound  $\text{ClF}_7$ . The following results were obtained for the displacement reaction:



This indicates that  $\text{ClF}_7$  under the given reaction conditions is unstable at temperatures as low as  $-78^\circ$  towards decomposition into  $\text{ClF}_5$  and  $\text{F}_2$ .

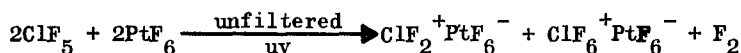
Both cations,  $\text{ClO}_2\text{F}_2^+$  (1) and  $\text{ClF}_6^+$ , are now well characterized. This suggested the possible synthesis of the intermediate  $\text{ClF}_4\text{O}^+$  cation from  $\text{ClF}_3\text{O}$  and  $\text{PtF}_6$ . At  $25^\circ$ , the main reaction was:



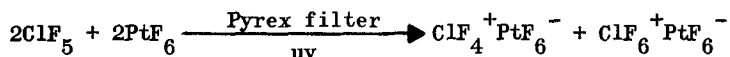
In addition, small amounts of  $\text{FClO}_2$  and  $\text{ClF}_5$  were observed among the volatile reaction products. When the reaction temperature was lowered to  $-45^\circ$ , the main products were again  $\text{ClF}_2\text{O}^+ \text{PtF}_6^-$  and  $\text{F}_2$ . However, small amounts of  $\text{ClO}_2\text{F}_2^+$  and  $\text{ClF}_6^+ \text{PtF}_6^-$  had also formed. No evidence for the presence of any  $\text{ClF}_4\text{O}^+$  could be obtained. This suggests that tetrahedral

$\text{ClF}_2\text{O}_2^+$  and octahedral  $\text{ClF}_6^+$  are more favorable products than the pseudo trigonal bipyramidal  $\text{ClF}_4\text{O}^+$ .

In the low-temperature reaction between  $\text{FClO}_2$  and  $\text{PtF}_6$ , the yield of  $\text{ClF}_6^+$  can be at best 1/6 based on  $\text{PtF}_6$ . Since Roberto had previously obtained (5) for the  $\text{ClF}_5$ - $\text{PtF}_6$  system a solid showing a strong  $890\text{ cm}^{-1}$  infrared absorption, we have also studied this system in order to increase the possible yield of  $\text{ClF}_6^+$  to 50% and to verify that the products from both systems contain the same species,  $\text{ClF}_6^+$ . Two reactions were carried out at  $25^\circ$  with uv irradiation. When unfiltered uv irradiation was used, the reaction was complete in several hours:



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



Since unfiltered uv light can decompose  $\text{ClF}_5$  into  $\text{ClF}_3 + \text{F}_2$  (6) and since  $\text{ClF}_2^+$  salts are more stable than  $\text{ClF}_4^+$  salts (7), the observed displacement of  $\text{ClF}_4^+$  by  $\text{ClF}_3$  is not surprising. The results from our vibrational spectroscopic study confirm that the products obtained from the reactions of  $\text{PtF}_6$  with either  $\text{FClO}_2$ ,  $\text{ClF}_3\text{O}$ , or  $\text{ClF}_5$  contain indeed the identical new species,  $\text{ClF}_6^+$ .

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