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THE HEXAFLUOROCHLORINE (VII) CATION, ClF_6^+

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It was recently shown (1) by Christe that PtF_6 can oxidatively fluorinate $FClO_2$ to form the novel $ClO_2F_2^+$ cation according to:

$$2FClO_2 + 2PtF_6 \xrightarrow{25^0} ClO_2^+PtF_6^- + ClO_2F_2^+PtF_6^-$$

The infrared spectrum of the solid reaction product exhibited, in addition to the bands characteristic of the $ClO_2F_2^+$, ClO_2^+, and PtF_6^- ions, a new band of medium intensity at 890 cm^{-1}. This band could not be assigned to any known species. The yield of $ClO_2F_2^+$ obtained from the PtF_6 fluorination reaction at 25^0 was relatively low, owing to the following competing reaction:

$$2FClO_2 + 2PtF_6 \longrightarrow 2ClO_2^+PtF_6^- + F_2$$

In order to suppress this competing reaction, we have studied the $FClO_2$-PtF_6 system at -78^0. When PtF_6 was exposed for 48 hours to an excess of $FClO_2$ at -78^0, the following unexpected reaction occurred:

$$6FClO_2 + 6PtF_6 \xrightarrow{-78^0} 5ClO_2^+PtF_6^- + ClF_6^+PtF_6^- + O_2$$

The observed $FClO_2$-PtF_6 combining ratio, weight gain, and O_2 evolution deviated by less than 3% from those calculated for the above equation. The infrared spectrum of the solid reaction product showed $ClO_2^+PtF_6^-$ as the main product, a trace of $ClO_2F_2^+$, and a strong 890 cm^{-1} absorption. The identity of the novel, stable species having an 890 cm^{-1} infrared absorption as ClF_6^+ was unambiguously established by ^{19}F nmr and vibrational spectroscopy, and its reaction chemistry. The ^{19}F nmr spectrum of the product dissolved in HF contains two sets of quadruplets at -391 ppm relative to $CFCl_3$ (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}ClF = 337 and J ^{37}ClF = 281 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 ClF_6^+ cation.

The vibrational spectrum of ClF_6^+ is given in Table I and is compared to that of isoelectronic SF_6 (2,3).

TABLE I

Vibrational Spectrum of ClF_6^+ and its Assignment

Frequency (cm^{-1}), intensity				Assignment for
ClF_6^+		SF_6		Point Group O_h
IR	RA	IR	RA	
	679 vs		769 vs	ν_1 (A_{1g})
	580 m		640 m	ν_2 (E_g)
890 vs		948 vs		ν_3 (F_{1u})
582 m		615 m		ν_4 (F_{1u})
	513 m		522 m	ν_5 (F_{2g})

As can be seen, the observed spectrum closely resembles that of SF_6 and confirms the octahedral structure of ClF_6^+. The 890 cm^{-1} infrared band shows a ^{35}Cl-^{37}Cl isotopic splitting. The observed value of about 13 cm^{-1} is in excellent agreement with the value of 12.5 cm^{-1} computed for octahedral ClF_6^+, assuming 100% characteristic modes.

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^+ can be considered as a Lewis acid adduct of ClF_7, the products from the FNO displacement reaction should allow some conclusions concerning the stability of the hypothetical compound ClF_7. The following results were obtained for the displacement reaction:

$$ClF_6^+PtF_6^- + FNO \xrightarrow{-78^0} NO^+PtF_6^- + ClF_5 + F_2$$

This indicates that ClF_7 under the given reaction conditions is unstable at temperatures as low as -78^0 towards decomposition into ClF_5 and F_2.

Both cations, $ClO_2F_2^+$ (1) and ClF_6^+, are now well characterized. This suggested the possible synthesis of the intermediate ClF_4O^+ cation from ClF_3O and PtF_6. At 25^0, the main reaction was:

$$2ClF_3O + 2PtF_6 \xrightarrow{25^0} 2ClF_2O^+PtF_6^- + F_2$$

In addition, small amounts of $FClO_2$ and ClF_5 were observed among the volatile reaction products. When the reaction temperature was lowered to -45^0, 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^+.

In the low-temperature reaction between $FClO_2$ and PtF_6, the yield of ClF_6^+ can be at best 1/6 based on PtF_6. Since Roberto had previously obtained (5) for the ClF_5-PtF_6 system a solid showing a strong 890 cm^{-1} infrared absorption, we have also studied this system in order to increase the possible yield of ClF_6^+ to 50% and to verify that the products from both systems contain the same species, ClF_6^+. Two reactions were carried out at 25° with uv irradiation. When unfiltered uv irradiation was used, the reaction was complete in several hours:

$$2ClF_5 + 2PtF_6 \xrightarrow[uv]{unfiltered} ClF_2^+PtF_6^- + ClF_6^+PtF_6^- + F_2$$

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

$$2ClF_5 + 2PtF_6 \xrightarrow[uv]{Pyrex\ filter} ClF_4^+PtF_6^- + ClF_6^+PtF_6^-$$

Since unfiltered uv light can decompose ClF_5 into $ClF_3 + F_2$ (6) and since ClF_2^+ salts are more stable than ClF_4^+ salts (7), the observed displacement of ClF_4^+ by ClF_3 is not surprising. The results from our vibrational spectroscopic study confirm that the products obtained from the reactions of PtF_6 with either $FClO_2$, ClF_3O, or ClF_5 contain indeed the identical new species, ClF_6^+.

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