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# The Difluoroperchloryl Cation, $ClO_2F_2^+$

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The reaction of $FClO_2$ with $PtF_6$ yields a product containing $ClO_2F_2^+PtF_6^-$. A synthetic method is described that converts this salt into $ClO_2F_2^+BF_4^-$ or $ClO_2F_2^+AsF_6^-$. All three salts are stable at 25° and according to their infrared, Raman, and $^{19}F$ nmr spectra are ionic in both the solid state and HF solution. The vibrational spectrum of $ClO_2F_2^+$ closely resembles that of isoelectronic $SO_2F_2$, suggesting a pseudotetrahedral structure of symmetry $C_{2v}$. A modified valence force is reported for $ClO_2F_2^+$.

## Introduction

A preliminary note on the existence of $ClO_2F_2^+PtF_6^-$ has recently been published by Christe. This salt was prepared from $FClO_2$ and $PtF_6$.[1] A detailed report on this interesting system, yielding under different reaction conditions $ClF_6^+PtF_6^-$, has been given elsewhere.[2] A $^{19}F$ nmr chemical shift of −310 ppm relative to external $CFCl_3$ has been tentatively assigned to $ClO_2F_2^+$.[3] A more complete characterization of the $ClO_2F_2^+$ cation in the original $PtF_6^-$ salt, however, was preempted by interference from the $PtF_6^-$ anion and from substantial amounts of by-products such as $ClO_2^+PtF_6^-$. Consequently, efforts were made to prepare $ClO_2F_2^+$ salts containing different anions and to eliminate the undesirable by-products. We have now succeeded in preparing $ClO_2F_2^+BF_4^-$ and $ClO_2F_2^+AsF_6^-$ and in more fully characterizing the $ClO_2F_2^+$ cation. These results are described below.

## Experimental Section

**Apparatus and Materials.** The stainless steel–Teflon-FEP vacuum system, the glove box, the infrared, Raman, and $^{19}F$ nmr spectrometers and sampling techniques, and the syntheses and purification of $PtF_6$, $AsF_5$, and $FClO_2$ have been described elsewhere.[2,3] Nitryl fluoride, prepared from $N_2O_4$ and $F_2$, and $BF_3$ (from The Matheson Co.) were purified by fractional condensation. Debye–Scherrer X-ray diffraction powder patterns were taken as previously described.[4]

**Syntheses of $ClO_2F_2^+$ Salts.** The synthesis of $ClO_2F_2^+PtF_6^-$ has been described elsewhere.[2] For the synthesis of $ClO_2F_2^+BF_4^-$, a mixture of $ClO_2F_2^+PtF_6^-$ (4.8 mmol) and $ClO_2^+PtF_6^-$ (12.2 mmol) was treated in a passivated (with $ClF_3$ and $BrF_5$) 75-ml stainless steel cylinder with $FNO_2$ (25.3 mmol) at −78° for 48 hr. The reaction products volatile at 25° consisted of $FClO_2$, $ClF_3O_2$, and unreacted $FNO_2$ and were separated by fractional condensation through a series of traps kept at −112, −126, −142, and −196°. The −126° fraction contained most of the $ClF_3O_2$ and some $FClO_2$. Attempts to separate further the $ClF_3O_2$ and $FClO_2$ mixture by fractional condensation were unsuccessful. Consequently, 2.76 mmol of this mixture was combined with $BF_3$ (3.00 mmol) at −196° in a passivated Teflon-FEP ampoule and the temperature was cycled several times between −196 and +25°. The product was kept at −78° for several hours and unreacted $BF_3$ (0.22 mmol) was removed at this temperature *in vacuo*. Removal of volatile material *in vacuo* was continued at 20°. The volatile material (2.60 mmol) consisted according to its infrared spectrum of a 1:1 mixture of $FClO_2$ and $BF_3$. The white, solid, nonvolatile residue (280 mg, 1.46 mmol) was identified by infrared, Raman, and $^{19}F$ nmr spectroscopy as $ClO_2F_2^+BF_4^-$.

For the preparation of the $AsF_6^-$ salt, $ClO_2F_2^+BF_4^-$ (0.62 mmol) and $AsF_5$ (1.43 mmol) were combined at −196° in a passivated Teflon-FEP ampoule. The contents of the ampoule were kept at −78° for 30 min and at 25° for 1 hr. Volatile products were removed at 25° and consisted of unreacted $AsF_5$ (0.79 mmol) and $BF_3$ (0.59 mmol). The white, stable solid weighed 185 mg (weight calculated for 0.62 mmol of $ClO_2F_2^+AsF_6^-$ is 183 mg) and was identified as $ClO_2F_2^+AsF_6^-$ by infrared, Raman, and $^{19}F$ nmr spectroscopy.

## Results and Discussion

**Syntheses and Properties of $ClO_2F_2^+$ Salts.** The synthesis of $ClO_2F_2^+PtF_6^-$ from $FClO_2$ and $PtF_6$ and its temperature dependence have been discussed elsewhere.[1,2] Since the $PtF_6^-$ anion interfered with the vibrational spectroscopic studies of $ClO_2F_2^+$, the $BF_4^-$ and $AsF_6^-$ salts were prepared according to the reaction

$$ClO_2^+PtF_6^- + ClO_2F_2^+PtF_6^- + FNO_2 \rightarrow FClO_2 + ClF_3O_2 + 2NO_2^+PtF_6^-$$

Unreacted $FNO_2$ and some of the $FClO_2$ could be separated from $ClF_3O_2$ by fractional condensation. The remaining $FClO_2$ was separated from $ClF_3O_2$ by complexing with $BF_3$. Since the resulting $ClO_2^+BF_4^-$ has a dissociation pressure[5] of 182 mm at 22.1° while $ClO_2F_2^+BF_4^-$ is stable, the former salt could be readily removed by pumping at 20°. Conversion of $ClO_2F_2^+BF_4^-$ to the corresponding $AsF_6^-$ salt was accomplished through displacement of $BF_4^-$ by the stronger Lewis acid $AsF_5$.

All three salts, $ClO_2F_2^+PtF_6^-$, $ClO_2F_2^+AsF_6^-$, and $ClO_2F_2^+BF_4^-$, are solids, stable at 25°, and react violently with water or organic materials. The $PtF_6^-$ compound is canary yellow, while those of $AsF_6^-$ and $BF_4^-$ are white. The salts dissolve in anhydrous HF without decomposing. They are crystallinic in the solid state and the X-ray powder diffraction patterns of $ClF_2O_2^+BF_4^-$ and $ClO_2F_2^+AsF_6^-$ are listed in Table I. The powder pattern of $ClO_2F_2^+BF_4^-$ is much simpler than that of $ClO_2F_2^+AsF_6^-$. This is not surprising since the anion and cation in the former salt are both of approximately tetrahedral shape and of similar size. The powder pattern of $ClO_2F_2^+BF_4^-$ can be indexed on the basis of an orthorhombic unit cell with $a = 5.45$, $b = 7.23$, and $c = 13.00$ Å. Assuming four molecules per unit cell and neglecting contributions from the highly charged central atoms to the volume,[6,7] a plausible average volume of 16 Å$^3$ per F or O atom is obtained. However, the agreement between the observed and calculated reflections is somewhat poor for several lines and, hence, the above unit cell dimensions are tentative.

The thermal stability of $ClO_2F_2^+BF_4^-$ is higher than those of $ClO_2^+BF_4^-$,[5] $ClF_2^+BF_4^-$,[8] or other similar salts. This is in good agreement with the previously made correlations[9] between the stability of an adduct and the structure of the

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(1) K. O. Christe, *Inorg. Nucl. Chem. Lett.*, **8**, 453 (1972).

(2) K. O. Christe, *Inorg. Chem.*, in press.

(3) K. O. Christe, J. F. Hon, and D. Pilipovich, *Inorg. Chem.*, **12**, 84 (1973).

(4) K. O. Christe and D. Naumann, *Inorg. Chem.*, **12**, 59 (1973).

(5) K. O. Christe, C. J. Schack, D. Pilipovich, and W. Sawodny, *Inorg. Chem.*, **8**, 2489 (1969).

(6) W. H. Zachariasen, *J. Amer. Chem. Soc.*, **70**, 2147 (1948).

(7) F. H. Ellinger and W. H. Zachariasen, *J. Phys. Chem.*, **58**, 405 (1954).

(8) H. Selig and J. Shamir, *Inorg. Chem.*, **3**, 294 (1964).

(9) K. O. Christe, C. J. Schack, and D. Pilipovich, *Inorg. Chem.*, **11**, 2205 (1972).

**Table I.** X-Ray Powder Patterns for $ClO_2F_2^+BF_4^-$ and $ClO_2F_2^+AsF_6^-$

| $ClO_2F_2^+BF_4^-$ | | $ClO_2F_2^+AsF_6^-$ | | | |
|---|---|---|---|---|---|
| d, Å | Intens | d, Å | Intens | d, Å | Intens |
| 5.47 | s | 7.49 | w | 2.12 | w |
| 5.06 | m | 5.50 | ms | 2.01 | w |
| 4.37 | ms | 4.98 | w | 1.94 | mw |
| 4.15 | w | 4.35 | ms | 1.90 | mw |
| 3.70 | vs | 4.02 | w | 1.86 | w |
| 3.56 | s | 3.86 | s | 1.80 | w |
| 3.00 | m | 3.70 | w | 1.76 | mw |
| 2.77 | m | 3.57 | m | 1.72 | w |
| 2.57 | vw | 3.40 | mw | 1.70 | mw |
| 2.41 | m | 3.02 | mw | 1.65 | w |
| 2.18 | s | 2.77 | m | 1.62 | w |
| 2.08 | s | 2.69 | m | 1.59 | w |
| 1.86 | ms | 2.60 | w | 1.54 | w |
| 1.80 | w | 2.41 | w | 1.50 | w |
| | | 2.30 | w | 1.41 | w |
| | | 2.20 | w | 1.37 | w |
| | | | | 1.34 | w |

parent molecule and its ions. Thus, tetrahedral $ClO_2F_2^+$ (see below) should be energetically much more favorable than trigonal-bipyramidal $ClF_3O_2$.[10,11]

**$^{19}F$ Nmr Spectra.** A broad singlet at −310 ppm relative to external $CFCl_3$ has previously been observed for $ClO_2F_2^+PtF_6^-$ at low concentration in anhydrous HF and was tentatively assigned to $ClO_2F_2^+$.[3] This tentative assignment is confirmed by the present study. The spectrum of $ClF_2O_2^+BF_4^-$ in HF shows a strong temperature dependence. At 30° it consists of a single peak at 185 ppm relative to external $CFCl_3$. With decreasing temperature the peak at first becomes broader and then separates at about 0° into three signals at −301 ($ClO_2F_2^+$), 146 ($BF_4^-$),[12] and 194 ppm (HF) which become narrower with further decrease in temperature. The observed peak area ratio of approximately 2:1 for the 146 and −301 ppm signals confirms their assignment to $BF_4^-$ and $ClO_2F_2^+$, respectively, and proves the ionic nature of the $ClF_3O_2 \cdot BF_3$ adduct in HF solution.

The spectrum of $ClF_2O_2^+AsF_6^-$ in HF (which was acidified with $AsF_5$)[3] consists of two resonances at −307 ($ClO_2F_2^+$) and 105 ppm (HF, $AsF_5$, $AsF_6^-$),[3] respectively. Rapid exchange among HF, $AsF_5$, and $AsF_6^-$ preempted the measurement of the $ClO_2F_2^+$ to $AsF_6^-$ peak area ratio.

**Vibrational Spectra.** Figure 1 shows the infrared and Raman spectra of solid $ClO_2F_2^+BF_4^-$ and the Raman spectrum of an HF solution of $ClO_2F_2^+BF_4^-$. Figure 2 depicts the infrared and Raman spectra of solid $ClO_2F_2^+AsF_6^-$. Figure 3 shows the infrared spectrum of a mixture of solid $ClO_2F_2^+PtF_6^-$ and $ClO_2^+PtF_6^-$. The observed frequencies are listed in Table II and are compared with those reported for isoelectronic $SO_2F_2$.[12]

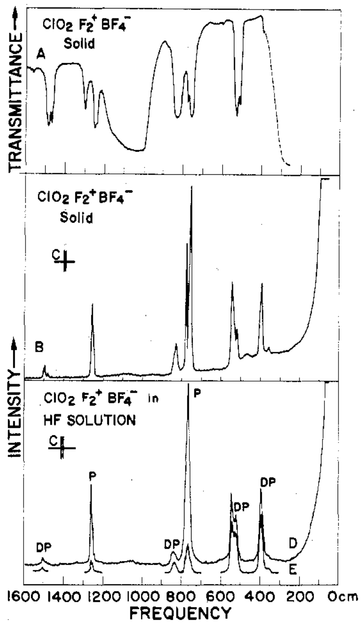

**Figure 1.** Vibrational spectra of $ClO_2F_2^+BF_4^-$: A, infrared spectrum of the solid as a AgCl disk; B, Raman spectrum of the solid; D and E, Raman spectrum of the HF solution, incident polarization perpendicular and parallel, respectively; exciting line is 4880-Å and C indicates spectral slit width.

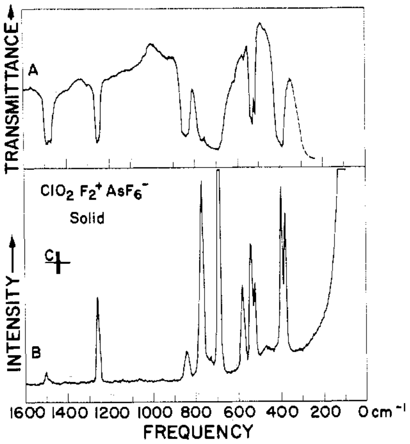

**Figure 2.** Vibrational spectra of solid $ClO_2F_2^+AsF_6^-$: A, infrared spectrum (AgCl disk); B, Raman spectrum; exciting line 4880 Å.

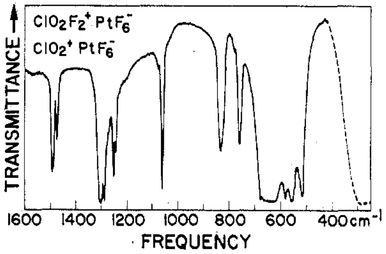

**Figure 3.** Infrared spectrum of a mixture of solid $ClO_2F_2^+PtF_6^-$ and $ClO_2^+PtF_6^-$ as a AgCl disk.

Inspection of Figures 1-3 and of Table II reveals that the spectra of $ClF_3O_2 \cdot BF_3$, $ClF_3O_2 \cdot AsF_5$, and $ClF_3O_2 \cdot PtF_5$ contain the bands characteristic for $BF_4^-$,[13-16] $AsF_6^-$,[16-19] and $PtF_6^-$,[2,20] respectively. Furthermore, the Raman spectra of $ClF_3O_2 \cdot BF_3$ are practically identical for both the solid and its HF solution. These observations, together with the $^{19}F$ nmr spectrum of the $BF_3$ adduct in HF solution, establish

(10) K. O. Christe, *Inorg. Nucl. Chem. Lett.*, **8**, 457 (1972).

(11) E. L. Muetterties and W. D. Phillips, *J. Amer. Chem. Soc.*, 81, 1084 (1959).

(12) D. R. Lide, Jr., D. E. Mann, and J. J. Comeford, *Spectrochim. Acta*, 21, 497 (1965).

(13) J. Goubeau and W. Bues, *Z. Anorg. Allg. Chem.*, **268**, 221 (1952).

(14) N. N. Greenwood, *J. Chem. Soc.*, 3811 (1959).

(15) H. A. Bonadeo and E. Silberman, *Spectrochim. Acta, Part A*, 26, 2337 (1970).

(16) K. O. Christe, E. C. Curtis, and C. J. Schack, *Inorg. Chem.*, 11, 2212 (1972).

(17) K. O. Christe and W. Sawodny, *Inorg. Chem.*, **6**, 313 (1967).

(18) K. O. Christe, J. P. Guertin, A. E. Pavlath, and W. Sawodny, *Inorg. Chem.*, 6, 533 (1967).

(19) K. O. Christe, C. J. Schack, D. Pilipovich, and W. Sawodny, *Inorg. Chem.*, **8**, 2489 (1969).

(20) N. Bartlett, *Angew. Chem., Int. Ed. Engl.*, 7, 433 (1968); N. Bartlett and S. P. Beaton, *Chem. Commun.*, 167 (1966); F. O. Sladky, P. A. Bulliner, and N. Bartlett, *J. Chem. Soc. A*, 2179 (1969).

**Table II.** Raman and Infrared Vibrational Spectra of $ClO_2F_2^+$ Salts Compared to Those of $SO_2F_2$

| Obsd freq, cm$^{-1}$, and rel intens[a] | | | | | | | | | | Assignment (point group) | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $SO_2F_2$ | | | $ClO_2F_2^+BF_4^-$ | | | $ClO_2F_2^+AsF_6^-$ | | $ClO_2F_2^+PtF_6^-$ + $ClO_2^+PtF_6^-$ | | | | | |
| R[b] | | Ir[c] | R | | | | | | | $XO_2F_2$ ($C_{2v}$) | $YF_6^-$ ($O_h$)[d] | $BF_4^-$ ($T_d$) | $ClO_2^+$ ($C_{2v}$) |
| Gas | Liquid | Gas | HF soln | Solid | Ir | R | Ir | R | Ir | | | | |
| | | | | | | | | | 2340 } w | | | | $\nu_1 + \nu_3$ ($B_1$) |
| | | | | | | | | | 2320 } | | | | |
| | | | | | | | | | 2115 vw | | | | $2\nu_1$ ($A_1$) |
| 1502 | 1497 (1) dp | 1502 vs | 1495 (0.3) dp | 1485 (0.6) | 1485 } s | 1492 (0.25) | 1489 } s | | 1486 } s | $\nu_6$ ($B_1$) | | | |
| | | | | 1469 (0.2) | 1469 } | | 1473 } | | 1470 } | | | | |
| | | | | | 1295 m | | | | | | | $\nu_1 + \nu_4$ ($F_2$) | |
| | | | | | | | | 1299 (0.5) } | 1297 vs } | | | | |
| | | | | | | | | 1285 (0.17) } | 1283 s } | | | | $\nu_3$ ($B_1$) |
| 1270 vs | 1263 (7) p | 1269 vs | 1252 (4.4) } p | 1245 (3.9) } | 1245 } s | 1252 } (1.9) | 1250 } s | 1246 (0+) | 1245 } s | $\nu_1$ ($A_1$) | | | |
| | | | 1244 (1.5) } | 1237 (1.3) } | 1237 } | 1244 } | 1242 } | | 1237 } | | | | |
| | | | | | | | | 1051 (2.7) | 1052 s } | | | | $\nu_1$ ($A_1$) |
| | | | | | | | | | 1047 m } | | | | |
| | | | 1050 (0+) br | 1050 (0+), br | 990–1150 vs, br | | | | | | | $\nu_3$($F_2$) | |
| 883 | 887 (1) | 885 vs | 834 (0.7) dp | 823 (1.6) | 824 s | 834 (0.6) | 832 s | | 827 s | $\nu_8$ ($B_2$) | | | |
| | | | 771 sh, p | 772 (6.3) | 772 w | | | | | | | $\nu_1$ ($A_1$) | |
| 847 vs | 846 (10) p | 848 vs | 761 (10) p | 753 (10) | 754 s | 761 (4.5) | 759 s | 754 (0.1) | 756 s | $\nu_2$ ($A_1$) | | | |
| | | | | | | | 700 vs, br | 617 (2.5) | 640 vs, br | | $\nu_3$ ($F_{1u}$) | | |
| | | | | | | 683 (10) | | 642 (10) | | | $\nu_1$ ($A_{1g}$) | | |
| | | | | | | | | 564 (1.3) } | 580 w } | | $\nu_2$ ($E_g$) | | |
| | | | | | | 573 (1.9) | 564 w | 552 (1.8) } | 552 s } | | | | |
| 543 vbr | 547 (6) dp | 552.8 } s | 538 (3.8) } dp | 534 (4.7) } | 534 sh } | 534 (2.9) } | 534 sh } | | 532 w | $\nu_7$ ($B_1$) | | | |
| | | 544.3 } | 533 sh } | 530 sh } | 529 s } | 528 sh } | 527 s } | 514 (0.4) | 514 s | $\nu_3$ ($A_1$) | | $\nu_4$ ($F_2$) | $\nu_2$ ($A_1$) |
| | | 539.4 } | 517 (1.6) } | 515 (1.5) } | 516 w } | 514 (1) } | 514 m } | | | $\nu_9$ ($B_2$) | | | |
| | | | | 394 sh | | | | | | | | | |
| 388 vbr | 389 (4) dp | 384.5 w | 388 (4.0) dp | 387 (3.9) | 395 w | 390 (3.8) | 395 sh | | | { $\nu_4$ ($A_1$)<br>{ $\nu_5$ ($A_2$) | | | |
| | | | | | | | 385 vs | | 284 m } | | $\nu_4$ ($F_{1u}$) | | |
| | | | | | | | | | 265 s } | | | | |
| | | | | | | 373 (3) | | | 239 (2.9) | | $\nu_5$ ($F_{2g}$) | | |
| | | | 355 sh | 355 (0.3) | | | | | | | | $\nu_2$ (E) | |
| | | | | | | | | | 180 (0+) | | $\nu_6$ ($F_{2u}$) | | |

[a] Uncorrected Raman intensities. [b] P. Bender and J. M. Wood, Jr., *J. Chem. Phys.*, **23**, 1316 (1955). [c] D. R. Lide, Jr., D. E. Mann, and J. J. Comeford, *Spectrochim. Acta*, **21**, 497 (1965); G. R. Hunt and M. K. Wilson, *ibid.*, 16, 570 (1960). [d] Assignments for $PtF_6^-$ are made for simplicity on the basis of point group $O_h$ though the site symmetry of $PtF_6^-$ is lower than $O_h$: K. O. Christe, *Inorg. Chem.*, in press.

**Table III.** Observed Frequencies (cm$^{-1}$), Approximate Description of Modes, Computed Symmetry, and Most Important Internal Force Constants of $ClO_2F_2^+$ [a]

| | | | | | ∠OClO, ∠FClF, deg | | | | | Obsd isotopic shifts |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | 124, 96 (I) | 114, 105 (II) | 109, 109 (III) | 124, 96 (IV) | 114, 105 (V) | |
| $A_1$ | $\nu_1$ | 1241 | $\nu_{sym}(ClO_2)$ | $F_{11} = f_D + f_{DD}$ | 11.33 [9.2] | 10.66 [10.7] | 10.12 [12.4] | 11.74 [8.0] | 11.38 [8.5] | 7.5–8.5 |
| | | | | $F_{12} = 2f_{DR}$ | | | | 0.50 | 1.00 | |
| | $\nu_2$ | 756 | $\nu_{sym}(ClF_2)$ | $F_{22} = f_R + f_{RR}$ | 4.28 [5.4] | 4.85 [3.4] | 4.83 [3.5] | 4.08 [6.4] | 4.56 [4.9] | ~5 |
| | $\nu_3$ | 514 | $\delta_{sym}(ClO_2)$ | $F_{33} = 0.56f_\alpha + 0.06f_\beta + 0.38f_\gamma - 0.72f_{\alpha\beta} + 0.06\cdot(f_{\beta\beta} + f_{\beta\beta}' + f_{\beta\beta}'') + 0.59f_{\beta\gamma} - 0.93f_{\alpha\gamma}$[c] | 1.62 [0.6] | 1.85 [0.2] | 1.79 [1.6] | 1.64 [0.4] | 1.86 [0.1] | |
| | | | | $F_{34} = 0.32f_\alpha + 0.13f_\beta - 0.45f_\gamma - 1.01f_{\alpha\beta} + 0.13\cdot(f_{\beta\beta} + f_{\beta\beta}' + f_{\beta\beta}'') + 0.31f_{\beta\gamma} + 0.28f_{\alpha\gamma}$ | (0)[b] | (0)[b] | (0)[b] | (0)[b] | (0)[b] | |
| | $\nu_4$ | 390 | $\delta_{sym}(ClF_2)$ | $F_{44} = 0.18f_\alpha + 0.29f_\beta + 0.52f_\gamma - 0.91f_{\alpha\beta} + 0.29\cdot(f_{\beta\beta} + f_{\beta\beta}' + f_{\beta\beta}'') - 1.56f_{\beta\gamma} + 0.63f_{\alpha\gamma}$ | 1.29 [1.0] | 1.06 [1.9] | 1.16 [0.1] | 1.29 [1.0] | 1.07 [1.8] | |
| $A_2$ | $\nu_5$ | 390 | $\tau$ | $F_{55} = f_\beta - f_{\beta\beta} - f_{\beta\beta}' + f_{\beta\beta}''$ | 1.16 | 1.16 | 1.16 | 1.16 | 1.16 | |
| $B_1$ | $\nu_6$ | 1479 | $\nu_{asym}(ClO_2)$ | $F_{66} = f_D - f_{DD}$ | 11.48 [18.7] | 11.98 [17.9] | 12.25 [17.5] | 12.66 [16.2] | 12.70 [16.4] | 15.9–16.7 |
| | | | | $F_{67} = \sqrt{2}(f_{D\beta} - f_{D\beta}')$ | (0)[b] | (0)[b] | (0)[b] | 1.00 | 0.60 | |
| | $\nu_7$ | 530 | $\delta_{rock}(ClO_2)$ | $F_{77} = f_\beta + f_{\beta\beta} - f_{\beta\beta}' - f_{\beta\beta}''$ | 1.61 [2.7] | 1.78 [3.3] | 1.89 [4.5] | 1.54 [3.6] | 1.71 [3.8] | |
| $B_2$ | $\nu_8$ | 830 | $\nu_{asym}(ClF_2)$ | $F_{88} = f_R - f_{RR}$ | 4.71 [10.9] | 4.50 [11.5] | 4.43 [11.7] | 4.71 [10.9] | 4.50 [11.5] | ~11 |
| | | | | $F_{89} = \sqrt{2}(f_{R\beta} - f_{R\beta}')$ | (0.5)[b] | (0.5)[b] | (0.5)[b] | (0.5)[b] | (0.5)[b] | |
| | $\nu_9$ | 514 | $\delta_{rock}(ClF_2)$ | $F_{99} = f_\beta - f_{\beta\beta} + f_{\beta\beta}' - f_{\beta\beta}''$ | 2.01 [2.5] | 1.72 [2.2] | 1.61 [2.1] | 2.01 [2.5] | 1.72 [2.2] | |
| | | | | $f_D$ | 11.41 | 11.32 | 11.19 | 12.20 | 12.04 | |
| | | | | $f_{DD}$ | −0.08 | −0.66 | −1.07 | −0.46 | −0.66 | |
| | | | | $f_R$ | 4.50 | 4.68 | 4.63 | 4.40 | 4.53 | |
| | | | | $f_{RR}$ | −0.21 | 0.17 | 0.20 | −0.32 | 0.03 | |

[a] Stretching constants in mdyn/Å, deformation constants in mdyn Å/radian$^2$, and stretch–bend interaction constants in mdyn/radian. Values listed in brackets are the computed $^{35}Cl$–$^{37}Cl$ isotopic shifts (cm$^{-1}$). Symmetry force constants not shown were assumed to be zero. $f_{\beta\beta}$, $f_{\beta\beta}'$, and $f_{\beta\beta}''$ refer to the interactions between the deformations of two angles having a common oxygen atom, a common fluorine atom, and no common oxygen or fluorine atom, respectively. [b] Assumed valucs. [c] The numerical coefficients in the $F$ matrix are based on the 124 and 96° bond angle geometry.

that these adducts are ionic and contain the $ClO_2F_2^+$ cation. The assignments for the anions are well established and are summarized in Table II. Consequently, only the assignments for $ClO_2F_2^+$ will be discussed in more detail. The $ClO_2F_2^+$ cation is isoelectronic with $SO_2F_2$ which was shown by microwave spectroscopy to possess symmetry $C_{2v}$.[21] The $SO_2F_2$ structure can be derived from a tetrahedron with two oxygen and two fluorine ligands occupying the corners and with the O=S=O angle increased to 123° 58′ and the F–S–F angle compressed to 96° 7′. Comparison of the bands due to $ClO_2F_2^+$ with those previously reported[12,22,23] for $SO_2F_2$ (see Table II) reveals a pronounced similarity indicating closely related structures and bonding. Therefore, assignments for $ClO_2F_2^+$ were made by analogy with those of $SO_2F_2$ which were reliably established by infrared,[23] Raman,[22] matrix-isolation,[12] and microwave[12] studies. The analogy appears to include the triple and double coincidences among $\nu_7$ ($B_1$), $\nu_3$ ($A_1$), and $\nu_9$ ($B_2$) at about 530 cm$^{-1}$ and between $\nu_4$ ($A_1$) and $\nu_5$ ($A_2$) at about 390 cm$^{-1}$, respectively. As for $SO_2F_2$,[12] only tentative assignments to the individual modes can be made for the bands observed in the 520-cm$^{-1}$ region.

The close analogy between the vibrational spectra of isoelectronic $ClO_2F_2^+$ and $SO_2F_2$ parallels those found for the isoelectronic pairs $ClF_2O^+$-$SF_2O$,[16] $ClF_6^+$-$SF_6$,[2] $ClF_5$-$SF_5^-$,[24] and $ClF_4^+$-$SF_4$.[25] It demonstrates the usefulness of knowing the vibrational spectra of the corresponding sulfur compounds for predicting and assigning those of the isoelectronic chlorine fluorides.

Additional evidence for the pseudotetrahedral structure of symmetry $C_{2v}$ of $ClO_2F_2^+$ consists of the $^{35}Cl$-$^{37}Cl$ isotopic splittings observed for the stretching modes (see Table III and Force Constant section).

**Force Constants.** Three sets of force constants were computed for $ClO_2F_2^+$ assuming different geometries. Two additional sets were computed requiring agreement between observed and computed $^{35}Cl$-$^{37}Cl$ isotopic shifts (see Table III). The potential and kinetic energy matrices were computed using a machine method.[26] The three different geometries adopted for $ClO_2F_2^+$ differ only in the bond angles but not in the bond lengths. The bond lengths were estimated to be $D$(ClO) = 1.41 Å and $R$(ClF) = 1.53 Å by comparison with related molecules and on the basis of the correlation of Robinson[27] between frequencies and bond lengths. The bond angles of set I, $\alpha$(∠OClO) = 124°, $\beta$(∠OClF) = 108° 15′, and $\gamma$(∠FClF) = 96°, were chosen to be identical with those of isoelectronic $SO_2F_2$.[21] For set III, tetrahedral bond angles were used, and for set II, a geometry was selected intermediate between those of sets I and III. The redundant coordinate was found numerically, and the deformation symmetry coordinates $S_3$ and $S_4$ were made orthogonal to it. To demonstrate that the redundancy condition was correct, it was verified that the frequencies of each block taken separately and the corresponding frequencies of the direct sum of all symmetry coordinates were the same.

The force constants were computed by trial and error with

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(21) D. R. Lide, Jr., D. E. Mann, and R. M. Fristrom, *J. Chem. Phys.*, **26**, 734 (1957).

(22) P. Bender and J. M. Wood, Jr., *J. Chem. Phys.*, **23**, 1316 (1955).

(23) G. R. Hunt and M. K. Wilson, *Spectrochim. Acta*, **16**, 570 (1960).

(24) K. O. Christe, E. C. Curtis, C. J. Schack, and D. Pilipovich, *Inorg. Chem.*, **11**, 1679 (1972).

(25) K. O. Christe and W. Sawodny, to be submitted for publication.

(26) E. C. Curtis, *Spectrochim. Acta, Part A*, **27**, 1989 (1971).

(27) E. A. Robinson, *Can. J. Chem.*, **41**, 3021 (1963).

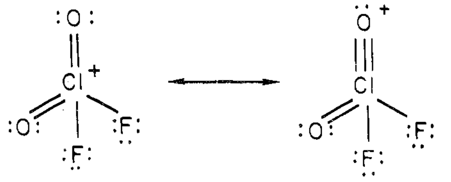
**Table IV.** Stretching Force Constants (mdyn/Å) of $ClO_2F_2^+$ Compared to Those of Related Compounds

| | $f_{ClO}$ | | $f_{ClF}$ | $f_{ClF}'$ [a] |
|---|---|---|---|---|
| $ClO_2F_2^+$ | 12.1 | $ClF_6^+$ [i] | 4.7 | |
| $ClF_2O^+$ [b] | 11.2 | $ClF_2^+$ [j] | 4.7 | |
| $FClO_3$ [c] | 9.4 | $ClF_4^+$ [k] | 4.5 | 3.2 |
| $ClF_3O$ [d] | 9.4 | $ClO_2F_2^+$ | 4.46 | |
| $FClO_2$ [e] | 9.1 | $ClF_3$ [l] | 4.2 | 2.7 |
| | | $FClO_3$ [c] | 3.9 | |
| $ClO_2^+$ [f] | 9.0 | $ClF_5$ [m] | 3.5 | 2.7 |
| $ClF_4O^-$ [g] | 8.9 | $ClF_2O^+$ [b] | 3.4 | |
| $ClF_2O_2^-$ [h] | 8.3 | $ClF_3O$ [d] | 3.2 | 2.3 |
| | | $FClO_2$ [e] | 2.5 | |
| | | $ClF_2^-$ [n] | | 2.4 |
| | | $ClF_4^-$ [o] | | 2.1 |
| | | $ClF_4O^-$ [g] | | 1.9 |
| | | $ClF_2O_2^-$ [h] | | 1.6 |

[a] ClF bonds for which strong contributions from semiionic three-center, four-electron bonds can be invoked. [b] Reference 16. [c] W. Sawodny, A. Fadini, and K. Ballein, *Spectrochim. Acta,* **21,** 995 (1965). [d] K. O. Christe and E. C. Curtis, *Inorg. Chem.,* **11,** 2196 (1972). [e] D. F. Smith, G. M. Begun, and W. H. Fletcher, *Spectrochim. Acta,* **20,** 1763 (1964). [f] Reference 19. [g] K. O. Christe and E. C. Curtis, *Inorg. Chem.,* **11,** 2209 (1972). [h] K. O. Christe and E. C. Curtis, *ibid.,* **11,** 35 (1972). [i] K. O. Christe, *ibid.,* in press. [j] K. O. Christe and C. J. Schack, *ibid.,* **9,** 2296 (1970). [k] Reference 25. [l] R. A. Frey, R. L. Redington, and A. L. K. Aljibury, *J. Chem. Phys.,* **54,** 344 (1971). [m] Reference 24. [n] K. O. Christe, W. Sawodny, and J. P. Guertin, *Inorg. Chem.,* **6,** 1159 (1967). [o] K. O. Christe and W. Sawodny, *Z. Anorg. Allg. Chem.,* **374,** 306 (1970).

the aid of a computer, requiring exact fit between the observed and computed frequencies. The results are given in Table III where the force constants not shown were assumed to be zero. The values shown for sets I-III were the simplest set that would give an exact fit and, with the exception of $F_{89}$, represent a diagonal symmetry force field. By analogy with isoelectronic $SO_2F_2$,[28] a nonzero value was required for $F_{89}$ to fit the observed frequencies. Its value was assumed to be 0.5 to obtain a plausible value for $F_{99}$. Table III demonstrates the dependence of the force constants on the chosen bond angles and the impossibility to achieve a fit between the observed and the computed $^{35}Cl-^{37}Cl$ isotopic shifts by simple variation of the bond angles. Numerical experiments confirmed that nonzero off-diagonal symmetry force constants are required to fit the observed isotopic shifts. The results for the more likely geometries I and II are listed as sets IV and V, respectively, in Table III. In the $A_1$ symmetry block, the only interaction constant capable of sufficiently decreasing the $\nu_1$ isotopic shift is $F_{12}$. The experimental data do not permit us to distinguish between sets IV and V. However, the variation in the two force constants of greatest interest, $f_D$ and $f_R$, is relatively small. Consequently, their values might be expected to approach those of a general valence force field. A statistically meaningful uncertainty estimate cannot be made for the force constant values owing to their underdetermined nature and to the lack of exact structural data. However, the numerical data of Table III allow some conclusions concerning the ranges of possible solutions. It should also be mentioned that the observed $^{35}Cl-^{37}Cl$ isotopic shifts varied slightly depending on the nature of the anion. In $ClO_2F_2^+BF_4^-$ for both the solid state and the HF solution, isotopic shifts of 7.5 and 15.9 $cm^{-1}$ were observed for $\nu_1$ $(A_1)$ and $\nu_6$ $(B_1)$, respectively. For solid $ClO_2F_2^+PtF_6^-$ the corresponding values were 8.5 and 16.6 $cm^{-1}$.

Of the internal force constants, the stretching force constants are of greatest interest since they can be used as a measure for the relative covalent bond strength. The stretching force constants of $ClO_2F_2^+$ are listed in Table IV and compared to those of related molecules and ions. Comparison of the ClO stretching force constant of $ClO_2F_2^+$ (12.1 mdyn/Å) with those listed in Table IV shows that it is the highest value known for a ClO bond. This is not surprising, since the central atom in $ClO_2F_2^+$ has a high oxidation state (+VII), highly electronegative ligands, and a formal positive charge (cation). The influence of these factors on $f_{ClO}$ has previously been discussed[16] for $ClF_2O^+$ and, hence, will not be reiterated. By analogy with $ClF_2O^+$, the only other known species exhibiting a $f_{ClO}$ value of similar magnitude, contributions from the resonance structure



might be invoked[16] to explain the high $f_{ClO}$ value. The value of the ClF stretching force constant (4.46 mdyn/Å) falls within the range expected for a predominantly covalent ClF bond. The interpretation of relatively small differences (~0.3 mdyn/Å) in the ClF stretching force constant values listed in Table IV should be done only with caution since most values were computed from underdetermined systems and might be significantly influenced by the chosen stretch-bend interaction constants.

**Registry No.** $ClF_3O_2$, 38680-84-1; $BF_3$, 7637-07-2; $AsF_5$, 7784-36-3; $(ClO_2F_2)BF_4$, 38682-34-7; $(ClO_2F_2)AsF_6$, 39003-82-2; $(ClO_2F_2)PtF_6$, 36609-92-4; $(ClO_2)PtF_6$, 38123-66-9.

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(28) W. D. Perkins and M. K. Wilson, *J. Chem. Phys.,* **20,** 1791 (1952).