# The Cl$_2$O$_2^+$ Cation: Preparation and Structural Investigation of Cl$_2$O$_2^+$SbF$_6^-$ and Cl$_2$O$_2^+$Sb$_2$F$_{11}^-$

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**Abstract:** Cl$_2$ reacts with O$_2^+$SbF$_6^-$ in anhydrous HF, forming subsequently a violet, a blue, and a yellow solution. Crystals from the violet solution are identified as Cl$_2$O$_2^+$SbF$_6^-$ or Cl$_2$O$_2^+$Sb$_2$F$_{11}^-$ by means of single-crystal structural determinations, Raman spectroscopy, magnetic and EPR measurements, and ab initio calculations. The cation has a planar trapezoid structure with Cl−Cl distances of 190.9(1)−191.6(5) pm, O−O distances of 118.5(11)−120.7(5) pm, and Cl−O distances of 240.8(4)−242.8(4) pm. The bonding between the two parts of the cation may be described as a $\pi^*-\pi^*$ interaction, resulting in a charge transfer of about 0.6 electrons with respect to isolated Cl$_2^+$ and O$_2$ fragments. The bonding of O$_2$ to Cl$_2^+$ is reversible, as is shown by $^{18}$O isotope exchange. The nature of the blue solution remains unknown. Both deeply colored compounds turn into yellow Cl$_3^+$ if warmed to room temperature, especially in the presence of excess Cl$_2$. The Cl$_3^+$ cation is symmetrical and bent with Cl−Cl = 197.23−199.44 pm and Cl−Cl−Cl = 104.51(10)−105.62(7)°.

## Introduction

A violet product in the system Cl/O/F was possibly first observed by Grosse et al. while reacting O$_2$F$_2$ and ClF.[2] It has been tentatively formulated as (ClF$_3$O$_2$)$_n$. Violet products have also been obtained by reacting O$_2$F$_2$ with BrF$_3$ and SF$_4$.[3,4] Early infrared and visible spectra of these materials were assigned to F$_2$ClOOClF$_2$.[5] Reacting O$_2^+$SbF$_6^-$ or O$_2^+$AsF$_6^-$ with various reactants always gave colored species, and the conclusion was drawn that they all belong to one or two species which could be oxygen fluoride radicals.[6] These mysterious compounds showed a solid-state EPR spectrum, and besides their characteristic color, an infrared absorption around 1540 cm$^{-1}$ has been found.[5,6]

Obviously these compounds are nonvolatile, so ionic compositions should have been considered also. We approached this problem during an investigation of the O$_2^+$/H$_2$O reaction, which resulted in a chemical synthesis of ozone, including isotopically labeled ozone.[7] The ozone lends the HF solution a deep blue color; however, this one is quickly removed by pumping at −78 °C. We found that by adding additional SbF$_5$ to O$_2^+$SbF$_6^-$ solutions in HF violet colors of varying intensity appear. Isotropic EPR spectra of these solutions indicated a hyperfine structure due to nuclei with spin > $^1/_2$. So the compound(s) in search must contain elements other than oxygen and fluorine also. The EPR spectrum is best interpreted as a 1:2:3:4:3:2:1 septet due to presence of two equivalent nuclei with spin $^3/_2$.

At this stage only antimony- or chlorine-containing radicals remained realistic. A scrutiny of the starting materials O$_2^+$SbF$_6^-$, HF, and SbF$_5$ revealed that SbF$_5$ almost always contains chlorine, be it as Cl$_2$ or SbF$_4$Cl. Even contact of SbF$_5$ with Kel-F [poly(chlorotrifluoroethene)] brings in traces of chlorine. Addition of Cl$_2$ to solutions of O$_2^+$SbF$_6^-$ in anhydrous HF then resulted in deep violet colored and, if more concentrated, even black solutions.

## Experimental Section

**Reagents.** O$_2^+$SbF$_6^-$ was prepared by UV irradiation of O$_2$/F$_2$/SbF$_5$ gaseous mixtures in large glass containers, following literature procedures.[8] HF was purified by 2-fold distillation in a stainless steel vacuum line and poly(perfluoroethylene)−perfluorovinyl ether (PFA) container. Cl$_2$ was dried over P$_2$O$_5$ and distilled in a 50 cm glass column filled with stainless steel rings.$^{18}$O$_2$ (>97%) and $^{17}$O$_2$ (30%) were purchased from Matheson Co. (Ohio). SbF$_5$ was distilled in a glass vacuum line into a −30° cold trap before use. Cl$_3^+$AsF$_6^-$ was prepared from ClF, Cl$_2$, and AsF$_5$ by following the literature method.[9]

**Spectroscopy**. Raman spectra were taken on a Bruker RFS 100 S instrument, with Nd:YAG laser excitation of 1064 nm. EPR spectra were taken on a Bruker ER 200 X band spectrometer. UV−visible spectra were taken on a Perkin-Elmer Lambda 9 instrument. Magnetic measurement was performed on a magnetic balance, built from a Sartorius microbalance S3D and a Varian electromagnet.

**Crystal Structures**. A suitable crystal was mounted on the tip of a glass fiber at low temperatures and under dry N$_2$ with the help of a special device,[10] mounted on the Enraf-Nonius CAD4 four-cycle diffractometer, and kept at temperatures between 120 and 130 K. Lattice constants were established by fine orientation of 25 reflections with 20° < $\theta$ < 25°. Intensities were measured by an $\omega$-scan of 1−2° and a maximum measurement time of 60 s, leaving thereof 25% for background measurement. Orientations and intensities of three reference

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**Table 1.**   Crystallographic Data

| formula | formula weight | crystal class | space group | color | unit cell parameters (pm, deg) | Z | R | GOF |
|---|---|---|---|---|---|---|---|---|
| $Cl_2O_2SbF_6$ | 338.65 | triclinic | $P1$ | black-violet | $a = 539.8(2)$ $b = 634.7(3)$ $c = 1151.8(6)$ $\alpha = 75.73(5)$ $\beta = 80.48(4)$ $\gamma = 81.94(3)$ | 2 | 0.0507 | 1.053 |
| $Cl_2O_2Sb_2F_{11}$ | 555.40 | monoclinic | $P2_1/c$ | black-violet | $a = 928.4(2)$ $b = 1062.5(2)$ $c = 1133.3(2)$ $\beta = 90.040(10)$ | 4 | 0.0241 | 1.187 |
| $Cl_3SbF_6$ | 342.1 | orthorhombic | $Cmca$ | orange-yellow | $a = 1055.3(2)$ $b = 1136.1(3)$ $c = 1208.1(3)$ | 8 | 0.0189 | 1.013 |
| $Cl_3Sb_2F_{11}$ | 558.85 | monoclinic | $P2_1/n$ | yellow | $a = 765.30(1)$ $b = 1262.3(2)$ $c = 1220.70(1)$ $\beta = 104.200(10)$ | 4 | 0.0291 | 1.088 |
| $Cl_3Sb_3F_{16}$ | 387.80 | monoclinic | $C2/c$ | yellow | $a = 1121.3(2)$ $b = 1189.8(1)$ $c = 1130.8(2)$ $\beta = 90.450(10)$ | 4 | 0.0206 | 1.032 |
| $Cl_3AsF_6$ | 295.27 | monoclinic | $P2_1/n$ | orange-yellow | $a = 704.5(2)$ $b = 1100.1(3)$ $c = 929.9(4)$ $\beta = 94.42(4)$ | 4 | 0.0255 | 1.118 |

reflections were measured from time to time. After Lorentz−polarization correction, a correction for decay if necessary, and a $\psi$-scan absorption correction, the structures were solved and refined by the Shelx procedures.[11]

**Computational Details.** The geometry of the $^2A_2$ electronic ground state of $Cl_2O_2^+$ was manually optimized by varying one parameter at a time using the CASPT2 approach, a multireference extension of regular second-order perturbation theory.[12] The full iterative scheme was employed. The orbitals were determined by complete-active-space self-consistent field (CASSCF) calculations, in which all orbitals stemming from the 2p and 3p valence orbitals of oxygen and chlorine, respectively, defined the active space. The resulting 14 110 configuration state functions represented also the reference space for the subsequent CASPT2 calculation. The orbitals were expanded in atomic natural orbital (ANO) basis sets of (14s9p4d3f) → [5s4p2d1f] and (17s12p5d4f) → [6s5p3d2f] quality for oxygen[13] and chlorine,[14] respectively. The energies of the lowest lying excited states were obtained at the same level of theory, while the transition dipole moments were computed at the CASSCF level. All calculations were performed by utilizing the MOLCAS-4 program[15] installed on IBM RS/6000 workstations. The Møller/Plesset and density functional calculations were done with the GAUSSIAN program package.[16]

**$Cl_2O_2^+SbF_6^-$.** $O_2^+SbF_6^-$ (200 mg, 0.75 mmol) $^+$was weighed under exclusion of water into a 8 mm o.d. PFA tube of approximately 20 cm length. After connection to the metal vacuum line 2−5 mL of anhydrous HF was condensed on it, then 55 mg (0.77 mol) of $Cl_2$ was condensed onto the latter. The reaction mixture was warmed to −40 °C and occasionally shaken. The yellow pearls of undissolved chlorine disappeared quickly, while the solution turned violet, then almost black. Slow cooling to −80° gave black needles. These were difficult to free from adhering HF, in which they melted under decomposition if warmed above −60° in a vacuum. For crystallographic data see Table 1.

**$Cl_2O_2^+Sb_2F_{11}^-$.** $O_2^+SbF_6^-$ (200 mg, 0.75 mmol) $^+$was weighed under exclusion of moisture into a PFA tube of 8 mm diameter and approximately 20 cm length, then 170 mg (0.78 mmol) of SbF$_5$ was added. HF (2−5 mL) and 60 mg (0.84 mmol) of chlorine were added at the metal vacuum line. The mixture was warmed to −30° and shaken, until the yellow droplets of chlorine had disappeared, and slow cooling to −80° afforded black crystals of approximately octahedral shape. Raman spectrum: 1534(5), 672(8), 646(5), 591(8), 584(7), 497(2), 414(5), 379(1), 336(br,4), 304(2), 261(100), 227(sh), 170(3), 133(1) cm$^{-1}$. For crystallographic data see Table 1. The black crystals were easily separated from colorless crystals under a microscope.

**$Cl_2{}^{18}O_2^+Sb_2F_{11}^-$ and $Cl_2{}^{17}O_2^+Sb_2F_{11}^-$** were prepared similarly from $^{18}O_2^+SbF_6^-$ and $^{17}O_2^+SbF_6^-$ and $Cl_2$. Raman spectrum of $Cl_2{}^{18}O_2^+$-$SbF_6^-$: 1448(5), 672(12), 646(4), 593(6), 586(6), 497 (br, 3), 395(3), 379(1), 341(br,3), 294(4), 255(100), 193(6), 170(1), 133(1) cm$^{-1}$.

**Oxygen Isotope Exchange Reaction.** $Cl_2{}^{18}O_2^+Sb_2F_{11}^-$ was kept as a solid at −60° under a pressure of 1 bar of $^{16}O_2$. The exchange was followed by Raman spectroscopy and gave after 24 h a 60/40% mixture of $Cl_2{}^{16}O_2^+$ and $Cl_2{}^{18}O_2^+$.

**$Cl_3^+SbF_6^-$, $Cl_3^+Sb_2F_{11}^-$, and $Cl_3^+Sb_3F_{16}^-$.** Samples of $Cl_2O_2^+SbF_6^-$ or $Cl_2O_2^+Sb_2F_{11}^-$ with varying amounts of SbF$_5$, dissolved in liquid anhydrous HF, were warmed to room temperature, until all violet, blue, or green colors had disappeared and a yellow color remained. This took 1 day or more. The yellow solutions were slowly cooled to −78 °C, while yellow and colorless crystals appeared. The yellow crystals contained the $Cl_3^+$ cation. No attempt was undertaken to optimize the conditions for the formation of one of the three compounds. Suitable crystals were mounted on the diffractometer; for experimental details see Table 1. The colorless crystals were shown to be $H_2F^+Sb_2F_{11}^-$ and $H_3F_2^+Sb_2F_{11}^-$.[17]

## Results

The reaction of $Cl_2$ with $O_2^+SbF_6^-$ in anhydrous HF at −78 °C gives deep violet solutions. Elemental chlorine can be replaced by any low-valent chlorine-containing compound, which can serve as a $Cl_2$ donor. As will be shown below, the violet color is due to the $Cl_2O_2^+$ cation. Warming to −50 °C and the use of an excess of chlorine results in an intensively

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*Cl2O2+ Cation*

*J. Am. Chem. Soc., Vol. 121, No. 18, 1999* 4381
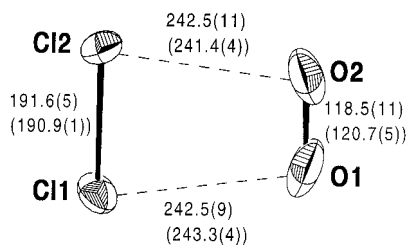


**Figure 1.** The $Cl_2O_2^+$ cation in $Cl_2O_2^+SbF_6^-$. The cation in $Cl_2O_2^+Sb_2F_{11}^-$ is essentially identical. Numerical values in brackets are those of $Cl_2O_2^+Sb_2F_{11}^-$. Dihedral angles in both cations are all smaller than 1°.

blue solution. Characteristically, the blue color disappears reversibly upon cooling to −78 °C. Usually a faint violet color remains at this temperature. The nature of the blue color remains unknown until now. Warming briefly to room temperature or for prolonged time to −30 °C gives orange-yellow solutions. Green colors that appear intermediately are clearly a mixture of blue and yellow. The yellow color, as will be also shown below, is due to the known $Cl_3^+$ cation.

**$Cl_2O_2^+$.** From the concentrated violet solution, needle shaped, black crystals of $Cl_2O_2^+SbF_6^-$ can be obtained by slow cooling from −40 to −78 °C. Addition of $SbF_5$ to the reaction mixture before or after the reaction affords black crystals of $Cl_2O_2^+$-$Sb_2F_{11}^-$. While crystals of $Cl_2O_2^+SbF_6^-$ are always obtained, crystallization of $Cl_2O_2^+Sb_2F_{11}^-$ needs some patience. $Cl_2O_2^+$-$Sb_2F_{11}^-$ is stable under exclusion of moisture until 40 °C, while $Cl_2O_2^+SbF_6^-$ decomposes well below 0 °C. The single-crystal structure determinations of $Cl_2O_2^+SbF_6^-$ and $Cl_2O_2^+Sb_2F_{11}^-$ prove that both salts have the same cation, which is shown in Figure 1. Cation−anion interactions do not seem to influence the cation. The structure is trapezoid, and planar, with a maximum dihedral angle of 0.58°. It looks like a pair of $Cl_2$ and $O_2$ molecules.

The chlorine−chlorine distances of 191.6(5) and 190.9(1) pm are well below that of molecular chlorine (198 pm), so from this information alone, one can draw the conclusion that the major part of the positive charge resides on the chlorine side of the cation. However, the Cl−Cl distance remains larger than that in free (gaseous) $Cl_2^+$ (189 pm).[18] Considering the larger vibrational amplitudes of the oxygen atoms and with this the larger esd's, the oxygen−oxygen distances of 118.5(11) and 120.7(5) do not differ significantly from molecular oxygen (120.74 ppm). Of special interest are the large chlorine oxygen distances of 240.8(4)−242.8(4) pm, approximately 75% of the sum of the van der Waals radii (330 pm). So the bonding between the chlorine part and the oxygen part of the cation is weak, as also shown in the chapter on ab initio calculations.

The EPR spectrum of $Cl_2O_2^+$ is shown in Figure 2. The seven lines with an approximate intensity ratio of 1:2:3:4:3:2:1 are assigned to the hyperfine structure due to the chlorine atoms. Since both naturally occurring chlorine isotopes have the nuclear spin = $3/2$, and their gyromagnetic factor varies only by 7.5%, no isotopic splitting is observed. Only the broadening of the outer lines is indicative of less than perfect overlap between the $^{35}Cl$ and $^{37}Cl$ fine structures. This EPR spectrum resembles very much the one that has been assigned to $Cl_2^+$ long ago.[19] The authors did not comment on any intense color. The assignment has been questioned because among other reasons

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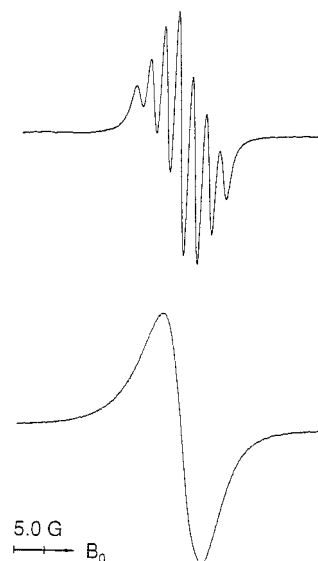


**Figure 2.** EPR spectrum of a $Cl_2O_2^+$ solution in HF at 270 K (above) and 230 K (below); $g = 1.9988(1)$, hyperfine splitting 2.23 G.
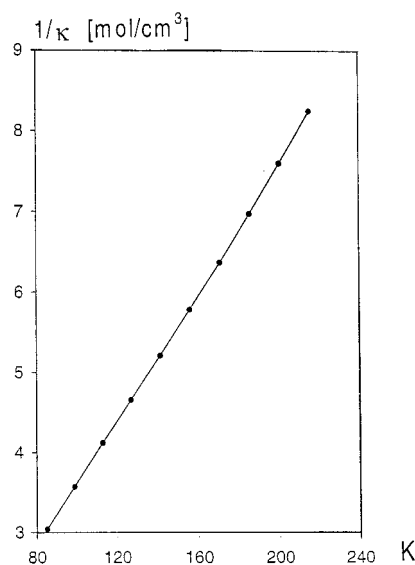


**Figure 3.** Magnetic measurement on solid $Cl_2O_2^+Sb_2F_{11}^-$; $1/\kappa$ versus temperature plot.

$Br_2^+$ does not show any hyperfine splitting in the EPR spectrum and $I_2^+$ does not show any EPR spectrum at all.[18,20,21] By reacting $^{17}O_2^+SbF_6^-$ with $Cl_2$ the $Cl_2^{17}O_2^+$ cation is obtained. EPR spectra of this do not show any fine structure due to the $5/2$ nuclear spin of $^{17}O$. From this we conclude that the hyperfine constant toward $^{17}O$ is close to zero and tentatively reason that the unpaired electron resides largely on the chlorine atoms.

Magnetic measurement with a magnetic balance over a wide temperature range shows simple paramagnetic behaviors down to −180 °C (see Figure 3). Calculation of the unpaired electron density gives 1.5 $\mu_B$, close to the value of 1.73 $\mu_B$ of the spin-only approximation.

To gain a deeper understanding of the bonding within the $Cl_2O_2^+$ cation, we performed quantum chemical calculations on several levels of theory. As indicated in Table 2, widely used methods, such as Moller−Plesset perturbation theory to

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**Table 2.**   Ab Initio Calculations of $Cl_2O_2^{+}$ [a]

| | state | Cl−Cl (pm) | O−O (pm) | Cl−O (pm) | energy (au) | dissociation energy into $Cl_2^{+} + {}^3O_2$ (kcal) |
|---|---|---|---|---|---|---|
| CASPT2: | ${}^2A_2$ | 190.6 | 122 | 242 | −1069.14943 | 12.8 |
| HF/6-311+G(d,p) | ${}^2A_2$ | 199.3 | 106.8 | 290.9 | −1068.18951 | |
| MP2/6-311+G(d,p) | ${}^2A_2$ | 194.5 | 121.8 | 287.7 | −1068.86304 | |
| MP4(SDQ)/6-311+G(d,p) | ${}^2A_2$ | 235.8 | 119.9 | 294.5 | −1068.82748 | |
| Becke 3LYP/6-311+G(3d,p) | ${}^2A_2$ | 198.7 | 116.2 | 273.4 | −1070.38212 | |
| Becke 3LYP/6-311++G(3df,3pd) | ${}^2A_2$ | 194.5 | 116.1 | 264.7 | −1070.41459 | 18.5 |
| Cl−O−O−Cl$^{+}$, trans (as above) | ${}^2B_g$ | | 142.8 | 163.5 | −1070.36642 | |
| Cl−O−Cl=O$^{+}$ (as above) | ${}^2A''$ | | | 162.3, 179.8, 146.4 | −1070.36456 | |
| Cl−ClO$^{+}_2$ (as above) | ${}^2A''$ | 285.2 | | 141.4 | −1070.34205 | |

| transition | $T_v$ (eV) | $|\langle Z|\mu|{}^2A_2\rangle|$ (au) | $f$ (au) |
|---|---|---|---|
| ${}^2B_2 \leftarrow {}^2A_2$ | 1.45 | 0.3629(y) | $4.68 \times 10^{-3}$ |
| ${}^2B_1 \leftarrow {}^2A_2$ | 3.89 | 0.0067(x) | $4.33 \times 10^{-6}$ |
| ${}^2A_2 \leftarrow {}^2A_2$ | 4.69 | 0 (forbidden) | 0.00 |

[a] Vertical transition energies $T_v$ calculated on the CASPT2 level, transition dipole moments $|{<}Z|\mu|{}^2A_2{>}|$, and oscillator strengths calculated on the CASSCF level.

second- or even fourth-order or density functional theory based approaches, fail significantly in reproducing the experimentally observed equilibrium geometry. In particular the predicted Cl−O distances scatter between 264.7 and 294.5 pm, while the experimental number is around 242 pm! If we instead use the CASPT2 method, which offers a promising approach to cover nondynamical as well as dynamical electron correlation effects,[12] the computed geometrical parameters agree very well with the experimental ones. For example, the critical Cl−O distance is computationally predicted as 242.0 pm, in perfect harmony with the experimental results. The ground state of $Cl_2O_2^{+}$ is ${}^2A_2$, and the formally singly occupied molecular orbital (the corresponding natural orbital in the CASPT2 wave function is occupied with 1.03 electrons) consists mainly of an antibonding $\pi$-orbital localized on the two oxygens with a smaller contribution from the corresponding $\pi^*$ orbital constructed from the 3p atomic orbitals on the $Cl_2$ unit. This orbital has an additional nodal plane between the $Cl_2$ and $O_2$ subunits. The ${}^2A_2$ state asymptotically correlates with the molecular ground states of $Cl_2^{+}$ (${}^2\Pi$) and $O_2$ (${}^3\Sigma_g^{-}$). This dissociation is connected with a binding energy of 0.55 eV (12.8 kcal/mol), neglecting zero-point energy contributions. According to a Mulliken population analysis, the $O_2$ unit bears a positive partial charge of 0.42 e$^{-}$ while the $Cl_2$ unit carries the remaining 0.58 e$^{-}$. The distribution of the spin density is similar. According to a B3LYP calculation with a cc-pvtz basis set at the CASPT2 optimized geometry, 62% of the spin density is on the $Cl_2$ moiety. (At this level of theory, the Mulliken partial charges amount to 0.34 e$^{-}$ on the oxygens and 0.66 e$^{-}$ on the chlorines).

We investigated also the vertical transitions from the ground state into the lowest lying excited states of ${}^2B_1$, and ${}^2B_2$ symmetry (the ${}^2A_1 \leftarrow {}^2A_2$ transition is forbidden by symmetry). As summarized in Table 2 the excitation into the ${}^2B_2$ state is of particular interest, since its transition energy of 1.45 eV is in the visible region and the transition dipole moment as well as the corresponding oscillator strength are fairly large. The Mulliken charge analysis on the ${}^2B_2$ state indicates a charge transfer of 0.3 e$^{-}$ from the $O_2$ unit to the $Cl_2$ unit, with respect to the ${}^2A_2$ ground state. So the intense color of $Cl_2O_2^{+}$ which is due to a broad absorption at 540 nm, in accord with earlier observations,[5] is of the charge-transfer type.

Due to the lack of analytical gradients, we did not attempt to compute the harmonic vibrational frequencies for this ion. However, to arrive at least at a semiquantitative information about the force field, we calculated the harmonic frequencies
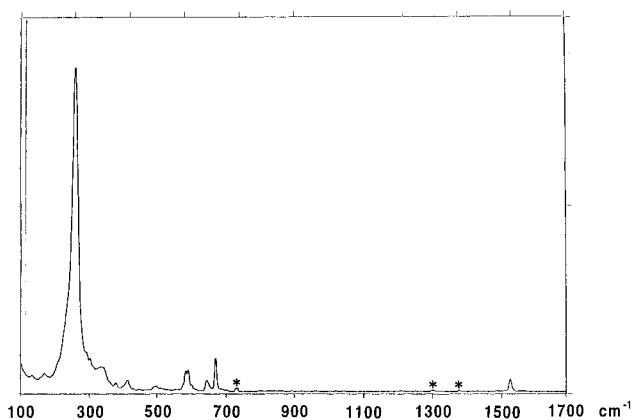


**Figure 4.**  Raman spectrum of $Cl_2O_2^{+}Sb_2F_{11}^{-}$ at −80 °C. Lines of the PEA container are marked with an asterisk.

using the Becke 3LYP density functional in combination with a 6-311++G(3df,3pd) basis set.

The Raman spectrum of $Cl_2O_2^{+}Sb_2F_{11}^{-}$ is shown in Figure 4. The band at 1534 cm$^1$ is clearly the oxygen−oxygen stretching vibration; in $Cl_2{}^{18}O_2^{+}$ it moves down to 1448 cm$^{-1}$. The bands at 646 and 672 cm$^{-1}$ are due to Sb−F stretching vibrations. The bridging Sb−F−Sb mode can be assigned to $\nu$ = 497 cm$^{-1}$. The Cl−Cl stretching vibration is visible at 586 and 593 cm$^{-1}$. The splitting is due to the different chlorine isotopomers; the ${}^{37}$Cl−${}^{37}$Cl vibration may be seen only as a shoulder to the lower frequency side of the band group. The ${}^{18}$O labeling is of help to assign the $Cl_2O_2^{+}$ bands (see Table 3). Two bands (414 and 263 cm$^{-1}$) show a pronounced isotopic effect (395 and 255 cm$^{-1}$), and a third line is observed only in $Cl_2{}^{18}O_2^{+}$ (193 cm$^{-1}$) because its ${}^{16}$O counterpart may be obscured by the enormous intensity of the 263 cm$^{-1}$ band. This remarkable intensity may be a result of an onset of a Raman resonance effect. However, no overtones are observed, since the laser excitation at 1064 nm is too far away from the charge-transfer absorption at 540 nm. In accordance with the calculated ${}^2A_2 \leftarrow {}^2B_2$ excitation this Raman line is therefore assigned to $\nu_s$ Cl−O (A$_1$), the breathing mode of the charge-transfer complex.

**$Cl_3^{+}$.** $Cl_2O_2^{+}$ finally decomposes into $Cl_3^{+}$, especially if excess chlorine is present. Depending on the SbF$_5$ concentration of the $O_2^{+}$SbF$_6$/HF/Cl$_2$/SbF$_5$ reaction mixture, $Cl_3^{+}$SbF$_6^{-}$, $Cl_3^{+}$Sb$_2$F$_{11}^{-}$, or $Cl_3^{+}$Sb$_3$F$_{16}^{-}$ are formed, each of them as yellow-orange crystals. Formation of $Cl_3^{+}$AsF$_6^{-}$ from ClF and AsF$_5$ has been described previously,[9] so we crystallized this

**Table 3.** Vibrational Frequencies of $Cl_2O_2^+$ in $Cl_2O_2^+Sb_2F_{11}^-$ and Assignment (cm$^{-1}$)

| | Raman spectrum | |
|---|---|---|
| calcd for $Cl_2^{16}O_2^{+\ a}$ | $Cl_2^{16}O_2^+$ | $Cl_2^{18}O_2^+$ |
| 1697.3 (A$_1$, $\nu_{OO}$) | 1534 | 1448 |
| 586.7 (A$_1$, $\nu_{ClCl}$) | 593 ($^{35}Cl_2O_2^+$) | 593 |
| | 586 ($^{35}Cl^{37}ClO_2^+$) | 586 |
| 338.0 (B$_2$, $\nu_{Cl-O}$) | 414 | 395 |
| 160.3 (A$^2$, out of plane ring deformation) | − | − |
| 143.6 (A$_1$, $\nu_{Cl-O}$) | 263 | 255 |
| 116.27 (B$_2$, in plane ring deformation) | 227(?) | 193 |

$^a$ Becke 3LYP/6-311/++G(3df,3pd). Note that the calculated ground-state geometry is unsatisfactory. Because of the too long Cl···O distance all vibrations except $\nu_{OO}$ and $\nu_{ClCl}$ are expected to have too small calculated wavenumbers.

**Table 4.** Bond Distances and Angles in $Cl_3^+$

| | distance (pm) | angle (deg) |
|---|---|---|
| $Cl_3^+SbF_6^-$ | 197.23(8) | 105.55(5) |
| $Cl_3^+Sb_2F_{11}^-$ | 199.4(1) | 105.62(7) |
| $Cl_3^+Sb_3F_{16}^-$ | 198.3(2) | 104.51(10) |
| $Cl_3^+AsF_6^-$ | 198.0(1) | 105.1(4) |
| $Br_3^{+\ a}$ | 227.0(5) | 102.5(2) |
| $I_3^{+\ b}$ | 266.0, 266.9(2) | 101.75(6) |

$^a$ Reference 30. $^b$ Reference 31.

compound too. In every case the $Cl_3^+$ cation shows the expected symmetric bent structure, as is found for $Br_3^+$ and $I_3^+$ also (see Table 4).

## Discussion

**$Cl_2O_2^+$.** The $Cl_2O_2^+$ structure is unique, if compared to the structures of all known chlorine oxides, independent of whether they are neutral, cationic, or anionic. In contrast to $Cl_2O_2^+$ all previously known structures can be visualized by using Lewis formula. It may be of interest that calculations have been undertaken on $Cl_2O_2^+$, where the three conventional structures $Cl-O-O-Cl^+$, $Cl-ClO_2^+$, and $Cl-O-ClO^+$ were investigated and found to be minima on the potential hypersurface.[22] However, there is little or no experimental evidence for these, except for the ionization threshold of $Cl-O-O-Cl^+$, measured by synchroton radiation.[23]

According to our calculations, the experimentally found connectivity is certainly the global minimum for $Cl_2O_2^+$ on the hypersurface (see Table 2).

We interpret the bonding of $Cl_2O_2^+$ in terms of a charge transfer between $Cl_2^+$ and $O_2$. In the CASPT2 calculation, there are two bonding interactions between $\pi^*$ of $Cl_2^+$ and $\pi^*$ of $O_2$, namely one in plane ($\sigma$) interaction of 1.88 electrons and one out of plane ($\pi$) interaction of 1.97 e$^-$. The corresponding antibonding $\pi^*-\pi^*$ interactions are occupied by 0.19 and 1.03 e$^-$, respectively. $Br_2^+$ [24] and $I_2^+$ [25] are both well-characterized. If one keeps in mind the increasing electron affinities of $I_2^+$ (9.22 eV), $Br_2^+$ (10.51 eV), and $Cl_2^+$ (11.51 eV), then it becomes clear that $I_2^+$ and $Br_2^+$ can exist unsupported by a

ligand molecule, and $Cl_2^+$ does (so far) not. The dissociation energy $Cl_2O_2^+ \rightarrow Cl_2^+ + {}^3O_2$ is calculated to be 12.8 kcal/mol. This value leaves room for the speculation that $O_2$ might bind reversibly to $Cl_2^+$. Whereas prolonged pumping on $Cl_2O_2^+$ at $-78$ °C with a good vacuum does not indicate loss of oxygen, $Cl_2^{18}O_2^+$ exchanges up to 60% with $^{16}O_2$ and vice versa within 1 day at $-78$ °C, as evidenced by Raman spectroscopy. No $^{16}O/^{18}O$ isotopic scrambling is observed within the $O_2$ units. The idea of a reversible $O_2$ binding under these extremely oxidative conditions is particularly appealing. One can also predict that under special conditions uncomplexed $Cl_2^+$ should be capable of existence.

The formation of $Cl_2O_2^+$ is at first certainly a redox process. Complexation may occur simultaneously or after the redox process.

$$Cl_2 + O_2^+ \rightarrow Cl_2^+ + O_2 \rightarrow [Cl_2 \cdots O_2]^+$$
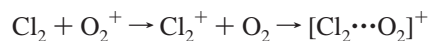
The difference of 0.5 eV between the ionization potentials of $O_2$ and $Cl_2$ is the driving force of this reaction.[26] Also it is safe to assume that the major part of the charge resides on the chlorine part of the cation, as is predicted by the ab initio calculation. Experimental evidence for this may be found in the shorter contacts of the chlorine atoms to fluorine atoms of the anions (minimum of 256 pm in $Cl_2O_2^+SbF_6^-$), whereas oxygen atoms have longer contacts to fluorine atoms of the anions (minimum of 276 pm) in $Cl_2O_2^+SbF_6^-$. Similarly, it can be said that the unpaired electron density resides largely on the chlorine atoms, as predicted by the ab initio calculation and the EPR measurements on $Cl_2^{17}O_2^+$.

We find it difficult to compare the $Cl_2O_2^+$ ion with any other known system. The cations $S_2I_4^{2+}$ and $I_4^{2+}$ may be the closest known relatives.[26,27] $S_2I_4^{2+}$ can be viewed as two $I_2^+$ units, complexed by one $S_2$ unit. So, a structure is obtained that is made up from two trapezoids intersecting at the S–S bond, which are almost perpendicular to each other. The rectangular $I_4^{2+}$ can be looked at as a complex between two $I_2^+$ units; in fact, there exists an equilibrium showing that the binding force between the two $I_2^+$ parts is particularly week.

**$Cl_3^+$.** The $Cl_3^+$ cation has been prepared as $Cl_3^+SbF_6^-$, $Cl_3^+Sb_2F_{11}^-$, and $Cl_3^+Sb_3F_{16}^-$ and also as $Cl_3^+AsF_6^-$. The latter is not stable at room temperature, but vibrational spectra have been recorded previously. Detailed information on the structure is missing, in contrast to $Br_3^+AsF_6^-$ [28] and $I_3^+AsF_6^-$.[29] The $Cl_3^+$ cation in all of these salts exists as the discrete cation $Cl_3^+$ as a symmetric, but bent, entity. The Cl–Cl distances vary between 197.2(1) and 199.4(1) pm. The bond angle increases from $I_3^+$ (101.75(6)°) to $Br_3^+$ (102.5(2)°) and $Cl_3^+$ (104.5(1)–105.62(7)°). This is in accord with conventional chemical bond models. No indication could be obtained so far for a $Cl_5^+$ cation, whereas $Br_5^+$ and $I_5^+$ are both known.[30,31]

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**Supporting Information Available:** Tables of crystal data, structure solution and refinement, atomic coordinates, bond lengths and angles, and anisotropic thermal parameters for $Cl_2O_2{}^+SbF_6{}^-$, $Cl_2O_2{}^+Sb_2F_{11}{}^-$, $Cl_3{}^+SbF_6{}^-$, $Cl_3{}^+Sb_2F_{11}{}^-$, $Cl_3{}^+Sb_3F_{16}{}^-$, and $Cl_3{}^+AsF_6{}^-$ in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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