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Dioxygenyl Pentafluorogermanate(IV), $O_2^+GeF_5^-$

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The novel compound $O_2^+GeF_5^-$ was prepared by uv photolysis of a GeF_4–F_2–O_2 mixture in quartz at −78 °C. The compound is a white crystalline solid and is unstable at 25 °C. It was characterized by infrared, Raman, and ESR spectroscopy. The vibrational spectra indicate for the anions a polymeric cis-fluorine-bridged structure similar to that found for NbF_5. The possibility to convert O_2GeF_5 into $(O_2)_2GeF_6$ by HF treatment at low temperature was briefly studied. For comparison, $(NO)_2GeF_6$ was prepared and characterized by vibrational spectroscopy. The Raman spectrum of solid GeF_4 has also been recorded and longitudinal components were observed for each of the two F_2 modes.

Introduction

The synthesis of $O_2^+PtF_6^-$, the first known example of a dioxygenyl salt, was reported[1] in 1962 by Bartlett and Lohmann. Since then numerous other O_2^+ salts have been synthesized and studied. However, all of the reported[1–16] dioxygenyl salts belong to one of the following three types: $O_2^+MF_6^-$ (M = P, As, Sb, Bi, Pt, Ru, Rh, Pd, or Au), $O_2^+M_2F_{11}^-$ (M = Sb, Bi, Nb, or Ta), or $O_2^+MF_4^-$ (M = B). In view of the interesting physical and chemical properties of these paramagnetic and strongly oxidizing salts, we have studied the possible synthesis of O_2^+ salts containing new types of anions. In this paper we report the synthesis and characterization of $O_2^+GeF_5^-$, the first known representative of the type $O_2^+MF_5^-$. Further interest was added to this study by the fact that the GeF_5^- anion has only recently been discovered.[17] Except for quaternary ammonium salts,[17] no other GeF_5^- salts have been reported and no structural data on GeF_5^- were available.

Experimental Section

Materials and Apparatus. Volatile materials were manipulated in a well-passivated (with ClF_3) Monel vacuum line equipped with Teflon FEP U-traps and bellows-seal valves. Pressures were measured with a Heise Bourdon tube-type gauge (0–1500 mm ± 0.1%) or a Validyne Model DM56A pressure transducer. Nonvolatile materials were handled outside of the vacuum system in the dry nitrogen atmosphere of a glovebox.

Germanium tetrafluoride (Ozark Mahoning), F_2 (Rocketdyne), and O_2 (research purity, 99.99% minimum, Matheson Gas Products) were used without further purification. Nitrosyl fluoride was prepared from NO and F_2 at −196 °C and purified by fractional condensation.

The infrared spectra were recorded in the range 4000–250 cm^{-1} on a Perkin-Elmer Model 457 infrared spectrophotometer. The spectra of gases were obtained using Monel cells of 5-cm path length fitted with AgCl windows. The spectra of solids at room temperature 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 low-temperature spectra were recorded at −196 °C using a cell and transfer technique similar to those previously described.[18] The inner windows of the cell were AgCl or CsI; the outer ones, CsI disks. The instrument was calibrated by comparison with standard calibration points.[19]

The Raman spectra were recorded on a Cary Model 83 spectrophotometer using the 4880-Å exciting line and a Claassen filter[20] for the elimination of plasma lines. Sealed quartz or Teflon FEP tubes were used as sample containers in the transverse-viewing, transverse-excitation technique. The low-temperature spectra were recorded using a previously described[21] device. Polarization measurements were carried out according to method VIII listed by Claassen et al.[20]

ESR spectra were recorded as previously described.[15] The ^{19}F NMR spectra were recorded at 56.4 MHz on a Varian Model DA60 spectrometer equipped with a variable-temperature probe. Chemical shifts were determined by the side-band technique relative to external $CFCl_3$. Teflon FEP liners (Wilmad Glass Co.) inserted into glass NMR tubes were used as sample containers and anhydrous HF was used as a solvent. Debye–Scherrer powder patterns were taken using a GE Model XRD-6 diffractometer. Samples were sealed in quartz capillaries (~0.5-mm o.d.)

Synthesis of $O_2^+GeF_5^-$. A 1-l. quartz bulb containing 500 cm^3 of O_2, 250 cm^3 of F_2, and 250 cm^3 of GeF_4 was exposed for 7 days to uv radiation from a high-pressure mercury lamp (Hanovia 616A, 100 W) equipped with a water filter. The condensing tip and the bottom of the reactor were kept at −78 °C. The solid $O_2^+GeF_2^-$ accumulated in the cold section of the reactor which also contained some solid GeF_4. After completion of the photolysis, products volatile at −31 °C were removed in vacuo. The white solid residue (about 500 mg) was transferred, while cold, from the quartz bulb to cold quartz or Teflon FEP tubes in an inert-atmosphere glovebox.

The composition of the solid was determined by allowing weighed samples contained in a Teflon FEP ampule to decompose completely at 25 °C and by separating and measuring the gases noncondensable (O_2 and F_2) and condensable (GeF_4) at −196 °C. The identity of the decomposition products was established by mass and infrared spectroscopy. In a typical experiment, 82 mg of the solid, corresponding to 0.411 mmol of $O_2^+GeF_5^-$, produced upon decomposition 0.63 mmol of O_2 + F_2 and 0.42 mmol of GeF_4, thus establishing its composition as O_2GeF_5. The ionic structure of the solid was established by vibrational spectroscopy.

Synthesis of $(NO^+)_2GeF_6^{2-}$. Germanium tetrafluoride (2.17 mmol) and FNO (5.40 mmol) were combined at −196 °C in a passivated Teflon FEP ampule. The mixture was warmed first to −78 °C, then to −45 °C, and then to 25 °C for 30 min. Unreacted FNO (1.05 mmol) was removed by pumping at 25 °C, leaving behind 532 mg of a stable white solid (weight calculated for 2.17 mmol of $(NO)_2GeF_6$ is 535 mg). The ionic structure of the solid was established by vibrational spectroscopy.

Results and Discussion

Synthesis and Properties of $O_2^+GeF_5^-$. Uv photolysis of a mixture of O_2, F_2, and GeF_4 in quartz at −78 °C produces a white crystalline solid according to

$$2O_2 + F_2 + 2GeF_4 \xrightarrow[-78\ °C]{h\nu} 2O_2GeF_5$$

The composition of the solid was established by quantitative thermal decomposition at 25 °C which produces the starting materials. It was found that the decomposition rate is suppressed by a pressure buildup of the gaseous decomposition products. A similar suppression of the decomposition rate of a dioxygenyl salt by the corresponding gaseous Lewis acid has previously been observed[22] for $O_2^+BF_4^-$.

The thermal stability of $O_2^+GeF_5^-$ is similar to that[22] of $O_2^+BF_4^-$. It was stored at −20 °C for over 4 months in either quartz or Teflon FEP containers without noticeable decomposition. It reacts violently with water producing a gas with typical fluorine odor.

$O_2^+GeF_5^-$ is the first example of a dioxygenyl salt of the type $O_2^+MF_5^-$. The relatively good thermal stability of $O_2^+GeF_5^-$ is surprising in view of the fact that GeF_5^- salts are difficult to prepare and that the only known examples possess bulky and strongly stabilizing counterions, such as quaternary ammonium cations.[17] A plausible explanation for the relative stability of GeF_5^- in the presence of a small cation,

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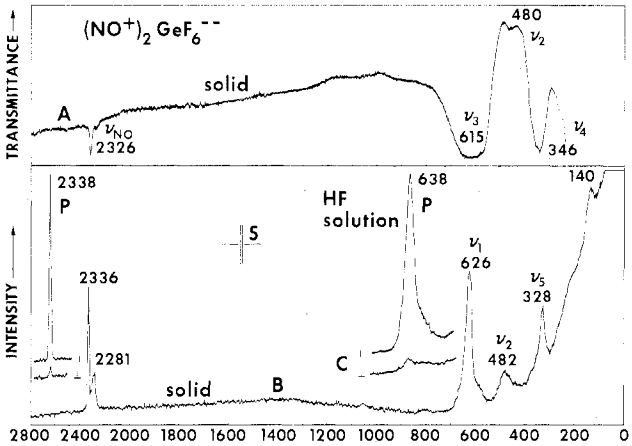

Figure 1. Vibrational spectra of $(NO^+)_2GeF_6^{2-}$ at 25 °C: trace A, infrared spectrum of the dry powder as a AgBr disk; trace B, Raman spectrum of the solid; trace C, Raman spectrum of an HF solution. P indicates polarized bands, and S the spectral slit width.

such as O_2^+, will be given below.

Since a trigonal-bipyramidal GeF_5^- anion would possess an energetically unfavorable structure, it might be possible to convert it to the more favorable and stable octahedral GeF_6^{2-} anion. For NF_4^+ salts, we have found that such a conversion can be achieved by treatment with anhydrous HF. This type of conversion was also studied for $O_2^+GeF_5^-$ as a possible route to $(O_2^+)_2GeF_6^{2-}$ which would be the first known example of a bis(dioxygenyl) salt and should possess very interesting magnetic properties. Unfortunately, the treatment of O_2^+-GeF_5^- with HF in the temperature range −78 to −31 °C did not produce any product of sufficient stability and purity to allow its unambiguous identification.

Synthesis, Properties, and Spectra of $(NO^+)_2GeF_6^{2-}$. The knowledge of the vibrational spectra of $(NO^+)_2GeF_6^{2-}$, which should be isostructural with $(O_2^+)_2GeF_6^{2-}$, was desirable to predict the spectrum of GeF_6^{2-} in its hypothetical dioxygenyl salt. The synthesis of $(NO^+)_2GeF_6^{2-}$ by the interaction of either GeO_2 with ClNO and BrF_3[23] or Ge with $FNO{\cdot}3HF$[24] has previously been reported but the compound was not characterized. For our study, $(NO^+)_2GeF_6^{2-}$ was prepared in quantitative yield by direct combination of GeF_4 with a slight excess of FNO. It is a white crystalline solid, stable at room temperature.

The vibrational spectrum of $(NO^+)_2GeF_6^{2-}$ is shown in Figure 1. The observed bands and their frequencies agree well with those previously reported for the NO^+ cation[25,26] and the GeF_6^{2-} anion,[27-29] thus confirming the ionic nature of the adduct. The spectra were recorded at 25 and −120 °C but showed no pronounced temperature-dependent order–disorder phenomena caused by reorientational motion of the ions.[14,30,31] The splitting of the NO stretching mode into two bands for the solid disappears in the spectrum of the HF solution (see Figure 1) and, hence, is due to crystal effects. The ^{19}F NMR spectrum of $(NO^+)_2GeF_6^{2-}$ in HF solution was also recorded, but only a single resonance was observed for both GeF_6^{2-} and HF solvent indicating rapid exchange of fluorine.

The x-ray powder diffraction pattern of $(NO^+)_2GeF_6^{2-}$ was also recorded and was tentatively indexed for a hexagonal unit cell with $a = 11.78$ Å, $c = 9.78$ Å, and $Z = 8$; a unit cell apparently related to that of $(NH_4)_2GeF_6$ for which $a = 5.862$ Å, $c = 4.817$ Å, and $Z = 1$ was found.[32] The similarity of the unit cell dimensions per formula unit is not surprising in view of the previous observation[30] that at 25 °C $O_2^+AsF_6^-$ and $OH_3^+AsF_6^-$ possess almost identical unit cells.

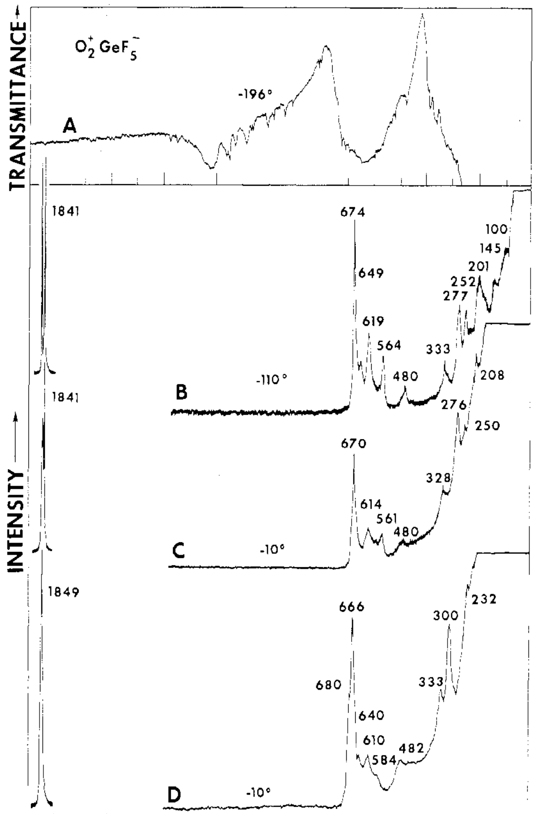

Figure 2. Vibrational spectra of $O_2^+GeF_5^-$: trace A, infrared spectrum of the solid recorded as a dry powder between CsI disks; traces B and C, Raman spectra of a well-aged solid sample; trace D, Raman spectrum of a freshly prepared sample. The spectral slit width used for the recording of the Raman bands in the 1800–1900-cm^{-1} region was half of that (3 cm^{-1}) used for the recording of the rest of the spectrum at the same gain setting.

Vibrational Spectrum and Structure of $O_2^+GeF_5^-$. The vibrational spectra of $O_2^+GeF_5^-$ are shown in Figures 2 and 3. These spectra are relatively complex and rule out the presence of both GeF_6^{2-} (see above) and solid GeF_4 (see below). Since the Raman spectra show lines between 1840 and 1860 cm^{-1}, characteristic[6,20] for O_2^+, the solid must be ionic and have the composition $O_2^+GeF_5^-$. The Raman spectra were recorded over the temperature range −5 to −130 °C and show a pronounced temperature dependence. At the higher temperatures, the anion bands are broader and fewer in number. By analogy with $O_2^+AsF_6^-$, $O_2^+SbF_6^-$,[14,30,31] and $OH_3^+AsF_6^-$,[31] this might be explained by order–disorder phenomena (see above). Similarly, freshly prepared samples showed a somewhat simpler spectrum (Figure 2, trace D) than well-aged samples.

A closer inspection of the O_2^+ bands in $O_2^+GeF_5^-$ also shows some interesting effects. Whereas a freshly prepared sample showed a single sharp line at 1849 cm^{-1}, the aged samples exhibited two lines at 1841 and 1847–1855 cm^{-1}, respectively. The frequency of the higher energy line and its intensity relative to that of the lower energy decreased with decreasing temperature (see Figure 3). This observation is further evidence for the existence of ordering effects and for a unit cell containing more than one O_2^+ cation.

While the vibrational spectra establish beyond doubt the presence of discrete O_2^+ cations, there is considerable direct and indirect evidence against the presence of discrete GeF_5^- anions, particularly in the well-aged samples. The GeF_5^- anion is isoelectronic with AsF_5 and therefore, should possess a

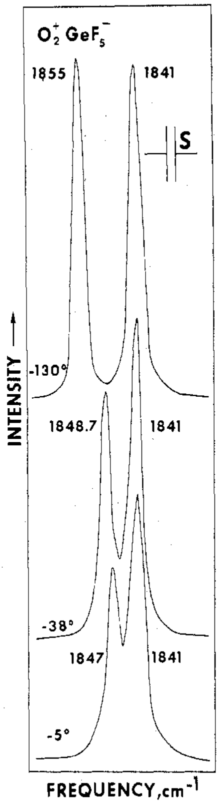

Figure 3. Temperature dependence of the O_2^+ stretching mode in the Raman spectra of $O_2^+GeF_5^-$ recorded with tenfold scale expansion and a spectral slit width of 1.5 cm^{-1}.

trigonal-bipyramidal structure of symmetry D_{3h}. Whereas AsF_5 and PF_5 are highly volatile and on the basis of their vibrational spectra[33,34] are little associated in the liquid and solid state, SbF_5 has a high boiling point and is associated in the gas, liquid, and solid states[35,36] through the formation of cis-fluorine bridges. Since the size of Ge(IV) should be intermediate between those of As(V) and Sb(V), GeF_5^- might very well be polymeric, particularly in an anion-dominated crystal lattice.

Comparison of the Raman spectrum of $O_2^+GeF_5^-$ with those of unassociated PF_5,[33] AsF_5,[34] or SbF_5[35] and associated SbF_5[35] or tetrameric NbF_5[16,36] was found helpful for distinguishing between discrete and polymeric GeF_5^- anions. The observation of at least five Ge–F stretching modes, with one of them (480 cm^{-1}) occurring in the frequency range expected for fluorine-bridged structures, argues against the presence of a discrete GeF_5^- anion. Furthermore, the Raman spectrum of GeF_5^- in $O_2^+GeF_5^-$ closely resembles that[16,36] of solid tetrameric NbF_5, indicating a similar polymeric structure. The crystal structure of solid NbF_5 has been determined by Edwards[37] and its vibrational spectrum was thoroughly analyzed by Beattie and co-workers.[36] Assignments for GeF_5^- on the basis of a cis-fluorine-bridged tetrameric polyanion can therefore be made by analogy with those[36] given by Beattie and co-workers for solid NbF_5. The possibility of a polymeric trans-fluorine-bridged structure for GeF_5^- can be eliminated based on the study of Beattie and co-workers on the vibrational spectrum of trans-fluorine-bridged α-BiF_5 which exhibits a much simpler Raman spectrum.[38]

The infrared spectrum of $O_2^+GeF_5^-$ also supports a polymeric structure for the anion. The 480-cm^{-1} band, indicative of fluorine bridges, was observed and the remaining part of the spectrum is very complex. Although the Raman spectra of the anions in $O_2^+GeF_5^-$ and $NF_4^+GeF_5^-$ [39] are relatively similar, the corresponding infrared spectra are more distinct. This indicates that the structure of polymeric GeF_5^- may be significantly influenced by the nature of the cations.

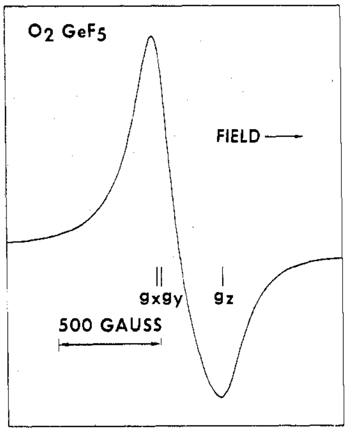

Figure 4. ESR spectrum of $O_2^+GeF_5^-$ recorded at −196 °C.

Additional indirect evidence for a polymeric structure of GeF_5^- in $O_2^+GeF_5^-$ can be derived from the following considerations. (i) The observed thermal stability of $O_2^+GeF_5^-$ would be surprisingly high (see above) for a salt containing discrete GeF_5^- anions. (ii) The GeF_5^- anion shows a strong tendency[17] to add a sixth ligand, such as H_2O or NH_3. Since the O_2^+ cation is quite small, there should be anion–anion contact in the crystal lattice and fluorine bridging appears likely. (iii) The splitting of the O_2^+ stretching mode in the Raman spectrum of $O_2^+GeF_5^-$ indicates a large unit cell containing more than one O_2^+ cation, contrary to $O_2^+MF_6^-$ for which only one very narrow line is observed for the O_2^+ stretch even at low temperatures. (iv) The observed orthorhombic crystal field splitting parameter in the ESR spectrum (see below) is compatible with a structure containing a polyanion. (v) The large number of combination bands observed for $O_2^+GeF_5^-$ in the infrared spectrum indicates many fundamentals and, hence, a rather complex anion.

ESR Spectrum of $O_2^+GeF_5^-$. The ESR spectrum of $O_2^+GeF_5^-$, recorded at −196°, is shown in Figure 4. The peak to peak line width is 283 G. The *g* factors were determined from computer-simulated spectra[15] as $g_x = 2.00$, $g_y = 1.98$, and $g_z = 1.86$. The natural line width used was Lorentzian with a peak to peak width of about 140 G. The orthorhombic crystal field splitting parameter[15] determined from g_z was 2.7×10^3 cm^{-1}. This value is larger than those reported[12,15] for $O_2^+AsF_6^-$ and $O_2^+BF_4^-$. This larger crystal field could be caused by effects, such as multiple charges or lower symmetry of the anion, and is not surprising in view of the probably polymeric nature of the GeF_5^- anion (see above).

Raman Spectrum of Solid GeF_4. The Raman spectrum of solid GeF_4 was recorded to demonstrate the absence of decomposition products in the spectra of $O_2^+GeF_5^-$. The observed spectrum is shown in Figure 5. It will be briefly discussed since it shows a remarkable deviation from the spectrum expected for a tetrahedral species of symmetry T_d. The observation of six sharp bands instead of the four, expected for T_d, resembles the previous reports for solid SiF_4[40] and CF_4.[41] By analogy with the spectrum of SiF_4 which has been thoroughly analyzed,[40] we assign the additional Raman bands observed for solid GeF_4 to a splitting of the two F_2 modes into longitudinal and transverse components. Longitudinal and transverse waves propagate with different frequencies in cubic or uniaxial crystals with the longitudinal component having the higher frequency.[40] Since the splitting of the F_2 modes into two components might also be explained by lowering of the site symmetry of GeF_4 from T_d to either C_{3v} or C_3, the infrared spectrum of solid GeF_4 was also recorded. However, such a site symmetry lowering seems less likely for the fol-

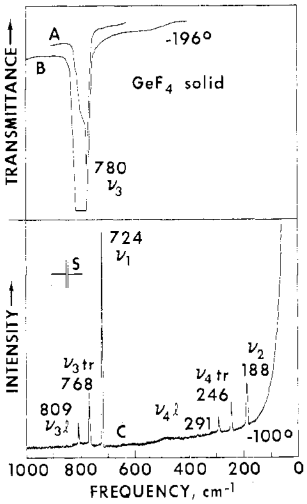

Figure 5. Vibrational spectra of solid GeF$_4$: traces A and B, infrared spectra recorded at two different concentrations; trace C, Raman spectrum; ℓ and tr indicate the longitudinal and transverse components, respectively, of the F$_2$ modes.

lowing reasons. (i) No evidence was found in the infrared spectrum for ν_1 which for C_{3v} or C_3 should become infrared active. (ii) The frequency separations between the F$_2$ components are larger than expected for site symmetry effects. (iii) The infrared spectrum shows only one intense component for ν_3. For C_{3v} or C_3, both components should be infrared active, whereas for a splitting into longitudinal and transverse components only the latter one should be infrared active. A more detailed study of these effects was beyond the scope of this investigation concerned with dioxygenyl salts.

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Registry No. $O_2^+GeF_5^-$, 58672-97-2; $(NO^+)_2GeF_6^{2-}$, 58673-00-0; GeF$_4$, 7783-58-6.

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