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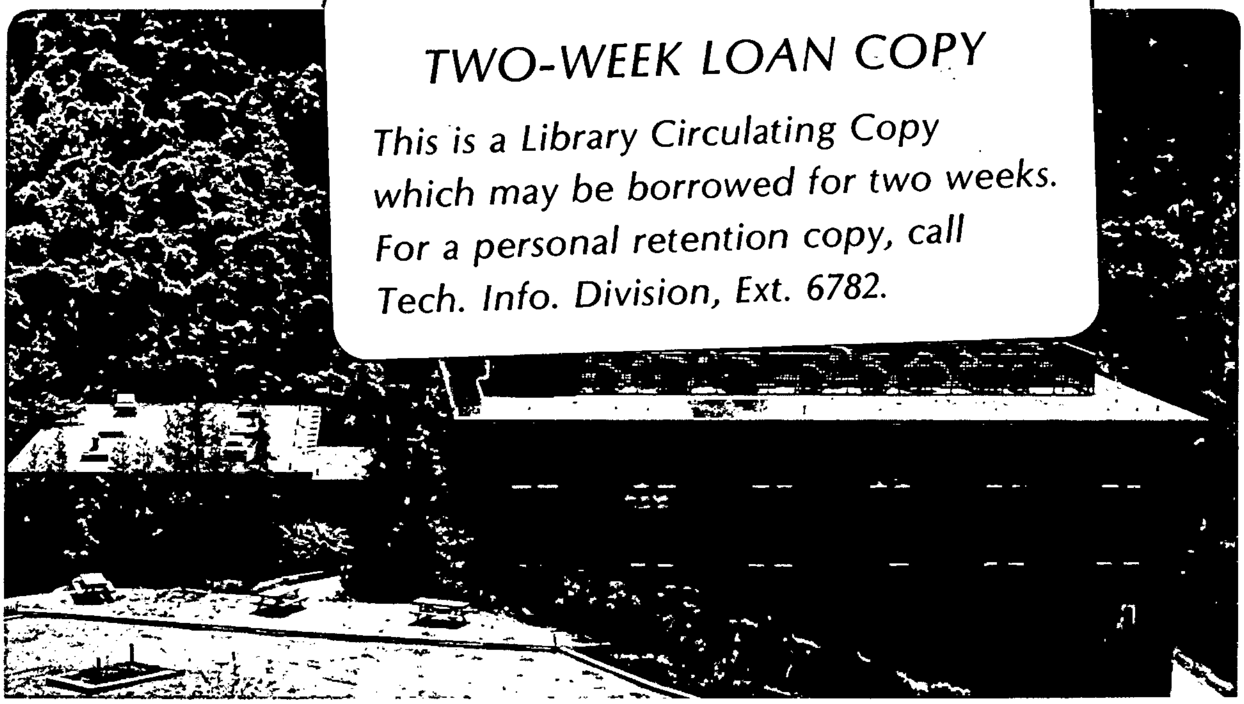

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Structural Studies, of Salts of *cis* and *trans* μ-Fluoro-Bridged Polymers of GeF_5^-, and of GeF_5^- Monomer

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ABSTRACT

$XeF_5^+GeF_5^-$ is orthorhombic and at 20°: a_o = 7.119(2); b_o = 12.986(4); c_o = 7.398(1) Å; V = 683.9(5) Å^3; Z = 4; space group Pmnb (a non-standard setting of Pnma, no. 62). From 437 independent X-ray diffraction data, the structure was refined to a weighted R of 0.018 (unweighted R = 0.021) a standard deviation of an observation of unit weight = 0.725. The structure contains infinite chains of GeF_6 octahedra sharing *trans* vertices. The XeF_5 cations are arranged alternately to left and right along the chain such that each cation approaches symmetrically two of the *μ* fluoro-bridged GeF_6 units. The non-bridging GeF_4 units are planar and approximately square, with Ge-F = 1.75(2) Å. The *μ* bridging Ge-F distance = 1.890(1) Å.

$ClO_2^+GeF_5^-$ is orthorhombic, and at -105±10°: a_o = 14.648(2); b_o = 7.576(1); c_o = 8.894(2) Å; V = 987.0(4) Å^3; Z = 8; space group $C222_1$ (no. 20). From 645 independent X-ray diffraction intensity data, refinement led to convergence with a weighted R factor = 0.068 (unweighted R = 0.059) a standard deviation of an observation of unit weight = 3.938. In the structure, infinite chains

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of approximately octahedral GeF_6 units are joined by sharing cis vertices. This is an infinite helix having all Ge atoms of the chain nearly coplanar. The non-bridging Ge-F distances are in two sets, the shorter (Ge-F = 1.737(4) and 1.728(3) Å) being cis to the bridging Ge-F bonds, and the longer (Ge-F = 1.776(3) and 1.768(3) Å) being trans to the Ge-F bridging. The two μ-bridging Ge-F distances are not significantly different, at 1.887(1) Å. The anion chains are held together by interactions with the cations. There are two crystallographically distinguishable ClO_2^+ units. Each lies on a two-fold axis and the closest cation to anion contacts (Cl_1-F_1 = 2.539(3)); Cl_2-F_4 = 2.625(3) Å) involve approach of F to Cl normal to the ClO_2 triangle.

Infrared and Raman spectra of the $XeF_5^+GeF_5^-$ and $ClO_2^+GeF_5^-$ salts have been assigned. Similarities of the vibrational spectra of the latter to the spectra of the O_2^+ salt indicate that the same anion occurs in both. The vibrational data show that a third oligomeric form of the anion must occur in the NO_2^+, NF_4^+ and SF_3^+ salts. The tetrabutyl ammonium salt contains a monomeric anion of approximately D_{3h} symmetry.

Introduction

The GeF_5^- anion is stabilized by a variety of cations including some of high electron affinity.[1-4] To date such salts have been characterized by their vibrational spectra. Those studies[2-4] have indicated that monomeric and oligomeric forms of the anion can occur. A need for detailed structural information for lattice energy evaluations, based upon the method of Bertaut[5] as modified by Templeton,[6] prompted the structural work reported in this paper. Salts were selected for those studies for which thermodynamic data, to complete the Born-Haber cycles, were accessible. The lattice energy evaluations and fluoride ion affinities derived using them are given in the accompanying paper.[7] The present studies include the crystal and molecular structures and vibrational spectra of the previously known compound[1] $XeF_6 \cdot GeF_4$ (for which x-ray structural work[8,9,10,11] had suggested the formulation $XeF_5^+GeF_5^-$) and similar studies of the new compound $ClO_2^+GeF_5^-$. The present crystallographic studies have provided a basis for the assignment of the structural form present in other salts.

Experimental Section

Apparatus and Materials: A Monel vacuum line was used. It was equipped with stainless steel or Monel 1KS4 Kel-F tipped Whitey valves and a Monel Acco Helicoid pressure gauge (0 - 1400 torr ± .3%). Reaction vessels were made from ¼" or 3/8" Teflon-FEP tubing (Penntube Plastics Co.) sealed at one end and degassed for several hours at 65-70°. A J-Y Ramanor spectrometer with a double holographic grating monochrometer, using either argon (514 or 488 nm) or krypton (647 nm) laser excitation provided the Raman spectra. Infrared spectra were recorded on a Perkin-Elmer 597 spectrometer using an air-tight Kel-F sample cell with AgCl windows cut from 1 mm thick sheet (Harshaw Chemical

Co., Solon, Ohio). X-ray powder diffraction patterns were obtained from a General Electric Co. precision camera (circumference 45 cm), with a Ni-filtered $CuK_{\bar{\alpha}}$ source.

GeF_4 was made from GeO_2 powder (Alfa Inorganics, 99.995%) and F_2 in a Monel bomb at 250°. It was purified by trap to trap distillation. XeF_6 was prepared by heating a F_2/Xe mixture (10/1 mole ratio) at 300° in a Monel bomb previously passivated with F_2. The small quantities of XeF_4 and $XeOF_4$ also formed were removed by condensing the crude product on to an excess of NaF to form NaF/XeF_6 complexes.[12] This mixture was heated in a dynamic vacuum at 50° to remove the impurities. XeF_6 was liberated by heating the remaining salt, Na_2XeF_8, in the range 100-150°.

ClO_2F was prepared by the method of Smith _et al._[13] from $KClO_3$ and ClF_3. The product was purified by trap to trap distillation. SF_4 and NO_2F were made and purified as described elsewhere.[14,15]

Preparation and X-Ray Structure Determinations. _$XeF_5^+GeF_5^-$_: XeF_6 (0.653 mmol) was combined with GeF_4 (0.878 mmol) at 50° for 20 minutes in a FEP U-tube which was then pumped out briefly at room temperature. The residual weight indicated the 1:1 compound $XeF_6.GeF_4$ (0.636 mmol). A Debye-Scherrer photograph yielded _d_ spacings in agreement with those previously reported.[1] The solid was handled in the dry nitrogen atmosphere of a (Vacuum Atmospheres Corp.) DRILAB.

Colorless crystals were formed upon sublimation of the microcrystalline solid at 40-50° in 0.7 mm diameter quartz X-ray capillaries. These had been sealed under an atmosphere of nitrogen. Precession photographs indicated a primitive orthorhombic cell, space group Pnma or $Pna2_1$.

A crystal was mounted on an Enraf-Nonius CAD-4 four circle diffractometer, and accurate cell dimensions were obtained by a least-squares fit to three sets of eight symmetry-equivalent reflections with 2θ between 25 and 29°. The cell dimensions and data collection parameters are summarized in Table I.

The structure was solved by heavy-atom methods[16] at the U. C. Berkeley CHEXRAY facility using full-matrix least-squares refinement procedures detailed elsewhere.[18] Systematically absent reflections were eliminated from the data set and those remaining were corrected for absorption by means of the calculated absorption coefficient. A three dimensional Patterson synthesis gave peaks which were consistent with Xe atoms in Wyckoff position 4$\underline{c}$ and Ge atoms in 4$\underline{a}$ in space group P$\underline{nmb}$ (see P$\underline{nma}$, no. 62). Three cycles of least-squares refinement for Xe and Ge with isotropic thermal parameters followed by a difference-Fourier synthesis gave the locations of the fluorine atoms (four in 4$\underline{c}$, three in 8$\underline{d}$). Three more cycles of isotropic least-squares refinement resulted in an R-factor of 0.110, indicating that the centric space group was probably the correct choice. Symmetry-equivalent reflections were averaged and the refinement continued with the inclusion of anisotropic thermal parameters and an extinction coefficient.[19] This led to final convergence with a weighted R factor of 0.018, unweighted R = 0.021, standard deviation of an observation of unit weight = 0.725 for 65 parameters, and 437 independent data. A final difference Fourier showed no peaks with intensity greater than 0.33 e/Å^3.

The positional and thermal parameters for XeF_5GeF_5 are listed in Table II.

$C\ell O_2^+GeF_5^-$: $C\ell O_2F$ and GeF_4, condensed in equimolar proportions into a FEP tube, produced a pale yellow solid. This was purified by briefly subjecting it to a dynamic vacuum at 0°, followed by sublimation at 22° to a trap held at -78°. Yellow crystals were obtained by sublimation at 30-35° in closed 0.5 mm diameter quartz capillaries under an atmosphere of nitrogen.

The ready sublimation of these crystals required that the collection of data be at low temperature; an apparatus was constructed for the CAD-4 which provided a stream of dry nitrogen to maintain the crystal at -105 ± 10° in all orientations. Apart from this modification the data collection (see Table I) and structure solution proceeded as for XeF_5GeF_5, except that loss of the crystal following data collection precluded the application of an absorption correction. Positional and thermal parameters for $C\ell O_2GeF_5$ are included in Table II.

Refinement of intensity data for $C\ell O_2GeF_5$ led to convergence with a weighted R factor = .068, unweighted R = .059, std. dev. obs. unit wt. = 3.938. The largest peak on a final difference electron density map was .285 e/Å^3.

$SF_3^+GeF_5^-$: This compound was prepared by displacement of BF_3 from SF_3BF_4 with GeF_4. The product is unstable with respect to disproportionation to $(SF_3)_2GeF_6$ and GeF_4 at room temperature, except under liquid (i.e., several atmospheres of) GeF_4, when SF_3GeF_5 can be stabilized. SF_3BF_4 (.35 mmol) was prepared[14] by interaction of equimolar quantities of SF_4 and BF_3 in FEP tubes. The compound was transferred by sublimation into a ¼" diam. quartz tube, the end of which had been drawn down to a capillary (0.7 mm diam.). GeF_4 (.50 mmol) was condensed into the reactor and after one minute at 10° the BF_3 liberated was pumped off at -126°. After two such treatments the powder was tapped down into the capillary, excess GeF_4 condensed upon it and the capillary sealed off. The X-ray powder pattern of this material (see supplementary material, Table V) was indexed to an orthorhombic cell, $\underline{a}$ = 11.66(2), $\underline{b}$ = 7.69(1), $\underline{c}$ = 6.36(1)Å, V = 569(1)Å^3, Z = 4 (consistent with Zachariasen's criterion[20] of 18Å^3 per fluorine atom). The Raman spectrum confirmed the formulation of this material as an SF_3^+ salt.

$\underline{NO_2^+GeF_5^-}$: NO_2F and GeF_4 were mixed at room temperature in equimolar proportions to produce a colorless vacuum-stable material, which was identified by its Raman and infrared spectra as an NO_2^+ salt.

Results and Discussion

$\underline{\text{The } XeF_5^+GeF_5^- \text{ Structure.}}$ A stereo view of the $XeF_5^+GeF_5^-$ structure is shown in Fig. 1. The anion consists of infinite chains of GeF_6 octahedra which share *trans* vertices. The cations are arranged alternately to left and right along the chain. Each XeF_5^+ cation has close contacts (2.75 - 2.76 Å) to four fluorine atoms of two neighboring μ-F-bridged GeF_6 groups in the chain. The coordination of the xenon atom is nearly that of a capped square antiprism of C_{4v} symmetry. The dimensions of the cation are close to those reported previously[8,9,10,11] for XeF_5^+ salts, and for the XeF_5^+ in the cubic form[21] of XeF_6. The μ-fluoro bridging of the anion with the cation is similar to that observed in the $XeF_5^+MF_6^-$ salts (M = Ru, Ir, Pt).[8,9] The bridging (and probably least negatively charged) fluorine atoms in the $(GeF_5^-)_n$ chain are apparently screened from interaction with the xenon atom by the non-bonding valence-electron pair of the latter. Note that the Ge-F-Ge linkage is kinked away from the Xe atom and its supposed sterically active non-bonding valence-electron pair. The coordination around each Ge atom is essentially an elongated octahedron of fluorine atoms, with cis F-Ge-F angles within the non-bridging fluorine GeF_4 set being 87.9° and 92.1°, the angle between this approximately square set and the bridging fluorine atoms is a right angle within one standard deviation. All Ge-F distances within the square plane are equal at 1.745(2) Å, and the Ge-bridging-F distance is 1.890(1). This difference in length of bridging and non-bridging M-F bonds of 0.14 Å is similar to that observed in other systems, and is consistent with the bridging bonds being essentially one-electron bonds.[22] Interactions between the chains are limited to F-F van der Waals' contacts ranging from 2.99 Å (F1-F4) to 3.26 Å (F2-F4). Selected bond lengths and angles are presented in Table III.

The $ClO_2^+GeF_5^-$ Structure. Figure 2 shows a stereo view of the $ClO_2^+GeF_5^-$ structure. Here the infinite chains are formed from approximately octahedral GeF_6 units which share cis vertices; the chain is an extended helix with all germanium atoms of a chain nearly coplanar. The shortest Ge-F bonds (1.73 - 1.74 Å) are cis to the bridging fluorine atoms but those trans are only slightly longer (1.77 - 1.78 Å). The Ge-bridging F-distances are the same (1.887(1)) within one standard deviation. The anion chains are linked together, by the close contacts (2.54 and 2.90 Å) of the chlorine atoms of the cations, to fluorine atoms <u>trans</u> to bridging F atoms of the anionic chains. There are two crystallographically distinguishable chlorine atoms in the structure, but each lies on a twofold rotation axis. The coordination of each is shown in Fig. 3. The closest cation-to-anion contacts (Cℓ1-F1 and Cℓ2-F4) are made on the faces of the triangle defined by the two oxygen atoms and the chlorine atom. Presumably the non-bonding electron pair is in the plane of the triangle and exo to it at the Cℓ apex. The screening of the cation charge by the Cl non-bonding electron pair is the probable cause of the long Cℓ to F contacts in the plane of the $C\ell O_2$ triangle, which contrast with the short Cℓ to F contacts roughly perpendicular to that plane. This differs from the coordination of the $C\ell F_2^+$ ion. As Lynton and Passmore point out in their discussion of the $C\ell F_2^+AsF_6^-$ structure[23] (and this view is supported by ab initio calculations[24] for the free $C\ell F_2^+$ ion), the $C\ell F_2^+$ ion is a slightly distorted $C\ell F_2E_2$ tetrahedron. In the $C\ell F_2^+AsF_6^-$ structure and also that[25] of $C\ell F_2^+SbF_6^-$ the closest anion-to-chlorine contacts are made on the FE_2 faces of the tetrahedron, giving a distorted square planar arrangement of fluorine atoms about each Cℓ atom.

A summary of bond distances and angles for $C\ell O_2^+GeF_5^-$ is presented in Table IV.

<u>Vibrational Analysis of Salts Containing the GeF_5^- Ion.</u> The Raman and infrared spectra of the GeF_5^- salts of XeF_5^+, NO_2^+, and SF_3^+ are shown in Figures 4 and 5.

$\underline{XeF_5^+GeF_5^-}$. Assignments for the XeF_5^+ ion in $XeF_5^+GeF_5^-$ are given in Table VI. In polarized Raman spectra recorded from a single crystal, the cation stretching bands which transform as A_g in the point group of the crystal (D_{2h}) are most intense for the I_{vv} polarization. The correlation $\underline{D}_{2h} \rightarrow C_s \rightarrow \underline{C}_{4v}$ shows that these are the A_1, B_2, and E modes of the approximately $\underline{C}_{4v}$ XeF_5^+ ion; hence the bands at 669, 622, and 602 cm^{-1} are attributed to the $\nu_1(A_1)$, $\nu_4(B_2)$, and $\nu_2(A_1)$ modes, respectively. The other Raman and infrared bands are assigned by analogy to published spectra of XeF_5^+ salts.[26,27] The assignments have been made according to the approximate $\underline{C}_{4v}$ symmetry of the ion, but since the crystallographic symmetry is C_s, the degeneracy of the E modes ought to be lifted.

Since the germanium atoms in $XeF_5^+GeF_5^-$ lie on crystallographic inversion centers, the Raman and infrared spectra are mutually exclusive for $(GeF_5)_n^{n-}$; it is important to note also that the Raman-active modes will involve no motion of the germanium atoms. To simplify the enumeration of the vibrations of the $(GeF_5)_n^{n-}$ chain, the normal modes of the square plane formed by the germanium and four non-bridging fluorine atoms are considered separately from those of the germanium and the bridging F atoms. For a GeF_4 square plane of $\underline{D}_{4h}$ symmetry we expect seven vibrations, of which three are stretching modes: $\nu_1(A_{1g})$, $\nu_4(B_{2g})$, and $\nu_7(E_u)$. The ν_1 vibration should be the most intense, but since a Ge-F bond is less easily polarized than an Xe-F bond, its intensity in the Raman will be rather low. Thus ν_1 is assigned to the band at 654 cm^{-1}. The ν_4 stretch is not as firmly assigned, but by comparison with the same type of vibration[28] in GeF_6^{2-} we associate it with the weak band found at 463 cm^{-1}. On similar grounds the doublet at 339, 331 cm^{-1} is attributed to the deformational modes of the square GeF_4 group. The ν_7 stretch, observable only in the infrared, is found at 700 cm^{-1}. The other vibrations of the square GeF_4 group, also infrared-active, are of a frequency too low (<300 cm^{-1}) to be observed.

The remaining bands must arise, therefore, from vibrations of the infinite chains. In the 500-600 cm^{-1} region, the observed infrared (600 and 500 cm^{-1}) and Raman bands (518 and 526 cm^{-1}) are attributed to chain stretching modes. Chain-square plane deformational (381 cm^{-1}) and torsional-rotational modes (184, 124 cm^{-1}) are also seen in the Raman.

$ClO_2^+GeF_5^-$. The cation and anion bands for $ClO_2^+GeF_5^-$ are shown in Table VI. The frequencies observed for ClO_2^+ correspond well to those given previously by Christe and his coworkers.[29]

Because the anion in $ClO_2^+GeF_5^-$ consists of infinite chains of octahedra which share cis-vertices, its symmetry is lower than that of the trans-bridged anion found in $XeF_5^+GeF_5^-$, and the IR-Raman selection rules are not very restrictive. If one considers the group formed by the germanium and four non-bridging fluorine atoms, it approaches C_{2v} symmetry with four stretching modes which transform as $2A_1 + B_1 + B_2$, all active in both infrared and Raman. Those of type A_1 are primarily observable in the Raman, while those of type B_1 and B_2 will be most intense in the infrared. Therefore we assign the IR bands at 695 and 650 cm^{-1} to the B_1 and B_2 vibrations, and the most intense Raman band (657 cm^{-1}) to the in-phase symmetric stretch (A_1) of the GeF_4 group. The bands between 500 and 600 cm^{-1} may then be attributed to the stretching modes of the chain. By analogy to the vibrational frequencies of the trans-bridged $(GeF_5)_n^{n-}$ ion in $XeF_5^+GeF_5^-$, we assign the 395, 399 cm^{-1} band to a deformation of the angle between the GeF_4 group and the bridging fluorines; the bands between 290 and 337 cm^{-1} are attributed to deformations of the GeF_4 group, and the lower frequency bands (133 to 232 cm^{-1}) to torsional and rotational motions of the infinite chains.

The published spectra[3] of $O_2^+GeF_5^-$ are similar to those of $ClO_2^+GeF_5^+$. It is therefore probable that the anion has nearly the same structure in both compounds.

The NO_2^+, SF_3^+ and NF_4^+ Salts of GeF_5^-. The vibrational spectra and assignments for the NO_2^+ and SF_3^+ salts are given in Table VI. Both compounds show Raman bands in the chain stretching region (507, 583 cm^{-1} in $SF_3^+GeF_5^-$ and 501, 606 cm^{-1} in $NO_2^+GeF_5^-$), indicating polymeric, cis-bridged $(GeF_5)_n^{n-}$ ions. Both compounds have a vibration of medium intensity near 500 cm^{-1} and a particularly simple bond bending region with only one strong band at 355 cm^{-1}. For this reason we conclude that the anions are structurally similar, and yet different from $(GeF_5)_n^{n-}$ in $ClO_2^+GeF_5^-$, wherein the infinite chains of bridged octahedra form an extended helix with the Ge atoms nearly coplanar. The anion in $NF_4^+GeF_5^-$, because its vibrational spectra[4] are very like those of $NO_2^+GeF_5^-$, is probably of the same structural type.

<u>$C_4H_9N^+GeF_5^-$</u>. The Raman and infrared spectra of the tetrabutylammonium salt, first prepared by Wharf and Onyszchuk[2], are shown in Figure 6. The vibrations of the anion may be readily assigned on the basis of $\underline{D}_{\underline{3h}}$ symmetry, from selection rules and by comparison to other MX_5 species. The ν_7 band (IR and Raman active) which we expect to find near 100 cm^{-1}, is obscured by a band of the tetrabutylammonium ion at 117 cm^{-1}. In measuring the intensity of this band relative to the tetrabutylammonium band at 260 cm^{-1} in this compound and in $C_4H_9N^+Br^-$, we find that its intensity is enhanced in the GeF_5^- salt. It seems therefore that the ν_7 vibration of GeF_5^- should be located near 117 cm^{-1}. The vibrational assignments for GeF_5^- in $(C_4H_9)_4N^+GeF_5^-$ are given in Table VII, and assignments for other MX_5^- species are tabulated for comparison.

<u>General Discussion</u>. Onyszchuk and his coworkers[2] had previously established that the monomeric GeF_5^-, of $\underline{D}_{\underline{3h}}$ symmetry, is stabilized by large mono-cations. It seems that such cations cannot make the close anion-cation contacts necessary to sustain a clustered anion arrangement. It is pertinent to examine why such large cations do not sustain relatives of the $[XeF_5]_n^+$ $[GeF_5]_n^-$ structure.

Clearly the effective diameter of a cation in the XeF_5GeF_5 structure cannot exceed the span of an atomic sequence F_b - Ge - F_b - Ge - F_b. By allowing linear bridge bonds (Ge-F_b-Ge = 180°) this span can be maximized to ∿ 7.6 Å, thus accommodating large cations. A cation such as tetra-<u>n</u>-butyl ammonium however (which has a minimum effective radius[30] of 4.1 Å) would require appreciable stretching and weakening of the bridge bonds. But there may be another factor contributing to the instability of the chain structure with a such a large cation. The closest approach of the center of any cation, to any atom of the chain, would be the sum of the large-cation radius and the van der Waals radius of the closest atom of the chain. Although XeF_5^+ is a large cation (with an effective volume of ∿ 95 $Å^3$) it is highly unsymmetrical. As has been pointed out previously[9,10] the positively charged xenon atom is effectively screened by the five F ligands and by the Xe-valence-electron pair, which is situated on the four-fold axis of the cation, trans to the axial ligand. The positive charge of the Xe atom is exposed on the pseudo-octahedral faces defined by the Xe-valence electron pair, and pairs of adjacent equatorial F ligands of the cation. It is very much a one-sided cation. This accounts for the short contacts between each Xe atom and four (two sets at 2.75 and 2.76 Å) F ligands of the $(GeF_5^-)_n$ chain.

The development of the XeF_5GeF_5 structure appears to be a consequence (given the tendency of GeF_5^- to polymerize) of the cation to interact strongly with four anionic ligands, all on one side of it. This results in the cation interacting with two non-bridging (and hence more negative) F ligands of each of two F-bridged $[GeF_4]$ units. The repulsive effect of the Xe-valence-electron pair, causes the bridging F ligand to be pushed away from the cation (this Xe-F distance is 3.890(3) Å). These interactions, combined with the requirements that the cations be separated to maximum extent, and that the F ligand configuration about Ge be approximately octahedral, account for the observed structure.

That the ClO_2GeF_5 and XeF_5GeF_5 structures are different is presumably a consequence of the different interactive geometries of the cations. The ClO_2^+

has a Cl-valence-electron pair (on the twofold axis, opposite the O ligands) and the structure reveals that the Cl atom does not make close contacts to anionic ligands in this direction. Unlike XeF_5^+ however, the ClO_2^+ makes two strong, almost centrosymmetric interactions with anionic ligands. These are approximately normal to the ClO_2 plane. To accommodate such approximately centrosymmetric interactions of the cation with the $(GeF_5^-)_n$ chain of XeF_5GeF_5 type, would require the Cl atom to be brought closer to the bridging F ligands of the anion, than to other F ligands of the GeF_6 polyhedra. Clearly such a structure is not tenable for the ClO_2^+. Thus the observed structure, with its cis-bridging ligand configuration for the $[GeF_6]$ unit must be an accommodation to the cation coordination requirements. The NO^+ [Ref. 31] and O_2^+ salts presumably adopt the same kind of structure because they also are able to interact approximately centrosymmetrically with anions.

Evidently the choice of cis versus trans bridging for polymerized GeF_5^- is one of energetic subtlety. Indeed both bridging modes occur[32] in $SrAlF_5$. The vibrational data show that the NO_2^+, NF_4^+ and SF_3^+ stabilize yet another polymeric form of $(GeF_5^-)_n$, although again, as in ClO_2GeF_5, the polymer must be cis bridged. Whether it is another chain or a ring is not clear, but the same form appears to be common to all.

Although the bridging Ge-F-Ge angles in XeF_5GeF_5 and ClO_2GeF_5 are similar, we believe that this coincidence is accidental. There is a systematic trend in related transition metal M-F-M bridging angles, such as those observed in the pentafluorides,[22] but similar trends for non-transition elements appear not to exist. Thus Edwards and Taylor[33] in their structure of crystalline SbF_5, have found Sb-F-Sb angles of both 141° and 170°. Also, in $BrF_4^+Sb_2F_{11}^-$ Lind and Christe[34] found Sb-F-Sb = 173 ± 6.4°, whereas Bartlett and his co-workers[35] found the Sb-F-Sb angle in $XeF_3^+Sb_2F_{11}^-$ to be 155.4(2)°. In α-BiF_5, the linear chain polymer[36] involves Bi-F-Bi = 180°.

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$$R = \frac{\Sigma||F_o|-|F_c||}{\Sigma|F_o|};\ R_w = \left(\frac{\Sigma w(|F_o|-|F_c|)^2}{\Sigma w|F_o|^2}\right)^{1/2},\ \text{e.s.d.o.u.w.} =$$

$$\left(\frac{\Sigma w(|F_o|-|F_c|)^2}{(n_o - n_v)}\right)^{1/2},$$

where n_o is the number of observations and n_v the number of variables.

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Table I. Crystallographic Data

	XeF_5GeF_5	ClO_2GeF_5
Crystal dimensions:	.15 x .14 x .10 mm	.30 x .10 x .10 mm
Space group:	Pmnb (non-std. setting of Pnma, #62)	$C222_1$
Volume ($\mathring{A}^3$) :	683.9(5) Z = 4 calc'd = 3.825	987.0(4) Z = 8 calc'd = 3.163
Cell dimensions ($\mathring{A}$):	$\underline{a}$ = 7.119(2) $\underline{b}$ = 12.986(4) $\underline{c}$ = 7.398(1)	$\underline{a}$ = 14.6480(15) $\underline{b}$ = 7.5762(11) $\underline{c}$ = 8.8941(15)
radiation:	MoK_α, monochromatized (λ = .71073$\mathring{A}$)	
2θ range:	2-45°	
hkl range:	+h, +k, $\pm$l	−h, +k, $\pm$l h+k=2n
scan mode:	θ-2θ	
background:	.25 x$\Delta\theta$, where = .70 + .347 tanθ	
scan rate:	variable, maximum 50 sec.	
absorption coefficient (μ):	98.9 cm^{-1}	---
transmission:	29.4% max., 11.7% min.	---
orientation and intensity stds.:	(272), (442), (124) every 250 reflections--no decay	($\bar{3}$15), ($\bar{8}$21), ($\bar{4}$42) every hour--no decay
reflections measured:	1054	645

Table IIa. Positional and Thermal Parameters for $XeF_5^+GeF_5^-$

ATOM	X	Y	Z	B(1,1)	B(2,2)	B(3,3)	B(1,2)	B(1,3)	B(2,3)
Xe	0.2500(0)	0.13903(3)	0.36600(5)	0.00810(5)	0.00386(2)	0.0000(0)	0.0000(0)	0.0000(0)	-0.00363(7)
Ge	0.0000(0)	0.0000(0)	0.0000(0)	0.00243(8)	0.00318(3)	0.00818(9)	-0.00007(8)	-0.0006(2)	-0.0007(1)
F1	0.0597(2)	-0.0269(1)	0.2242(3)	0.0059(3)	0.0054(1)	0.0094(4)	0.0035(4)	-0.0013(6)	0.0014(5)
F2	0.0567(2)	0.1283(1)	0.0423(3)	0.0070(3)	0.0032(1)	0.0160(4)	0.0014(4)	-0.0001(7)	-0.0009(5)
F3	0.2500(0)	-0.0269(2)	-0.0708(4)	0.0026(4)	0.0040(2)	0.0100(6)	0.0000(0)	0.0000(0)	-0.0018(7)
F4	0.2500(0)	0.2688(2)	0.2698(6)	0.0208(7)	0.0040(2)	0.0249(8)	0.0000(0)	0.0000(0)	-0.0034(10)
F5	0.5030(2)	0.1530(2)	0.4057(3)	0.0094(4)	0.0062(1)	0.0196(5)	-0.0029(4)	-0.0053(8)	-0.0061(6)
F6	0.2500(0)	0.0342(2)	0.5314(5)	0.0150(6)	0.0064(2)	0.0118(6)	0.0000(0)	0.0000(0)	0.0024(8)
F7	0.2500(0)	0.2136(3)	0.5741(5)	0.0194(7)	0.0084(3)	0.0186(7)	0.0000(0)	0.0000(0)	-0.0157(9)

THE FORM OF THE ANISOTROPIC THERMAL PARAMETER IS:

$$\mathrm{EXP}\ (-[B(1,1)xh^2 + B(2,2)xk^2 + B(3,3)x\ell^2 + B(1,2)xhk + B(1,3)xh\ell + B(2,3)xk\ell])$$

Table IIb. Positional and Thermal Parameters for $ClO_2^+GeF_5^-$

ATOM	X	Y	Z	B(1,1)	B(2,2)	B(3,3)	B(1,2)	B(1,3)	B(2,3)
Ge	0.11474(7)	0.11118(1)	0.3194(1)	0.00085(5)	0.0027(2)	0.0015(1)	-0.0000(1)	0.0000(1)	0.00004(2)
CL1	-0.3858(3)	0.0000(0)	0.0000(0)	0.0017(2)	0.0060(6)	0.0041(5)	0.0000(0)	0.0000(0)	0.0025(8)
CL2	0.2708(3)	0.0000(0)	0.0000(0)	0.0013(2)	0.0063(6)	0.0034(5)	0.0000(0)	0.0000(0)	-0.0004(9)
F1	0.1386(4)	0.2148(8)	0.1444(7)	0.0016(3)	0.0081(10)	0.0026(7)	0.0009(9)	0.0007(8)	0.006(2)
F2	0.0000(0)	0.0331(10)	0.2500(0)	0.0008(4)	0.0041(13)	0.0033(11)	0.0000(0)	-0.0015(12)	0.000(0)
F3	0.0601(4)	0.2980(7)	0.3863(8)	0.0017(3)	0.0033(9)	0.0059(8)	0.0017(8)	-0.0007(9)	-0.005(2)
F4	0.2196(4)	0.1734(7)	0.4027(7)	0.0013(3)	0.0048(8)	0.0042(8)	-0.0001(8)	0.0000(8)	-0.002(2)
F5	0.1571(4)	-0.0890(8)	0.2558(8)	0.0018(3)	0.0047(10)	0.0047(8)	0.0017(9)	0.0008(8)	-0.001(1)
F6	0.0793(6)	0.0000(0)	0.5000(0)	0.0012(4)	0.0084(15)	0.0026(12)	0.0000(0)	0.0000(0)	0.004(2)
01	-0.4339(5)	0.0864(10)	0.1144(9)	0.0032(4)	0.005(1)	0.0040(9)	-0.000(1)	-0.001(1)	0.000(2)
02	0.3189(5)	0.0669(9)	0.1231(9)	0.0022(4)	0.005(1)	0.0025(9)	-0.001(1)	-0.001(1)	-0.000(2)

THE FORM OF THE ANISOTROPIC THERMAL PARAMETER IS:

$$\mathrm{EXP}\ (-[B(1,1)xh^2 + B(2,2)xk^2 + B(3,3)x\ell^2 + B(1,2)xhk + B(1,3)xh\ell + B(2,3)xk\ell])$$

Table III. Selected Internuclear Distances and Angles for $XeF_5^+GeF_5^-$

Distances:

Ge	F1	1.745(2)	Xe	F3	3.890(3)
Ge	F2	1.745(2)	Xe	F4	1.828(5)
Ge	F3	1.890(1)	Xe	F5	1.831(3)
Xe	F1	2.752(3)	Xe	F6	1.826(4)
Xe	F2	2.764(3)	Xe	F7	1.813(4)

Angles:

F1-Ge-F1	180	F5-Xe-F5	158.26(20)
F1-Ge-F2	87.86(13)	F5-Xe-F6	88.18(11)
F1-Ge-F3	90.07(13)	F5-Xe-F7	79.13(10)
F2-Ge-F2	180	F6-Xe-F7	79.70(23)
F2-Ge-F3	90.48(13)	Ge-F3-Ge	140.70(20)
F4-Xe-F5	88.25(12)	Xe-F1-Ge	109.09(12)
F4-Xe-F6	160.94(21)	Xe-F2-Ge	108.58(11)
F4-Xe-F7	81.25(24)		

Table IV - Selected Bond Lengths and Angles for $ClO_2^+GeF_5^-$

Ge - F1	1.776(3)	Cℓ1 - 54	2.898(4)
Ge - F2	1.887(1)	Cℓ1 - 01	1.401(5)
Ge - F3	1.728(3)	Cℓ2 - F1	2.837(4)
Ge - F4	1.768(3)	Cℓ2 - F4	2.625(3)
Ge - F5	1.737(4)	Cℓ2 - F5	2.900(4)
Ge - F6	1.888(2)	Cℓ2 - 02	1.396(5)
Cℓ1 - F1	2.539(3)		

F1 - Ge - F2	91.57(12)	F3 - Ge - F5	172.92(17)
F1 - Ge - F3	91.97(18)	F3 - Ge - F6	86.89(16)
F1 - Ge - F4	94.60(17)	F4 - Ge - F5	93.31(16)
F1 - Ge - F5	91.66(18)	F4 - Ge - F6	90.04(18)
F1 - Ge - F6	175.26(18)	F5 - Ge - F6	88.99(15)
F2 - Ge - F3	87.59(16)	01 - Cℓ1 - 01	119.5(4)
F2 - Ge - F4	173.82(14)	02 - Cℓ2 - 02	119.5(4)
F2 - Ge - F5	86.24(16)	Ge - F2 - Ge	143.2(2)
F2 - Ge - F6	83.79(15)	Ge - F6 - Ge	148.1(3)
F3 - Ge - F4	92.46(16)		

Table V - X-ray Powder Data for $SF_3^+GeF_5^-$

line #	intensity*	$10^4/d^2$ (obs)	$10^4/d^2$ (calc)	h	k	ℓ
1	s	167	170	0	1	0
2	w	245	244	1	1	0
3	s	416	418	0	1	1
4	s	465	468	2	1	0
5	s	669	671	3	0	0
6	s	703	717	2	1	1
7	s	761	755	1	2	0
8	m	912	919	3	0	1
9	w	1095	1090	3	1	1
10	m	1167	1163	0	1	2
11	m, broad	1281	1292	2	0	2
12	m	1417	1442	4	0	1
13	w	1516	1530	0	3	0
14	vw	1589	1600	3	2	1
15	w	1662	1665	3	0	2
16	w	1788	1779	0	3	1
17	w, broad	1889	1874	4	2	0
18	w, broad	2115	2113	5	0	1

* CuK$\bar{\alpha}$ radiation, $\lambda = 1.5418$ Å

s = strong
m = medium
w = weak
vw = very weak

orthorhombic, $\underline{a} = 11.66(2)$, $\underline{b} = 7.69(1)$, $\underline{c} = 6.36(1)$ Å

Table VI - Vibrational Assignments for GeF_5^- Salts

$XeF_5^+GeF_5^-$

obs. freq.(cm^{-1}) IR	obs. freq.(cm^{-1}) Raman	assignment $XeF_5^+(C_{4v})$	assignment $(GeF_5)_n^{n-}(D_{4h})$
700			ν_6 (E_u)
680	675	ν_7 (E)	
645	648		
	669	ν_1 (A_1)	
	654		ν_1 (A_{1g})
	622	ν_4 (B_2)	
	602	ν_2 (A_1)	
600			stretching vibrations of the chains
	526		
	518		
500			
	463		ν_4 (B_{2g})
413	417	ν_8 (E)	
400	402		
			deformation of the chain-square plane angle
	381		
355	354	ν_3 (A_1)	
	339		ν_2 (B_{1g})
	331		
	300	ν_6 (B_1)	
	263	ν_5 (B_2)	
	220	ν_9 (E)	
	208		
	184		chain torsional-rotational modes
	124		

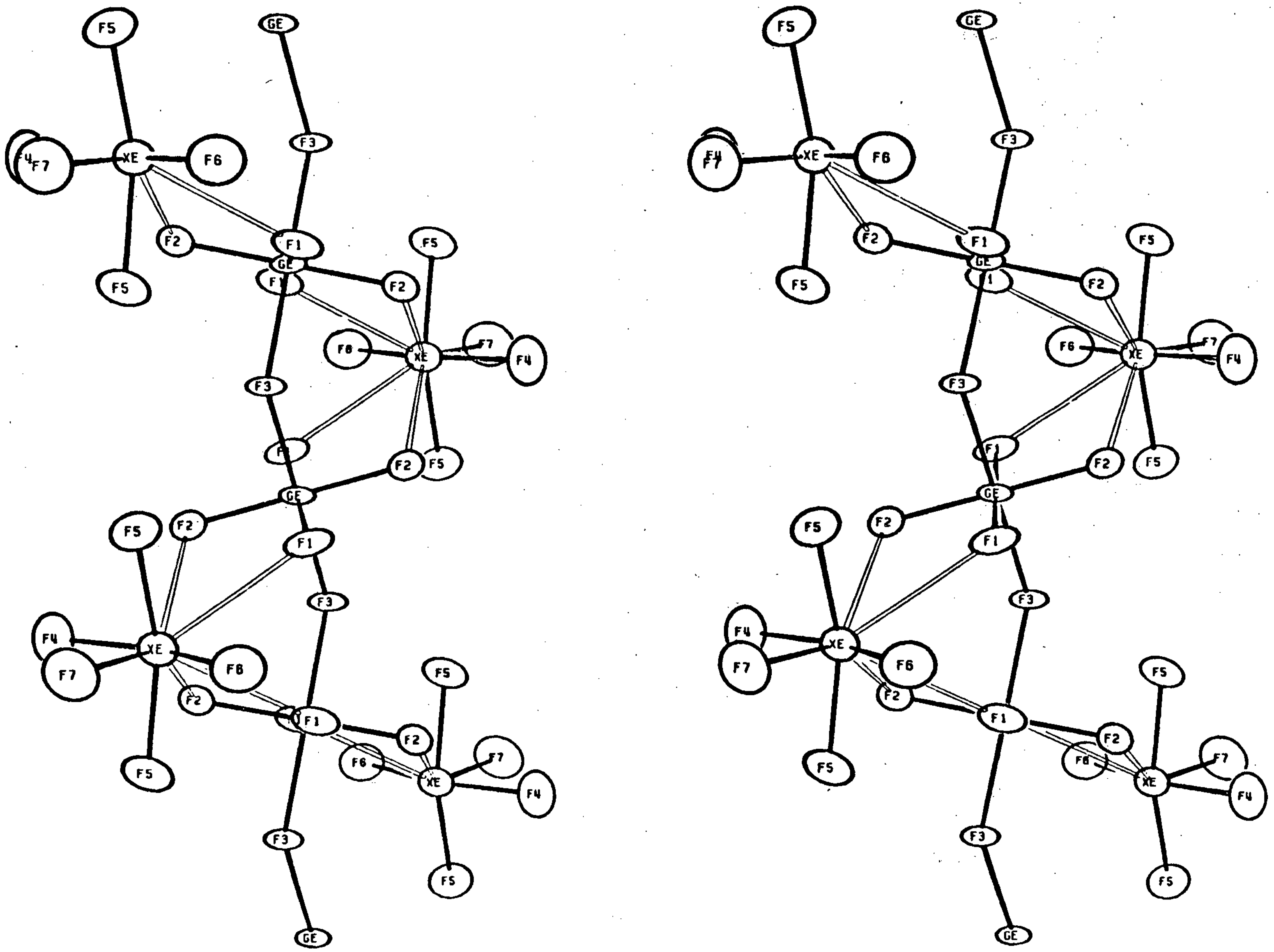
$ClO_2^+GeF_5^-$

obs. freq.(cm^{-1}) IR	obs. freq.(cm^{-1}) Raman	assignment $ClO_2^+(C_{2v})$	assignment $(GeF_5)_n^{n-}$
1303	1307	ν_3 (B_1)	
1293	1294		
1086			
	1065	ν_1 (A_1)	
	1057		
1040		2 x ν_2	
1018			
	713		Ge-non-bridging F stretching vibrations
695			
	657		
650			
	603		stretching vibrations of the chains
595	590		
	559		
	525		
	512	ν_2 (A_1)	
395	399		chain-GeF_4 group angle deformation
	337		bending modes of the GeF_4 group
	303		
290	292		
	232		chain torsional-rotational modes
	160		

$NO_2^+GeF_5^-$ observed freq. (cm^{-1}) IR	$NO_2^+GeF_5^-$ observed freq. (cm^{-1}) Raman	$SF_3^+GeF_5^-$ observed freq. (cm^{-1}) Raman	assignment $NO_2^+(D_{\infty h})$	assignment $SF_3^+(C_{3v})$	assignment $(GeF_5)_n^{n-}$
3765			ν_1 + ν_3		
2388			ν_3 (Σ_u^+)		
2378					
	1409		ν_1 (Σ_g^+)		
	1405				
		945		ν_1 (A_1)	
		932			
		916		ν_3 (E)	
		904			
		887			
		874			
		708			Ge-non-bridging F stretching vibrations
687					
		669			
660	654				
618					stretching vibrations of the chains
	606				
		583			
587	592		ν_2 (Π_u)		
		538		ν_4 (E)	
	501	507			stretching vibrations of the chain
		410		ν_2 (A_1)	
382					
362	354	353			bending modes of the GeF_4 group
343					
	265				chain torsional-rotational modes
	156				

Table VII - Vibrational Assignments for GeF_5^- in $Bu_4N^+GeF_5^-$

	GeF_5^- (this work)	SiF_5^- (ref. 25)	$GeC\ell_5^-$ (ref. 26)
ν_1 (cm^{-1})	665	708	348
ν_2 (cm^{-1})	520	519	236
ν_3 (cm^{-1})	654	785	310
ν_4 (cm^{-1})	345	481	200
ν_5 (cm^{-1})	690	874	395
ν_6 (cm^{-1})	317	449	200
ν_7 (cm^{-1})	∿ 117	-	-
ν_8 (cm^{-1})	337	-	-



XBL 835-9964

Figure 1. $XeF_5^+GeF_5^-$ Structure

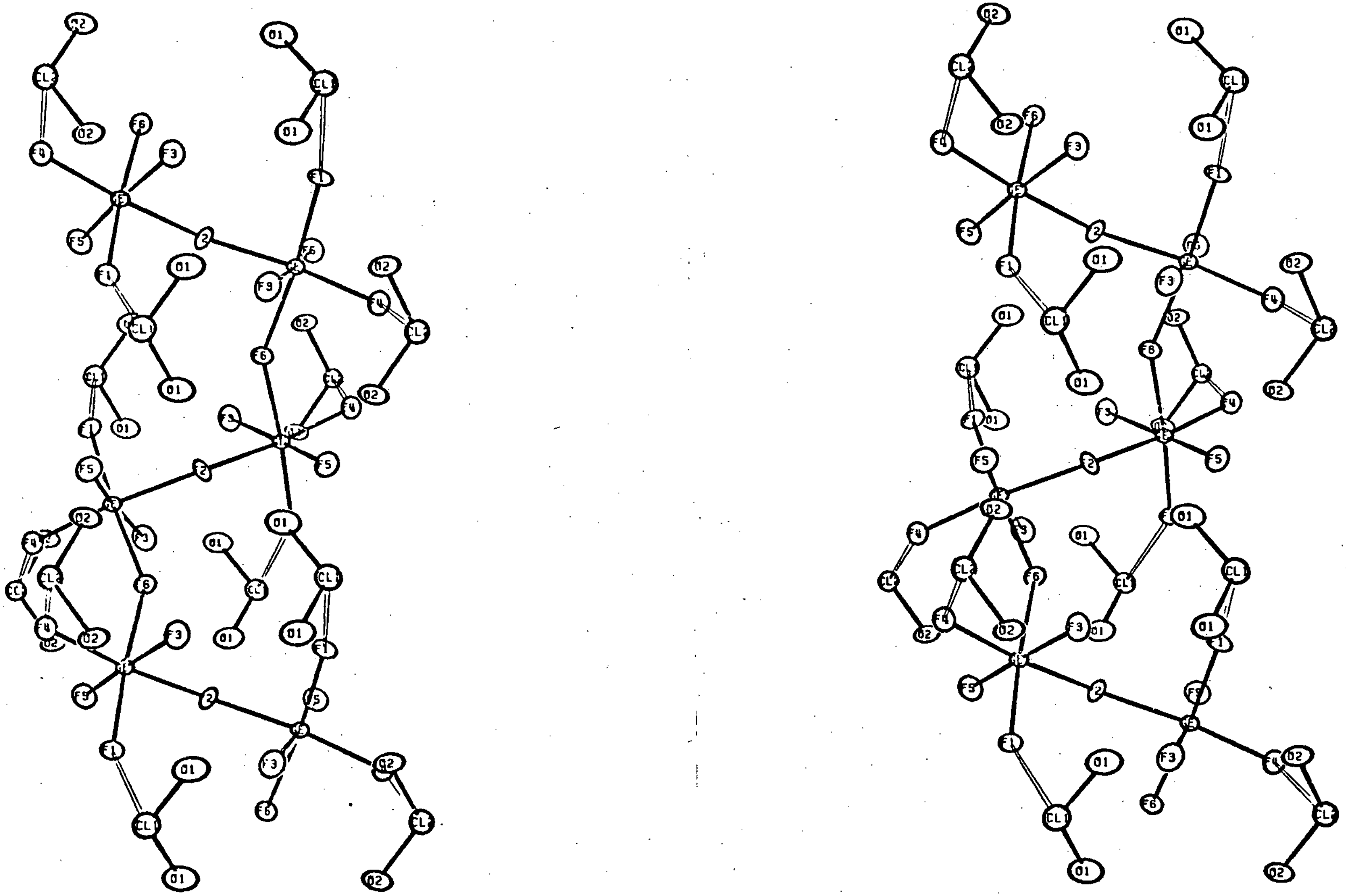


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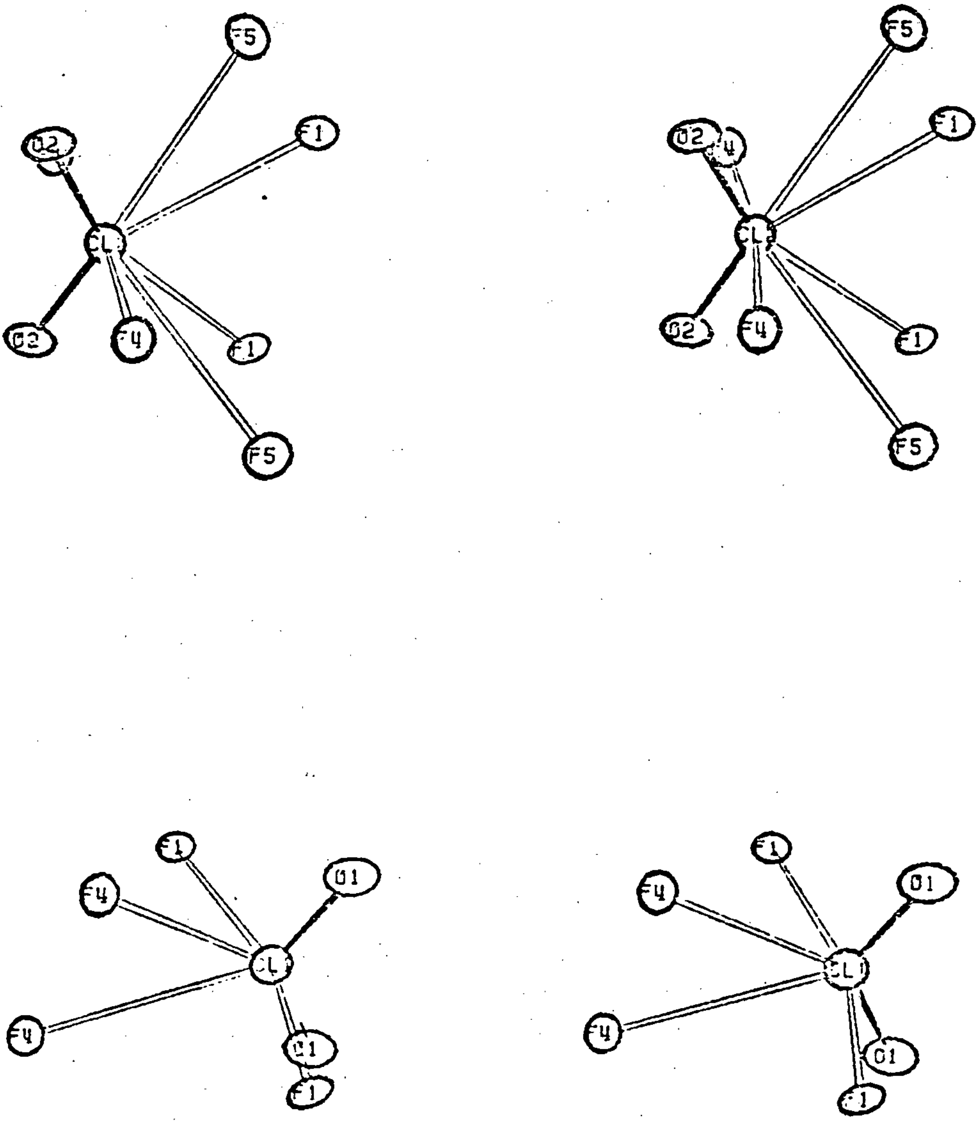
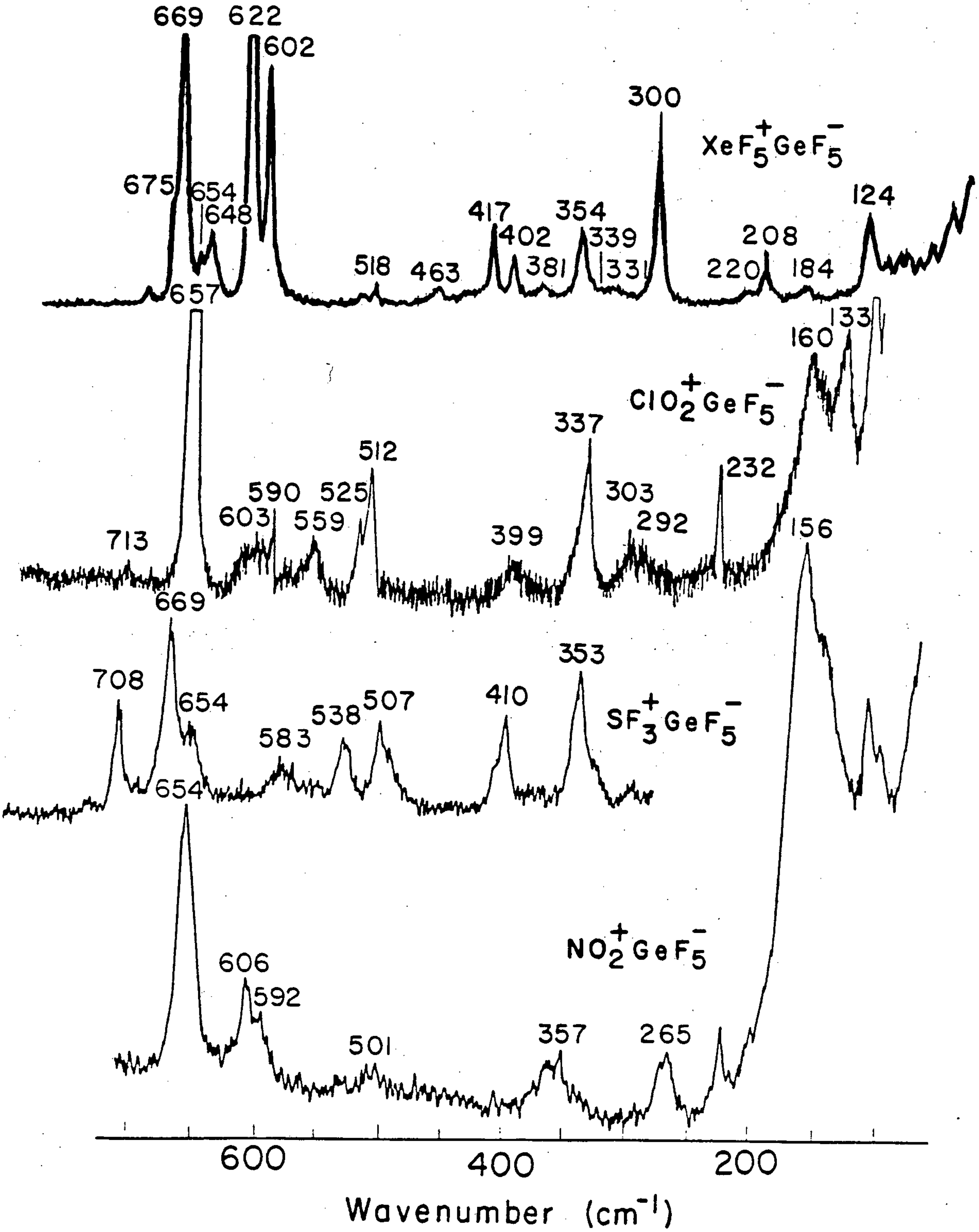
Figure 2. $ClO_2{}^+GeF_5{}^-$ Structure



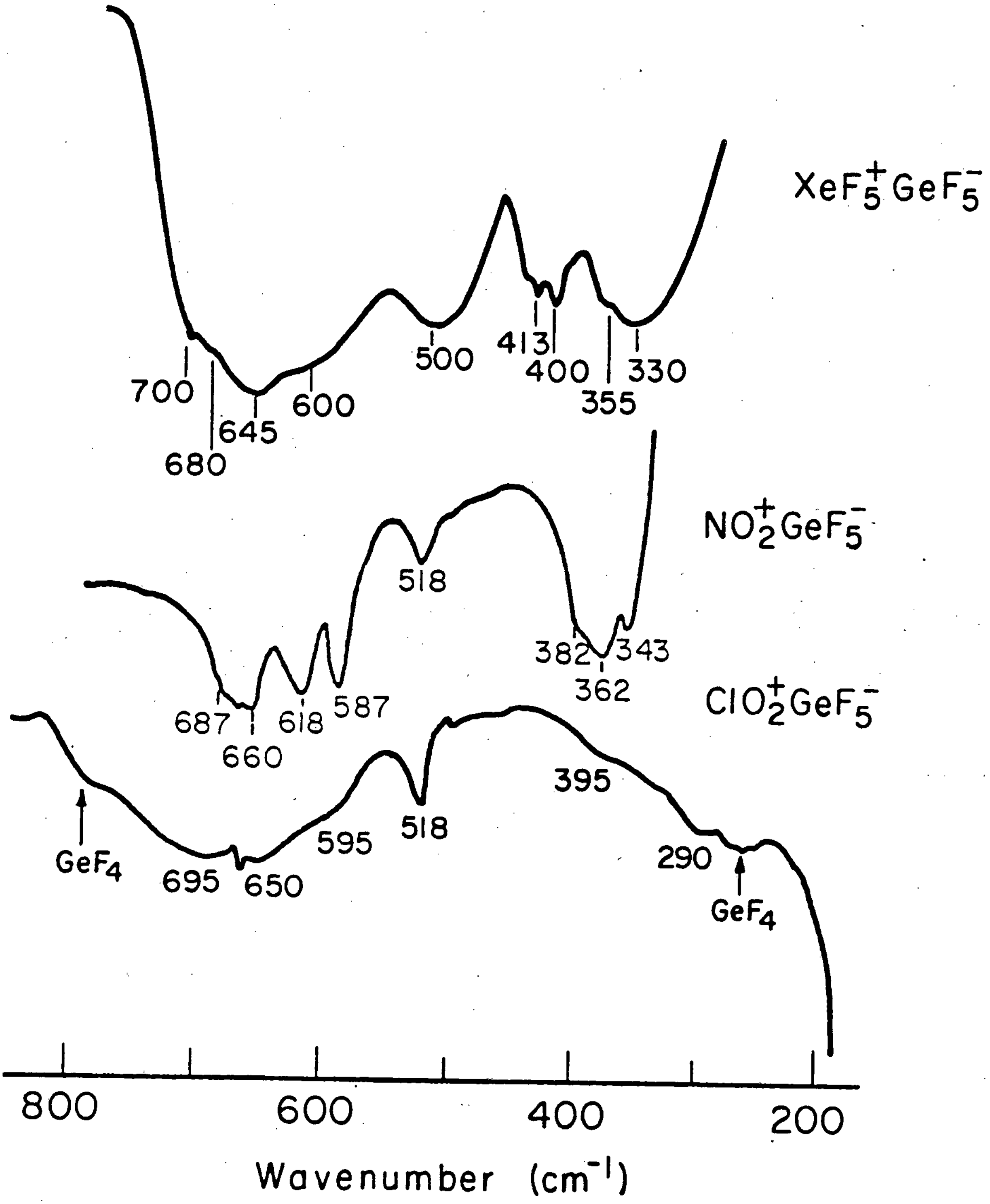
XBL 835-9962

Figure 3. Chlorine Coordination Environments in $C\ell O_2^+GeF_5^-$



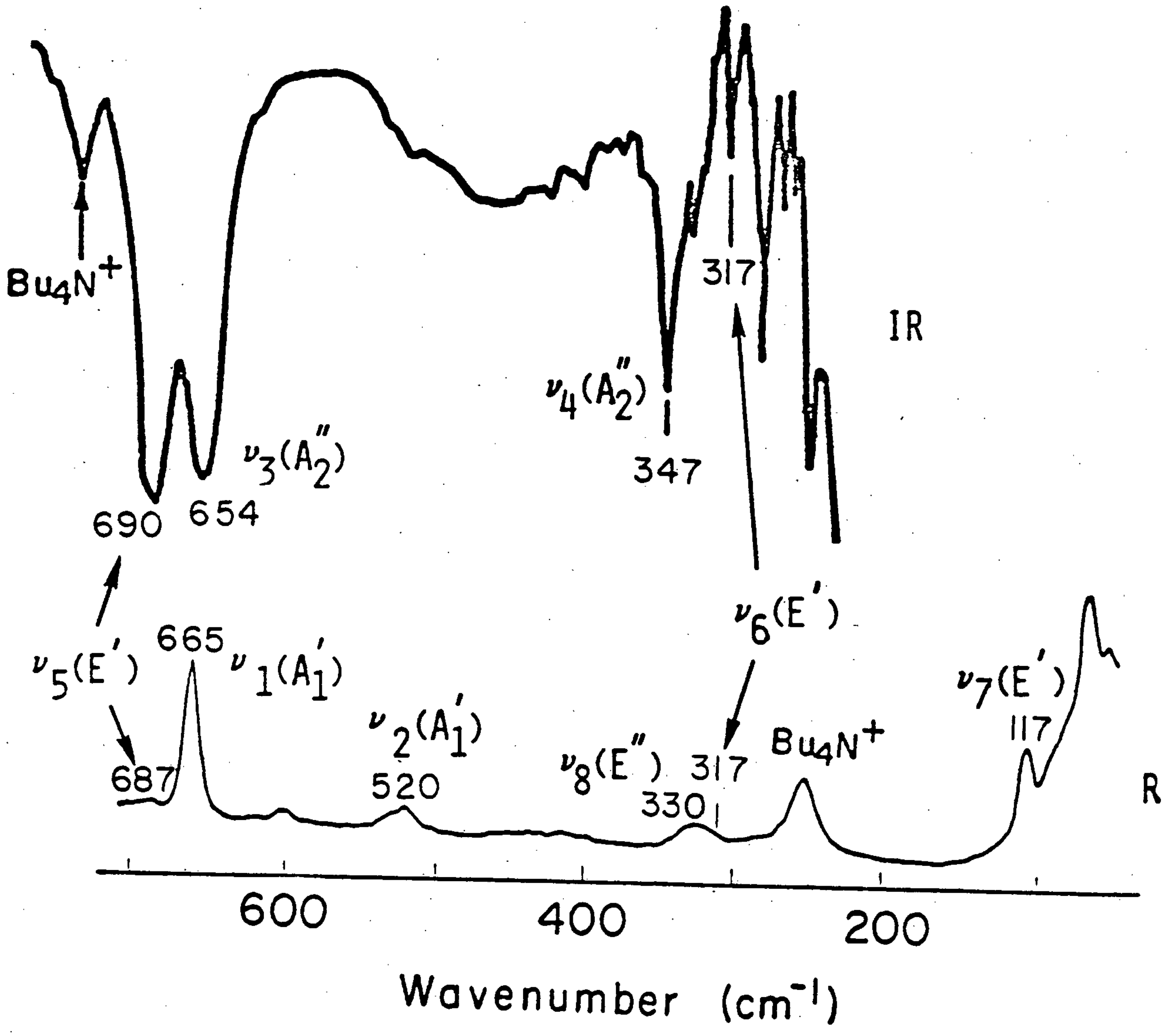
XBL 835-9970

Figure 4. Raman Spectra of GeF_5^- Salts



XBL 835-9971

Figure 5. Infrared Spectra of GeF_5^- Salts



XBL 835-9966

Figure 6. Raman and Infrared Spectra of Bu$_4$N$^+$GeF$_5^-$

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