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Infrared Matrix Isolation Studies of the Pentahalogermanate Anions

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The gas-phase reaction of CsF with GeF_4 diluted in argon, followed by rapid condensation at 15 K into an inert matrix, has led to the formation of the GeF_5^- anion ion paired with Cs^+. At higher concentrations, the GeF_6^{2-} anion was observed as well. The GeF_5^- anion was characterized by Ge–F stretching modes at 679, 696, and 730 cm^{-1}, indicative of a trigonal-bipyramidal structure perturbed by the cesium counterion. The reactions of CsCl with GeF_4 and CsF with $GeCl_4$ gave rise to the $Cs^+GeClF_4^-$ and $Cs^+GeCl_4F^-$ ion pairs, respectively, but with decreasing yields. The synthesis of the $GeCl_5^-$ anion by the reaction of CsCl with $GeCl_4$ was not successful, indicating either marginal stability of this anion or an inherent limitation to the salt/molecule technique.

Introduction

Many octahedral complexes[1] of the germanium tetrahalides have been synthesized in the past 20 years; these are generally 1:2 adducts with strong Lewis bases[2–4] such as F^- or amines. Much less is known about the intermediate 1:1 trigonal-bipyramidal adducts, with either neutral or anionic ligands. For example, the octahedral GeF_6^{2-} anion[5] has been well characterized, while there have been only a few conflicting reports concerning the GeF_5^- anion. The synthesis of GeF_5^- was first reported[6,7] in 1970, but later studies have suggested a polymeric, fluorine-bridged structure rather than a discrete anionic species.[8] Similarly, little is known about the $GeCl_5^-$ anion,[9] and there have been no reports to date concerning the mixed chloro/fluoro anions, $GeCl_xF_y^-$, $x + y = 5$.

The matrix isolation technique has been applied successfully numerous times to the study of intermediate complexes, both neutral and anionic.[10,11] The salt/molecule reaction technique, in which a gas-phase alkali halide salt molecule is reacted with a Lewis acid to bring about ion-pair formation, has been coupled with matrix isolation for the formation of unusual anionic species.[12–15] The reaction of CsF, after vaporization from a high-temperature oven, with samples of Ar/GeF_4 followed by condensation at 15 K might allow the formation of the GeF_5^- anion in the $Cs^+GeF_5^-$ ion pair. Infrared spectra of the discrete GeF_5^- anion might then be obtained and structural information deduced. Likewise, the synthesis of the chloro and mixed chloro/fluoro anions might be achieved in this manner.

Experimental Section

All of the experiments described here were carried out on a conventional matrix isolation apparatus which has been reported previously.[16] CsF (Alfa) and CsCl (Fisher) were the two salts employed in this study; previous studies employing the salt/molecule technique have shown that the cesium cation provided the best yields and lowest distortion of the product anion.[17] The salts were loaded into a stainless steel Knudsen cell and heated under vacuum to drive off residual water and CO_2. Vaporization temperature was the same for both salts, roughly 500 °C, which is sufficient to provide 1 μm vapor pressure of the salt. GeF_4 (Ozark-Mahoning) and $GeCl_4$ (Alfa) were employed after purification by two freeze/thaw cycles under vacuum prior to sample preparation. Argon was used as the matrix gas in all experiments and was used without further purification.

Table I. Infrared Band Positions for the Reaction Products of CsF and CsCl with GeF_4 and $GeCl_4$ in Argon Matrices (cm^{-1})

CsF + GeF_4	CsCl + GeF_4	CsF + $GeCl_4$	assignt
730	739	735	Ge–F str, GeF_5^- ($GeClF_4^-$)
696	722		Ge–F str, GeF_5^- ($GeClF_4^-$)
697	657		Ge–F str, GeF_5^- ($GeClF_4^-$)
595			Ge–F str, GeF_6^{2-}
	399	340	Ge–Cl str, $GeClF_4^-$ ($GeCl_4F^-$)
		311	Ge–Cl str, $GeCl_6^{2-}$

Matrix samples were deposited for approximately 20–22 h at 2 mmol h^{-1} before final infrared scans were recorded on a Beckman IR-12 infrared spectrophotometer. Survey scans were recorded from 200 to 4000 cm^{-1}, followed by expanded-scale scans over the regions of interest. Occasionally, infrared scans were also recorded of the solid residue left on the cold window after warmup to room temperature.

Results

Prior to the study of the reaction products of the cesium halide salts with GeF_4 and $GeCl_4$, blank experiments were conducted with the germanium halide compounds. The intense, triply degenerate stretching mode of the tetrahedral monomer was observed in each case, in good agreement with literature spectra.[18,19] In addition, weak aggregate bands were observed in blank experiments conducted at higher concentrations, M:R = 250 and 500. Blank experiments of the cesium halide salts have been recorded previously in this laboratory; CsF is characterized by an intense monomer band near 313 cm^{-1} and dimer bands near 250 and 210 cm^{-1}. The fundamental of CsCl is not observed above 200 cm^{-1}, the spectral limit of the spectrometer, but evidence for CsCl was obtained by the observation of bands at 462 and 3116 cm^{-1}, which have been assigned previously[16] to a complex of CsCl with impurity H_2O.

CsF + GeF_4. When CsF was vaporized and codeposited with a sample of Ar:GeF_4 = 1000, four new product bands were observed, which could not be attributed to parent species. These bands were located at 595 (0.09), 679 (0.04), 696 (0.04), and 730 (0.06) cm^{-1} (optical densities given parenthetically), as can be seen in the second trace of Figure 1. When a similar experiment was conducted at a concentration of 500:1, the same set of four bands was observed, all with increased in-

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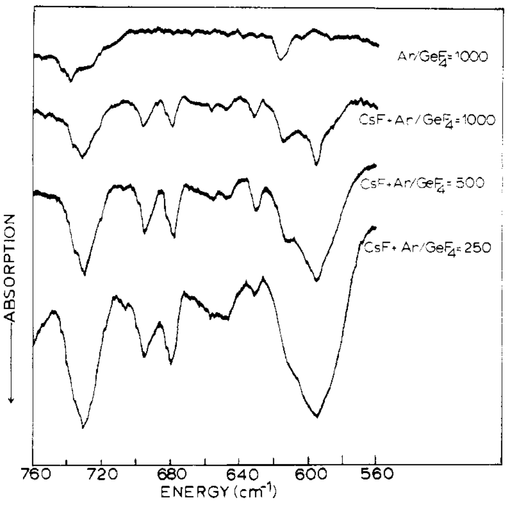

Figure 1. Infrared spectra of the reaction product of CsF with samples of Ar/GeF_4 at varying dilutions. The top traces shows a blank spectrum of Ar:GeF_4 = 1000, while the next three traces show the reaction products of CsF with samples of Ar:GeF_4 = 1000, Ar:GeF_4 = 500 and Ar:GeF_4 = 250, respectively.

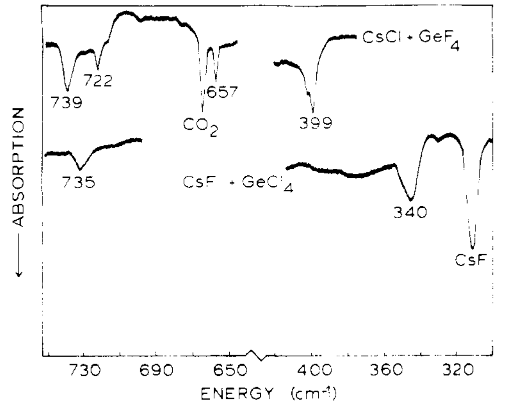

Figure 2. Infrared spectra of the reaction products of CsCl with GeF_4 and CsF + $GeCl_4$, both in argon matrices.

tensity. However, the band at 595 cm^{-1} appeared to grow more rapidly than the remaining three bands, which showed a roughly constant intensity ratio. when the concentration was increased to 250:1, the band at 595 cm^{-1} was the dominant feature in the spectrum, being very broad and with an optical density of 0.50. The remaining three bands also grew in intensity, but not nearly as rapidly as the 595-cm^{-1} band, and maintained a roughly constant relative intensity ratio to one another. After several of these experiments, a scan was recorded of the solid residue on the cold window after warming to room temperature. a single, very broad intense band was observed in each of these spectra, at 595 cm^{-1}. Finally, in an attempt to vary the cation in these studies, TlF was vaporized and cocondensed with a sample of Ar/GeF_4. Weak bands were observed in the 600–750-cm^{-1} spectral region, but the spectra were not nearly the quality of those obtained with CsF, and further studies with TlF were not attempted.

CsCl + GeF_4. CsCl was vaporized and codeposited with samples of Ar:GeF_4 = 500 and 1000, and similar spectra were obtained in each experiment. Four new, relatively weak product bands were observed in each experiment, near 399, 657, 722, and 739 cm^{-1}. In addition, the product bands at 679, 696, and 730 cm^{-1} observed in the reaction of CsF + GeF_4 were also detected, although with quite low intensity.

CsF + $GeCl_4$. These two reactants were codeposited in an experiment with M:R = 500, and two product bands were observed which could not be assigned to either parent species. These were located at 340 and 735 cm^{-1}; the band at 340 cm^{-1} was of medium intensity and the band at 735 cm^{-1} was quite weak, although distinct. Additional product bands in the low-energy region may have been masked by the bands due to parent CsF monomer and dimers.

CsCl + $GeCl_4$. CsCl was vaporized and codeposited with samples of Ar/$GeCl_4$ in five experiments, with M:R values of 1000 and 500. Considerable difficulties were encountered in the spectral region below 400 cm^{-1}, due to interference from atmospheric water. No distinct product bands were observed in these experiments although, after warmup of the cold window, an intense band was observed near 310 cm^{-1}.

Discussion

The codeposition of CsF and samples of Ar/GeF_4 at a variety of concentrations gave ample evidence that a reaction did occur. Four product bands were detected, at 595, 679, 696, and 730 cm^{-1}, and all grew with increasing GeF_4 concentration. However, the four bands did not grow at the same rate, but rather the band at 595 cm^{-1} was dominant at high concentrations. This suggests that more than one species was formed during this reaction, which is consistent with the fact that the species responsible for the 595-cm^{-1} band remained as a solid residue after warmup, while the other three bands disappeared. Moreover, the 595-cm^{-1} band matches very closely the position of the intense, triply degenerate stretching mode of the GeF_6^{2-} anion.[20] In view of the concentration dependence of the species responsible for this band, and agreement with crystal spectra, the 595-cm^{-1} band is assigned to the GeF_6^{2-} anion in the Cs_2GeF_6 triple ion.

The three remaining bands were relatively more significant at high dilutions, persisting up to M:R = 1000. Moreover, they maintained a constant intensity ratio to one another, indicating that they can be assigned to a single absorber. These three bands also disappeared during warmup, at the expense of GeF_6^{2-}, marking them as due to an intermediate species between the parent GeF_4 and the final product GeF_6^{2-}. The reaction of CsF with GeF_4 to ultimately form Cs_2GeF_6 is likely stepwise, suggesting an intermediate $Cs^+GeF_5^-$ ion pair. The GeF_5^- anion has been observed in mass spectral studies,[6] demonstrating that it is a stable anion and has been reported in crystalline studies with tetraalkylammonium cations.[7] In view of this observation, and the previous results of the salt/molecule reaction technique where ion-pair formation has been observed, the three product bands at 679, 696, and 730 cm^{-1} are assigned to the GeF_5^- anion in the $Cs^+GeF_5^-$ ion pair.

All three bands lie in a region easily assignable to Ge–F stretching vibrations, between the triply degenerate mode of GeF_4 at 795 cm^{-1} and the triply degenerate mode of GeF_6^{2-} at 595 cm^{-1}. For the analogous silicon system, it has been observed that Si–F stretching bands for a trigonal-bipyramidal structure lie intermediate between the tetrahedral and octahedral band positions.[12,21] Since a trigonal-bipyramidal structure is anticipated for five-coordinate anions, and a similar structure has been observed for the SiF_5^- anion, it may safely be concluded that the basic arrangement about the central germanium is trigonal bipyramidal. However, a strict D_{3h} trigonal-bipyramidal geometry will give rise to only two infrared-active Ge–F stretching modes.[22] Three bands were observed here, suggesting that the effective symmetry of the anion in the ion pair is less than D_{3h}, presumably due to distortion by the cesium cation. A similar situation was observed for the matrix-isolated $Cs^+SiF_5^-$ ion pair, and in that case three Si–F stretching modes were also detected.[12] In $Cs^+SiF_5^-$ ion pair, no definitive conclusion could be reached about the position of the cation, but a C_{3v} structure was preferred, with

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the cation coordinated to an axial fluorine. For the present $Cs^+GeF_5^-$ ion pair, it is likewise impossible to reach any conclusion about the structure of the ion pair, but the simplistic analogy to the $Cs^+SiF_5^-$ species tentatively suggests a C_{3v} structure for the ion pair. Reference 12 provides a more detailed discussion as to why the C_{3v} structure was preferred for the $M^+SiF_5^-$ ion pair. These arguments can be extended rather directly to the $M^+GeF_5^-$ ion pair studied here. If this structure is assumed, the upper band at 730 cm^{-1} is assigned to the doubly degenerate equatorial Ge–F stretching mode, which is in quite close agreement with the analogous mode for the $GeF_4{\cdot}NH_3$ adduct.[23] This assignment is also consistent with the somewhat greater bandwidth of this band compared to the 679- and 696-cm^{-1} bands. The lower two bands at 696 and 679 cm^{-1} are assigned to the Ge–F stretching modes of the noncoordinated and coordinated axial fluorines, respectively. The remaining Ge–F stretching mode, the symmetric equatorial stretch, is expected to be very weak and was not observed. It should be noted that the spectra are also consistent with a C_{2v} structure with equatorial ion-pair interaction, and such a structure cannot be ruled out. Finally, it has been suggested that GeF_5^- is polymeric with certain cations in the solid state, with fluorine bridges between anions.[8] The spectra of these solids included a Ge–F stretching mode of the bridging fluorine near 480 cm^{-1}, which is certainly not observed here. Rather, it is clear that the isolated GeF_5^- anion, ion paired with Cs^+, has been formed.

The reaction of CsCl with GeF_4 gave rise to a series of four product bands, at 399, 657, 722, and 739 cm^{-1}, which may be ascribed to a 1:1 reaction product, namely, the $GeClF_4^-$ anion. The upper three bands are in the Ge–F stretching region, not far from the bands observed for the GeF_5^- ion pair, and are readily assigned as such. The band at 399 cm^{-1} lies some 60 cm^{-1} below the $GeCl_4$ stretching fundamental and roughly 90 cm^{-1} above the $GeCl_6^{2-}$ fundamental,[9] and thus in a region readily ascribed to a Ge–Cl stretching vibration. It is noteworthy that the 722- and 739-cm^{-1} bands are nearly symmetric about the 730-cm^{-1} band of the GeF_5^- anion, suggesting that this doubly degenerate mode is split in the $GeClF_4^-$ anion. This would come about most readily by substitution of the chlorine into an equatorial site in the trigonal-bipyramidal structure, a substitution which is likely on valence-bond considerations as well.

The reaction of CsF with $GeCl_4$, which might give rise to the $Cs^+GeCl_4F^-$ ion pair, produced two new absorptions, both of relatively low intensity. The upper band, near 735 cm^{-1} can be assigned to the Ge–F stretching mode of the product anion, while the 340-cm^{-1} band is likely due to one of the several anticipated Ge–Cl stretching modes of the anion. The remaining Ge–Cl stretching modes are either too weak to be observed or masked by the absorptions of parent CsF and $(CsF)_2$ at 313, 250, and 210 cm^{-1}. In any event, it is apparent that while the synthesis of the GeF_5^-, $GeClF_4^-$, andd $GeCl_4F^-$ anions has been achieved, the yield drops off as the number of chlorine atoms in the product anion increases. This pattern continued when the reaction of CsCl with $GeCl_4$ was attempted, in that no product bands were observed until very high concentrations were employed. Only then was a band observed at 310 cm^{-1}, which matches closely the triply degenerate stretching mode of $GeCl_6^{2-}$, and is so assigned. There is no evidence that detectable amounts of $GeCl_5^-$ were formed, although this anion has been reported at room temperature.[9] This result either may indicate marginal stability for the $GeCl_5^-$ anion or may reflect an inherent limitation in the salt/molecule technique. The $GeCl_6^{2-}$ which was observed may be formed either through a stepwise process involving only small amounts of the $GeCl_5^-$ anion or more likely by the reaction of $GeCl_4$ with $(CsCl)_2$, which is known to be present in equilibrium with monomeric CsCl. No firm conclusions may be drawn about the stability of the $GeCl_5^-$ anion until more is known about the limitations of the salt/molecule technique.[24]

Conclusions

The salt/molecule technique, coupled with matrix isolation, has allowed for the formation of the GeF_5^- anion in isolated $Cs^+GeF_5^-$ ion pairs. Definitive infrared spectra have been obtained of the distinct, rather than polymeric, anion, with the observation of three Ge–F stretching modes. A structure which is basically trigonal bipyramidal, but perturbed by the cesium counterion, is suggested. At higher concentrations, and upon warmup, formation of the GeF_6^{2-} is observed as well. The synthesis of the intermediate anions $GeClF_4^-$ and $GeCl_4F^-$ was successful as well, but with decreasing yield. The synthesis, in this fashion, of the $GeCl_5^-$ anion was not successful, indicating either marginal stability for this anion or a limit to the applicability of the salt/molecule reaction technique.

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Registry No. CsF, 13400-13-0; CsCl, 7647-17-8; GeF_4, 7783-58-6; $GeCl_4$, 10038-98-9; GeF_5^-, 28407-33-2; $GeCl_4F^-$, 81315-96-0; GeF_4Cl^-, 81315-97-1; GeF_6^{2-}, 16920-88-0; $GeCl_6^{2-}$, 18588-21-1.

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