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Infrared Matrix Isolation Spectra of the $Cs^+PF_4^-$ and $Cs^+PClF_3^-$ Ion Pairs

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The tetrafluorophosphoranyl anion PF_4^- has been isolated for the first time in argon matrices ion paired with the Cs^+ cation, after formation through the gas-phase reaction of CsF with PF_3. Infrared spectra of the anion show four bands, at 621, 710, 780, and 789 cm^{-1}, which are assigned to P–F stretching vibrations and suggest a symmetry no higher than C_{2v}. Normal coordinate calculations, combined with analogy to the isoelectronic SF_4 species, suggest a folded-square, C_{2v}, structure for the anion, with the cesium cation in an axial monodentate arrangement. Similar spectra were obtained for the $Cs^+PClF_3^-$ ion pair, while attempts to form the $Cs^+PCl_4^-$ ion pair were unsuccessful, supporting the notion that PCl_3 is a weaker Lewis acid than PF_3.

Introduction

While the phosphorus trihalides have long been used as Lewis bases, it was not until recently that they were shown to have limited acceptor, or Lewis acid, properties. At this time, Dillon and Waddington[1] isolated compounds of PBr_4^-, and Rhyne and Dillard observed PF_4^- by high-pressure mass spectrometry.[2,3] Shortly thereafter, ion cyclotron resonance studies by Beauchamp et al. indicated that PF_4^- is quite stable, with a heterolytic bond dissociation energy of near 50 kcal/mol.[4] None of the tetrafluoro- or tetrachlorophosphoranyl anions have been isolated, however, and the only available spectroscopic data deals with PBr_4^-. A rational approach to the study of the tetrahalophosphoranyl anions might involve matrix isolation infrared spectroscopy, coupled with the salt/molecule reaction technique. This method has been used to investigate a number of thermodynamically stable halide anion adducts to Lewis acids[5–8] and is especially valuable for examining highly reactive or labile adducts, as might be expected for PF_4^-. In this salt/molecule technique, an alkali halide salt molecule is vaporized and codeposited with a matrix gas/Lewis acid mixture. A reaction can occur in the gas phase just above the surface of the cold window, leading to halide ion transfer from the salt to the Lewis acid and ion pair formation. Anions including HF_2^-, F_3^-, BF_4^-, and SiF_5^- have been studied in this fashion, with a variety of alkali metal cations.[5–9] The spectra obtained in this manner are gas phase like, with minimal interaction between trapped species in the inert matrix, generally leading to sharp absorption bands.

Experimental Section

The experiments described in this paper were conducted with use of a conventional matrix isolation apparatus, including a CTi closed cycle refrigerator, and has been described previously.[10] Earlier studies employing the salt/molecule reaction technique have shown that the cesium cation provides the least perturbation for the anion under investigation, as well as the highest product yields. Moreover, the cesium halide salts are readily vaporized, so that only CsF and CsCl were employed in this study. CsF (Alfa) and CsCl (Fisher) were both vaporized at about 500 °C from a stainless steel Knudsen cell, after outgassing to nearly this temperature, to remove impurities. PF_3 (Ozark-Mahoning) was purified immediately prior to use in an experiment by one or more freeze–thaw cycles under high vacuum. PCl_3 was purified by vacuum distillation from a −70 °C slush bath to remove impurity HCl, followed by one or more freeze–thaw cycles.

Table I. Band Positions (cm^{-1}) and Assignments for the $Cs^+PF_4^-$ and $Cs^+PClF_3^-$ Ion Pairs in Argon Matrices

$Cs^+PF_4^-$	$Cs^+PClF_3^-$	assignt[a]
789	780	ν_1, A_1 sym eq P–F st
780	767	ν_8, B_2 antisym eq P–F st
710		ν_6, B_1 noncoord ax P–F st
621	621	ν_2, A_1 coord ax P–F st

[a] Assignments based on C_{2v} point group.

$PClF_2$ was prepared following the general procedure of Cavell,[11] involving the formation of PF_2NH_2 from PF_3 and dimethylamine, followed by chlorination by HCl to yield the desired product. $PClF_2$ was purified by freeze–thaw cycles over a pentane slush bath at −131 °C and still contained slight HCl and PF_3 impurities. Argon was used as the matrix gas in all experiments and was used without further purification.

Matrix samples were generally deposited for 20–24 h, at 2 mmol/h, before final infrared scans were recorded on a Beckman IR 12 infrared spectrophotometer. Both survey scans and high-resolution scans were recorded over the regions of interest. Normal coordinate calculations were performed with use of a program from the National Research Council of Canada, employing a Urey-Bradley force field. The computer of the University of Cincinnati computing center was used for all calculations.

Results

Prior to the experiments in which the reactions between phosphorus trihalides and cesium halides were carried out, blank experiments of PF_3, PCl_3, and $PClF_2$ in argon were conducted at several reagent/matrix ratios. The results of these blank experiments were in good agreement with reported spectra.[12,13] The Ar/PF_3 samples showed a broad, complex series of band between 790 and 900 cm^{-1}; two, at 849 and 884 cm^{-1}, can be assigned to monomeric PF_3 while the remainder can be assigned to aggregate species. Aggregate formation was observed at Ar/PF_3 ratios as high as 2000 but predominated in more concentrated experiments. Samples of Ar/$PClF_2$ were contaminated by small amounts of PF_3 and HCl, while the PCl_3 samples contained traces of HCl.

PF_3 + CsF. Numerous experiments were conducted in which CsF and PF_3 were reacted in argon matrices over a wide range of concentrations; each experiment showed several new product bands in the final spectrum. At a PF_3/Ar ratio of 1/2000, product bands were observed near 622, 710, 721, 742, 781, and 789 cm^{-1}. At PF_3/Ar concentrations of 1/1000, reproducible bands centered near 622, 711, 741, 757, 780, and

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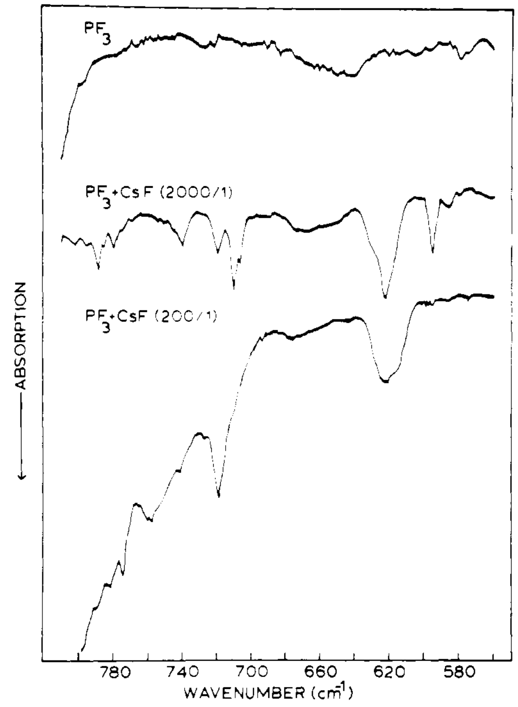

Figure 1. Infrared spectra of the reaction products of CsF with PF_3 in argon matrices. The top trace shows a blank spectrum of Ar/PF_3, while the middle and lower traces show the reaction products at two different Ar/PF_3 ratios.

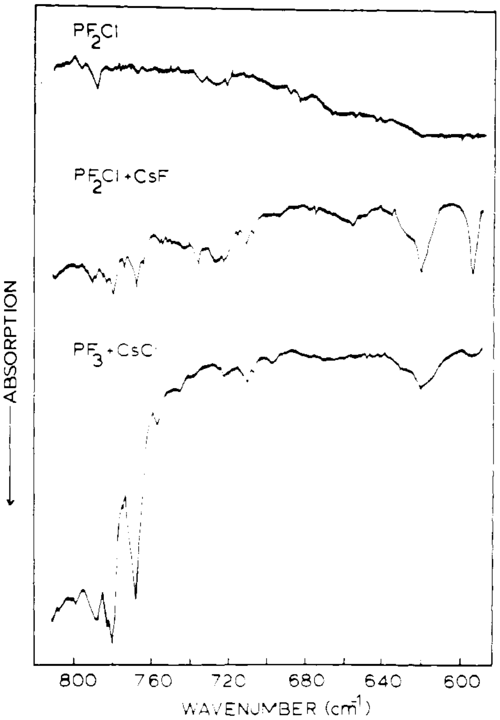

Figure 2. Infrared spectra of the mixed chloro–fluoro reaction products of the MX/PX_3 system. The top trace shows the infrared spectrum of a sample of $Ar/PClF_2$, while the middle trace shows the reaction product of CsF with $Ar/PClF_2$ and the lower trace shows the spectrum of the reaction products of CsCl with Ar/PF_3.

789 cm^{-1} appeared. These listed bands were often comprised of several sharp bands separated by 1–2 cm^{-1}, apparently due to matrix site splitting. As the PF_3/Ar ratio was increased to 1/200, the broad aggregate bands of parent PF_3 began to interfere down to about 780 cm^{-1}. In these experiments, bands at 620, 720, 742, 780, and 789 cm^{-1} were observed, the latter two appearing on the slope of the PF_3 aggregate band. Band broadening was also observed in these concentrated experiments, indicative of increased interactions in the matrix. The bands near 622, 710, 780, and 789 cm^{-1} appeared to show a roughly constant intensity ratio throughout these experiments, although the band at 622 cm^{-1} was quite broad in all experiments, presenting some difficulty in determining its integrated intensity. The relative intensity of the band at 742 cm^{-1} suggests that it is not due to the same species associated with the absorptions at 622, 711, 780, and 789 cm^{-1}. Spectra of the reaction products of CsF with PF_3 at two different concentrations are shown in Figure 1, and band positions are listed in Table I.

CsCl + PF_3. When CsCl was deposited with PF_3/Ar at a ratio of 1/500, product bands were observed at 621, 745, 756, 767, 779, 787, and 797 cm^{-1}, while a similar experiment employing a PF_3/Ar ratio of 1/1000 produced similar results. The most intense, reproducible bands were at 621, 767, 779, and 787 cm^{-1}, and as in the experiments employing CsF and PF_3, the 621-cm^{-1} absorption was quite broad. Site splitting of these product bands was also quite common.

CsF + $PClF_2$. A series of experiments in which CsF and samples of $Ar/PClF_2$ = 1/1000 were codeposited resulted in product bands at 622, 767, 779, and 790 cm^{-1}, and again site splitting was prevalent. The spectra obtained in these experiments were quite similar to those obtained in the CsCl + PF_3 experiments described above. In addition, weak product bands due to the CsF + PF_3 reaction product were observed, due to PF_3 impurity in the $PClF_2$ sample.

CsCl + $PClF_2$. The codeposition of CsCl with samples of $PClF_2$ in argon at 1/1000 produced spectra with weak absorptions at 445, 621, 697, 737, 760, 773, 780, and 798 cm^{-1}, with the band at 445 cm^{-1} being rather broad. Spectra of the reactions leading to mixed chloro–fluoro reaction products are shown in the traces of Figure 2.

CsF (CsCl) + PCl_3. Several experiments were conducted in which either CsF or CsCl were codeposited with samples of Ar/PCl_3 over the concentration range 1/1000 to 1/250, and no detectable product bands were observed in any of these experiments.

Discussion

The reaction of CsF with PF_3 in an argon matrix gave rise to a number of bands which cannot be assigned to either parent species. The complexity of the spectrum is reduced somewhat when the observation is made that several bands are very close to one another and can be attributed to site splitting of a single fundamental vibration. Further, concentration dependence studies demonstrate that only four bands maintain a roughly constant intensity ratio, the bands near 621, 710, 780, and 789 cm^{-1}. It is noteworthy that these are the four bands that persist at dilutions as high as 1/2000. The remaining bands in the 700–800 cm^{-1} region show a different concentration dependence, and are more dominant at high concentrations. This marks these bands as due to aggregate reaction products, while the four primary product bands can be confidently assigned to a 1/1 reaction product between CsF and PF_3. In view of the prior results of the salt/molecule reaction technique, where ion pairs are known to be formed, combined with the known gas-phase stability of the PF_4^- anion, and the above observations, the product bands observed here at 621, 710, 780, and 789 cm^{-1} are assigned to the PF_4^- anion in the $Cs^+PF_4^-$ ion pair.

The reaction products of CsF with $PClF_2$ and CsCl with PF_3 were investigated as well, and the spectra observed for both of the reactions were nearly identical, suggesting that the same product is formed in both experiments. In view of the above discussion, these bands are assigned to the $PClF_3^-$ anion, again in the $Cs^+PClF_3^-$ ion pair. The observed concentration dependence suggests that the 779 and 787 cm^{-1} bands are

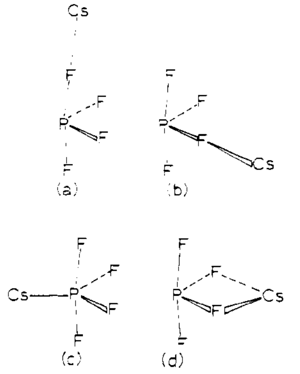

Figure 3. Possible structures for the $Cs^+PF_4^-$ ion pair.

probably site split components of a single band, leading to three bands in the P–F stretching region, near 621, 767, and 780 cm^{-1}. Three P–F stretching vibrations might be anticipated for the $PClF_3^-$ anion, while the anticipated P–Cl stretching vibration of this anion was not observed, presumably due to low intensity.

The reaction of CsCl with $PClF_2$ is more complex, as a large number of product bands were observed. One, at 445 cm^{-1}, appears to be a P–Cl stretching mode for a reaction product, while numerous bands were observed in the P–F stretching region. The complexity of the spectra suggests that aggregate formation is likely, and it would be nearly impossible to pick out a well-defined seet of bands to assign to the $PCl_2F_2^-$ anion. Consequently, this system was not investigated further.

The reaction of either CsF or CsCl with PCl_3 gave no reaction product, suggesting that PCl_3 is a weaker Lewis acid or acceptor than PF_3. This result is not surprising in view of the fact that PF_5 is a considerably stronger Lewis acid than PCl_5,[14] and similar results have been observed[9] for SiF_4 vs. $SiCl_4$.

The structure of PF_4^- can be inferred to some degree from the spectra as well. The most likely structures include a tetrahedral arrangement and a folded-square arrangement derived from a trigonal-bipyramidal configuration with one lone pair. The tetrahedral structure can be ruled out rapidly in as much as four P–F stretching bands were observed, and only one triply degenerate mode is anticipated for the T_d point group. Even upon reduction in symmetry by the metal cation, only two modes are likely to be observed under C_{3v} symmetry, by analogy to the $Cs^+BF_4^-$ ion pair.[8] The C_{2v} distorted trigonal-bipyramidal structure is much more likely for PF_4^- and is the structure determined[15] for SF_4, with which PF_4^- is isoelectronic. Here, the lone pair on the central atom occupies an equatorial position in the trigonal bipyramid, giving rise to a folded–square arrangement. Four P–F stretching modes are anticipated for this structure, in agreement with the observed spectra, supporting this geometric arrangement.

The role and influence of the cesium cation cannot be directly deduced in this ion pair, as all P–F stretching vibrations in the C_{2v} structure are both singly degenerate and infrared active. Molecular orbital arguments suggest that the axial fluorines of SF_4 are more electron rich than the equatorial fluorines and that the axial S–F bonds are weaker than the equatorial S–F bonds.[16,17] Experimentally, it is known that Lewis acids will abstract a fluoride anion from SF_4 to leave SF_3^+, rather than coordinate through the sulfur lone pair.[18] In addition, the $S{-}F_{ax}$ vibrations occur at much lower energy than do the $S{-}F_{eq}$ vibrations, suggesting lower stretching force constants.[19]

This analogy to SF_4 would indicate that the alkali metal cation might coordinate through an axial fluorine, as shown in Figure 3a. However, a number of other possible arrangements might be envisioned, all possessing C_{2v} or lower symmetry, and the spectroscopic data obtained here does not readily distinguish between these configurations. To provide some clarification as to the structure of the ion pair, normal coordinate calculations were undertaken. However, with only four vibrational bands observed and no isotopic data available, at least five force constants were available, so that a nonredundant fit was not possible. So that this problem could be avoided, force constants were taken by scaling from SF_4, SF_6, and PF_6^- [20,21] and applied to each of the structures shown in Figure 3. Then, by analogy to other studies of ion pairs, the stretching force constant of the coordinated fluorine was lowered relative to the noncoordinated fluorines until a fit was reached. Of the possible structures, only the structures involving a monodentate axial interaction (Figure 3a) or a cation interaction with the phosphorus lone pair (Figure 3c) gave an acceptable fit to the spectrum for a reasonable set of force constants. Of these two, the fact that the axial monodentate structure was anticipated from analogy with SF_4 makes it the more likely structure for this ion pair, although the latter possibility cannot be ruled out.

The calculated spectrum for this structure assigns the two higher energy vibrations near 780 cm^{-1} to the two equatorial PF stretching vibrations and the lower two to the axial vibrations. In addition, the vibration of the coordinated fluorine is matched up with the 621-cm^{-1} band, which might rationalize the breadth of this band relative to the other P–F stretching bands. These assignments are in good agreement with those found for SF_4.

The infrared spectrum of the $Cs^+PClF_3^-$ ion pair shows three P–F stretching vibrations, as might be anticipated, at 621, 767, and 780 cm^{-1}. The upper two bands are near the P–F equatorial stretching bands of the PF_4^- anion, suggesting a similar assignment here. The lowest energy band at 621 cm^{-1} is identical with the stretching mode of the coordinated fluorine of the PF_4^- anion, indicating a similar assignment for $PClF_3^-$. The second $P{-}F_{ax}$ stretching vibration, near 710 cm^{-1}, has disappeared upon substitution of a chlorine into the anion, indicating that the chlorine occupies the noncoordinated axial position. This result is contrary to chemical intuition, which would have predicted that the larger, less electronegative chlorine[22] would occupy an equatorial site. However, there may be some form of inductive trans effect due to the alkali metal cation in an axial position which brings about this result. Regardless of rationale, the spectra do point toward a structure with the chlorine atom axial, trans to the coordinated fluorine.

In view of the fluoride affinity of PF_3 and the ease of formation of $Cs^+PF_4^-$ in the matrix, it is somewhat puzzling why observation of PF_4^- has not been acheived in solution studies. The work of Muetterties and co-workers[23] provides some insight on this point; they observed that the reaction of PF_3 with either KF or CsF lead ultimately to red phosphorus and a PF_6^- salt. This would indicate that PF_4^- is the likely initial reaction product (as they suggest) but that disproportionation occurs to form elemental phosphorus and the very stable hexafluorophosphate anion.

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Conclusions

The salt/molecule technique has allowed for the synthesis of the $Cs^+PF_4^-$ ion pair in argon matrices, through the codeposition of CsF and PF_3. The spectra obtained here represent the first spectral data obtained for the PF_4^- anion and support the notion that PF_3 has a least limited acceptor properties. The spectrum is suggestive of a folded-square, C_{2v}, structure for the anion, and normal coordinate calculations support this structure as well. In addition, normal coordinate calculations support a structure for the ion pair which has the Cs^+ cation sitting along an axial P–F bond, in a monodentate arrangement. The salt/molecule reaction technique also leads to the synthesis of the $PClF_3^-$ anion and the possible synthesis of the $PCl_2F_2^-$ anion, while the synthesis of the PCl_3F^- and PCl_4^- anions could not be achieved.

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Registry No. $Cs^+PF_4^-$, 76173-91-6; $Cs^+PClF_3^-$, 76173-92-7; PF_3, 7783-55-3; $PClF_2$, 14335-40-1; CsCl, 7647-17-8; CsF, 13400-13-0.

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Proton Magnetic Resonance Study of *cis*-Bis(ethylenediamine)cobalt(III) Complexes. Assignment and Deuteration of Amine Hydrogens and the Structure of Ion Pairs and Ion Triplets[1]

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The amine portion of the ^{1}H NMR spectra has been investigated for *cis*-bis(ethylenediamine)cobalt(III) complexes, *cis*-$[Co(en)_2(X)_2]^{n+}$, with $(X)_2 = (CN)_2$, $(NO_2)_2$, acetylacetonate, malonate, and oxalate, in dimethyl-d_6 sulfoxide and D_2O. One of the NH hydrogens undergoes large, counterion-dependent shifts in dimethyl-d_6 sulfoxide and is assigned to the trans hydrogens pointing approximately parallel to the molecular twofold axis. In the nitro compound, this hydrogen is deuterated first in D_2O. In the other complexes, this hydrogen is exchanged with deuterium second, the fastest exchanging hydrogen being the other trans NH. The peculiar behavior of the nitro compound has been explained by intramolecular hydrogen bonding between nitro oxygen and trans amine hydrogen(s). The structure of ion pairs between complex cations and counteranions (Cl^-, Br^-, I^-) and of the ion triplet in the acetylacetonato complex, in dimethyl-d_6 sulfoxide, has been deduced.

Recently, we have reported that the magnetic anisotropy of a cobalt(III) ion dominates the proton chemical shift of coordinated amine groups. Yoneda and Nakashima[2] advanced a theory of proton chemical shift based on this hypothesis. More recently, Nakashima, Sakaguchi, and Yoneda[3] refined the theory so as to be suitable for practical applications and established a correlation between ^{59}Co chemical shifts and proton chemical shifts. The theory has been tested for a series of pentaamminecobalt(III) complexes with quantitative sucess, except for the trans (to substituent) ammine groups of cyano- and nitropentaamminecobalt(III) ions. The theory has also been examined on various types of complexes[4] and supported in the main by other groups of workers. The disparity noted for the trans ammine groups of the cyano and nitro complexes suggested an increase in the electron density on these ammine hydrogens. To test this view, we have measured the hydrogen-exchange rates at ammine groups.[5] The results of HD exchange studies pointed to the importance of the trans influence in $[Co(NH_3)_5(X)]^{2+}$ complexes; trans ammine hydrogens are deuterated faster than cis ones for weak-field ligand X, whereas for strong-field ligands, CN^- and possibly NO_2^-, trans hydrogens are slower exchanging. The effect of the X ligand upon the exchange rate is less prominent for cis ammines.

In contrast to the nitropentaammine complex, the *cis*-$[Co(en)_2(NO_2)_2]^+$ ion[6] suggested smaller rate of deuteration for cis amine than for trans ones.[5] The reason for this difference and the assignment of NH absorptions were not clear at that time. The chemical shift of amine hydrogens in a series of *cis*-$[Co(en)_2(X)_2]^+$ has been calculated by using a procedure similar to that used for the pentaammine series, but the agreement with the observed shifts was not so good, especially again for the cyano complex.[7] Further, the amine portion of the ^{1}H NMR spectra of *cis*-$[Co(en)_2(X)_2]^+$ in trifluoroacetic acid solvent exhibited two to four absorptions depending upon the X ligand, and the assignment of each of these absorptions could not be made. Though the ^{1}H NMR spectra of this type of complexes have been reported previously by several workers, no definite conclusions has been reached about the assignment of the NH absorptions.[8-11]

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(6) Abbreviations: en, ethylenediamine; acac 2,4-pentanedionate ion; mal, malonate ion; ox, oxalate ion; Me_2SO, dimethyl sulfoxide; DMF, dimethylformamide.

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