of ca. −9 cm^3 mol^{-1} is now reported for this reaction involving a neutral leaving group. It follows that this value indicates the volume decrease on substituting a water molecule ($\bar{V}$ = 18 cm^3 mol^{-1}) with $SC(MNe_2)_2$ ($\bar{V}$ = 130 cm^3 mol^{-1}) on a square-planar metal ion. The significantly more positive values observed for the other systems quoted in Table IX can be ascribed to an increase in molar volume due to charge neutralization and a decrease in electrostriction for these reactions.

The results of this investigation are in good agreement with those reported recently[31] for solvent exchange on and anation of $Pd(H_2O)_4^{2+}$ by MeCN and Me_2SO. Here too, $\Delta V^{\ne}$ decreases along the series, viz. −2.2 ± 0.2 (H_2O), −4.0 ± 0.8 (MeCN), and −9.2 ± 0.6 cm^3 mol^{-1} (Me_2SO), compared to almost constant values for the reverse aquation reactions, viz. −2.2 ± 0.2 (H_2O), −1.5 ± 0.5 (MeCN), and −1.7 ± 0.6 cm^3 mol^{-1} (Me_2SO). The construction of a volume profile for the anation of $[Pd(Me_5dien)H_2O]^{2+}$ by $SC(NMe_2)_2$ reveals that the transition state for the forward and reverse reaction is significantly more compact than either the reactant or product states. A similar finding was reported for the other anation reactions included in Table IX[15] as well as for those of $Pd(H_2O)_4^{2+}$ mentioned above.[31] It follows that the solvent exchange and anation data reported in this study once again underline the operation of an associative substitution mechanism in these systems. The results of this investigation also demonstrate that steric hindrance on the dien ligand can slow down the ligand substitution process significantly but does not change the basic nature of the mechanism. Earlier work[5,7,15] has demonstrated this more explicitly for an extended series of complexes. It has been suggested[33] that strong nucleophiles can in some cases overcome the steric barrier. However, bulky entering groups, even when they are strong nucleophiles, can be less effective than small ligands having poor nucleophilicity but being capable of penetrating the coordination sphere.

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Registry No. $[Pd(Me_5dien)H_2O]^{2+}$, 85344-11-2; $[Pd(Et_5dien)H_2O]^{2+}$, 118169-65-6; $SC(NH_2)_2$, 62-56-6; $SC(NHMe)_2$, 534-13-4; $SC(NMe_2)_2$, 2782-91-4; H_2O, 7732-18-5.

Supplementary Material Available: Tables of the chemical shift as a function of pH, the relaxation rate as a function of temperature at various pH values, and rate constants for the anation reactions as a function of ligand concentration and a figure presenting the temperature dependence of the relaxation rate at various pH values (6 pages). Ordering information is given on any current masthead page.

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Notes

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Structure and Vibrational Spectra of $NF_4^+BF_4^-$: A Reappraisal

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In a recent publication in this journal,[1] a fascinating problem was posed on connection with the reconciliation between the crystal structure and vibrational spectra of $NF_4^+BF_4^-$. This compound crystallizes in the $P\bar{4}2_1m$ space group with $Z = 4$. In contrast, the infrared and Raman spectra of the crystal are consistent with a uniaxial space group with $Z = 1$, although the authors did not summarize the spectral observations in this way. In order to reconcile these rather different results, the authors postulated the occurrence of a rotation or large amplitude oscillation of the BF_4^- groups about one B–F bond so that they have an effective C_{3v} symmetry, in contrast to their crystallographic C_s site symmetry, and that the vibrations take place within this rotationally smeared-out environment. They used this model to explain not only the simple BF_4^- anion spectrum but also the NF_4^+ spectrum, the latter ion occupying two distinct sites, one of C_{2v} symmetry and the other of S_4 symmetry (although the molecule in the latter site is actually of strict D_{2d} symmetry). However, there is one significant problem with this model that was not discussed: the problem of time scale. Typically, a rotation is rather slower than a vibrational motion—the corresponding transitions occur in different spectral regions. One additional consequence of the model is therefore that some, if not all, of the vibrations explore a wide range of rotationally different local environments and so should show a marked broadening. In fact, the spectra reported have quite normal band widths. We believe that there is an alternative explanation of the spectroscopic observations. Our explanation is based, in part, on the recognition that a vibrational space group may differ from the crystallographic one.[2] In the present case it is important also to recognize certain crystal structure insensitive aspects of vibrational spectroscopy. Finally, we take this opportunity to present a method of analysis appropriate when more than one site is occupied by chemically equivalent groups (in the present case, NF_4^+).

Although our conclusions do not strictly depend upon it, it is simplest to assume that there is strong vibrational coupling between NF_4^+ groups and, separately, between BF_4^-. In making this assumption we follow Christe et al.;[1] without it the problem that arises is much less severe—all spectra are expected to be site-symmetry determined and so the only residual problem arises from the C_{2v}–S_4 duality of the NF_4^+ sites. Let us first consider the NF_4^+ ions. All are arranged with a tetrahedral 2-fold axis along the crystallographic z axis. Further, sets of four NF_4^+ cations, two on C_{2v} sites and two on S_4 sites, are coplanar to ± 0.05 Å along z, and, within error, are interrelated by an S_4 operation of the space group $P\bar{4}2m$ (D_{2d}^1) with $Z = 1$. Of course, NF_4^+ groups on C_{2v} and S_4 sites differ in their static geometries, but these differences can be ignored. There are two reasons for this. First, the zero-point and lattice vibrational motions both will tend to smear out the static distinctions. Second, vibrational coupling, which, it is generally accepted, is expected to occur, will mean that normal coordinates involve both types of NF_4^+ groups; their individuality is lost. The spectra reported are entirely consistent with the conclusion that the NF_4^+ groups subtend a $P\bar{4}2m$ (D_{2d}^1) vibrational space group with $Z = 1$. The observed splitting of NF_4^+ T_2 modes into two components with a 2:1 intensity ratio, is entirely consistent with $D_d \rightarrow D_{2d}$ ($T_2 \rightarrow E + B_2$), as is the splitting of the E (T_d) mode into two peaks of equal intensity ($E \rightarrow A_1 + B_1$). Finally, the analysis requires coincident infrared and Raman peaks when both are active, as observed.

The analysis of the NF_4^+ features that we have just presented is the simplest available. At a more detailed level, we may wish

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to explicitly recognize two different NF_4^+ sites in the analysis. In this case, the actual spectral predictions may be obtained by a procedure that we have detailed elsewhere for the case of disorder.[3] In the latter case, the space group of each alternative ordered lattice is determined, and the spectral predictions are obtained by correlation between them. In the present case, in addition to the S_4 site-only space group for NF_4^+ ($P\bar{4}2m$, D_{2d}^1), we need the corresponding C_{2v} site-only space group, $Pmm2$ (C_{2v}^1), with $Z = 1$. We would expect correlation between D_{2d} and C_{2v} to give the spectral predictions—in particular, to predict a splitting of the degenerate E mode of the former. Such a splitting is reported in the ν(N-F) feature but not in the δ(N-F) feature.

We now turn to the BF_4^- anion. As noted by Christe et al.,[1] these anions are all arranged with one B-F bond parallel to the crystallographic z axis to within experimental error. Such an arrangement has been noted elsewhere, as have its significant spectroscopic consequences.[4] As far as the BF_4^- anion is concerned, then, it has 3-fold rotational symmetry about the local z axis. Surely no less important is that it occupies, to within about 1%, the S_4 site of the $P\bar{4}2m$ NF_4^+ lattice discussed above. That is, the BF_4^- anion is at a site of near-perfect 4-fold cation site symmetry; it is surely this combination of C_3 and C_4 coincident sites, leading to a 12-fold potential energy profile and the consequent low librational barrier, that is responsible for the large temperature coefficients reported for three of the fluorines of the BF_4^-—we have incipient disorder of the BF_4^- anions. Turning now to the vibrational properties of the BF_4^- anion, we note that both its own (C_3) and site (C_4) rotational symmetries preserve x,y degeneracy. To a first approximation, the fact that a C_3 molecule occupies a C_4 site is irrelevant—they are equivalent in that the modes and multipoles of the C_3 molecule have a 1:1 mapping onto the corresponding modes of a similar C_4 molecule—the "missing" modes of the latter are not of relevance. As far as the NF_4^+ is concerned, we could either work in terms of C_3 (or, more conveniently, C_{3v}) or C_4 (or, more conveniently, C_{4v})—the predictions do not differ. Herein lies, we believe, one aspect of the basis of Christe et al.'s choice of C_{3v} as the symmetry explaining the vibrational properties of the BF_4^- anion in NF_4^+-BF_4^-. Vibrationally, the different orientations of the F_3BF^- group with respect to the crystallographic axes are unimportant. Irrespective of this orientation, for each F_3B unit, vectors parallel to x and y crystal axes exist—this is simply a restatement of the common x,y isotropy of C_3 and C_4. That is, $Z = 1$ not only for the NF_4^+ cations but also for the BF_4^- anions; no factor group effects are predicted and none observed. The second aspect of Christe's choice of C_{3v} symmetry is also explained. The correlation $T_d \rightarrow C_{3v}$ leads to a 2:1 splitting of T_2 modes and a 1:1 splitting of E (T_d) modes. The present example provides an even better example of the consequences of the C_{3v} orientation of a T_d group than does $(NH_4)_2SO_4$.[4]

Conclusion

In the present paper, we have presented an alternative explanation to that of Christe et al.[1] of the vibrational spectra of NF_4BF_4. It has been found possible to dispense with the emphasis placed on the rotational-oscillation motion of the BF_4^- anion by these authors. In so doing, we believe that we have restored physical meaning to those details of their X-ray results that they themselves doubted. In particular, we regard the presence of two crystallographically independent sets of NF_4^+ cations as entirely consistent with the spectroscopic data. The long wavelength of the radiation associated with infrared and Raman spectroscopies (implicitly assumed to be infinite, $k = 0$, when one applies the factor group method) means that vibrationally coupled molecules cannot be distinguished—their relative phases are locked together.

In contrast, diffraction methods involve wavelengths exploring a quite different part of k space, the difference in phase associated with the scattering from each of the vibrationally coupled molecules enabling a distinction between them. The present work underlines the fact that an assumption is involved when a crystallographic space group is taken to be that appropriate for a spectroscopic (and not just vibrational spectroscopic) analysis. In addition, we have suggested a method of analysis appropriate to structures in which one species occupies more than one site. Taken together with earlier work on disorder,[3] the present approach provides hope that disordered structures with multiple site occupancy may be amenable to vibrational analysis.

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Registry No. $NF_4^+BF_4^-$, 15640-93-4.

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Preparation, Characterization, and Chemistry of $F_4S{=}\overline{CCF_2O}SO_2$

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Recently, we found a convenient route to synthesize the ketene $F_5SC(SO_2F){=}C{=}O$ (**1**) from the acyl fluoride $F_5SCH(SO_2F)$-COF (**2**) and the base $F_3B{\cdot}N(C_2H_5)_3$ (**3**).[1] In an attempt to prepare ketene **1** directly, the dehydrohalogenation of the sultone $F_5S\overline{CHCF_2O}SO_2$ (**4**) with base **3** was tried. Unlike as was found for the sultone $F_3C\overline{CHCF_2O}SO_2$,[2] where the sole product was the ketene $F_3CC(SO_2F){=}C{=}O$, a mixture of two compounds was obtained, ketene **1** and what has now been shown to be its isomer, $F_4S{=}\overline{CCF_2O}SO_2$ (**5**). Compound **5** is the first cyclic example of a novel class of compounds, the alkylidenesulfur tetrafluorides. We are now studying this compound, because it could serve as an important intermediate in the synthesis of a number of new sultones. Since sultones play an important part in the synthesis of sulfonic acids, esters, and polymers containing the SO_2F group, pathways to novel sultones are of interest.

The first member of the alkylidenesulfur tetrafluorides, methylenesulfur tetrafluoride, $CH_2{=}SF_4$, was obtained by Kleemann and Seppelt.[3-6] This compound undergoes facile addition reactions with the polar agents HF, HCl, HBr, ICl, HgF_2, and AsF_5 and with chlorine.[7] These additions are such that *cis*-SF_4X systems are obtained, in contrast to the *trans*-SF_4X compounds from the fluorination of (fluoroalkyl)sulfenyl chlorides.[8] Additional members of this series include $FC(O)CH{=}SF_4$,[9] $H_3CCH{=}SF_4$,[10] $F_3CCH{=}SF_4$, and $F_3CC(CH_3){=}SF_4$.[11,12]

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