Inorg. Chem. **2006**, *45*, 7981−7984

Inorganic Chemistry

Article

Are the NF_4^+ Cations in NF_4BF_4 Really Nontetrahedral?

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Received June 30, 2006

The crystal structure of NF_4BF_4 has been reexamined. The low-temperature X-ray structure and solid-state ^{19}F MAS NMR spectra are in agreement with the conclusions reached from the vibrational spectra, that solid NF_4^+ salts contain only tetrahedral NF_4^+ cations. The alleged observation of two kind of nontetrahedral NF_4^+ cations in several previous crystal structures is attributed to incorrectly solved structures and, possibly, problems caused by disorder or twinning. It is further evidence for the dangers of over-reliance on crystal structures. Flawed crystal structures can give rise to either bad or unwarranted theory.

Introduction

The NF_4^+ cation is an ideal oxidizer. It exhibits high oxidizing power while at the same time possessing an unusually high kinetic stability due to nitrogen having its maximum coordination number of four. These properties have made NF_4^+ salts the key ingredient for solid propellants, NF_3/F_2 gas generators for chemical HF/DF lasers,[1] and a powerful, yet mild, electrophilic fluorinating agent.[2]

Historically, attempts to synthesize NF_4^+ salts had been discouraged by two theoretical predictions that NF_4^+ salts cannot exist[3] and that NF_4BF_4 should be stable only below −150 °C.[4] Furthermore, all complex fluoro cations known at that time had been prepared by fluoride-ion abstraction from a parent molecule by a strong Lewis acid. For the synthesis of NF_4^+, such an approach was not possible, because NF_5, the hypothetical parent molecule of NF_4^+, does not exist,[5,6] and the use of a F^+ equivalent was required to oxidize NF_3 to NF_4^+. However, F^+ is not accessible by chemical means, because fluorine is the most electronegative element. This big challenge was overcome in 1965.[7] Using NF_3, F_2, AsF_5, and electric glow discharge as an activation-energy source, researchers prepared NF_4AsF_6 (eq 1).

$$NF_3 + F_2 + AsF_5 \rightarrow NF_4AsF_6 \qquad (1)$$

It represented the first example of a synthesis of a complex fluoro cation derived from a nonexisting parent molecule. Subsequently, a large number of other stable NF_4^+ salts were prepared and characterized.[8] Although multinuclear NMR spectroscopy had established[9,10] beyond a doubt that, in solution, NF_4^+ was perfectly tetrahedral, and vibrational spectroscopy had suggested that, in the solid salts, NF_4^+ was also approximately tetrahedral,[8,9] the N−F bond length in NF_4^+ had been estimated only from a force constant−bond distance extrapolation[11] using a general valence force field obtained with the help of $^{14}N/^{15}N$ isotopic shifts[12] and by a theoretical calculation.[13] Although numerous attempts had been made to obtain crystal structures for different NF_4^+ salts, it was not until 1988 that the first crystal structure of a NF_4^+ salt, NF_4BF_4, was published.[14]

This crystal structure, however, was in serious conflict with the results from the vibrational analyses. Although the

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10.1021/ic061206p CCC: $33.50

vibrational spectra were in excellent agreement with all NF_4^+ ions being identical and possessing either tetrahedral or almost tetrahedral symmetry, the room-temperature crystal structure showed the presence of two different sets of NF_4^+ cations. One set was approximately tetrahedral, with a N−F bond length of 1.301(6) Å, but the second one was strongly distorted, with N−F bond lengths ranging from 1.265(9) to 1.321(10) Å. The BF_4^- anion exhibited rotational disorder about one of its B−F bonds. The discrepancy between the X-ray diffraction data and the vibrational spectra was attributed[14] to the description of a rotationally disordered dynamic structure with a static X-ray model with nonrotating ions. Because the time scale of vibrational spectroscopy is much shorter than that of a time-averaged X-ray structure, vibrational spectroscopy was assumed to be the superior method for detecting any nonequivalency of the ions. These circumstances prompted the authors of ref 14 to favor the vibrational results and to attribute "no real physical meaning" to the observation of two crystallographically very different NF_4^+ cations, thus leaving the question about the exact structure of NF_4^+ unsettled.

An alternative explanation for the apparent discrepancy between the reported crystal structure and the vibrational spectra was subsequently provided by Arif and Kettle.[15] They attempted to restore physical meaning to the crystal structure and the existence of two sets of nonequivalent NF_4^+ ions by the assumption of strong vibrational coupling among the different NF_4^+ cations due to the long wavelength of the radiation used for the vibrational spectroscopy, resulting in a locking of the relative phases. This supposedly renders them undistinguishable on the vibrational spectroscopy time scale. In contrast, the X-ray diffraction method, involving much shorter wavelengths, was assumed to enable a distinction between the two sets of cations because of the difference in phase associated with the scattering from each of the vibrationally coupled ions. These arguments, although not unreasonable, were nevertheless not very convincing.

Very recently, two crystal structures were also obtained for $NF_4Sb_3F_{16}$ and $NF_4Sb_2F_{11}$ that seemed to support the coexistence of nonequivalent NF_4^+ cations within the same unit cells. In $NF_4Sb_3F_{16}$, one NF_4^+ was weakly distorted from tetrahedral symmetry, with bond lengths ranging from 1.289(14) to 1.319(16) Å, whereas the second one was grossly distorted, with bond lengths ranging from 1.24(3) to 1.49(3) Å.[16] In $NF_4Sb_2F_{11}$, four distorted NF_4^+ ions were indicated, with bond lengths ranging from 1.235(15) to 1.309(11) Å.[17] Again, the vibrational spectra of these compounds showed no evidence for nonequivalent nontetrahedral NF_4^+ cations. Because several examples are known in which flawed crystal structures have resulted in the proposition of either unusual effects, such as stretch bond isomerism,[18−21] or very unusual bond lengths,[22,23] we decided to reexamine the solid-state structure of NF_4BF_4 by X-ray diffraction and solid-state NMR spectroscopy.

Experimental Section

Caution! Anhydrous HF can cause serious burns and must be handled using appropriate protective gear with immediate access to proper treatment procedures[24−26] in the event of contact with liquid HF, HF vapor, or HF containing solutions.

Materials and Apparatus. High-purity NF_4BF_4 was prepared by low-temperature UV photolysis using a literature method.[27] All reactions were carried out in Teflon-FEP ampules that were closed by stainless steel valves. Volatile materials were handled in a stainless steel/Teflon-FEP vacuum line.[28] All reaction vessels were passivated with ClF_3 prior to use. Nonvolatile materials were handled in the dry argon atmosphere of a glovebox.

Crystal Growth of NF_4BF_4. Inside the drybox, approximately 0.05 g of NF_4BF_4 was loaded into a 9 mm FEP tube, which was sealed on one side and fused to a 3/8 in. long piece of FEP tubing equipped with a Whitey SS-IRF2 valve on the other side. On the vacuum line, anhydrous HF (0.8 mL) was condensed into the tube at −196 °C. After being warmed to room temperature to dissolve all the NF_4BF_4, the tube was cooled to −20 °C; the HF solvent was removed slowly under a dynamic vacuum at this temperature, yielding a colorless crystalline solid. The ampule was cut open at −78 °C under a dry nitrogen stream, and the crystals were immediately transferred into a glass trough, kept at −100 °C by a stream of cold dry nitrogen. A crystal was selected in the cold stream and mounted on a glass fiber by rapidly bringing it into contact with a droplet of Fomblin oil (Z-60) that adhered to the tip of the fiber. The mounted crystal was quickly transferred into the cold nitrogen stream of the goniometer head.

Crystal Structure Determination. The single-crystal X-ray diffraction data of NF_4BF_4 was collected on a Bruker three-circle platform diffractometer, equipped with a SMART CCD (APEX) detector with the χ-axis fixed at 54.74°, and using Mo Kα radiation (graphite monochromator) from a fine-focus tube. The diffractometer was equipped with an LT-3 apparatus for low-temperature data collection using controlled liquid nitrogen boil-off. Cell constants were determined from 90 10 s frames. A complete hemisphere of data was scanned on ω (0.3°) with a run time of 30 s per frame at a detector resolution of 512 × 512 pixels using the SMART software package.[29] A total of 1271 frames were collected in three sets and a final set of 50 frames, identical to the first 50 frames, was also collected to determine any crystal decay. The frames were then processed on a PC, running Windows 2000 software, by using the SAINT software package[30] to give the *hkl* files corrected for Lp/decay. The absorption correction was performed using the SADABS program.[31] The structure was solved

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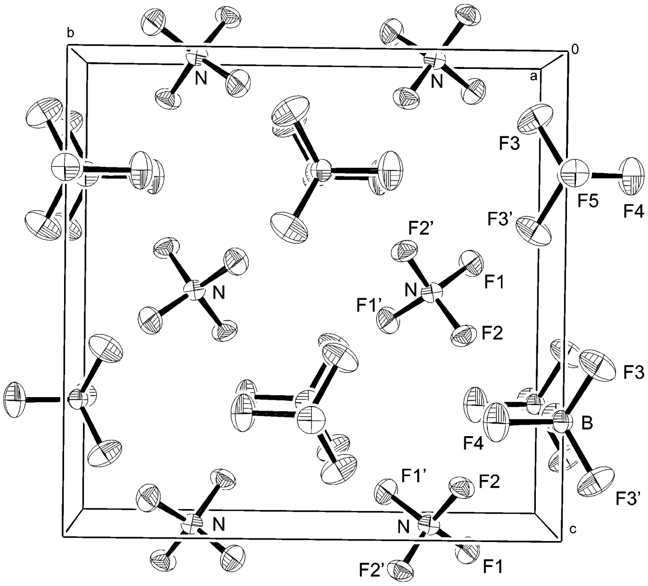

Figure 1. Packing diagram for the low-temperature structure of NF_4BF_4. Thermal ellipsoids are shown at the 50% probability level. The BF_4^- ions are situated on a mirror plane that passes through B, F4, and F5, whereas the NF_4^+ cations are situated on a 2-fold rotation axis located perpendicular to the plane of the paper.

by the direct method using the SHELX-90 program and refined by the least-squares method on F^2, SHELXL-97 incorporated in SHELXTL Suite 6.12 for Windows NT/2000.[32] All non-hydrogen atoms were refined anisotropically. For the anisotropic displacement parameters, the U_{eq} was defined as one-third of the trace of the orthogonalized U_{ij} tensor. ORTEP drawings were prepared using the ORTEP-3 for Windows V1.076 program.[33]

X-ray crystallographic file (CIF) can be obtained from the Inorganic Crystal Structure Database (ICSD, Fachinformationzentrum (FIZ) Karlsruhe, Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany, (fax: (49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de) on quoting deposition no. CSD 415904.

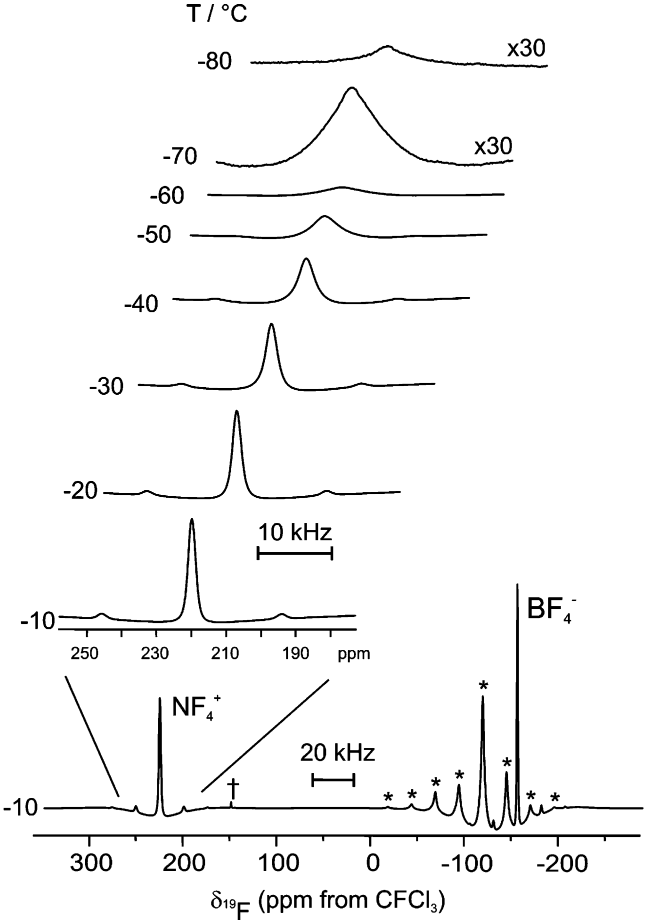

Figure 2. Solid-state ^{19}F MAS NMR spectrum of NF_4BF_4 inside an FEP insert at a spinning speed of 11.2 kHz. Asterisks (*) denote the spinning sideband manifold arising from FEP; the dagger (†) denotes an unidentified impurity.

Table 1. Refinement Data for the Low-Temperature Structure of NF_4BF_4

empirical formula	BF_8N
fw	176.82
T (K)	153(2)
cryst syst	orthorhombic
space group	*Pbcm*
a (Å)	5.1733(4)
b (Å)	9.9020(8)
c (Å)	9.7533(7)
α (deg)	90
β (deg)	90
γ (deg)	90
V (Å^3)	499.62(7)
Z	4
ρ_{calcd} g/cm^3	2.351
F(000)	336
index ranges	$-6 \leq h \leq 6, -12 \leq k \leq 10, -12 \leq l \leq 11$
μ (mm^{-1})	0.351
cryst size (mm^3)	0.23 × 0.17 × 0.09
λ (Å)	0.71073
no. of reflns collected	2802
no. of independent reflns	606
R_{int}	0.0587
no. of params	52
R1, wR2 [$I > 2\sigma(I)$]	0.0329, 0.0983
R1, wR2 (all data)	0.0380, 0.1000
$(\Delta/\rho)_{min/max}$ (e Å^{-3})	0.266/−0.375

Results and Discussion

The crystal structure of NF_4BF_4 was determined at different temperatures. In contrast with the previous room-temperature structure, which was refined in the tetragonal space group $\bar{P}42_1m$ and contained two crystallographically different NF_4^+ cations and rotationally disordered BF_4^- anions, the −120 °C structure belongs to the orthorhombic space group *Pbcm* (see Figures 1 and 2 and Tables 1−3). It is well-ordered and contains only one type of NF_4^+ cations. These cations, which, within the experimental uncertainties, are tetrahedral, are located on special positions with a 2-fold screw axis, giving them S_4 site symmetry. This site symmetry is in excellent agreement with the previously reported low-temperature vibrational spectra, obeying all the selection rules for S_4. There is no evidence for any additional factor group

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Table 2. Bond Lengths (Å) and Angles (deg) for NF_4BF_4[a]

NF_4^+		BF_4^-	
F1−N1	1.3079(13)	F3−B1	1.3785 (17)
F2−N1	1.3073(13)	F4−B1	1.391(3)
F1−N1−F1′	109.46(15)	F5−B1	1.389(3)
F1−N1−F2	109.02(6)	F3−B1−F3′	110.4(2)
F1−N1−F2′	109.70(6)	F3−B1−F4	109.03(13)
F2−N1−F2′	109.91(16)	F3−B1−F5	109.77(13)
		F4−B1−F5	108.76(19)

[a] Symmetry transformations used to generate equivalent atoms: $-x, -y + 1/2, -z + 2$; $x, y, -z + 1/2$.

Table 3. Atomic Coordinates (1 × 10^4) and Isotropic Displacement Factors U_{eq} ($Å^2$ × 10^3) for NF_4BF_4[a]

	x	y	z	U_{eq}[a]
B(1)	8961(5)	9910(2)	2500	20(1)
F(1)	3314(2)	1619(1)	10631(1)	30(1)
F(2)	6221(2)	1871(1)	9111(1)	27(1)
F(3)	8036(2)	10541(1)	3661(1)	45(1)
F(4)	8145(3)	8572(2)	2500	42(1)
F(5)	11646(3)	9938(1)	2500	27(1)
N(1)	4773(3)	2500	10000	21(1)

[a] Symmetry transformations used to generate equivalent atoms: $-x, -y + 1/2, -z + 2$; $x, y, -z + 1/2$. [b] U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

splittings. The BF_4^- anions are also well-ordered but are located on a mirror plane and are slightly distorted from perfect tetrahedral symmetry. The resulting C_s site symmetry is again in perfect agreement with the previously reported low-temperature vibrational spectra. Consequently, the low-temperature crystal structure of NF_4BF_4 is in perfect agreement with the vibrational spectra, thus bringing the vibrational spectra into harmony with the crystal structures. It should be noted that the unit-cell dimensions of the orthorhombic low-temperature structure are very similar to those of the tetragonal room-temperature structure and that the packing arrangements in both structures are almost identical. It was, therefore, of interest to examine whether the original room-temperature data set could be refined with a single set of tetrahedral NF_4^+ ions. Whereas the original data set could be fitted best with the previously published tetragonal $P\bar{4}2_1m$ structure with two sets of different NF_4^+ cations, it was found that the structure could also be solved with an only slightly higher R factor in the same tetragonal space group when constraining all NF_4^+ cations and BF_4^- anions to have ideal tetrahedral symmetry. A redetermination of the room-temperature unit-cell dimensions showed that they were identical to those originally published.

Additional evidence for the equivalency of all NF_4^+ cations in NF_4BF_4 was obtained by solid-state NMR spectroscopy. In contrast to solution-state NMR spectroscopy, where molecules tumble rapidly in a time-averaged solvent environment, solid-state NMR spectroscopy of crystalline or microcrystalline samples can detect different signals for different environments in the crystal lattice. Hence, the NMR spectra of microcrystalline solids can be directly related to the asymmetric unit of a crystal lattice and the number of crystallographically different species. The ^{19}F nucleus is sufficiently sensitive to changes in its environment to result in separate signals for chemically identical but crystallographically different species. In accord with the results from vibrational spectroscopy and the redetermined crystal structure, the solid-state ^{19}F MAS NMR spectra of NF_4BF_4 (Figure 2) showed only two signals, one at 220 ppm for NF_4^+ and one at −160 ppm for BF_4^-. Indirect spin−spin coupling was not resolved, because of the line width of the ^{19}F resonances (at −10 °C and MAS = 11.2 kHz: $\Delta\nu_{1/2} = 1130$ Hz (220 ppm) and $\Delta\nu_{1/2} = 470$ Hz (−160 ppm)). All fluorines in the cation and in the anion are rendered equivalent because of rapid rotation, confirming the previously suggested fluxional behavior in the crystal lattice.[14] The rapid motion could not be stopped at −80 °C; however, the NF_4^+ resonance showed significant broadening upon lowering the temperature to −70 °C, whereas further cooling to −80 °C resulted in a small narrowing of the resonance, suggesting the approach of the coalescence temperature. The BF_4^- resonance exhibited broadening only below −70 °C (at −80 °C: $\Delta\nu_{1/2} = 590$ Hz).

Acknowledgment. This paper is dedicated to Professor Kurt Dehnicke on the occasion of his 75th birthday. This work was funded by the Air Force Office of Scientific Research, the Office of Naval Research, the National Science Foundation, and the Natural Sciences and Engineering Research Council of Canada. We thank Dr. M. Yousufuddin for help with the structure refinement, Dr. T. Schroer for some theoretical calculations, and Prof. Dr. G. A. Olah for his steady support.

IC061206P