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Crystal Structure of NF_4^+ Salts

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Received December 14, 1987

The room-temperature tetragonal structure of NF_4BF_4 has been determined by a combination of single-crystal X-ray diffraction analysis and vibrational spectroscopy. This compound crystallizes in the tetragonal space group $P\bar{4}2_1m$ with $Z = 4$ and unit cell dimensions $a = 9.92$ (1) and $c = 5.23$ (1) Å. The structure was refined to an R value of 0.071 by using 325 independent observed reflections. The structure is made up from an approximately tetrahedral NF_4^+ cation with a bond length of 1.30 Å and a BF_4^- anion that rotates or oscillates around a 3-fold axis along one of its bonds. This rotation of the BF_4^- ion provides a mechanism for averaging the anisotropic fluorine-fluorine repulsion effects caused by the packing requirements of two sets of tetrahedral ions in a primitive cubic type of arrangement. The use of a static X-ray model with nonrotating ions results in artifacts, such as an apparent lowering of the site symmetries of the ions and two sets of different NF_4^+ cations, which have no real physical meaning. Additional data, such as vibrational spectra or improved models incorporating dynamic effects, are required for an adequate description of structures exhibiting this type of ion rotation. Due to this ion rotation and/or disorder problems and the lack of a successful static model, only partial X-ray structures could be obtained for NF_4SbF_6 and $\text{NF}_4\text{Sb}_2\text{F}_{11}$. Although these partial structures yielded N-F bond lengths with apparently small estimated standard deviations, these values were either much too large or small, depending on the constraints employed for obtaining a structure solution.

Introduction

Although NF_4^+ salts have been known for 20 years, the exact structure of the NF_4^+ cation is still unknown. From ^{19}F NMR spectra it is known that in solution NF_4^+ is an ideal tetrahedron. Vibrational spectra of many NF_4^+ salts indicate that in the solid state the NF_4^+ cations are also essentially tetrahedral.² From the general valence force field, the bond length in NF_4^+ has been estimated as 1.31 Å.³ This value is supported by ab initio calculations, which resulted in a value of 1.32 Å.⁴ Numerous unsuccessful attempts were made, in both our and other laboratories, to determine a crystal structure for one of the NF_4^+ salts, and the only reported structure was incomplete, giving a range of 1.30–1.40 Å for the N-F bond length.⁵ In this paper we report the crystal structure of $\text{NF}_4^+\text{BF}_4^-$ and partial structures of $\text{NF}_4^+\text{SbF}_6^-$ and $\text{NF}_4^+\text{Sb}_2\text{F}_{11}^-$ and address the problem of ion rotation and its effects on crystal structure determinations.

Experimental Section

Literature methods were used for the synthesis of $\text{NF}_4^+\text{BF}_4^-$,⁶ $\text{NF}_4^+\text{SbF}_6^-$,⁷ and $\text{NF}_4^+\text{Sb}_2\text{F}_{11}^-$.⁸ The single crystals were grown from either anhydrous HF or BrF_3 solutions, with the latter generally giving better results. The crystals were handled in the dry nitrogen atmosphere of a glovebox that was equipped with a microscope and were sealed in quartz capillaries. Infrared spectra were recorded on a Perkin-Elmer Model 283 spectrophotometer using dry powders pressed between AgCl or AgBr windows in an Econo press (Barnes Engineering, Co.). The Raman spectra were obtained with a Spex Model 1403 spectrophotometer using the 647.1-nm exciting line of a Kr ion laser and sealed melting point capillaries as sample containers.

Results and Discussion

Single-Crystal Analysis of $\text{NF}_4^+\text{BF}_4^-$.^{1b,c} The crystal data and details of the intensity data measurement and structure refinement are given in Table I. The lattice parameters and possible space groups were determined from Buerger precession photographs taken at 23 °C with Zr-filtered Mo $K\alpha$ X-rays. Symmetry and

Table I. Crystallographic Data for $\text{NF}_4^+\text{BF}_4^-$

fw	176.80
space group	$P\bar{4}2_1m$ (tetragonal; No. 113)
a , Å	9.92 (1)
c , Å	5.23 (1)
c/a	0.527
V , Å ³	514.7
Z	4
ρ (calcd), g/cm ³	2.281
radiation	Mo $K\alpha$
abs coeff (μ), cm ⁻¹	3.75
no. of reflns measd	388
no. of reflns used in refinement	325
no. of params refined	55
function minimized	$\sum w(F_o - F_c)^2$
weighting scheme	$1/w = 1 + [(F_o - 50)/100]^2$
$R = \sum F_o - F_c / \sum F_o $	0.071
$R_w = [\sum w(F_o - F_c)^2 / \sum w F_o ^2]^{1/2}$	0.077
residual electron density, e/Å ³	-0.4 to +0.3

Table II. Fractional Atomic Coordinates with Estimated Standard Deviations for $\text{NF}_4^+\text{BF}_4^-$

atom	x	y	z
B	0.2460 (5)	0.7460	-0.3961 (14)
N(1)	0	0	0
N(2)	0	0.5	-0.0172 (21)
F(1)	-0.0641 (4)	0.0874 (4)	0.1401 (17)
F(2)	0.0737 (4)	0.5737	0.1221 (19)
F(3)	0.0759 (5)	0.4241	-0.1668 (19)
F(4)	0.2789 (8)	0.6205 (5)	-0.3101 (11)
F(5)	0.2460 (4)	0.7460	-0.6591 (8)
F(6)	0.3321 (5)	0.8321	-0.3039 (18)

systematic absences on those photographs indicated space group $P\bar{4}2_1m$ or $P4_22$, but no solution was found for the latter space group. X-ray diffraction intensities were measured with a Supper-Pace/Picker automatic diffractometer using Mo $K\alpha$ X-rays and balanced Zr and Y filters. The rotation axis was the a axis. Continuous scans of each diffraction maximum were made with a scan rate of 1°/min (the scan widths were 2° or more), and background counts were made for one-sixth of the scan time at the beginning and end of the scan interval. All independent $I(hkl)$ with $(\sin \theta)/\lambda \leq 0.65 \text{ \AA}^{-1}$ were measured. The crystal, sealed in a 0.5-mm capillary tube, was small enough to make absorption corrections negligible. The intensities were reduced to relative $|F_o(hkl)|^2$ values by application of the appropriate Lorentz-polarization factors.

The approximate structure was determined by a trial and error method using a ball-and-stick model, aided by the three-dimen-

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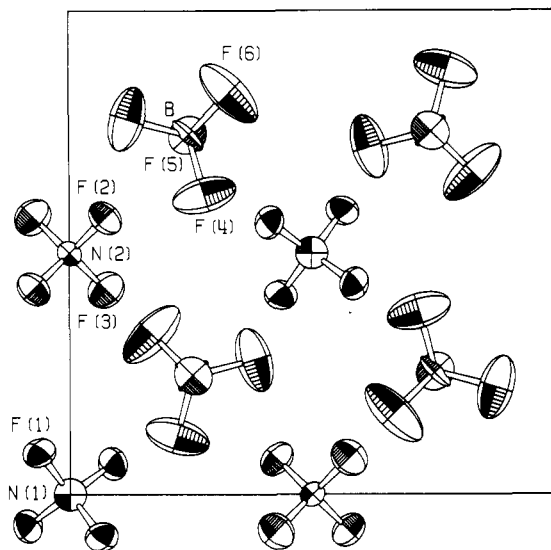


Figure 1. Crystal structure of $\text{NF}_4^+\text{BF}_4^-$ viewed along the c axis.

Table III. Bond Lengths (Å) and Bond Angles (deg) in NF_4^+ and BF_4^- with Esd's in Parentheses^a

N(1)–F(1)	1.301 (6)	B–F(4)	1.363 (8)
N(2)–F(2)	1.265 (9)	B–F(5)	1.376 (9)
N(2)–F(3)	1.321 (10)	B–F(6)	1.301 (8)
F(1)–N(1)–F(1)	108.5 (3), 111.5 (5)	F(4)–B–F(4)	109.2 (6)
F(2)–N(2)–F(2)	109.7 (10)	F(4)–B–F(5)	109.3 (5)
F(2)–N(2)–F(3)	109.9 (4)	F(4)–B–F(6)	108.7 (6)
F(3)–N(2)–F(3)	107.4 (9)	F(5)–B–F(6)	111.8 (6)

^aInterionic $\text{F}\cdots\text{F}$ distances: 2.66–2.78 Å.

sional Patterson function evaluated with a computer program written by M.D.L.

The trial model was refined by a least-squares technique using the program system SHELX-76.⁹ Neutral-atom scattering factors were taken from ref 10. Reflections with $I < \sigma(I)$ were omitted from refinement. Two reflections (020 and 040) were discarded because of poor agreement with calculated values as well as film intensities. The resultant atomic coordinates are listed in Table II, while the anisotropic thermal parameters are given in the supplementary material. A projection of the structure is depicted in Figure 1, which also shows the atom numbering as well as thermal ellipsoids. The program ORTEP¹¹ was used to produce the crystal structure illustration, and geometry calculations were made with the program system X-ray.¹² Bond lengths and angles are given in Table III.

The structure consists of isolated tetrahedra of NF_4^+ cations and BF_4^- anions. The interionic $\text{F}\cdots\text{F}$ contact distances are in the range of 2.66–2.78 Å, which is normal for such interactions. There are two crystallographically independent NF_4^+ ions corresponding to N(1) and N(2) on $\bar{4}$ and mm sites, respectively. This leads to four identical N(1)–F distances of 1.301 Å and two pairs of N(2)–F distances that are 1.265 and 1.321 Å, giving an overall average distance of 1.30 Å. The BF_4^- tetrahedron also has an imposed symmetry of mm . The B–F(6) distance appears significantly shorter than B–F(4) and B–F(5), even if esd's are underestimated.

To our knowledge, the NF_4BF_4 structure represents an original solution to the packing of two tetrahedral ions. The crystal packing

Table IV. Correlation Table for the Internal Vibrations of NF_4^+ on the S_4 Sites of Space Group $P\bar{4}2_1m$ in NF_4BF_4

assignment	point group T_d	site group S_4	factor group D_{2d}
ν_{sym}	$A_1(-RA)$	$A(-RA)$	$A_1(-RA)$ $A_2(-)$
δ_{sym}	$E(-RA)$	$A(-RA)$ $B(IR, RA)$	$A_1(-RA)$ $A_2(-)$ $B_1(-RA)$ $B_2(IR, RA)$
ν_{asym}	$F_2(IR, RA)$	$B(IR, RA)$ $E(IR, RA)$	$B_1(-RA)$ $B_2(IR, RA)$ $E(IR, RA)$
δ_{asym}	$F_2(IR, RA)$	$B(IR, RA)$ $E(IR, RA)$	$B_1(-RA)$ $B_2(IR, RA)$ $E(IR, RA)$

Table V. Correlation Table for the Internal Vibrations of NF_4^+ on C_{2v} Sites of Space Group $P\bar{4}2_1m$ in NF_4BF_4

assignment	point group T_d	site group C_{2v}	factor group D_{2d}
ν_{sym}	$A_1(-RA)$	$A_1(IR, RA)$	$A_1(-RA)$ $B_2(IR, RA)$
δ_{sym}	$E(-RA)$	$A_1(IR, RA)$ $A_2(IR, RA)$	$A_1(-RA)$ $B_2(IR, RA)$ $A_2(-)$ $B_1(-RA)$
ν_{asym}	$F_2(IR, RA)$	$A_1(IR, RA)$ $B_1(IR, RA)$ $B_2(IR, RA)$	$A_1(-RA)$ $B_2(IR, RA)$ $E(IR, RA)$ $E(IR, RA)$
δ_{asym}	$F_2(IR, RA)$	$A_1(IR, RA)$ $B_1(IR, RA)$ $B_2(IR, RA)$	$A_1(-RA)$ $B_2(IR, RA)$ $E(IR, RA)$ $E(IR, RA)$

can be considered as a superstructure of the primitive cubic CsCl structure, with the doubling of the cell in two directions being necessitated by the alternating orientations of identical ions. The NF_4^+ ions are stacked with their $\bar{4}$ or $mm2$ symmetry elements along the c axis, while the BF_4^- ions are packed with their pseudo-3-fold axis along the same axis. The stacks of N(1) F_4^+ and N(2) F_4^+ ions are rotated by 90° in relationship to each other in such a manner that room is made alternatively for either three or only one of the fluorine atoms of the BF_4^- anion. Therefore, the boron atoms are located either above or below the center of the small cubic cell depending on the up or down orientation of the BF_4^- ion in a given stack.

Analysis of the Vibrational Spectra of NF_4BF_4 . On the basis of the X-ray crystal structure, solid $\text{NF}_4^+\text{BF}_4^-$ possesses a strongly distorted BF_4^- anion on a C_s site and two kinds of NF_4^+ cations, one of nearly tetrahedral symmetry on an S_4 site and one with two significantly different bond lengths on a C_{2v} site. These results, however, disagree with the previously reported infrared^{6,13,14} and

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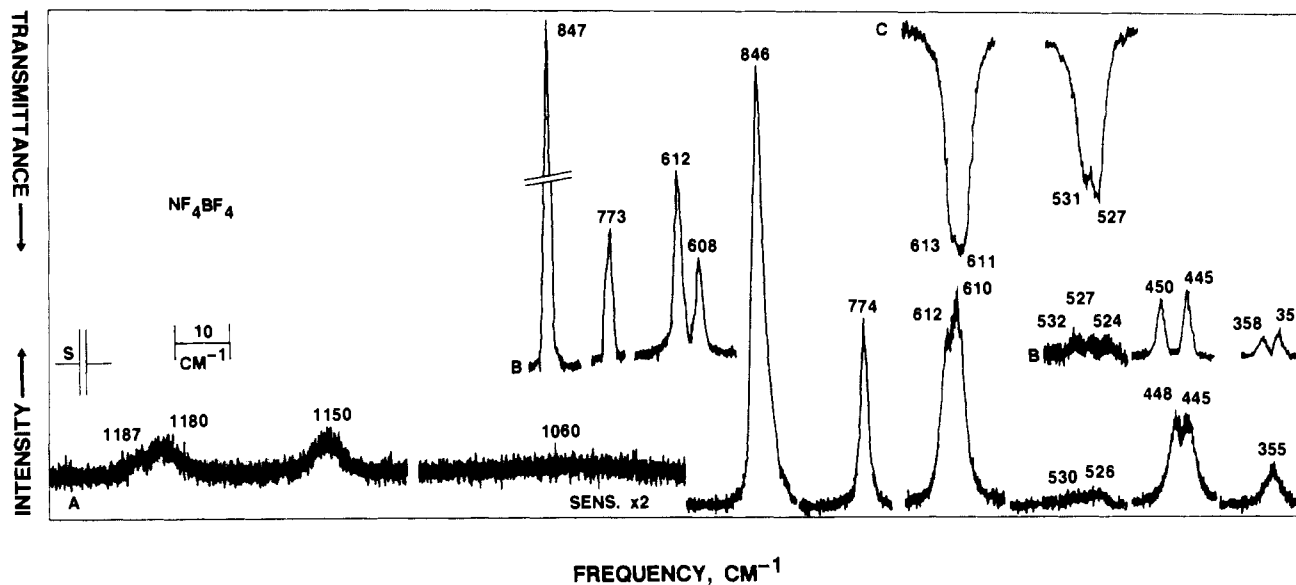


Figure 2. Vibrational spectra of NF_4BF_4 ; traces A and B, Raman spectra recorded at 25 and -140°C , respectively; trace C, infrared spectrum recorded at 25°C ; S indicates spectral slit width.

Table VI. Correlation Table for the Interval Vibrations of BF_4^- on C_s Sites of Space Group $P\bar{4}2_1m$ in NF_4BF_4

assignment	point group T_d	site group C_s	factor group D_{2d}
ν_{sym}	A_1 (— RA)	A' (IR, RA)	A_1 (— RA)
			B_2 (IR, RA)
			E (IR, RA)
δ_{sym}	E (— RA)	A' (IR, RA)	A_1 (— RA)
			B_2 (IR, RA)
			E (IR, RA)
δ_{sym}	E (— RA)	A'' (IR, RA)	A_2 (— —)
			B_1 (— RA)
			E (IR, RA)
ν_{asym}	F_2 (IR, RA)	A' (IR, RA)	A_1 (— RA)
			B_2 (IR, RA)
			E (IR, RA)
		A'' (IR, RA)	A_1 (— RA)
			B_2 (IR, RA)
			E (IR, RA)
δ_{asym}	F_2 (IR, RA)	A' (IR, RA)	A_1 (— RA)
			B_2 (IR, RA)
			E (IR, RA)
		A'' (IR, RA)	A_2 (— —)
			B_1 (— RA)
			E (IR, RA)

Raman^{6,14} spectra, which indicated nearly tetrahedral symmetry for both ions and only one kind of cation.⁶ Therefore, we have rerecorded the individual bands of $\text{NF}_4^+\text{BF}_4^-$ under higher resolution conditions and carried out a site group and factor group

Table VII. Observed Infrared and Raman Spectra of NF_4BF_4

freq, rel intens	approx description of mode in point group T_d		
IR	RA	NF_4^+ BF_4^-	
25°	25°	-140°	
1187s	1187sh	1190w	$\nu_3(F_2), \nu_{\text{asym}}$
1180s	1180w		
1159vs	1150w	1152w	
1130-1040vs, br	1060vw		$\nu_3(F_2), \nu_{\text{asym}}$
	846vs	847vs	$\nu_1(A_1), \nu_{\text{sym}}$
775w	774s	773s	$\nu_1(A_1), \nu_{\text{sym}}$
613ms	612s	612s	$\nu_4(F_2), \delta_{\text{asym}}$
611s	610s	608ms	
531m	530vw	532w	$\nu_4(F_2), \delta_{\text{asym}}$
527mw	526w	527vw	
		524w	
	448m	450m	$\nu_2(E), \delta_{\text{sym}}$
	445m	445m	
	355mw	358mw	$\nu_2(E), \delta_{\text{sym}}$
		354mw	

analysis for NF_4BF_4 in space group $P\bar{4}2_1m$ using the correlation method.¹⁵ The results are summarized in Tables IV–VII, and the vibrational bands of interest are depicted in Figure 2. A comparison of the observed spectra with the predictions from the factor group analysis for NF_4BF_4 in space group $P\bar{4}2_1m$ allows the following conclusions: (i) There is no spectroscopic evidence for the presence of two distinct NF_4^+ cations. For example, no infrared band and only one symmetrical, narrow Raman line with a half-width of about 2 cm^{-1} at a spectral slit width of 1 cm^{-1} are observed for the symmetric NF_4^+ stretching vibration. For two distinct NF_4^+ cations, at least three strong Raman bands should be observed in this region. (ii) For NF_4^+ , the number of bands and their infrared and Raman activities are incompatible with a C_{2v} site symmetry. However, they are acceptable for either an S_4 symmetry, i.e. identical NF_4^+ bond lengths with a slight compression of the tetrahedral angle in one direction, or a tetrahedral symmetry, where the degeneracies of the E and F_2 modes

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Table VIII. Correlation Table for the Internal Vibrations of BF_4^- of Symmetry C_{3v}

T_d	C_{3v}	obsd freq, rel int	
		IR	RA(25°)
$A_1(-RA)$	$A_1(IR, RA)$	775w	774s
$E(-RA)$	$E(IR, RA)$		355mw
$F_2(IR, RA)$	$A_1(IR, RA)$	1130-1040vw, br	1060vw, br
	$E(IR, RA)$		
$F_2(IR, RA)$	$A_1(IR, RA)$	531m	530w
	$E(IR, RA)$	527mw	526mw

are partially lifted due to solid-state effects. This interpretation is supported by the fact that the infrared and Raman selection rules for T_d symmetry are retained. (iii) For BF_4^- , again the number of observed bands and their Raman and infrared activities are incompatible with a C_s site symmetry in space group $P\bar{4}2_1m$, and the actual symmetry must be higher. The observation of the symmetric BF_4^- stretching mode in the infrared spectrum eliminates both T_d and S_4 symmetries and also suggests that the symmetries of NF_4^+ and BF_4^- are different.

Reconciliation of the X-ray Data with the Vibrational Spectra.

At first glance, the vibrational spectra and single-crystal X-ray data for NF_4BF_4 are incompatible. A closer inspection of the X-ray results, however, reveals the following facts. For the BF_4^- anion, three of the four fluorine atoms, F(6) and the two F(4) atoms, exhibit very large thermal parameters, and the orientations of their ellipsoids indicate rotation or oscillation around the B-F(5) axis.

If this rotating anion model is correct, the vibrational spectra of BF_4^- in NF_4BF_4 should exhibit approximately C_{3v} symmetry. The correlation for $T_d \rightarrow C_{3v}$ is given in Table VIII. As can be seen, the observed spectra are in excellent agreement with the predictions for C_{3v} symmetry. The only bands that, due to their very low intensities, have not been observed are the infrared component of the symmetric deformation and one of the two Raman components of the antisymmetric stretch.

The above model of a rotating BF_4^- anion can also nicely account for the discrepancies encountered with the NF_4^+ cations. With a static model, i.e. nonrotating BF_4^- anions, the fluorine-fluorine repulsions can be equalized within the tetrahedral packing requirements for only half of the NF_4^+ cations. The other half is then experiencing anisotropic repulsions, which lead to their distortion. If, however, the BF_4^- anion rotates or oscillates and thereby averages out the fluorine-fluorine repulsion effects, then all NF_4^+ cations become equivalent and should approximate ideal tetrahedra. This conclusion is in excellent agreement with the vibrational spectra, which show only one kind of NF_4^+ cation of tetrahedral or almost tetrahedral symmetry. From the small thermal parameters of the fluorines on nitrogen, it appears that in NF_4BF_4 the NF_4^+ cations do not appreciably rotate.

The discrepancy between the X-ray data and the vibrational spectroscopic results can therefore be attributed to the fact that a static model with nonrotating ions was used to solve a structure with rotating or oscillating ions. Therefore, the presence of two different sets of NF_4^+ cations, the strong C_{2v} distortion of one of them, and the strong C_s distortion of BF_4^- have no physical meaning and must be considered as artifacts of the method used.

The Raman spectrum of NF_4BF_4 was also recorded at -140°C . The observed spectrum (see Table VII) was very similar to the room-temperature spectrum, except for the expected line sharpening, minor frequency shifts, and splittings of the 355-cm^{-1} band into two and of the 530- and 526-cm^{-1} bands into three components. Some of these bands are shown in Figure 2. These results suggest that cooling to -140°C is insufficient to freeze out the rotational motion of the BF_4^- anions.

Most of the thermally more stable NF_4^+ salts undergo at elevated temperatures a phase change.² For NF_4AsF_6 and NF_4BF_4 this occurs at 145 ± 1 and $224 \pm 2^\circ\text{C}$, respectively. An X-ray

Table IX. Crystallographic Data for NF_4SbF_6 and $\text{NF}_4\text{Sb}_2\text{F}_{11}$

NF_4SbF_6	
Room Temperature	
tetragonal	$a = 7.956(5) \text{ \AA}$; $c = 5.840(4) \text{ \AA}$ $V = 369.63 \text{ \AA}^3$; $\rho(\text{calcd}) = 2.928 \text{ g cm}^{-3}$; $Z = 2$
Low Temperature (-120°C)	
tetragonal	$a = 7.979(4) \text{ \AA}$; $c = 11.428(4) \text{ \AA}$ $V = 727.56 \text{ \AA}^3$; $\rho(\text{calcd}) = 2.975 \text{ g cm}^{-3}$; $Z = 4$
$\text{NF}_4\text{Sb}_2\text{F}_{11}$	
Room Temperature	
tetragonal:	$a = 18.326(9) \text{ \AA}$; $c = 14.205(5) \text{ \AA}$ $V = 4770.6 \text{ \AA}^3$; $\rho(\text{calcd}) = 3.02 \text{ g cm}^{-3}$; $Z = 16$

powder pattern of the high-temperature phase of NF_4AsF_6 showed it to be cubic.¹⁶ This transition from a tetragonal to a cubic phase suggests that at elevated temperature all ions rotate freely and act as spheres. Although no X-ray data are available for the high-temperature phase of NF_4BF_4 , the cause for the phase transition is probably the same. A detailed study of the ion motions in NF_4^+ salts as a function of temperature, using methods such as second moment and relaxation time NMR measurements, would be most interesting but was beyond the scope of this study.

Partial Crystal Structures of NF_4SbF_6 and $\text{NF}_4\text{Sb}_2\text{F}_{11}$. Attempts to solve the X-ray crystal structures of NF_4SbF_6 and $\text{NF}_4\text{Sb}_2\text{F}_{11}$ were carried out at the University of Leicester and the University of Southern California, respectively. Both compounds exhibited ion rotation and possibly disorder problems, and, therefore, their structures could only partially be solved.

For NF_4SbF_6 , which appears to be isotypic with $\text{PCl}_4^+\text{PCl}_6^-$,¹⁷ the structure could be refined to $R_w = 0.084$ for the antimony, nitrogen, and the four fluorines on nitrogen but did not result in reasonable positions for the fluorines on antimony. This is not surprising in view of the fact that in the closely related $\text{PCl}_4^+\text{PCl}_6^-$ structure the chlorines on the octahedral phosphorus exhibit very large thermal parameters and two longer axial bonds, indicative of anion rotation around 3-fold axes. Attempts were unsuccessful to overcome the problem of ion rotation by collecting a data set at low temperature (-120°C). Although the c axis of the unit cell was doubled at -120°C , the structure again could not be solved. Some of the crystallographic data for NF_4SbF_6 and $\text{NF}_4\text{Sb}_2\text{F}_{11}$ are summarized in Table IX.

It was hoped that the anion rotation problem could be solved by substituting the octahedral SbF_6^- anion by the less symmetrical $\text{Sb}_2\text{F}_{11}^-$ anion. With the positions of the $\text{Sb}_2\text{F}_{11}^-$ anions fixed first, the NF_4^+ cations appeared clearly visible, but problems arose during the least-squares refinement. By applying constraints on the distances and angles of the $\text{Sb}_2\text{F}_{11}^-$ anion, it was possible to refine the structure to an R factor of 0.126.

It should be emphasized that, although N-F bond lengths with reasonably small estimated standard deviation values were obtained in both cases, these N-F bond length values significantly deviated from the more reliable value obtained for NF_4BF_4 . Furthermore, when the NF_4^+ geometry was fixed and the anion refined without constraints on symmetry, as for NF_4SbF_6 , the resulting N-F bond length ($1.25(2) \text{ \AA}$) was much too short. However, when the anion geometry was constrained, as for $\text{NF}_4\text{Sb}_2\text{F}_{11}$, the resulting N-F bond length (1.34 \AA) was much too long. Thus, values obtained from incomplete structures of this type should not be trusted because errors induced by ion rotation and repulsion effects can cause apparent lengthening or shortening of bonds, depending on the constraints used for the refinement.

Conclusions. The bond length in NF_4^+ has been determined experimentally for the first time. The found value of 1.30 \AA confirms the predictions of 1.31 and 1.32 \AA , made from force field³ and ab initio⁴ calculations, and is the shortest known N-F bond. Its shortness is attributed to the high oxidation state (+V) of and the formal positive charge on nitrogen and a maximal number

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of fluorine ligands. Partial double bonding, which can be invoked for the NF molecule



($r = 1.3173 \text{ \AA}$),¹⁸ is unlikely for NF_4^+ because all of its atoms already possess an electron octet.

The problems previously encountered with solving a crystal structure of an NF_4^+ salt appear to be largely due to ion rotation and/or disorder in these salts. The main difficulty consisted of finding a static model with nonrotating ions that could describe a dynamic structure with rotating ions. The thermal parameters of the atoms from the X-ray data and vibrational spectroscopy coupled with a group factor analysis were found to be very useful for the detection and understanding of ion rotation. In the case

of ion rotation, the X-ray analysis can result in an apparent lowering of the symmetry and in a nonequivalence of ions, which have no real physical meaning. Similarly, partial structure solutions or solutions in which the geometry of one set of ions has to be constrained can result in unreliable bond lengths with deceptively small estimated standard errors.

Acknowledgment. The work at Rocketdyne was sponsored by the Office of Naval Research and the U.S. Army Research Office. We thank Dr. M. Watkins and J. A. Feng for assistance during the structural analysis of $\text{NF}_4\text{Sb}_2\text{F}_{11}$ and Dr. P. Charpin for helpful comments.

Registry No. NF_4BF_4 , 15640-93-4; NF_4SbF_6 , 16871-76-4; $\text{NF}_4\text{Sb}_2\text{F}_{11}$, 58702-89-9.

Supplementary Material Available: A table of anisotropic thermal parameters for NF_4BF_4 (1 page); a listing of observed and calculated structure factors (2 pages). Ordering information is given on any current masthead page.

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Structural and Magnetic Properties of Dimorpholinium Hexahalodicuprate(II) Salts: Study of Two Planar $\text{Cu}_2\text{X}_6^{2-}$ Dimers

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Received January 6, 1988

The chloride and bromide analogues of the title compound were synthesized, and the X-ray crystal structure of the former compound was determined. Magnetic susceptibility and EPR studies were carried out on both compounds. The crystal structure of the chloride salt yielded a triclinic structure, space group $P\bar{1}$, with $a = 7.414(2) \text{ \AA}$, $b = 8.686(2) \text{ \AA}$, $c = 14.766(4) \text{ \AA}$, $\alpha = 79.16(2)^\circ$, $\beta = 82.20(2)^\circ$, $\gamma = 74.19(2)^\circ$, $Z = 2$, $d_{\text{calcd}} = 1.94 \text{ g/cm}^3$, and $R = 0.0527$. The structure consists of isolated planar dimers with each copper atom semicoordinated to two oxygen atoms in what may be described, on the average, as a 4+2 elongated octahedral geometry. The magnetic exchange interaction in the two compounds is predominantly antiferromagnetic with a singlet-triplet splitting energy of $J/k = -43.5(1) \text{ K}$ for the chloride and $J/k = -131(2) \text{ K}$ for the bromide. EPR and magnetic studies on both compounds indicate that magnetically these compounds are not isolated dimers. EPR studies supplement both the structural and magnetic studies.

Introduction

There have been numerous copper(II) halide dimers of $\text{Cu}_2\text{X}_6^{2-}$ stoichiometry studied in the last several years,^{1,2} but only recently have isolated planar dimers been discovered.³ The copper(II) halide dimers studied to date belong to one of the following geometries: planar, bifoldded, or twisted.⁴ The bifold distortion, which is symbolized by σ , involves the angle between the central Cu_2X_2 plane and the terminal CuX_3 planes,⁵ while the twist distortion, denoted by τ , refers to the angle between the bridging Cu_2X_2 plane and the terminal CuX_2 planes.⁴ The planar dimers normally form stacks with the Cu(II) ions in sites of 4+2 coordination geometry, while the bifoldded dimers form stacks with the Cu(II) ions in 4+1 coordination geometry. The twisted dimers are isolated species in which the Cu^{2+} ions in the $\text{Cu}_2\text{X}_6^{2-}$ units distort toward tetrahedral geometry in order to lower the chlorine-chlorine repulsion energy. The cations in these cases are large and do not hydrogen bond to the halide atoms in the dimer. Recently Tanaka discovered a planar isolated dimer with only a very small twist distortion,³ in which the planar geometry is stabilized by interaction with dibenzotetrafulvalenium (ab-

breviated DBTTF) counterions. The morpholinium salts presented here are the second example of isolated planar dimers, in this case with the planar configuration stabilized by interaction with the organic cations.

Hatfield, while studying a series of planar dihydroxo-bridged Cu(II) dimers,² discovered the relationship between the bridging angle, ϕ , and the magnetic properties of these compounds; the antiferromagnetic coupling increases with increasing bridging angle. It is the purpose of magneto-structural studies to elucidate such correlations between not only the strength but also the anisotropy of the magnetic interactions and the geometrical and electronic structure of materials. Such relationships hold very well for the copper(II) halide dimers. Studies have shown that for bifoldded chloride dimers, with $\phi \approx 95.5^\circ$, J is antiferromagnetic for small values of σ and becomes ferromagnetic for $\sigma \geq 25^\circ$.⁶

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