New Synthesis, Crystal Structure, and Vibrational Spectra of Tetramethylammonium Azide and Reactions of the Fluoride Anion with HN_3 and of the Azide Anion with HF[†]

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Abstract: Tetramethylammonium azide, $N(CH_3)_4^+N_3^-$, was obtained in high purity and quantitative yield by the reaction of $N(CH_3)_4^+F^-$ with $Si(CH_3)_3N_3$ in CH_3CN solution. This compound is isostructural with $N(CH_3)_4^+HF_2^-$ and crystallizes in the orthorhombic system: space group, $Pmn2_1$ (No. 31); a = 6.879 (5) Å; b = 5.479 (4) Å; c = 8.858 (7) Å; Z = 2; $R(F)$ = 0.0388. Its N_3^- anion is symmetric and linear and the $N(CH_3)_4^+$ cation is somewhat distorted from tetrahedral symmetry due to crystal packing effects. The infrared and Raman spectra of $N(CH_3)_4^+N_3^-$ were also recorded. The symmetric stretching mode of N_3^- exhibits the pronounced frequency decrease expected for increasing ionicity with increasing cation size. A study of the HN_3–MF systems [M = Na, K, Rb, Cs, $N(CH_3)_4$] revealed some unexpected chemistry. Even at −80 °C, HN_3 displaces F^- from MF with formation of equimolar amounts of $M^+N_3^-$ and HF. The latter reacts with MF to give $M^+HF_2^-$. On the other hand, HF quantitatively displaces N_3^- from MN_3 with formation of HN_3 and $M^+HF_2^-$. This apparent discrepancy can be explained by the vast difference in basicity between F^- and HF_2^-. Attempts to isolate stable $F–H–N_3^-$ or $N_3–H–N_3^-$ anions from HN_3 and either MF or MN_3, respectively, were unsuccessful.

Introduction

Although tetramethylammonium azide, $N(CH_3)_4^+N_3^-$, had been known[1] since 1918, only very little information has since been reported[2-6] for this interesting compound. According to the previous reports,[1-6] the compound was prepared by either the reaction of $N(CH_3)_4I$ with AgN_3 (1) in either water[1] or anhydrous

$$N(CH_3)_4I + AgN_3 \rightarrow N(CH_3)_4N_3 + AgI\downarrow \qquad (1)$$

ethanol[4] or the neutralization[3,5,6] of $N(CH_3)_4OH$ with aqueous HN_3 (2). Both preparations involve the use of shock-sensitive

$$N(CH_3)_4OH + HN_3 \rightarrow N(CH_3)_4N_3 + H_2O\downarrow \qquad (2)$$

starting materials, i.e. AgN_3 and HN_3, and suffer from solubility and purification problems. No structural or spectroscopic data had previously been reported for $N(CH_3)_4N_3$, except for partial vibrational spectra.[6] In this paper, we report an improved synthesis for $N(CH_3)_4N_3$ and its crystal structure and vibrational spectra.

Experimental Section

Caution! *Hydrazoic acid is shock sensitive when undiluted, and appropriate shielding and safety precautions must be used when working with this compound.*

Materials. CH_3CN (Baker, Bio-analyzed, having a water content of 40 ppm) was treated with P_2O_5 and freshly distilled prior to use, thereby reducing its water content to <4 ppm. The synthesis of $N(CH_3)_4F$ has previously been described.[7] $Si(CH_3)_3N_3$ (Petrarch) was distilled prior to use. Hydrazoic acid was generated from NaN_3 and stearic acid at about 110 °C, as previously described.[8] Dry KF, RbF, and CsF were obtained by fusing these materials in a platinum crucible and transferring the resulting clinkers into a drybox while still hot. The RbF single crystal (Semi-Elements, Inc.), used for the low-temperature infrared study, was freshly cleaved with a razor blade in the drybox and then mounted in a dry N_2 atmosphere into the tip of an Air Products Model DE 202S helium refrigerator equipped with external CsI windows. The HF (Matheson) was dried by storage over BiF_5.[9]

Apparatus. Volatile materials were handled either in a flamed-out Pyrex vacuum line equipped with Kontes Teflon valves, in a stainless-steel vacuum line equipped with Teflon-FEP U-traps,[10] or in the dry nitrogen atmosphere of a glovebox. Solids were manipulated exclusively in the drybox.

Raman spectra were recorded on either a Cary Model 83 or a Spex Model 1403 spectrophotometer by use of the 488-nm exciting line of an Ar ion or the 647.1-nm line of a Kr ion laser, respectively. Baked-out Pyrex melting point capillaries were used as sample holders. Infrared spectra were recorded as KBr disks on a Perkin-Elmer Model 283 spectrophotometer. The KBr disks were pressed in a Wilks minipress and left in the press for the recording of the spectra. The spectra obtained in this manner were identical with those obtained for pressed AgCl disks, indicating that no reaction between KBr and $N(CH_3)_4N_3$ had occurred during the pressing operation. The cryostat used for the low-temperature infrared studies has previously been described.[11]

Table I. Summary of Crystal Data and Refinement Results for $N(CH_3)_4^+N_3^-$

space group	$Pmn2_1$ (No. 31)
a (Å)	6.879 (5)
b (Å)	5.479 (4)
c (Å)	8.858 (7)
V (Å^3)	333.9 (7)
molecules/unit cell	2
formula weight (g/mol)	116.2
crystal dimens (mm)	0.28 × 0.34 × 0.88
calcd density (g cm^{-3})	1.156
wavelength (Å) used for data collecn	0.71069
sin (θ/λ) limit (Å^{-1})	0.6497
total no. of reflecns measured	1469
no. of independent reflecns	762
no. of reflecns used in structural analysis, $I > 3\sigma(I)$	427
no. of variable params	77
final agreement factor	$R(F)$ = 0.0388 $R_w(F)$ = 0.0359

Synthesis of $N(CH_3)_4N_3$. A solution of $Si(CH_3)_3N_3$ (29.92 mmol) in 15 mL of CH_3CN was slowly added in a dry atmosphere to $N(CH_3)_4F$ (24.10 mmol) dissolved in 29 mL of CH_3CN. In a mildly exothermic reaction, a white precipitate was formed instantaneously. The mixture was agitated for about 10 min, and then all volatile material was pumped off at room temperature. The white solid residue (2.794 g; weight calculated for 24.10 mmol of $N(CH_3)_4N_3$ = 2.797 g, corresponding to a 99.9% yield) was identified by vibrational spectroscopy and a crystal

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[†] Dedicated to Prof. Alois Haas on the occasion of his 60th birthday.

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(1) Friedländer, F. *J. Am. Chem. Soc.* **1918**, *40*, 1945.

(2) Straumanis, M.; Circulis, A. *Z. Anorg. Allg. Chem.* **1943**, *252*, 17.

(3) Gutmann, V.; Hampel, G.; Leitmann, O. *Monatsh. Chem.* **1964**, *95*, 1034.

(4) Weller, F.; Dehnicke, K. *J. Organomet. Chem.* **1972**, *35*, 237.

(5) Bojes, J.; Chivers, T. *Inorg. Chem.* **1978**, *17*, 318.

(6) Glavincevski, B.; Brownstein, S. *J. Inorg. Nucl. Chem.* **1981**, *43*, 1827.

(7) Christe, K. O.; Wilson, W. W.; Wilson, R. D.; Bau, R.; Feng, J. *J. Am. Chem. Soc.* **1990**, *112*, 7619.

(8) Krakow, B.; Lord, R. C.; Neely, G. O. *J. Mol. Spectrosc.* **1968**, *27*, 198.

(9) Christe, K. O.; Wilson, W. W.; Schack, C. J. *J. Fluorine Chem.* **1978**, *11*, 71.

(10) Christe, K. O.; Wilson, R. D.; Schack, C. J. *Inorg. Synth.* **1986**, *24*, 3.

(11) Christe, K. O.; Wilson, R. D. *Inorg. Chem.* **1987**, *26*, 920.

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Table II. Bond Distances (Å) for $N(CH_3)_4{}^+N_3{}^-$

N1–N2	1.155 (5)	C5–H9	0.944 (10)
N2–N3	1.176 (5)	C5–H11	0.961 (10)
N4–C5	1.496 (2)	C6–H10	1.046 (10)
N4–C6	1.470 (7)	C6–H14	0.981 (8)
N4–C7	1.529 (7)	C7–H12	1.001 (8)
C5–H8	1.030 (7)	C7–H13	0.990 (11)

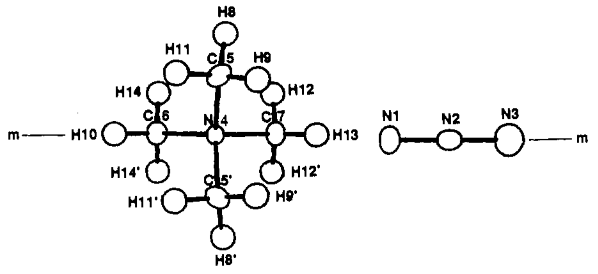

Figure 1. View of the molecular $N(CH_3)_4N_3$ unit showing the positions and labeling of the hydrogen atoms and the crystallographic mirror plane.

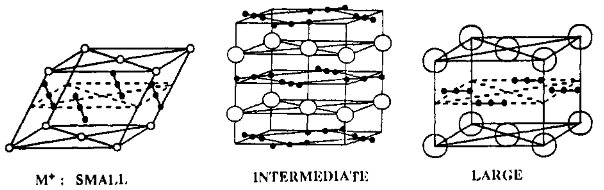

Figure 2. Packing in azides and bifluorides as a function of the cation size.

structure determination as $N(CH_3)_4N_3$. Its decomposition point was found to be 255 °C.

Crystal Structure of $N(CH_3)_4N_3$. Single crystals of $N(CH_3)_4N_3$ were grown from a hot CH_3CN solution. A suitable crystal was selected under the microscope and sealed in a glass capillary because the compound diliquesces slowly, and intensity data were collected at room temperature on a Nicolet/Syntex $P2_1$ automated four circle diffractometer, with Mo Kα radiation and a graphite crystal monochromator. The unit cell parameters were determined by least-squares refinement of 15 centered reflections. Data were collected with the ω-scan technique for all reflections such that $4.0° < 2\theta < 55.0°$. Throughout the data collection, three reflections were monitored periodically and no decay was observed. A set of 1469 intensity values, representing a hemisphere of data, was collected and the four equivalent octants were merged to give a total of 427 unique reflections. The R factor for averaging was 1.8%. The positions of the non-hydrogen atoms were obtained by direct methods using the computing package SHELX-86.[12] The hydrogen atoms were later located from a difference Fourier map. The structure was then refined to final agreement factors of $R(F) = 3.88\%$ and $R_w(F) = 3.59\%$, using 427 reflections with $I > 2\sigma(I)$. In the least-squares refinement, the H atoms were also varied and were assigned equal isotropic temperature factors. Details of the data collection parameters and other crystallographic information are given in Table I, and the final atomic coordinates and temperature factors are listed in Tables A and B, respectively, of supplementary material. Interatomic distances and angles are given in Tables II and III, respectively. A view of the molecular $N(CH_3)_4N_3$ unit showing the positions and labeling of the hydrogen atoms is given in Figure 1, and the packing in $N(CH_3)_4N_3$ is shown in Figure 2 for the large cation case.

Reactions of HN_3 with MF (M = Na, K, Rb, Cs, $N(CH_3)_4$). Samples of these fluorides were exposed at room temperature to about 100 Torr of HN_3 vapor for 12 h. The solid reaction products were weighed and identified by infrared and Raman spectroscopy and showed about equimolar amounts of $N_3{}^-$ and $HF_2{}^-$. No evidence for the formation of any new species, such as $F–H–N_3{}^-$ or $N_3–H–N_3{}^-$, was observed.

A sample of HN_3 was condensed at 12 K onto a RbF single crystal window. The temperature of the window was steadily increased, and infrared spectra were periodically recorded. Between 12 and 100 K the spectra showed only solid HN_3, with increasing temperature causing irreversible band broadening. At 130 K the HN_3 deposit was slowly pumped away. Therefore, the pumping was interrupted and the RbF window, while kept at 190 K, was exposed to an HN_3–He mixture (1:10 mole ratio) at a total pressure of about 35 Torr. The infrared spectrum, recorded at this temperature, showed only $N_3{}^-$ and $HF_2{}^-$ but no unreacted HN_3. This indicates that, even at 190 K, the reaction of RbF with HN_3 to give RbN_3 and $RbHF_2$ is fast and complete.

Table III. Bond Angles (deg) for $N(CH_3)_4{}^+N_3{}^-$

N1–N2–N3	179.0 (3)	N4–C7–H12	106.6 (7)
C5–N4–C6	111.8 (4)	N4–C7–H13	108.3 (6)
C5–N4–C7	107.3 (4)	H8–C5–H9	109.6 (9)
C5–N4–C5′	109.1 (3)	H8–C5–H11	109.6 (8)
C6–N4–C7	109.3 (2)	H9–C5–H11	112.0 (7)
N4–C5–H8	109.9 (4)	H10–C6–H14	109.2 (7)
N4–C5–H9	109.2 (6)	H14–C6–H14′	116.8 (8)
N4–C5–H11	106.5 (6)	H12–C7–H13	111.0 (7)
N4–C6–H10	107.9 (6)	H12–C7–H12′	113.1 (9)
N4–C6–H14	106.6 (7)		

Reactions of HF with MN_3 (M = Na, Cs, $N(CH_3)_4$). Weighed amounts of MN_3 were exposed to less than stoichiometric amounts of gaseous HF for several hours at room temperature. Essentially all of the HF was consumed, and HN_3 was liberated. The solid reaction products were identified spectroscopically as mixtures of $MF{\cdot}nHF$ and unreacted excess MN_3.

For NaN_3, a sample was treated at room temperature with a 31-fold excess of liquid anhydrous HF. After removal of the volatile products, which consisted of a mixture of HF and HN_3, the solid residue was identified as $NaHF_2$.

Results and Discussion

Synthesis and Properties of $N(CH_3)_4N_3$. The ready acess to truly anhydrous $N(CH_3)_4F$[7] combined with the commercial availability of $Si(CH_3)_3N_3$ provides a convenient and safe synthesis (3) for $N(CH_3)_4N_3$. Using a slight excess of $Si(CH_3)_3N_3$, $N(CH_3)_4N_3$ can be prepared in quantitative yield and excellent purity.

$$N(CH_3)_4F + Si(CH_3)_3N_3 \xrightarrow[\text{room temp}]{CH_3CN} N(CH_3)_4N_3 + Si(CH_3)_3F \quad (3)$$

The observed decomposition point of 255 °C is in good agreement with that previously reported[4] for a sample prepared from AgN_3 and $N(CH_3)_4I$ in C_2H_5OH and recrystallized from 2-propanol but disagrees with that of 125 °C originally reported[1] by Friedländer. The compound is a white, crystallinic, nonsensitive, and slightly hygroscopic solid. It has little solubility in cold CH_3CN, moderate solubility in hot CH_3CN, and is highly soluble in alcohol and water.

Crystal Structure of $N(CH_3)_4N_3$. The structure of $N(CH_3)_4N_3$ can be derived from a primitive cubic CsCl lattice which is orthorhombically distorted by the nonspherical $N_3{}^-$ anions. The packing in $N(CH_3)_4N_3$ is identical to that[13] found for $N(CH_3)_4HF_2$, and the two compounds are isotypic. In both, the $M^+HF_2{}^-$ and the $M^+N_3{}^-$ series, the packings are governed by the ionic radii of the M^+ cations. For small M^+ (Li^+, $r = 0.60$ Å; Na^+, $r = 0.95$ Å), the anion layers are stacked perpendicular to the M^+ layers; for intermediate M^+ (K^+, $r = 1.33$ Å; Rb^+, $r = 1.48$ Å; Cs^+, $r = 1.69$ Å), the anions are oriented with their axes parallel to the M^+ layers and perpendicular to each other;[14] and for large M^+ ($N(CH_3)_4{}^+$, $r \approx 2.74$ Å), the anions are oriented with their axes parallel both to the M^+ layers and to each other (see Figure 2).

Both the tetramethylammonium cation and the azide anion were found to be situated on crystallographic mirror planes. The cationic mirror plane bisects the angle C5–N4–C5′ and passes through atoms N4, C6, C7, H10, and H13, while the anionic mirror plane passes through all three N atoms N1, N2, and N3. The azide ion refined to an essentially linear, symmetrical structure [N1–N2 = 1.155 (5) Å, N2–N3 = 1.176 (5) Å, N1–N2–N3 = 179.0 (3)°], even though there are no symmetry constraints that require it to be linear and symmetric. Its N–N bond length of 1.16 Å is comparable to those found for other ionic azides.[14] The

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(12) Sheldrix, G. M. *SHELX System of Crystallographic Programs*; University of Goettingen: Germany, 1986.

(13) Wilson, W. W.; Christe, K. O.; Feng, J.; Bau, R. *Can. J. Chem.* **1989**, *67*, 1898.

(14) Choi, C. S. In *Energetic Materials*; Fair, H. D., Walker, R. F., Eds.; Plenum Press: New York, 1977; Vol. 1, p 97.

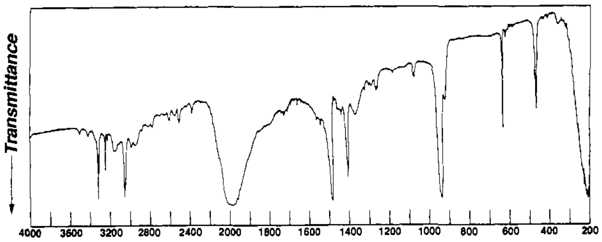

Figure 3. Infrared spectrum of solid $N(CH_3)_4N_3$ pressed in an AgBr disk. The absorption at 250 cm^{-1} is due to the window material.

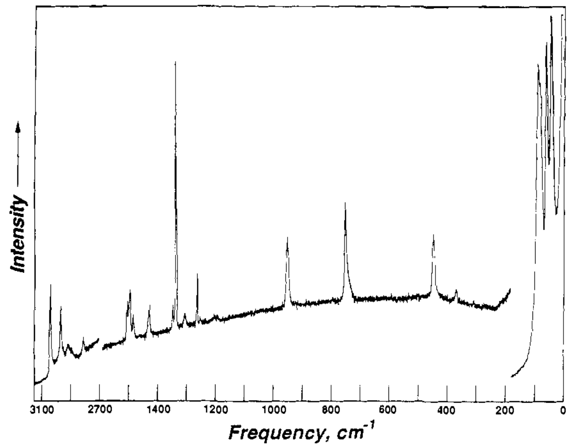

Figure 4. Raman spectrum of solid $N(CH_3)_4N_3$ recorded at ambient temperature. The region 0–200 cm^{-1} was recorded at a 10 times lower sensitivity.

tetramethylammonium cation is slightly but significantly distorted, with angles around N ranging from 107.3 (4)° to 111.8 (4)°, compared to angles ranging from 108.8 (2)° to 110.3 (2)° in isotypic $N(CH_3)_4HF_2$.[13] This increased distortion of the $N(CH_3)_4^+$ cations is attributed to packing effects caused by the slightly larger anion size on going from HF_2^- to N_3^-.

Vibrational Spectra. The infrared and Raman spectra of solid $N(CH_3)_4^+N_3^-$ are shown in Figures 3 and 4, respectively. The observed frequencies and their assignments are summarized in Table IV. The assignments and mode descriptions for $N(CH_3)_4^+$ follow those[15] published by Berg. These spectra confirm the findings from the crystal structure determination that the $N(CH_3)_4^+$ cation in $N(CH_3)_4^+N_3^-$ is more distorted from tetrahedral symmetry than that in $N(CH_3)_4^+HF_2^-$. This is manifested by the significant difference in the relative Raman intensities of the two NC_4 deformation modes, $\nu_{19}(F_2)$ and $\nu_8(E)$, in these two compounds. In $N(CH_3)_4HF_2$, the $\nu_8{:}\nu_{19}$ intensity ratio equals 3.6, whereas in $N(CH_3)_4N_3$ it is only 0.29. It has previously been demonstrated[16,17] that this ratio decreases with increasing distortion of the $N(CH_3)_4^+$ cation. Additional evidence for the increased cation distortion is the frequency decrease of the antisymmetric CH_3 stretching mode, $\nu_{13}(F_2)$,[16,17] from 3036 cm^{-1} in $N(CH_3)_4HF_2$ to 3022 cm^{-1} in $N(CH_3)_4N_3$, and the infrared activity of the F_1 modes, which for strict T_d symmetry should be inactive.[15]

The bands observed for the N_3^- anion (see Table I) are in excellent agreement with those previously reported for a symmetric linear ion of symmetry $D_{\infty h}$.[18-20] The frequency of ν_1 follows a trend previously noted[20] for the alkali metal azides, i.e. a decrease in ν_1 with increasing ionic radius and ionicity of the cation (Li^+, 1372; Na^+, 1360; K^+, 1343; Rb^+, 1335; Cs^+, 1328; $N(CH_3)_4^+$, 1317 cm^{-1}).

Table IV. Vibrational Spectra of Solid $N(CH_3)_4^+N_3^-$

obsd frequencies, cm^{-1} (rel intens)		assignments (point group)	
IR	R	$N(CH_3)_4$ (T_d)	N_3^- ($D_{\infty h}$)
3486vw			
3400vw			
3330sh			
3297ms			$\nu_1 + \nu_3$ (Σu^+)
3225mw			
3201vw			
3130w		$\nu_{13}(F_2)\nu_{as}CH_3$	
3031ms			
3023sh	3022 (7)		
2970w			
	2953 (5)	$\nu_5(E)\nu_{as}CH_3$	
2930w		$\nu_{14}(F_2)\nu_{sym}CH_3$	
	2900 (1)	$\nu_1(A_1)\nu_{sym}CH_3$	
	2882sh	+ combin. bands	
	2802 (1)		
2790vw			
2750vw			
2579w			
2529vw			
2480w			
2358w			
1998vs			$\nu_3(\Sigma u^+)\nu_{as}$
1492s		$\nu_{15}(F_2)\delta_{as}CH_3$	
	1480 (3)	$\nu_2(A_1)\delta_{sym}CH_3$	
	1473 (5)	$\nu_6(E)\delta_{as}CH_3$	
	1460 (2)		
1439vw		$\nu_{10}(F_1)\delta_{as}CH_3$	
1414ms	1407 (3)	$\nu_{16}(F_2)\delta_{sym}CH_3$	
1365mw			
	1327 (2)		
1319vw	1317 (30)		$\nu_1(\Sigma g^+)\nu_{sym}$
1299vw			
1288vw	1287 (1)	$\nu_{17}(F_2)CH_3$rock	
1263w			
1256w			
	1245 (5)		$2\nu_2(\Sigma g^+)$
1175vw	1180 (0+)	$\nu_7(E)CH_3$rock	
1077w			
1071w		$\nu_{11}(F_1)CH_3$rock	
959sh			
950s	947 (8)	$\nu_{18}(F_2)\nu_{as}CN_4$	
922m		$2\nu_{19}(F_2)$	
	756 (11)	$\nu_3(A_1)\nu_sCN_4$	
632ms			$\nu_2(\pi_u)\delta$
614vw			
462ms	459 (7)	$\nu_{19}(F_2)\delta CN_4$	
	383 (2)	$\nu_8(E)\delta CN_4$	
347w		$\nu_{12}(F_1)\tau CH_3$	
	105 (100)		
	78 (75)	Lattice Vibrations	
	61 (75)		

A comparison of our spectra with those previously reported[6] for $N(CH_3)_4N_3$ shows significant discrepancies. Thus, ν_3 of N_3^- differs by more than 60 cm^{-1} from the previous report, and numerous other bands differ in both frequencies and relative intensities. In view of the high purity of our sample, as shown by the crystal structure and correct decomposition point, our spectra should be preferred over those previously reported.[6]

Reactions of HN_3 with the F^- Anion and of HF with the Azide Anion. The N_3 group can be considered as a pseudohalogen[21] or para-halogen.[22] Since other pseudohalides, such as NO_3^- or ClO_4^-, are known to form the bihalide-type anions, $[O_2NO{-}H{-}ONO_2]^-$,[23-28] $[F{-}H{-}ONO_2]^-$,[29] and $[O_3ClO{-}H{-}OClO_3]^-$,[30] respec-

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(15) Berg, R. W. *Spectrochim. Acta, Part A* **1978**, *34A*, 655.
(16) Kabisch, G.; Klose, M. *J. Raman Spectrosc.* **1978**, *7*, 311.
(17) Kabisch, G. *J. Raman Spectrosc.* **1980**, *9*, 285.
(18) Bryant, J. I. *J. Chem. Phys.* **1964**, *40*, 3195; **1966**, *45*, 689.
(19) Hathaway, C. E.; Temple, P. A. *Phys. Rev. B* **1971**, *3*, 3497.
(20) Iqbal, Z.; Prask, H. J.; Trevino, S. F. In *Energetic Materials*; Fair, H. D., Walker, R. F., Eds.; Plenum Press: New York, 1977; Vol. 1, p 131.
(21) Golub, A. M.; Köhler, H.; Skopengo, V. V. Chemistry of Pseudohalides. In *Topics in Inorganic and General Chemistry*; Clark, R. J. H., Ed.; Monograph 21; Elsevier: Amsterdam, 1986; p 28.
(22) Haas, A. *Adv. Inorg. Chem. Radiochem.* **1984**, *28*, 167.
(23) Gillard, R. D.; Mitchell, S. H. *Polyhedron* **1987**, *6*, 1885.

tively, it was interesting to study the interaction of HN_3 with both the N_3^- and the F^- anions. With $N(CH_3)_4N_3$, HN_3 did not form an adduct stable at room temperature. With MF [M = Na, K, Rb, Cs, $N(CH_3)_4$], gaseous or liquid HN_3 reacted at or below room temperature with the formation of an equimolar mixture of MN_3 and MHF_2 (4). The products of reaction 4 are best

$$2MF + HN_3 \rightarrow MN_3 + MHF_2 \tag{4}$$

interpreted by the summation of (5) and (6), where step 5 might

$$MF + HN_3 \rightarrow MN_3 + HF \tag{5}$$

$$MF + HF \rightarrow MHF_2 \tag{6}$$

involve an intermediate $F{-}H{-}N_3^-$ anion which readily eliminates HF to give the final N_3^- product. Attempts were made to isolate this intermediate anion by reacting HN_3 with a RbF single crystal infrared window at low temperature. Below −100 °C, no reaction occurred, and above this temperature, the only new products observable by infrared spectroscopy were RbN_3 and $RbHF_2$.

Reaction 5, i.e. the displacement of F^- from M^+F^- by HN_3, was surprising since, in aqueous solution, HN_3 ($P_k = 4.77$) is a weaker acid than HF ($P_k = 3.18$). Furthermore, molten weak organic acids such as stearic acid also displace N_3^- from NaN_3.[8] Since reaction 5 was not carried out in aqueous solution in which the acidity of HF is enhanced by the hydration energy of F^-, but between solid MF and neat gaseous or liquid HN_3, it should not be governed by the above P_k values but by the proton affinities of F^- and N_3^-. In view of the proton affinity of F^- (371.5 kcal mol^{-1}) exceeding that of N_3^- (328.6 kcal mol^{-1}) by about 43 kcal mol^{-1}, it is then not surprising that HN_3 can displace F^- from M^+F^-.

On the other hand it was found that HF quantitatively displaces N_3^- from $M^+N_3^-$ (7). This reaction does not require the use of an excess of HF. If less than the stoichiometric amounts of HF are used, the resulting products still are MHF_2 and HN_3 and not MF and HN_3. Hence, it appears that both reactions 5 and 7 are

$$MN_3 + 2HF \rightarrow MHF_2 + HN_3 \qquad M = Na, Cs, N(CH_3)_4 \tag{7}$$

irreversible and that the puzzling observations that HN_3 displaces F^- from MF (5) while HF displaces N_3^- from MN_3 (7) are not due to the shifting of a single chemical equilibrium (8).

$$MF + HN_3 \rightleftarrows MN_3 + HF \tag{8}$$

The observed reaction chemistry can be explained by the vastly different Lewis basicities of F^- and HF_2^-. Thus, the very strong Lewis base F^- is readily displaced by the weak acid HN_3 (5), but the more acidic HF_2^- anion is the final product which, once it has been formed, cannot be displaced anymore by the weak acid HN_3.

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Registry No. Trimethylsilyl azide, 4648-54-8; tetramethylammonium fluoride, 373-68-2; tetramethylammonium azide, 999-77-9; hydrazoic acid, 7782-79-8; sodium fluoride, 7681-49-4; potassium fluoride, 7789-23-3; rubidium fluoride, 13446-74-7; cesium fluoride, 13400-13-0; azide, 14343-69-2; bifluoride, 18130-74-0; fluoride, 16984-48-8; hydrogen fluoride, 7664-39-3.

Supplementary Material Available: Tables of final atomic coordinates and anisotropic thermal parameters (2 pages); tables of calculated and observed structure factor amplitudes (2 pages). Ordering information is given on any current masthead page.

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(24) Al-Zamil, N. S.; Evans, E. H. M.; Gillard, R. D.; James, D. W.; Jenkins, T. E.; Lancashire, R. J.; Williams, P. A. *Polyhedron* **1982**, *1*, 525.

(25) Rozière, J.; Lehman, M. S.; Potier, J. *Acta Crystallogr.* **1979**, *B35*, 1099.

(26) Rozière, J.; Rozière-Bories, M. T.; Williams, J. M. *Inorg. Chem.* **1976**, *15*, 2490.

(27) Williams, J. M.; Dowling, N.; Gunde, R.; Hadzi, D.; Orel, B. *J. Am. Chem. Soc.* **1976**, *98*, 1581.

(28) Rozière, J.; Berney, C. V. *J. Am. Chem. Soc.* **1976**, *98*, 1582.

(29) Al-Zamil, N.; Delf, B. W.; Gillard, R. D. *J. Inorg. Nucl. Chem.* **1980**, *42*, 1117.

(30) Karelin, A. I.; Grigorovich, Z. I.; Rosolovskii, V. Ya. *Izv. Akad. Nauk. SSSR, Ser. Khim.* **1974**, 1228.

Formation of Fibrous Molecular Assemblies by Amino Acid Surfactants in Water

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Abstract: Gel-like solutions are obtained at medium pH and low temperature for aqueous solutions of *N*-acyl-L-aspartic acids (C_nAsp, n = 12–18). Electron microscopic observation reveals that helical, fibrous molecular assemblies are formed in the gel-like solutions. The rheological behavior reflects the formation of swarms or bundles of fibers. The hydrogen bonding of amide groups and the moderate degree of ionization of carboxyl groups are confirmed from the infrared absorption bands, consistent with the pH titration result. The possible models of helical, fibrous assemblies are the double stranded or the superhelical structure of helical bilayer strands or the twisted ribbon of a planar bilayer sheet. While *N*-dodecanoyl-L-glutamic acid (C_{12}Glu) molecules cannot be associated into fibrous assemblies, *N*-dodecanoyl-β-alanine (C_{12}Ala) molecules form cylindrical fibers which have no helical structure.

Biopolymers such as polynucleotides, polypeptides, and polysaccharides can take the helical structure which is very important in the occurrence of biological functions. The formation of similar helical structures has recently been reported for assemblies of some native and artificial amphiphiles.

When mineral oil was used as a dispersion medium, lithium 12-hydroxystearate formed fibers with the structure of a twisted ribbon or helical rope.[1] Twisted fibrous aggregates were also constructed by *N*-(2-hydroxydodecyl) amino acids in organic solvents.[2] Helical and cylindrical aggregates in an aqueous

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(1) Tachibana, T.; Kambara, H. *J. Am. Chem. Soc.* **1965**, *87*, 3015–3016.

(2) Hidaka, H.; Murata, M.; Onai, T. *J. Chem. Soc., Chem. Commun.* **1984**, 562–564.

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