Journal of Chemical Crystallography, Vol. 27, No. 11, 1997

Note

Crystal structure and hydrogen bonding of propargylammonium hexafluorosilicate, $2(C_3H_6N)^+ (SiF_6)^{2-}$

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Received October 28, 1996

The X-ray crystal structure of propargylammonium hexafluorosilicate, $2(C_3H_6N)^+ (SiF_6)^{2-}$, is determined. The SiF_6 anion is involved in N−H···F and C−H···F interactions with eight surrounding cations. This involves two- three- and four-center N−H···F hydrogen bonds, and additional C−H···F interactions with C···F distances down to 2.963(6) Å. The alkynyl C−H donors form only C−H···F interactions of unfavorable geometries.

KEY WORDS: Hexafluorosilicate; terminal alkyne; hydrogen bonding; x-ray crystal structure.

Introduction

Terminal alkynes, −C≡C−H, are among the strongest C−H hydrogen bond donors.[1,2] In numerous crystal structures, they have been found involved in directional C−H···A interactions, where A can be any hydrogen bond acceptor including π-bonded systems like Ph or C≡C.[3] In this context, it is of interest to study the behaviour of the terminal alkyne residue in different crystal environments, ranging from weakly polarized systems to ionic compounds. The present communication reports on the propargylammonium salt $2[NH_3{-}CH_2{-}C{\equiv}C{-}H]^+ [SiF_6]^{2-}$, in which the −C≡C−H residue finds itself competing for hydrogen bond acceptors with the much stronger ammonium donor. The crystal structure of a different propargylamminium salt, $[NH_3{-}CH_2{-}C{\equiv}C{-}H]^+ Cl^-$, has been reported previously.[4]

Experimental

The crystal was obtained by slow evaporation of a solution of propargylamine (C_3H_5N, Sigma) in dilute hydrofluoric acid, which was by accident kept in a glass tube. SiF_6^{2-} anions formed by reaction of hydrofluoric acid with the wall of glass tube, leading to crystallization of propargylammonium hexafluorosilicate. X-ray diffraction data was collected at room temperature on a crystal glued to a glass pin (Enraf-Nonius-Turbo-CAD4 single crystal diffractometer, Cu-*K*α-radiation, $\lambda = 1.54184$ Å, Ni-filter, three standard reflections monitored every 30 min., $2\theta_{max} = 60°$). Although the intensity of the standard reflections did not reduce significantly during data collection, there must have been some crystal instability because after data collection, the originally colorless crystal was found yellow. The structure was solved[5] and refined[6] with standard methods. H-atoms were treated in the default riding model of SHELXL93,[6] with ammonium groups allowed to rotate. Relevant numerical data are given in Table 1 and final fractional atomic coordinates are given in Table 2.

Results and discussion

The asymmetric crystal unit of the title compound contains one SiF_6^{2-} anion and two $(C_3H_6N)^+$ cations (Fig. 1). The hexafluorosilicate anion has the expected geometry with a mean Si−F bond length of 1.676(5) Å. The mode of intermolecular interactions is quite complex: each of the ammonium groups forms N−H···F hydrogen bonds with three anions, and each

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1074-1542/97/1100-0673$12.50/0

Table 1. Crystal data and experimental details

Crystal data	
Compound	$2(C_3H_6N)^+ (SiF_6)^{2-}$
Formula weight	254.3
Space group	$P2_1/c$
a, Å	9.444(1)
b, Å	11.511(1)
c, Å	10.167(2)
β, deg.	100.62(4)
Vol., Å^3	1086.3(3)
Z	4
D_{calc}, gcm^{-3}	1.56
Habit	Plate
Color	Colorless
Crystal dimensions, mm	0.70 × 0.40 × 0.07
Data collection and structure refinement	
Scan mode	$\omega-2\theta$
Independent reflections	1602
Reflections $I > 4\sigma(I)$	1476
Parameters	139
Extinction coeff. refined	0.017(3)
GOOF	1.061
$R(I > 4\sigma(I))$	0.082
R_W (all data)	0.26
Max. shift/esd	< 0.001

of the −C≡C−H group forms a C−H···F interaction with a further anion (Table 3). This way, each of the cations is coordinated to four symmetry related anions, and the anion is coordinated with eight cations. This leads to a complex crystal packing scheme which need not be discussed here in further detail.

Table 2. Fractional atomic coordinates (×10^4) and equivalent istoropic displacement parameters (Å × 10^3)

Atom	x/a	y/b	z/c	U(eq)^a
Si	676(1)	8933(1)	2643(1)	40(1)
F1	−391(3)	8933(2)	3815(2)	54(1)
F2	1730(3)	8893(2)	1497(3)	68(1)
F3	1428(3)	10155(2)	3294(3)	64(1)
F4	1896(3)	8155(2)	3679(2)	63(1)
F5	−557(3)	9706(2)	1607(2)	62(1)
F6	−138(3)	7690(2)	2022(3)	65(1)
N1	1768(3)	6087(3)	1281(3)	45(1)
C11	3081(4)	6093(4)	2330(5)	56(1)
C21	4225(5)	5425(4)	1907(5)	59(1)
C31	5160(6)	4892(6)	1608(5)	80(2)
N2	−1515(4)	8466(3)	−832(3)	55(1)
C12	−2728(6)	7671(6)	−780(8)	92(2)
C22	−3844(5)	8139(4)	−132(5)	65(1)
C32	−4760(6)	8478(5)	395(6)	78(2)

[a] U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

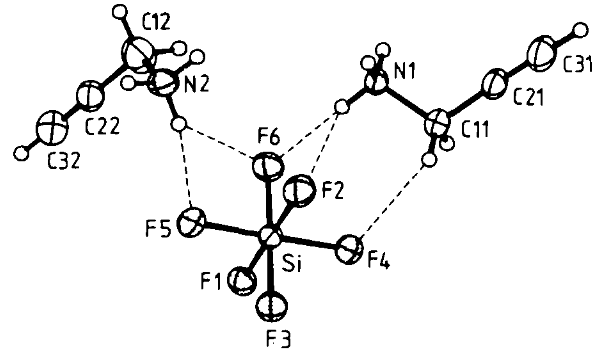

Fig. 1. One asymmetric crystal unit of the title compound. N and F atoms are drawn shaded. Thermal ellipsoids are drawn at the 30% probability level.

A closer look at the N−H···F interactions shows that there are two-, three- and four-center hydrogen bonds (i.e., hydrogen bonds with one, two, and three fluorine acceptors-simultaneously),[7] with the shortest hydrogen bond distance H···F = 1.76 Å in N1−H1···F6. Of the six independent ammonium−anion contacts, three are associated with a further $C(sp^3)$−H···F hydrogen bond, such as can be seen for the right cation in Fig. 1. The other three ammonium−anion contacts are free of a $C(sp^3)$−H contact, as for the left cation in Figure 1. This way, three of the four $C(sp^3)$−H groups are engaged in contacts to F which have surprisingly short C···F separations, the shortest C12···F1 (z, 3/2-y, z-1/2) = 2.963(6) Å [to be compared with the shortest N···F separation: N1···F6 = 2.778(4) Å].

The C≡C−H···F interactions formed by the terminal alkyne groups have quite unfavorable geometries. In particular C32−H is engaged only in a very long contact with C···F = 3.720(7) Å. This is an interesting situation because more typically, the C≡C−H donor is strong enough to find a mode of hydrogen bonding not far from optimal geometry. For C≡C−H···O hydrogen bonding, this would mean a roughly linear contact with H···O ~ 2.2 Å,[1,2] and for the smaller acceptor fluorine, even shorter contacts might be expected. It is assumed that these poor geometries are due to competitive hindrance by the ammonium donors, which are not only far stronger but also superior in number. In fact, the acceptor potentials of the six F-atoms are already essentially satisfied by interaction with the six N−H donors, so that the weaker C−H donors are left with what of the anion remains sterically accessible.

Table 3. Geometry of X−H···F hydrogen bonds with H···F < 2.8 Å, given for normalized H-atom positions (N−H = 1.03 Å, C−H = 1.09 Å) in Å and degrees

H−bond	H−F	X−F	X−H···F	Symm.
N−H···F bonds				
N1−H1···F6	1.76	2.778(4)	168	x, y, z
N1−H1···F2	2.75	3.239(4)	109	x, y, z
N1−H2···F1	1.80	2.793(4)	162	$-x, y - 1/2, 1/2 - z$
N1−H2···F5	2.65	3.057(4)	103	$-x, y - 1/2, 1/2 - z$
N1−H3···F4	1.81	2.809(4)	163	$x, 3/2 - y, z - 1/2$
N1−H3···F1	2.56	2.926(4)	100	$x, 3/2 - y, z - 1/2$
N1−H3···F3	2.79	3.318(4)	112	$x, 3/2 - y, z - 1/2$
N2−H1···F6	2.15	3.044(5)	144	$x, 3/2 - y, z - 1/2$
N2−H1···F1	2.28	3.003(4)	125	$x, 3/2 - y, z - 1/2$
N2−H2···F5	1.86	2.860(4)	163	x, y, z
N2−H2···F6	2.34	3.085(5)	128	x, y, z
N2−H3···F3	2.15	2.979(4)	135	$-x, 2 - y, -z$
N2−H3···F2	2.25	3.113(5)	140	$-x, 2 - y, -z$
N2−H3···F5	2.67	3.074(4)	103	$-x, 2 - y, -z$
C−H···F bonds				
C11−H1···F4	2.43	3.054(5)	115	x, y, z
C11−H2···F5	2.48	3.217(5)	124	$-x, y - 1/2, 1/2 - z$
C31−H···F3	2.51	3.220(6)	122	$1 - x, y - 1/2, 1/2 - z$
C31−H···F4	2.42	3.481(6)	165	$1 - x, y - 1/2, 1/2 - z$
C12−H2···F1	2.38	2.963(6)	112	$x, 3/2 - y, z - 1/2$
C32−H3···F	2.69	3.720(7)	156	$x - 1, y, z$

Acknowledgment

The author thanks Prof. Wolfram Saenger (Freie Universität Berlin) for giving him the opportunity to carry out this study in his laboratory.

Supplementary material. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-1003/5242. Copies of available material can be obtained, free of charge, on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, (fax: +44-(0)1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).

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