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Bis(diisopropylammonium) Hexafluorosilicate(IV)

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Abstract

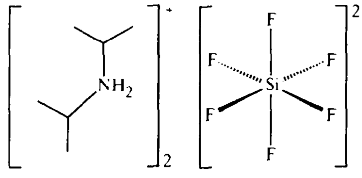
In bis(diisopropylammonium) hexafluorosilicate(IV), $[\{(CH_3)_2CH\}_2NH_2]_2[SiF_6]$, two symmetry-related diisopropylammonium cations in general positions are connected *via* two N—H···F hydrogen bonds to one hexafluorosilicate(IV) anion lying on a twofold axis to form a quasi-molecular 2:1 ion pair. These units are further connected by significantly weaker N—H···F bonds to form infinite chains along [001]. The $[SiF_6]^{2-}$ ion is distorted from the highest possible O_h symmetry to C_{4v} associated with the hydrogen-donating environment. The diisopropylammonium cation possesses approximately C_2 symmetry.

Comment

Salts of the diisopropylammonium cation with bromide (Kociok-Köhn *et al.*, 1996) and chloride (Prince *et al.*, 1990) are known to form isostructural hydrogen-bonded chain structures. Other polymeric diisopropylammonium salts with carbamoylplatinate (Dell'Amico *et al.*, 1979), tetrabromocuprate (Fernandez *et al.*, 1987) and carbonylferrate (Chen *et al.*, 1987), and a titanium(III) *N,N*-dialkylcarbamato complex (Dell'Amico *et al.*, 1987) have been reported. Two hydrogen-bonded dimeric structures of the diisopropylammonium salts of dithiocarbamate (Wahlberg, 1978) and (mercaptoacetato-*S,O*)triphenylstannate (Ng *et al.*, 1996) have also been described.

Only a few alkylammonium hexafluorosilicates have been structurally characterized, *e.g.* the salts of acetidinium (Calov & Jost, 1990), guanidinium (Waskowska, 1997), ethylenediammonium (Ben Ghozlen *et al.*, 1994) and dimethyldiethylenediammonium (Rother *et al.*, 1997).

In bis(diisopropylammonium) hexafluorosilicate(IV), (I), the diisopropylammonium ion lies in a general position, while atoms Si, F3 and F4 of the $[SiF_6]^{2-}$ anion occupy a twofold axis. Each anion is bonded to two cations *via* strong hydrogen bonds (Fig. 1). These quasi-molecular 2:1 ion pairs are connected to neighbouring units by extremely weak additional hydrogen bonds (Table 3) to form chains along [001]. The chains are shielded by their peripheral methyl groups, forming lipophilic channels (*e.g.* at $0,\frac{1}{2},z$); one H atom of each isopropyl group is directed towards the centre of the channels.



(I)

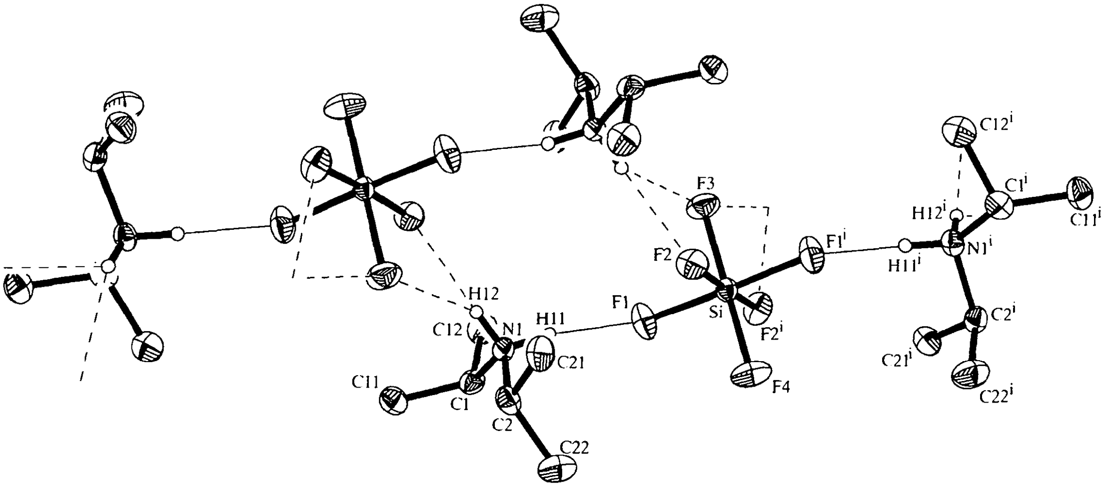


Fig. 1. Two quasi-molecular units of (I), each consisting of one hexafluorosilicate anion and two diisopropylammonium cations (displacement ellipsoids are at the 50% probability level, the symmetry code is as in Table 2, thin dashed lines show weak additional hydrogen bonds, and the H atoms at methyl and CH groups have been omitted for clarity).

The cation possesses approximately C_2 symmetry, and all bond lengths and angles are as expected (Table 2). The diisopropylammonium cation acts as a tridentate bridging ligand, with one strong monodentate bond within the quasi-molecule [H···F 1.89 (2) Å] and a forked hydrogen bond to the next unit (Fig. 1). The refined N—H distances differ slightly, with a value of 0.89 (2) Å for the atom involved in the strong N—H···F bond and a value of 0.86 (2) Å for the H atom that is only very weakly connected to the related F atoms.

The F atoms (F1, F2 and F3) that form at least weak hydrogen bonds to their hydrogen-donating environment show Si—F distances from 1.6830 (9) to 1.7018 (9) Å, whereas the F4 atom that is not hydrogen bonded to a diisopropylammonium cation has a significantly shorter Si—F distance [1.6519 (13) Å]. The distortion of the $[SiF_6]^{2-}$ anion from the highest possible O_h symmetry to C_{4v} can be explained in terms of its hydrogen-donating environment.

Experimental

Solutions of $H_2SiF_6.xH_2O$ were prepared by dissolving silicic acid in hydrofluoric acid. Reaction of diisopropylamine with a hydrofluoric acid solution of $H_2SiF_6.xH_2O$ yielded a clear colourless solution. Small colourless needle-shaped crystals grew at room temperature within a few days.

Crystal data

$(C_6H_{16}N)_2[SiF_6]$
$M_r = 346.49$
Monoclinic
$C2/c$
$a = 12.386 (2)$ Å
$b = 11.732 (2)$ Å
$c = 12.845 (2)$ Å
$\beta = 112.080 (10)^\circ$
$V = 1729.6 (5)$ Å^3
$Z = 4$
$D_x = 1.331$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 50 reflections
$\theta = 9.5–26.9^\circ$
$\mu = 0.189$ mm^{-1}
$T = 173 (2)$ K
Needle
0.30 × 0.14 × 0.10 mm
Colourless

Data collection

Siemens *P*4 four-circle diffractometer equipped with an LT2 cooling device
ω scans
Absorption correction: none
3574 measured reflections
1534 independent reflections
1238 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.023$
$\theta_{\rm max} = 25.09^\circ$
$h = -1 \rightarrow 14$
$k = -14 \rightarrow 14$
$l = -15 \rightarrow 14$
3 standard reflections every 100 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.030$
$wR(F^2) = 0.076$

$(\Delta/\sigma)_{\rm max} = 0.014$
$\Delta\rho_{\rm max} = 0.200$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.237$ e Å^{-3}

$S = 1.036$
1534 reflections
133 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0341P)^2 + 0.7508P]$
where $P = (F_o^2 + 2F_c^2)/3$

Extinction correction: *SHELXL*97
Extinction coefficient: 0.0045 (9)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_jU^{ij}a^ia^j\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Si	0	0.11118 (5)	3/4	0.01745 (17)
F1	−0.10199 (8)	0.10890 (9)	0.61689 (7)	0.0349 (3)
F2	−0.10613 (8)	0.10649 (8)	0.80185 (8)	0.0298 (3)
F3	0	−0.03325 (10)	3/4	0.0339 (4)
F4	0	0.25198 (10)	3/4	0.0346 (4)
N1	−0.12499 (11)	0.12123 (11)	0.39389 (11)	0.0200 (3)
C1	−0.25626 (13)	0.12055 (14)	0.33279 (13)	0.0235 (4)
C2	−0.06096 (14)	0.22713 (14)	0.38319 (13)	0.0248 (4)
C11	−0.28673 (15)	0.12586 (14)	0.20735 (13)	0.0298 (4)
C12	−0.30476 (15)	0.01477 (15)	0.36762 (14)	0.0306 (4)
C21	0.06877 (14)	0.20688 (15)	0.44522 (13)	0.0296 (4)
C22	−0.10294 (17)	0.32933 (14)	0.42901 (16)	0.0374 (4)

Table 2. *Selected geometric parameters (Å, °)*

Si—F4	1.6519 (13)	Si—F1	1.7018 (9)
Si—F2	1.6830 (9)	N1—C2	1.508 (2)
Si—F3	1.6945 (14)	N1—C1	1.517 (2)
F1—Si—F2	90.11 (5)	C11—C1—N1	109.93 (13)
F1—Si—F3	89.10 (4)	C11—C1—C12	112.34 (13)
F1—Si—F4	90.90 (4)	N1—C1—C12	108.53 (12)
F2—Si—F3	88.13 (4)	N1—C2—C22	110.40 (13)
F1—Si—F1$^{\rm i}$	178.19 (8)	N1—C2—C21	108.18 (12)
F2—Si—F2$^{\rm i}$	176.25 (7)	C22—C2—C21	111.74 (14)
C2—N1—C1	117.09 (12)		
C2—N1—C1—C11	64.74 (17)	C1—N1—C2—C22	60.43 (17)
C2—N1—C1—C12	−172.04 (13)	C1—N1—C2—C21	−177.02 (13)

Symmetry code: (i) $-x, y, \frac{3}{2} - z$.

Table 3. *Hydrogen-bonding geometry (Å, °)*

D—H···A	D—H	H···A	D···A	D—H···A
N1—H11···F1	0.89 (2)	1.89 (2)	2.7737 (17)	167.2 (17)
N1—H12···F2$^{\rm i}$	0.857 (18)	2.171 (18)	2.9661 (16)	154.2 (15)
N1—H12···F3$^{\rm ii}$	0.857 (18)	2.304 (18)	3.0049 (14)	139.1 (14)

Symmetry codes: (i) $x, -y, z - \frac{1}{2}$; (ii) $-x, -y, 1 - z$.

The atomic coordinates of the H atoms belonging to NH_2 and CH groups, and their individual $U_{\rm iso}$ values were refined freely. H atoms belonging to methyl groups were included in the refinement riding on their attached C atom, and were allowed to rotate about the C—C bond with one common $U_{\rm iso}$ value for each group.

Data collection: *XSCANS* (Siemens, 1994). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997*a*). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997*b*). Molecular graphics: *SHELXTL-Plus* (Sheldrick, 1992). Software used to prepare material for publication: *SHELXL*97.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1289). Services for accessing these data are described at the back of the journal.

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2-Oxo-1,2-dihydropyridine-6-carboxylic Acid

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Abstract

The molecular structure of the title compound, $C_6H_5NO_3$, clearly indicates the keto–enol tautomerism of the CONH moiety, although the keto form is more preferable than the enol form. Two molecules are connected by two N—H···O hydrogen bonds around an inversion center to form a dimer, and the dimers are linked in a planar fashion by O—H···O hydrogen bonds to form a sheet.

Comment

2-Pyridone derivatives have been extensively studied since they cause base mispairing and enzymatic reactions related to bifunctional catalysis (Beak *et al.*, 1976). Theoretical analysis and NMR measurements have been performed for these compounds (Kuzuya *et al.*, 1984; Facelli *et al.*, 1992), and the crystal structures of some 2-pyridone derivatives have been determined previously (Low & Wilson, 1983; Kvick & Booles, 1972). In order to compare the molecular structure of the title compound, 2-oxo-1,2-dihydropyridine-6-carboxylic acid, (I), with the 2-pyridone derivatives, the data were collected at 200 K.

Keto form
(I)

Enol form

The molecular structure of (I) with atomic numbering is shown in Fig. 1 and the crystal structure viewed along the *b* axis is shown in Fig. 2. There are two considerably strong hydrogen bonds (N—H···O) between the two molecules around an inversion center, forming a dimer [N1···O7(1 − *x*, 2 − *y*, 1 − *z*) 2.873 (3) Å]. The H1 atom, confirmed from a difference Fourier map, is clearly bonded to the N atom of the six-membered ring. This indicates that the molecule is not an enol, but is instead in the keto form. However, the C2—O7 distance is longer than C8—O9 and shorter than C8—O10. Moreover, N1—C2 is shorter than a usual N—C bond (1.469 Å; *International Tables for Crystallography*, 1974, Vol. C). These distances suggest that the molecule adopts partly the enol form. The molecule is approximately planar, excluding the carboxyl group (r.m.s. deviation of fitted atoms is 0.008 Å). The C5—C6—C8—O9 torsion angle is −15.1 (5)°. These parameters are essentially the same as those of the related derivatives.

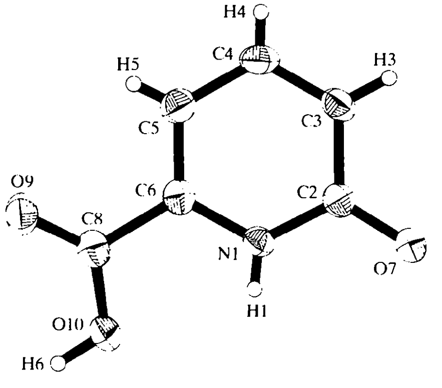

Fig. 1. The molecular structure of (I). Displacement ellipsoids are scaled to enclose 50% probability levels.