C8—S1—C7	100.0 (2)	C1—C7—S1	116.3 (3)
C12—S2—C11	101.6 (2)	C9—C8—S1	114.7 (3)
O—P—C13	113.20 (15)	C8—C9—P	110.9 (3)
O—P—C9	114.0 (2)	C11—C10—P	115.5 (3)
C13—P—C9	107.5 (2)	C10—C11—S2	115.1 (3)
O—P—C10	111.5 (2)	C2—C12—S2	116.6 (3)
C13—P—C10	104.9 (2)	C18—C13—P	124.5 (3)
C9—P—C10	105.0 (2)	C14—C13—P	117.7 (3)
C7—C1—C2—C12	−0.1 (5)	C9—P—C10—C11	−70.0 (3)
C2—C1—C7—S1	148.3 (3)	P—C10—C11—S2	167.7 (2)
C8—S1—C7—C1	−59.0 (3)	C12—S2—C11—C10	−79.0 (3)
C7—S1—C8—C9	−74.7 (3)	C1—C2—C12—S2	−120.3 (4)
S1—C8—C9—P	148.5 (2)	C11—S2—C12—C2	75.0 (4)
C10—P—C9—C8	−73.9 (3)		

H atoms were located from $\Delta\rho$ maps and refined with U_{eq} fixed to $1.2U_{eq}$ of the host atom.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1995). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1989). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *SHELXL*93.

This work is partly financed by Comision Interministerial de Ciencia y Tecnologia from the Spanish Government through project MAT94-0668. RK thanks Ministerio de Educación y Ciencia of the Spanish Government for grant SAB95-0249 and the Oskar Öflund's Foundation for financial support.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AB1413). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Caminade, A. M. & Majoral, J. P. (1994). *Chem. Rev.* **94**, 1183–1213.

Casabó, J., Escriche, L., Pérez-Jiménez, C., Muñoz, J. A., Teixidor, F., Baucells, J. & Errachid, A. (1996). *Anal. Chim. Acta*, **320**, 63–68.

Izatt, R. M., Pawlak, K., Brandshaw, J. S. & Bruening, R. L. (1991). *Chem. Rev.* **91**, 1721–2085.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Kivekäs, R., Sillanpää, R, Escriche, L., Almajano, M. P., Teixidor, F. & Casabó, J. (1994). *Acta Cryst.* C**50**, 2047–2049.

Kyba, E. P., Clubb, C. N., Larson, S. B., Schueler, V. J. & Davis, R. E. (1985). *J. Am. Chem. Soc.* **107**, 2141–2148.

Lockhart, J. C., Mousley, D. P., Stuart Hill, M. N., Tomkinson, N. P., Teixidor, F., Almajano, M. P., Escriche, L., Casabó, J. F., Sillanpää, R. & Kivekäs, R. (1992). *J. Chem. Soc. Dalton Trans.* pp. 2889–2897.

Molecular Structure Corporation (1989). *TEXSAN. Single Crystal Structure Analysis Software*. Version 5.0. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Molecular Structure Corporation (1995). *MSC/AFC Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Muñoz, J. A., Escriche, L., Casabó, J., Kivekäs, R. & Sillanpää, R. (1996). *Inorg. Chim. Acta*. In the press.

North, A. C. T., Phillips, D. C. & Mathews, F. C. (1968). *Acta Cryst.* A**24**, 351–359.

Sheldrick, G. M. (1985). *SHELXS86. Program for the Solution of Crystal Structures*. University of Göttingen, Germany.

Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.

Acta Cryst. (1997). C**53**, 128–130

Diguanidinium Hexafluorosilicate

ALICJA WAŚKOWSKA

Institute of Low Temperature and Structure Research, Polish Academy of Sciences, Okolna str. 2, 50 950 Wrocław, Poland. E-mail: waskowsk@highscreen.int.pan.wroc.pl

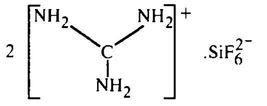
(*Received 23 April 1996; accepted 20 September 1996*)

Abstract

The crystal structure of diguanidinium hexafuorosilicate, $[C(NH_2)_3]_2SiF_6$, consists of regular octahedral SiF_6^{2-} anions linked through a system of hydrogen bonds to the guanidinium cations, which have a planar conformation. The striking feature of the structure is the high degree of hydrogen bonding. All H atoms of the guanidinium units are involved in hydrogen bonds of the type N—H···F of length 2.901 (2), 2.908 (2) and 2.891 (1) Å. Unlike other materials belonging to the family of compounds of general formula $R_x(NH_{4-x})_2MX_3$, the crystals of the present compound do not display ferroelectric/ferroelastic properties.

Comment

This paper is a continuation of earlier reports on structural studies of the complex compounds of metal halogenides with various N-atom containing organic ligands (*e.g.* Morimoto & Lingafelter, 1970; Adams & Small, 1974; Waśkowska, Czapla & Janczak, 1993). The general formula is $R_x(NH_{4-x})MX_3$ and $(R_xNH_{4-x})_2MX_4$, where R is an aliphatic or aromatic hydrocarbon, M is a metal atom and X is Cl, Br, I or F. Most of these compounds show phase transitions of ferroelectric or ferroelastic character which are related to the dynamics of the constituent organic or inorganic subunits (Doudin & Chapuis, 1988; Miyazaki, Irokawa, Komukae, Osaka & Makita, 1991; Katrusiak & Szafranski, 1994). The title compound could be a candidate for behaviour of this type, but our specific heat measurements by differential scanning calorimetry (DSC), performed in the temperature range 106–410 K, showed no anomalies which could be related to a phase transition. The X-ray diffraction study of the title crystal structure, (I), has been undertaken in order to try to provide a structural explanation for the distinct physical properties of this material. The crystal structure of the isomorphous compound with the TiF_6 anion has been published by Calov, Schneider & Leibnitz (1991). The diguanidinium titanium analogue, however, forms a non-centrosymmetric structure, with two symmetrically independent guanidinium cations.



(I)

The structure of (I) consists of SiF_6 octahedra located at centres of inversion and coordinated by twelve guanidinium ions which are linked to the octahedra by N—H···F hydrogen bonds (Fig. 1). The SiF_6 octahedron is regular; the lengths of two independent Si—F distances vary by one standard deviation and bond angles deviate from right angles by 0.4°. Unlike guanidinium hexachlorotellurate, where the guanidinium cation was partly disordered about one of the N—C bonds (Waśkowska *et al.*, 1993), there is no disorder observed in the present structure. In the guanidinium ion, the N atoms are coplanar with the C atom. The planar configuration of the guanidinium units has been observed in, for example, zinc guanidinium sulfate $Zn[C(NH_2)_3]_2SO_4$ (Morimoto & Lingafelter, 1970) and guanidinium carbonate $[C(NH_2)_3]_2CO_3$ (Adams & Small, 1974). As the variation of the C—N bond distances is not significant, all three C—N bonds acquire partial double-bond character (sp^2 hybridization). The coordination of the SiF_6 anion is shown in Fig. 2 and each N atom of the guanidinium cation forms two hydrogen bonds with the F atoms. In this way, the maximum hydrogen bonding in the structure is achieved, because each fluorine is an acceptor of two hydrogen bonds. The geometry of the hydrogen bonds is given in Table 3. The high degree of hydrogen bonding may arise from the fact that the donor and acceptor atoms are on oppositely charged ions, therefore, electrostatic forces participate in the formation of these contacts. As shown by the specific heat measurements, the temperature-dependent motions of the structural subunits, which are often associated with the phase transitions of the ferroelectric and/or ferroelastic character, are not capable of moving protons from their equilibrium sites before the decomposition temperature (about 405 K) is reached.

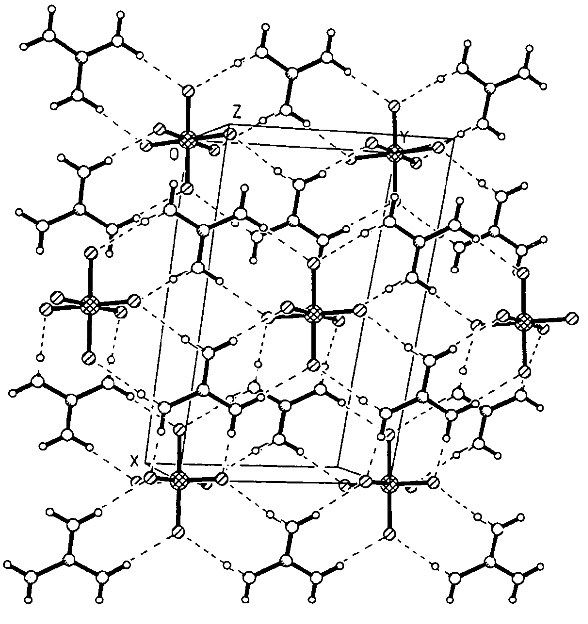


Fig. 1. The structure of diguanidinium hexafluorosilicate viewed down the *c* axis.

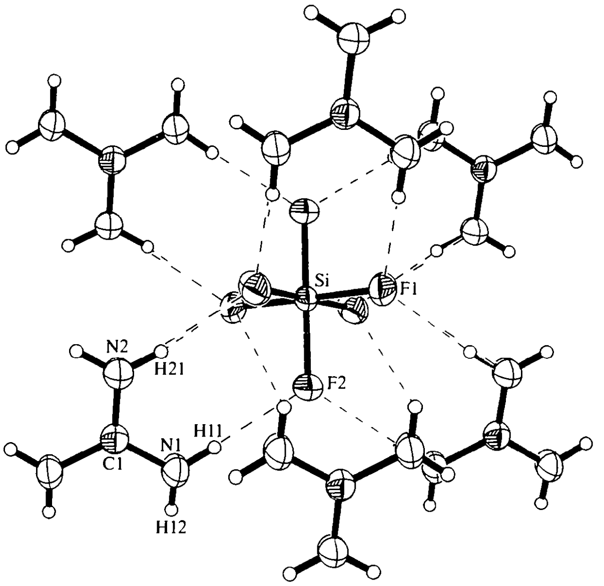


Fig. 2. The coordination of the SiF_6 anion. The displacement ellipsoids are drawn at the 50% probability level. The H atoms are represented as small circles of arbitrary size.

Experimental

Diguanidinium hexafluorosilicate was obtained from aqueous solutions containing stoichiometric quantities of guanidinium carbonate, $[C(NH_2)_3]_2CO_3$, and hexafluorosilicic acid, (H_2SiF_6). The mixture was maintained at 306 K and the solvent allowed to evaporate. The crystalline material obtained in this way was recrystallized by slowing down the rate of evaporation at a reduced temperature of 287 K.

Crystal data

$2CH_6N_3^+.SiF_6^{2-}$
$M_r = 262.27$
Monoclinic
$C2/m$

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 32 reflections

$a = 12.600\,(3)$ Å
$b = 7.258\,(1)$ Å
$c = 6.162\,(1)$ Å
$\beta = 114.49\,(3)°$
$V = 512.8\,(2)$ Å^3
$Z = 2$
$D_x = 1.698$ Mg m^{-3}
D_m not measured
$\theta = 11–18°$
$\mu = 0.299$ mm^{-1}
$T = 293\,(2)$ K
Transparent plate
0.40 × 0.35 × 0.25 mm
Colourless

Data collection

Kuma KM-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
2941 measured reflections
855 independent reflections
763 observed reflections
  $[I > 2\sigma(I)]$
$R_{\rm int} = 0.0378$
$\theta_{\rm max} = 31.06°$
$h = -18 \rightarrow 18$
$k = -9 \rightarrow 9$
$l = -8 \rightarrow 8$
2 standard reflections
  monitored every 50
  reflections
  intensity decay: 0.5%

Refinement

Refinement on F^2
$R(F) = 0.0304$
$wR(F^2) = 0.0620$
$S = 1.040$
855 reflections
54 parameters
H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0003P)^2$
  $+ 0.48P]$
  where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.001$
$\Delta\rho_{\rm max} = 0.328$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.201$ e Å^{-3}
Extinction correction:
  *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient:
  0.049 (2)
Atomic scattering factors
  from *International Tables for Crystallography* (1992, Vol. C)

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

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Si	0	0	0	0.0276 (2)
F1	−0.01623 (6)	0.16438 (11)	0.1766 (2)	0.0415 (2)
F2	0.14496 (8)	0	0.1630 (2)	0.0385 (3)
N2	0.61924 (15)	0	0.2735 (4)	0.0408 (4)
C1	0.72359 (14)	0	0.2692 (3)	0.0293 (3)
N1	0.77580 (11)	0.1579 (2)	0.2703 (2)	0.0371 (3)

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

Si—F2	1.6805 (12)	N2—C1	1.326 (2)
Si—F1	1.6833 (8)	C1—N1	1.3203 (14)
F2—Si—F2$^{\rm i}$	180.0	F1$^{\rm i}$—Si—F1	180.0
F2—Si—F1$^{\rm i}$	89.61 (4)	N1—C1—N1$^{\rm ii}$	120.5 (2)
F2—Si—F1	90.39 (4)	N1—C1—N2	119.73 (8)

Symmetry codes: (i) $-x, -y, -z$; (ii) $x, -y, z$.

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

D—H$\cdots$$A$	H$\cdots$$A$	$D\cdots A$	D—H$\cdots$$A$
N1—H11$\cdots$F2$^{\rm i}$	2.08 (2)	2.901 (2)	171 (2)
N1—H12$\cdots$F1$^{\rm ii}$	2.08 (2)	2.908 (2)	167 (2)
N2—H21$\cdots$F1$^{\rm iii}$	2.05 (2)	2.891 (1)	172 (2)

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

Data collection: KM-4 software (version 7.1). Cell refinement: KM-4 software (version 7.1). Data reduction: KM-4 software (version 7.1). Program(s) used to solve structure: *SHELXTL-Plus* (Sheldrick, 1991). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXS*86 (Sheldrick, 1990). Software used to prepare material for publication: *SHELXL*93.

The author is grateful to Professor Z. Czapla (Institute of Experimental Physics, Wrocław University) for the crystal sample and to M. Drozd (Institute of Low Temperature and Structure Research, Polish Academy of Sciences) for the DSC measurements.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: NA1247). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Adams, J. M. & Small, R. W. (1974). *Acta Cryst.* B**30**, 2191–2193.
Calov, U., Schneider, M. & Leibnitz, P. (1991). *Z. Anorg. Allg. Chem.* **604**, 77–83.
Doudin, B. & Chapuis, G. (1988). *Acta Cryst.* B**44**, 495–502.
Katrusiak, A. & Szafranski, M. (1994). *Acta Cryst.* C**50**, 1161–1163.
Miyazaki, A., Irokawa, K., Komukae, M., Osaka, T. & Makita, Y. (1991). *J. Phys. Soc. Jpn*, **60**, 3596–3599.
Morimoto, C. N. & Lingafelter, E. C. (1970). *Acta Cryst.* B**26**, 335–341.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1991). *SHELXTL-Plus*. Release 4.1. Siemens Analytical X-ray Instruments, Madison, Wisconsin, USA.
Sheldrick, G. M. (1993). *SHELXL*93. *Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
Waśkowska, A., Czapla, Z. & Janczak, J. (1993). *J. Alloys Compd*, **196**, 255–257.

Acta Cryst. (1997). C**53**, 130–132

2-Methylperimidinium Acetate Monohydrate

S. Patnaik,[a] Kodumuru Vishnumurthy,[b] Malayalam Sridhar,[b] Sosale Chandrasekhar,[b] K. Usha[a] and T. N. Guru Row[a,b]

[a]*Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore 560 012, India,* [b]*Organic Chemistry Department, Indian Institute of Science, Bangalore 560 012, India. E-mail: ssctng@sscu.iisc.ernet.in*

(*Received 30 September 1996; accepted 8 October 1996*)

Abstract

The title compound, $C_{12}H_{11}N_2^+.C_2H_3O_2^-.H_2O$, is a hydrated salt of 2-methylperimidinium acetate. The 2-methylperimidinium cations are protonated at the N atoms. In the acetate anions, the C—O bond distances

Acta Crystallographica Section C
ISSN 0108-2701 © 1997