Crystal structure of hexamethylguanidinium hexafluorosilicate hexahydrate

Xiongzhi Zhang[a], Robert Bau[a], Jeffrey A. Sheehy[b], Karl O. Christe[a,b*]
[a]*Loker Hydrocarbon Research Institute, University of Southern California, Los Angeles, CA 90089, USA*
[b]*Air Force Research Laboratory, Propulsion Directorate, Edwards Air Force Base, CA 93524, USA*

Abstract

Single crystals of the hexamethylguanidinium hexafluorosilicate hexahydrate salt, $[C(NMe_2)_3]_2^+SiF_6^{2-}\cdot 6H_2O$, were isolated when a product, obtained by water removal from aqueous $[C(NMe_2)_3]F$ in a glass vessel, was recrystallized from CH_3OH. The crystal structure of this salt was determined, and the structure of the free hexamethylguanidinium cation was calculated, showing that the propeller-shaped structure of the hexamethylguanidinium cation is not caused by solid state effects but is the true minimum energy structure.

Keywords: Hexamethylguanidinium hexafluorosilicate hexahydrate; X-ray structure; electronic structure calculation

1. Introduction

The synthesis of anhydrous tetramethylammonium fluoride (TMAF) [1] and its use as a "naked" fluoride ion source have led to a renaissance in high coordination number chemistry [2-4]. The main advantage of TMAF is the high chemical and thermal stability of the tetramethylammonium cation. However, the high symmetry of this cation often leads to disordered unsolvable crystal structures. To overcome this problem, the synthesis and characterization of alternate "naked" fluoride ion sources is of general interest [5,6]. One of the candidates, which were studied in our laboratory, was hexamethylguanidinium fluoride (HMGF) [7]. Although the thermal stability and inertness of HMGF were found to be inferior to those of TMAF [1], single crystals of a new hexamethylguanidinium salt,

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$(HMG)_2SiF_6 \cdot 6H_2O$, were isolated during recrystallization procedures, and their crystal structure was determined. Prior to this study, only one crystal structure containing the interesting HMG cation had been reported [8].

2. Isolation of $[(Me_2N)_3C^+]_2SiF_6^{2-} \cdot 6H_2O$

The hexamethylguanidinium hexafluorosilicate hexahydrate salt, $[HMG]_2SiF_6 \cdot 6H_2O$, was formed by reactions (1-5).

$$Me_2NC(=O)NMe_2 + COCl_2 \xrightarrow{EtOEt} (Me_2N)_2CCl^+Cl^- + CO_2 \quad (1)$$

$$(Me_2N)_2CCl^+Cl^- + Me_2NSiMe_3 \xrightarrow{CHCl_3} (Me_2N)_3C^+Cl^- + ClSiMe_3 \quad (2)$$

$$(Me_2N)_3C^+Cl^- + AgOH \xrightarrow{H_2O} (Me_2N)_3C^+OH^- + AgCl\downarrow \quad (3)$$

$$(Me_2N)_3C^+OH^- + HF \longrightarrow (Me_2N)_3C^+F^- + H_2O \quad (4)$$

$$2(Me_2N)_3C^+F^- + 4HF + SiO_2 \longrightarrow [(Me_2N)C^+]_2SiF_6^{2-} \cdot 6H_2O \quad (5)$$

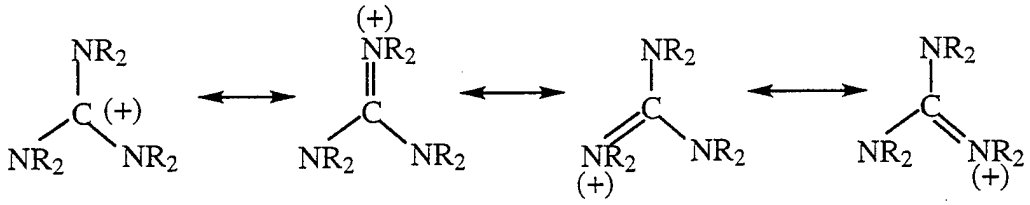
Reactions (1) and (2) were modifications of those previously reported by Eilingsfeld and coworkers [9] and Igumnov and coworkers [7], respectively. Steps (3) and (4) are analogous to those, previously reported for the preparations of hexamethylpiperidinium fluoride [5] and TMAF [1]. Reaction (5) is a side reaction, the extent of which can vary. The single crystals of $[HMG]_2SiF_6 \cdot 6H_2O$ were obtained during attempts in Pyrex vessels to purify the product from reaction (4) by water removal from an aqueous solution of HMGF in a dynamic vacuum at 50 °C, followed by recrystallization from pure methanol.

3. Crystal Structure of $[(Me_2N)_3C^+]_2SiF_6^{2-} \cdot 6H_2O$ (1) and Computational Results

The title compound crystallizes in the triclinic space group $P\bar{1}$, with a = 7.961(2), b = 8.068(2), c = 11.084(2)Å, α = 89.60(3), β = 71.37(3), γ = 79.89(3)°. A hemisphere of data

was collected at -100 °C and refined to a final agreement factor of R = 4.9% for 2843 reflections having $I > 2\sigma(I)$. The crystal and structure refinement data, atomic coordinates and isotropic and anisotropic displacement parameters, and selected bond distances and angles of (1) are summarized in Tables 1-5, respectively. The structure of the individual HMG ion and a packing diagram are shown in Figures 1 and 2, respectively.

The structure of (1) is ionic, containing discrete HMG cations and $[SiF_6]^{2-}$ anions, with the latter being situated on crystallographic inversion centers. The structure of the $[C(NMe_2)_3]^+$ cation is comparable with the one in $[C(NMe_2)_3][Fe(CO)_4C(O)NMe_2]$ [8]. The CN_3 unit is essentially planar, with N-C-N angles ranging from 117.9(3)° to 121.9(3) °. The C-N bond distances vary from 1.318(5)Å to 1.368(5)Å, just somewhat longer than an average C=N double bond (1.30 Å), indicating a significant degree of double bond character in the C-N bonds of this carbocation, as expected from the following resonance structures.



The significant double bond character of the C-N bonds and the resulting distribution of the positive charge over the three nitrogen ligands implies that the HMG cation should be considered as an iminium cation, rather than a carbenium ion [11]. For steric reasons, the NMe_2 groups are twisted out of the CN_3 plane like a propeller. The three dihedral angles are 32.3, 32.6 and 33.6 °, with an average of 32.8 °, very similar to that of 34.0 ° found for HMG $[Fe(CO)_4C(O)NMe_2]$ [8]. In contrast, in the parent guanidinium cation (as found, for example, in arginine [10]), the NH_2 groups are virtually coplanar with the CN_3 plane. In view of the very different anions and the different anion-cation stoichiometry in the SiF_6^{2-} and $[Fe(CO)_4C(O)NMe_2]^-$ salts of HMG, the similarity of their HMG dihedral angles suggested that these angles are not caused by crystal effects, but must represent a minimum energy structure. This was verified by a theoretical calculation at the B3LYP / 6-31G(d) level for the free gaseous

HMG cation. It resulted in a minimum energy structure (see Table 6) which, as shown by Figure 3, is very similar to that found for (1) by the x-ray diffraction study. Furthermore, the value of 35.0 ° calculated for the dihedral angle between the CN_3 and the three CNC planes is very close to the averages of 32.8 ° and 34.0 ° found in the present and the previous [8] x-ray diffraction studies. This result demonstrates that the propeller shape of the HMG cation is a true minimum energy structure and not caused by interionic packing effects in the solids. Also, the arrangement of the hydrogen atoms in the crystal structure of $(HMG)_2SiF_6$ is very similar to that calculated (see Figure 1). The nearest contact distances between the anion and cation are 2.36 Å (F2...H14B), 2.42 Å (F2...H12A), and 2.44 Å (F1...H13B) which imply only weak anion-cation interactions.

4. Experimental

4.1 Spectra

Raman spectra, Bruker Equinox 55, Nd-YAG laser (1064 nm). NMR spectra, Bruker AM-360, $CFCl_3$ and $Si(CH_3)_4$ were used as external standards with down field shifts being positive.

4.2. Tetramethylchloroformamidinium Chloride

Phosgen (90 mmol), $COCl_2$, was added at -196 °C on the vacuum line to a 100 ml reaction vessel, equipped with a valve, which contained 86.2 mmol of 1,1,3,3-tetramethylurea in 50 ml of ether. The mixture was slowly warmed to -78 °C and, then, under electromagnetic stirring to room temperature. After 12 hr, all volatile material was removed under vacuum. Yield, based on tetramethylurea, 84.5 mmol (98%); ^{1}H NMR ($CDCl_3$, $SiMe_4$): 2.77 ppm.

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4.3. N,N,N',N',N'',N''-Hexamethylguanidinium Chloride

N,N-Dimethyltrimethylsilylamine (18.7 mmol) was added slowly to 16.8 mmol of tetramethylchloroformamidinium chloride in 20 ml of chloroform under stirring and reflux.

This is an exothermic reaction. The solution was allowed to cool, and all volatile material was removed under vacuum. Yield, based on tetramethylchloroformamidinium chloride, 16.0 mmol (95%); ^{1}H NMR ($CDCl_3$, $SiMe_4$): 2.82 ppm, ^{13}C NMR ($CDCl_3$, $SiMe_4$): 162.7 (CN_3), 39.5 (CH_3) ppm. Ra (Solid): ν = 3016[27], 3003[46], 2992[38], 2959[100], 2915[76], 2889[62], 2858[45], 2839[22], 2804[55], 1514[6], 1493[31], 1465[26], 1441[14], 1429[5], 1412[7], 1371[24], 1075[5], 1049[4], 839[14], 657[27], 537[6], 395[24], 372[24], 314[4], 217[9], 132[9], 83[25].

4.4. N,N,N',N',N",N"-Hexamethylguanidinium Fluoride and Hexafluorosilicate Hexahydrate

The N,N,N',N',N",N"-hexamethylguanidinium chloride was converted to N,N,N',N',N",N"-hexamethylguanidinium hydroxide with a twofold excess of freshly prepared silver oxide. The clear solution was neutralized with diluted hydrofluoric acid in a polyethylene container using a pH-meter as an indicator. Water was removed at 40 °C by using a rotary evaporator equipped with a glass flask. The resulting solid was further dried in a glass flask in a dynamic vacuum at 50 °C. Recrystallization of this product from waterfree methanol resulted in the isolation of the $(HMG)_2SiF_6 \cdot 6H_2O$ single crystals.

4.5. Structure Determination of $(HMG)_2SiF_6 \cdot 6H_2O$

The single crystals were obtained by slowly evaporating a methanol solution at room temperature. Due to the strong hygroscopicity of the crystals, the whole process was carried out in a dry environment. A single crystal was selected and mounted under a dry nitrogen flow. The diffraction data were collected at -100 °C, using a Siemens/Nicolet/Syntex $P2_1$, diffractometer with MoKα radiation up to a 2θ limit of 55 °. 3498 intensity values for an entire reflection sphere were collected, within which a total of 3492 unique reflections were independent. The atomic positions of the $[SiF_6]^{2-}$ anion were obtained by direct methods using the computing package SHELX-86 [12]. The rest of the atoms were then located from a

difference-Fourier map, and the entire structure was anisotropically refined by SHELX-93 [13] to a final agreement factor of 4.87%. One minor complication encountered during the structural analysis was a slight packing disorder of the $[(Me_2N)_3C]^+$ cation: two sets of N positions were found, (see Figure 1) related by a 60° rotation, with an occupancy ratio of 5:1. However, the C atoms of the methyl groups were not disordered. A similar form of this disorder has previously been found [14] for $Fe_3(CO)_{12}$. Crystal data and refinement results are summarized in Table 1, the final atomic coordinates and temperature factors, and the bond distances and angles are given in Tables 2-5, respectively.

4.6. Computational Methods

The geometry of the free hexamethylguanidinium cation was optimized in D_3 symmetry using Hartree-Fock and density-functional-theory (DFT) methods and 6-31G(d) atomic basis sets [15]. The DFT calculations were performed with the so-called B3LYP functional [16]. Vibrational frequencies were obtained by computing analytic second derivatives of the energy with respect to nuclear coordinates, and these were examined to ensure that the structure obtained was a minimum on the potential-energy surface. The Gaussian 94 program system [17] was used for these calculations on IBM RS/6000 work stations.

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Table 1. Crystal data and structure refinement for ([C(NMe2)3]+)2[SiF6]2-.6H2O

Empirical formula	C14 H48 F6 N6 O6 Si
Formula weight	538.67
Temperature	193(2) K
Wavelength	0.71073 A
Crystal system	triclinic
Space group	P(-1)
Unit cell dimensions	a = 7.961(2) A alpha = 89.60(3) deg. b = 8.068(2) A beta = 71.37(3) deg. c = 11.084(2) A gamma = 79.89(3) deg.
Volume	663.2(3) A**3
Z	1
Density (calculated)	1.349g/cm**3
Absorption coefficient	0.169 mm**-1
F(000)	290
Crystal size	0.2 x 0.3 x 0.3 mm
Theta range for data collection	1.94 to 27.50 deg.
Index ranges	-9<=h<=10, -10<=k<=10, -14<=l<=13
Reflections collected	3498
Independent reflections	2843 [R(int) = 0.0288]
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2839 / 12 / 206
Goodness-of-fit on F^2	0.962
Final R indices [I>2sigma(I)]	R1 = 0.0487, wR2 = 0.1159
R indices (all data)	R1 = 0.0751, wR2 = 0.1479
Largest diff. peak and hole	0.288 and -0.327 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for {[C(NMe2)3]+}2[SiF6]2-.6H2O

	x	y	z	U(eq)
Si(1)	0	0	0	19(1)
F(1)	-1577(3)	-817(2)	1146(2)	29(1)
F(2)	-1569(3)	1654(3)	-47(2)	39(1)
F(3)	449(3)	1047(3)	1141(2)	42(1)
C(1)	-3027(4)	5746(4)	-2220(3)	22(1)
N(11)	-1695(5)	4482(4)	-2293(3)	26(1)
N(12)	-3613(4)	6930(4)	-1267(3)	25(1)
N(13)	-3873(5)	5864(4)	-3123(3)	26(1)
C(11)	-185(5)	4736(5)	-1827(4)	39(1)
C(12)	-1611(6)	2792(4)	-2837(4)	40(1)
C(13)	-3545(6)	6480(6)	20(3)	44(1)
C(14)	-4287(5)	8694(4)	-1466(4)	33(1)
C(15)	-2834(7)	5231(6)	-4447(3)	45(1)
C(16)	-5794(5)	6557(6)	-2804(4)	42(1)
N(11')	-2142(17)	5623(18)	-1357(11)	17(3)
N(12')	-2318(20)	4550(15)	-3182(11)	20(4)
N(13')	-4409(17)	7030(16)	-2127(15)	25(4)
O(1)	-43(4)	8389(4)	-3664(2)	41(1)
O(2)	3740(4)	1605(4)	-3476(3)	44(1)
O(3)	2666(4)	13(4)	-5272(3)	42(1)

Table 3. Bond lengths [A] and angles [deg] for ([C(NMe2)3]+)2[SiF6]2-.6H2O

Si(1)-F(1)	1.698(2)
Si(1)-F(2)	1.673(2)
Si(1)-F(3)	1.688(2)
C(1)-N(11)	1.318(5)
C(1)-N(12)	1.337(4)
C(1)-N(13)	1.368(5)
N(11)-C(11)	1.496(5)
N(11)-C(12)	1.477(5)
N(12)-C(13)	1.485(5)
N(12)-C(14)	1.471(5)
N(13)-C(15)	1.478(5)
N(13)-C(16)	1.461(5)
C(1)-N(11')	1.351(8)
C(1)-N(12')	1.351(8)
C(1)-N(13')	1.350(8)
F(2)-Si(1)-F(2')	180.0
F(2)-Si(1)-F(3')	90.27(13)
F(2)-Si(1)-F(3)	89.73(13)
F(3)-Si(1)-F(3')	180.0
F(2)-Si(1)-F(1')	89.96(10)
F(3)-Si(1)-F(1')	90.25(10)
F(2)-Si(1)-F(1)	90.04(10)
F(3)-Si(1)-F(1)	89.75(10)
F(1')-Si(1)-F(1)	180.0
N(13)-C(1)-N(11)	120.2(3)
N(13)-C(1)-N(12)	117.9(3)
N(11)-C(1)-N(12)	121.9(3)
C(1)-N(11)-C(12)	122.4(3)
C(1)-N(11)-C(11)	120.1(3)
C(12)-N(11)-C(11)	117.5(3)
C(1)-N(12)-C(14)	121.7(3)
C(1)-N(12)-C(13)	119.8(3)
C(14)-N(12)-C(13)	118.5(3)
C(1)-N(13)-C(16)	121.6(3)
C(1)-N(13)-C(15)	119.3(3)
C(16)-N(13)-C(15)	119.0(3)
N(13')-C(1)-N(12')	125.4(10)
N(13')-C(1)-N(11')	120.9(9)
N(12')-C(1)-N(11')	113.6(9)

Symmetry transformations used to generate equivalent atoms:
#1 -x,-y,-z

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for {[C(NMe2)3]+}2[SiF6]2-.6H2O.
The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
Si(1)	19(1)	23(1)	17(1)	2(1)	-5(1)	-8(1)
F(1)	24(1)	33(1)	26(1)	7(1)	-2(1)	-10(1)
F(2)	29(1)	40(1)	38(1)	15(1)	-1(1)	3(1)
F(3)	53(2)	53(1)	26(1)	-3(1)	-12(1)	-29(1)
C(1)	25(2)	23(2)	19(1)	3(1)	-4(1)	-10(1)
N(11)	34(2)	20(2)	28(2)	2(1)	-13(2)	-4(1)
N(12)	24(2)	27(2)	23(2)	0(1)	-7(1)	-6(1)
N(13)	26(2)	31(2)	20(2)	-1(1)	-7(1)	-4(1)
C(11)	29(2)	39(2)	49(2)	14(2)	-14(2)	-2(2)
C(12)	58(3)	20(2)	44(2)	-1(2)	-22(2)	-2(2)
C(13)	59(3)	59(3)	20(2)	2(2)	-8(2)	-35(2)
C(14)	28(2)	25(2)	40(2)	-3(1)	-4(2)	-1(1)
C(15)	65(3)	50(2)	19(2)	1(2)	-11(2)	-9(2)
C(16)	26(2)	56(3)	44(2)	2(2)	-15(2)	-5(2)
N(11')	12(7)	23(7)	13(7)	-7(5)	-2(5)	-1(5)
N(12')	30(8)	16(7)	15(7)	-2(5)	-7(6)	-6(6)
N(13')	15(7)	26(8)	29(9)	-12(6)	-8(6)	6(6)
O(1)	49(2)	46(2)	25(1)	4(1)	-9(1)	-8(1)
O(2)	37(2)	51(2)	30(1)	7(1)	3(1)	-2(1)
O(3)	32(2)	63(2)	28(1)	6(1)	-9(1)	-6(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for {[C(NMe2)3]+}2[SiF6]2-.6H2O

	x	y	z	U(eq)
H(11A)	944(6)	4397(35)	-2494(10)	58
H(11B)	-202(25)	4068(29)	-1104(18)	58
H(11C)	-329(22)	5905(8)	-1583(27)	58
H(12A)	-1400(40)	1956(5)	-2255(13)	60
H(12B)	-646(26)	2580(16)	-3634(14)	60
H(12C)	-2732(15)	2740(13)	-2975(26)	60
H(13A)	-4723(11)	6809(37)	636(5)	66
H(13B)	-2712(33)	7057(32)	232(13)	66
H(13C)	-3158(42)	5285(8)	24(9)	66
H(14A)	-3641(26)	9419(5)	-1177(24)	50
H(14B)	-5549(10)	8986(11)	-993(21)	50
H(14C)	-4110(34)	8829(9)	-2356(5)	50
H(15A)	-3046(34)	6071(17)	-5025(4)	68
H(15B)	-3209(31)	4221(23)	-4632(10)	68
H(15C)	-1572(7)	4989(38)	-4543(9)	68
H(16A)	-6396(9)	5731(15)	-3023(28)	62
H(16B)	-5952(5)	7545(23)	-3273(23)	62
H(16C)	-6298(10)	6852(37)	-1907(6)	62
HO11	-259(59)	8629(61)	-2929(13)	61
HO12	785(46)	8744(60)	-4131(31)	61
HO21	3148(44)	1351(61)	-2800(25)	65
HO22	4774(22)	1169(60)	-3695(41)	65
HO31	2827(66)	573(49)	-4746(37)	62
HO32	1993(58)	485(51)	-5613(42)	62

Table 6. Geometry of the free gaseous hexamethylguanidinium cation optimized at the B3LYP/6-31G(d) level

Distances (Å)		Angles (°)	
C(1)—N(11-13)	1.352	N—C—N	120.0
N(11-13)—C(11-16)	1.468	C(1)—N—C(11-16)	122.32
C(11-16)—H	1.09	C(11)—N—C(12)	115.37

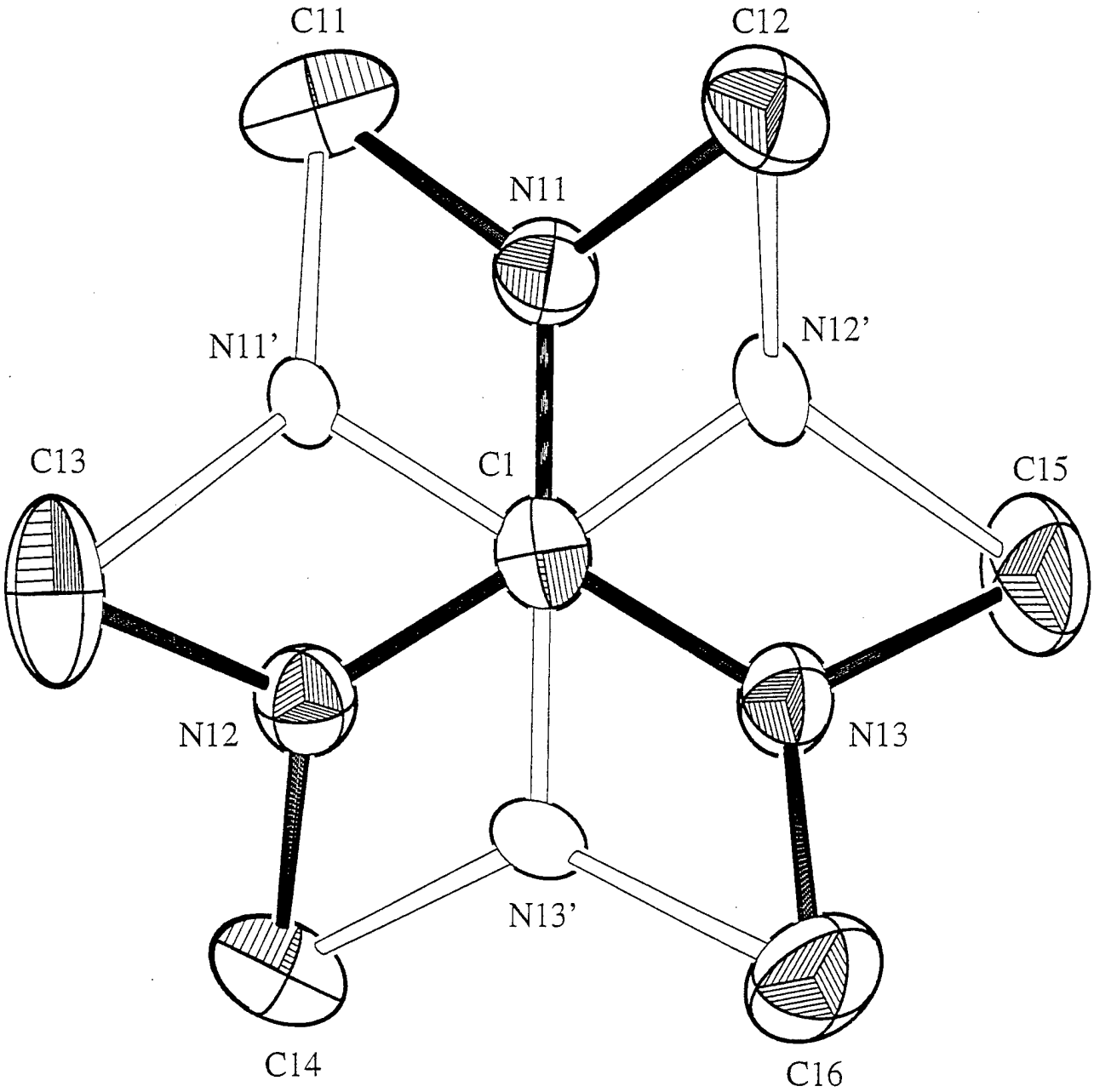
dihedral angle between the CN_3 an the three NC_2 planes 34.97

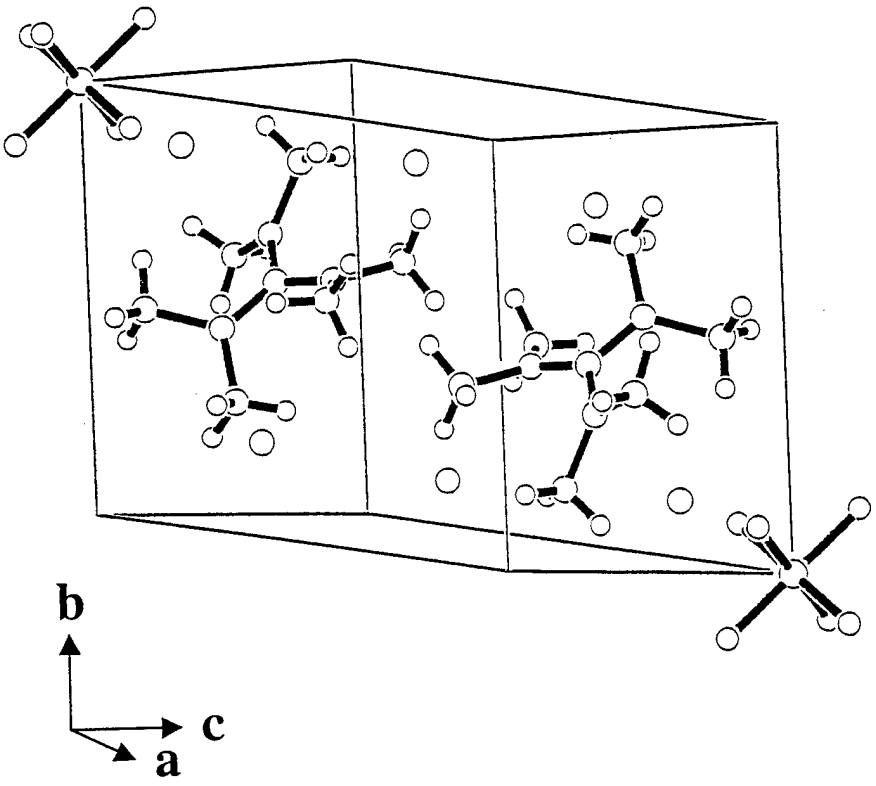
Diagram Captions

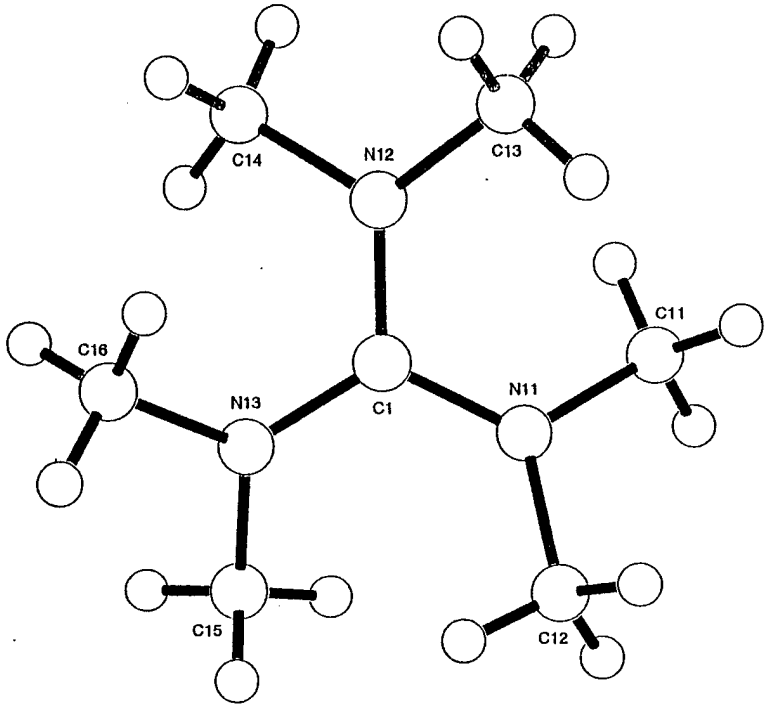
Figure 1. Structure and numbering scheme for the hexamethylguanidinium cation showing the packing disorder of the nitrogen atoms.

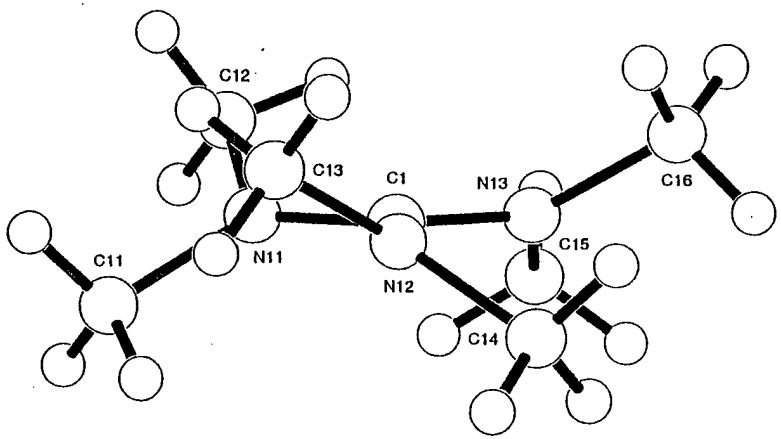
Figure 2. Packing diagram for $(HMG)_2SiF_6 \cdot 6H_2O$. The $[SiF_6]^{2-}$ anions are situated on all eight corners of the unit cell, but for clarity only two of these are shown. The isolated circles are the oxygen atoms of the water molecules.

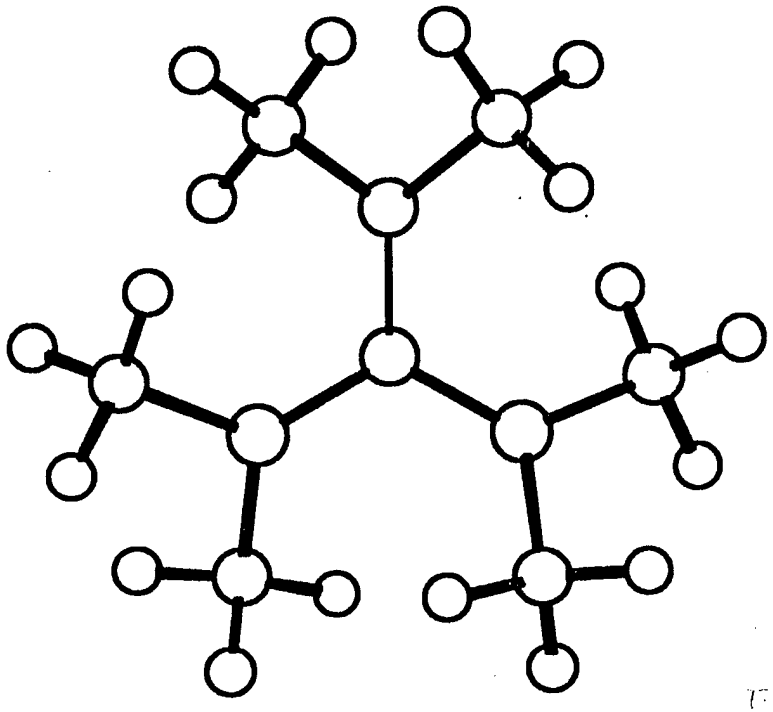
Figure 3. Structure of the hexamethylguanidinium cation from the crystal structure of $(HMG)_2SiF_6 \cdot 6H_2O$ (upper trace) and minimum energy structure from the B3LYP calculation (lower trace).


C11
C12
N11
N11'
N12'
C13
C1
C15
N12
N13
N13'
C14
C16


b
c
a


C14
N12
C13
C16
C11
N13
C1
N11
C15
C12


C12
C13
C1
N13
C16
C11
N11
N12
C15
C14



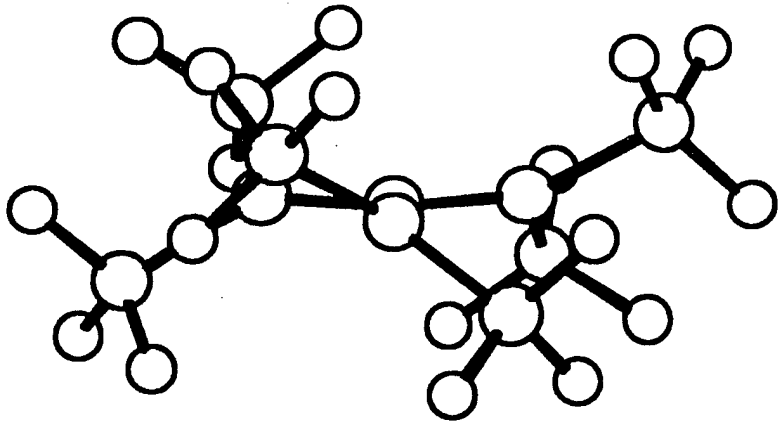


FIG. 3