

## Sodium tris(glycinium) bis(hexafluorosilicate) glycine trisolvate

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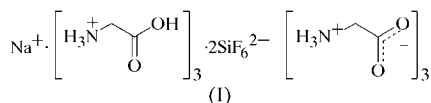
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The title compound,  $\text{Na}^+ \cdot 3\text{C}_2\text{H}_6\text{NO}_2^+ \cdot 2\text{SiF}_6^{2-} \cdot 3\text{C}_2\text{H}_5\text{NO}_2$ , arose from an unexpected reaction of glycine and HF with the glass container. It is an unusual hybrid organic–inorganic network built up from chains of vertex-sharing  $\text{NaF}_4\text{O}_2$  and  $\text{SiF}_6$  octahedra. A pair of glycinium/glycine molecules bridges the chains into a sheet *via* a centrosymmetric  $\text{O} \cdots \text{H} \cdots \text{O}$  link. The other organic species interact with the network by an extensive  $\text{N} \cdots \text{H} \cdots \text{F}$  hydrogen-bond network, including bifurcated and trifurcated bonds. Finally, an extremely short  $\text{C} \cdots \text{H} \cdots \text{O}$  interaction ( $\text{H} \cdots \text{O} = 2.25 \text{ \AA}$ ) is seen in the crystal structure. The Na atom has site symmetry  $\bar{1}$ .

### Comment

The title compound,  $\text{Na}(\text{SiF}_6)_2(\text{C}_2\text{H}_6\text{NO}_2)_3(\text{C}_2\text{H}_5\text{NO}_2)_3$ , (I), arose as an unexpected product during our studies of amino acid fluorides as possible nonlinear optical materials. The sodium and silicon were presumably incorporated from the walls of the glass reaction vessel, mediated by reaction with hydrofluoric acid.



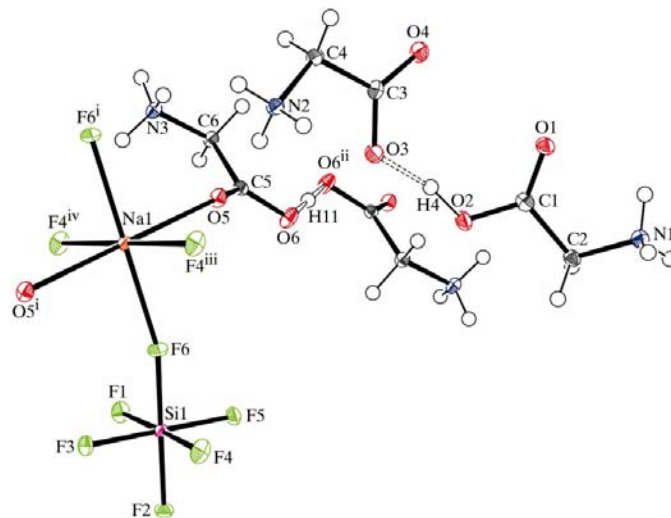
The structure of (I) (Fig. 1) is built up from *trans*- $\text{NaF}_4\text{O}_2$  octahedra (Na site symmetry  $\bar{1}$ ) and  $\text{SiF}_6$  octahedra, sharing corners *via* atoms F4 and F6. The geometries of the Na and Si atoms (Table 1) may be regarded as normal (Allen *et al.*, 1995). Considered by themselves, they form chains propagating in [100], with each Na octahedron linked to its neighbour by two Si polyhedra *via* F atoms, with notably large Na–F–Si bond angles greater than  $164^\circ$ . The square formed by atoms Na1, Si1, Na1<sup>i</sup> and Si1<sup>i</sup> [symmetry code: (i)  $1 - x, -y, -z$ ] is constrained to be exactly flat by symmetry and the  $\text{Na} \cdots \text{Si1} \cdots \text{Na1}^i$  [ $90.58(3)^\circ$ ] and  $\text{Si1} \cdots \text{Na1} \cdots \text{Si1}^i$  [ $89.42(3)^\circ$ ] angles barely deviate from  $90^\circ$ . The  $\text{NaF}_4\text{O}_2$  polyhedron is a

rare one, with only two other examples recorded in Version 5.27 of the Cambridge Structural Database (Allen, 2002), in structures otherwise unrelated to (I).

There are three organic molecules in the asymmetric unit of (I). The C1 species is a well defined  $\text{C}_2\text{H}_6\text{NO}_2^+$  glycinium cation, with  $\text{C1} \cdots \text{O2}$  [ $1.3018(14) \text{ \AA}$ ] much longer than  $\text{C1} \cdots \text{O1}$  [ $1.2175(14) \text{ \AA}$ ], indicating localized single and double bonds, respectively. The positive charge of the cation is localized on the N atom.

The C2 species is a neutral  $\text{C}_2\text{H}_5\text{NO}_2$  glycine molecule in its normal (Marsh, 1958) zwitterionic form (*i.e.* nominal H-atom transfer from O3 or O4 to N2). Consequently, the  $\text{C3} \cdots \text{O3}$  and  $\text{C3} \cdots \text{O4}$  bond lengths [ $1.2759(14)$  and  $1.2354(14) \text{ \AA}$ , respectively] approach each other, implying a degree of delocalization. The C1 and C3 molecules are linked by an  $\text{O2} \cdots \text{H4} \cdots \text{O3}$  hydrogen bond (Table 2) and it is possible that  $\text{C3} \cdots \text{O3}$  is lengthened relative to  $\text{C3} \cdots \text{O4}$  because atom O3 accepts this short strong bond, with an  $\text{O} \cdots \text{O}$  distance of  $2.4495(12) \text{ \AA}$ .

The C5 molecule sits close to an inversion centre, resulting in an  $\text{O6} \cdots \text{O6}^{\text{ii}}$  contact of  $2.4312(16) \text{ \AA}$  [symmetry code: (ii)  $-x, 1 - y, -z$ ], whereas atom O5 makes a bond to an adjacent  $\text{Na}^+$  cation [ $\text{C5} \cdots \text{O5} = 1.2366(14) \text{ \AA}$  and  $\text{C5} \cdots \text{O6} = 1.2796(14) \text{ \AA}$ ]. In order to achieve overall charge balance in the structure and to justify the very short  $\text{O} \cdots \text{O}$  contact, we have assumed a symmetrical (single potential well) hydrogen bond (Ichikawa, 1978), with atom H11 located on the inversion centre midway between the two crystallographically equivalent O6 atoms. This is strongly supported by our refinements of the structure in the space group  $P1$ , which resulted in a significant difference peak almost midway between the two non-equivalent O atoms in the noncentrosymmetric model. Even so, in the centrosymmetric model, when  $U_{\text{iso}}(\text{H11})$  was allowed to refine freely, a value of

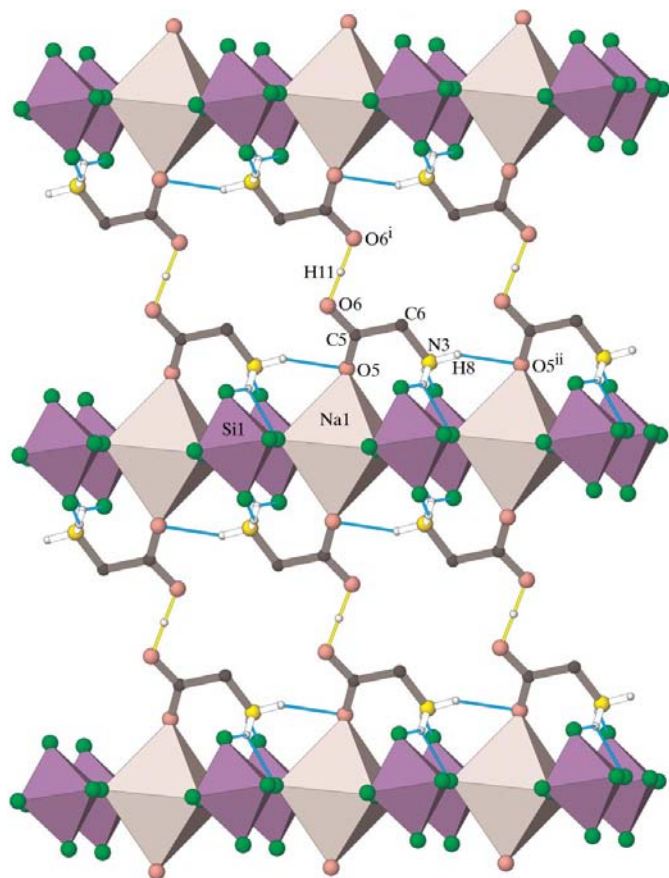


**Figure 1**

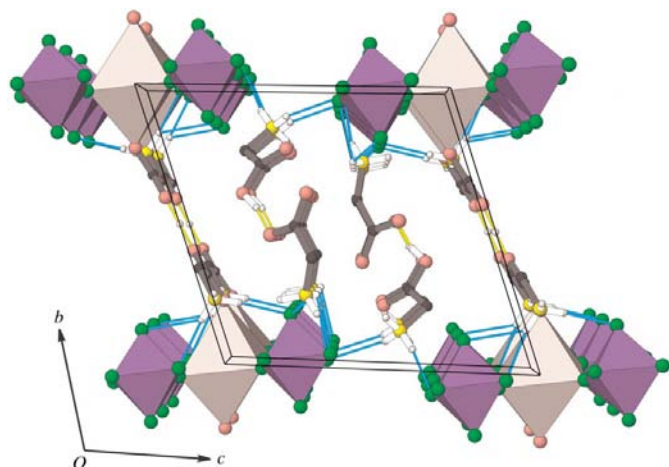
The asymmetric unit of (I), showing the atom-numbering scheme, expanded to show the Na coordination sphere and the organic molecules linked by the  $\text{O} \cdots \text{H} \cdots \text{O}$  bond. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as spheres of arbitrary radii. Hydrogen bonds are shown as double dashed lines or open bonds. [Symmetry codes: (i)  $-x, -y, -z$ ; (ii)  $-x, 1 - y, -z$ ; (iii)  $1 - x, -y, -z$ ; (iv)  $x - 1, y, z$ .]

0.062 (9) Å<sup>2</sup> resulted, significantly higher than those of the other H atoms, perhaps suggesting disorder.

Thus, based on the present data, a situation of disordered asymmetric O—H···O and O···H—O hydrogen bonds



**Figure 2**  
Part of the composite inorganic/organic (001) sheet structure in (I), with the inorganic species shown as polyhedra. The NaF<sub>2</sub>O<sub>4</sub> and SiF<sub>6</sub> octahedra are light and dark, respectively. The symmetric O6···H···O6<sup>i</sup> link is indicated. C-bound H atoms have been omitted for clarity. [Symmetry codes: (i)  $-x, 1 - y, -z$ ; (ii)  $x - 1, y, z$ .]



**Figure 3**  
The unit-cell packing for (I), viewed down [100], with drawing conventions as used in Fig. 2.

(double potential well) cannot be completely ruled out, as they are known to be hard to distinguish from X-ray data alone and indeed may be temperature dependent (Wilson, 2001). Either way, this ensemble in (I) has a formula of C<sub>4</sub>H<sub>11</sub>N<sub>2</sub>O<sub>4</sub>, *i.e.* equivalent to one glycinium cation and one glycine molecule (C<sub>2</sub>H<sub>6</sub>NO<sub>2</sub><sup>+</sup> + C<sub>2</sub>H<sub>5</sub>NO<sub>2</sub>). These glycinium/glycine pairs serve to bridge the [100] inorganic chains into (001) sheets (Fig. 2). For all three organic molecules, the N atom of the —NH<sub>3</sub> group and one of the O atoms of the —CO<sub>2</sub> group are close to being eclipsed (Table 1), which is not an uncommon conformation for glycine (Natarajan & Zangrando, 1992). The co-existence of glycine molecules and glycinium cations in the same structure is also very common (Nemec *et al.*, 1998).

A large number of N—H···F hydrogen bonds (Table 2) help to consolidate the crystal packing of (I). It is notable that some of these are bifurcated N—H···(F,F) bonds and some are trifurcated N—H···(F,F,F) links. Finally, an exceptionally short C6—H6A···O2( $x - 1, y, z$ ) interaction (Taylor & Kennard, 1982), with a H···O distance of 2.25 Å, occurs in the structure of (I), although its role in the complex crystal packing is not clear.

Together, these interactions generate a structure in which the (001) hybrid sheets sandwich the C1 and C2 organic molecules, with a dense mesh of N—H···F hydrogen bonds linking the two together (Fig. 3).

## Experimental

An aqueous solution of glycine was mixed with excess 2 *N* hydrofluoric acid. This solution was allowed to undergo evaporation by heating at 313 K. The resulting solid was dried and purified by repeated crystallization in water. The experiment was conducted in glass vessels. An aqueous saturated solution of the compound synthesized as described above was prepared in water at 323 K. The solution was filtered and kept to undergo slow evaporation by cooling at a rate of 0.5 K per day. A portion of the mother solution was poured into a Petri dish and allowed to undergo evaporation at room temperature. The nucleation time was very long, but optically good tiny crystals of (I) were seen in the Petri dish after about one month. These crystals were used as seeds and suspended in the super-saturated mother solution when the temperature reached 313 K. The growth temperature was maintained at 313 K and large crystals of (I) of dimensions 10 × 6 × 3 mm were harvested after a week.

### Crystal data

Na <sup>+</sup> ·3C <sub>2</sub> H <sub>6</sub> NO <sub>2</sub> <sup>+</sup> ·2SiF <sub>6</sub> <sup>2-</sup> · 3C <sub>2</sub> H <sub>5</sub> NO <sub>2</sub>	$\beta = 102.397 (1)^\circ$
$M_r = 760.61$	$\gamma = 93.562 (1)^\circ$
Triclinic, $P\bar{1}$	$V = 664.56 (2) \text{ \AA}^3$
$a = 5.5364 (1) \text{ \AA}$	$Z = 1$
$b = 10.9918 (2) \text{ \AA}$	Mo $K\alpha$ radiation
$c = 11.8432 (2) \text{ \AA}$	$\mu = 0.30 \text{ mm}^{-1}$
$\alpha = 107.631 (1)^\circ$	$T = 120 (2) \text{ K}$
	0.50 × 0.50 × 0.35 mm

### Data collection

Nonius KappaCCD area-detector diffractometer	14359 measured reflections
Absorption correction: multi-scan (SADABS; Bruker, 2003)	3041 independent reflections
$T_{\min} = 0.863, T_{\max} = 0.901$	2825 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.024$

## Refinement

$R[F^2 > 2\sigma(F^2)] = 0.024$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.061$	
$S = 1.07$	
3041 reflections	$\Delta\rho_{\max} = 0.39 \text{ e } \text{\AA}^{-3}$
212 parameters	$\Delta\rho_{\min} = -0.37 \text{ e } \text{\AA}^{-3}$

**Table 1**  
Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ).

Na1—F4 <sup>i</sup>	2.2150 (6)	Si1—F2	1.6871 (7)
Na1—F6	2.2529 (7)	Si1—F6	1.6922 (7)
Na1—O5	2.4085 (8)	Si1—F4	1.6938 (7)
Si1—F1	1.6730 (7)	Si1—F3	1.7008 (7)
Si1—F5	1.6741 (7)		
Si1—F4—Na1 <sup>ii</sup>	165.79 (5)	Si1—F6—Na1	164.78 (4)
O1—C1—C2—N1	19.66 (15)	O5—C5—C6—N3	-2.66 (14)
O3—C3—C4—N2	19.24 (14)		

Symmetry codes: (i)  $x - 1, y, z$ ; (ii)  $-x + 1, -y, -z$ .

**Table 2**  
Hydrogen-bond geometry ( $\text{\AA}$ ,  $^\circ$ ).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1 $\cdots$ F2 <sup>iii</sup>	0.91	1.91	2.8115 (12)	169
N1—H1 $\cdots$ F5 <sup>iii</sup>	0.91	2.45	3.0735 (12)	126
N1—H2 $\cdots$ O4 <sup>iv</sup>	0.91	2.18	2.8769 (13)	133
N1—H2 $\cdots$ O1 <sup>iv</sup>	0.91	2.52	3.2299 (13)	135
N1—H3 $\cdots$ F1 <sup>v</sup>	0.91	2.35	3.1782 (12)	151
O2—H4 $\cdots$ O3	1.031 (17)	1.435 (17)	2.4495 (12)	166.7 (16)
N2—H5 $\cdots$ F1 <sup>vi</sup>	0.91	2.20	3.0750 (12)	161
N2—H5 $\cdots$ O1 <sup>vii</sup>	0.91	2.38	2.8803 (13)	115
N2—H5 $\cdots$ F3 <sup>vi</sup>	0.91	2.43	2.8760 (12)	111
N2—H6 $\cdots$ F2 <sup>ii</sup>	0.91	2.30	2.7571 (12)	110
N2—H6 $\cdots$ O4 <sup>viii</sup>	0.91	2.34	3.0904 (13)	140
N2—H6 $\cdots$ F3 <sup>ii</sup>	0.91	2.36	3.0088 (12)	128
N2—H7 $\cdots$ O5	0.91	2.28	3.1710 (13)	165
N2—H7 $\cdots$ F4 <sup>ii</sup>	0.91	2.61	3.1022 (12)	115
N3—H8 $\cdots$ O5 <sup>i</sup>	0.91	2.03	2.8840 (12)	156
N3—H8 $\cdots$ O6 <sup>i</sup>	0.91	2.40	3.1720 (13)	143
N3—H9 $\cdots$ F3 <sup>vi</sup>	0.91	1.92	2.8014 (12)	163
N3—H10 $\cdots$ F6 <sup>i</sup>	0.91	2.15	2.9180 (12)	142
N3—H10 $\cdots$ F5 <sup>i</sup>	0.91	2.24	2.9383 (12)	133
O6—H11 $\cdots$ O6 <sup>viii</sup>	1.22	1.22	2.4309 (16)	180
C6—H6A $\cdots$ O2 <sup>i</sup>	0.99	2.25	3.2316 (14)	172

Symmetry codes: (i)  $x - 1, y, z$ ; (ii)  $-x + 1, -y, -z$ ; (iii)  $-x + 2, -y + 1, -z$ ; (iv)  $x + 1, y, z$ ; (v)  $x + 1, y + 1, z + 1$ ; (vi)  $-x, -y, -z$ ; (vii)  $-x + 1, -y + 1, -z + 1$ ; (viii)  $-x, -y + 1, -z$ .

O-bound H atoms were located in difference maps and their positions were freely refined, with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{O})$ . The other H atoms were positioned geometrically, with C—H = 0.99  $\text{\AA}$  and N—H = 0.91  $\text{\AA}$ , and refined as riding, with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C}, \text{N})$ . The  $-\text{NH}_3$  groups were allowed to rotate but not to tip in order to best fit the electron density.

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *SCALEPACK*, *DENZO* (Otwinowski & Minor, 1997) and *SORTAV* (Blessing, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ3076). Services for accessing these data are described at the back of the journal.

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