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The monoclinic polymorph of *rac*-5,7,7,12,12,14-hexamethyl-1,4,8,11-tetraazoniacyclotetradecane bis(hexafluorogermanate) tetrahydrate

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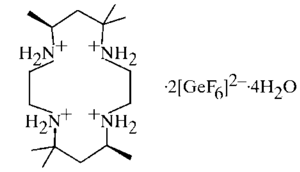
X-ray data were obtained for the monoclinic polymorph of *rac*-5,7,7,12,12,14-hexamethyl-1,4,8,11-tetraazoniacyclotetradecane bis(hexafluorogermanate) tetrahydrate, $(C_{16}H_{40}N_4)[GeF_6]_2\cdot 4H_2O$. The tetraaza-macrocyclic cations lie across inversion centers in space group $P2_1/c$. Water molecules and $[GeF_6]^{2-}$ anions form zigzag chains, which alternate in a three-dimensional network with the macrocyclic cations. The structure is sustained by multiple hydrogen bonds.

Comment

The ability of crown ethers to stabilize in the form of the proper host–guest complexes normally unstable or volatile species is well known (Bott *et al.*, 1991; Chuit *et al.*, 1993; Feinberg *et al.*, 1993). Previously, we have shown that crown ethers (18-crown-6, isomers of dicyclohexyl-18-crown-6, mono- and diaza-18-crown-6, and diaza-15-crown-5) provide the opportunity to hold harmful gaseous (SiF_4; Simonov *et al.*, 1994), intermediate [$(SiF_5\cdot H_2O)^-$ and SiF_5^-; Simonov *et al.*, 1996; Gelmboldt *et al.*, 1999] or low-melting substances ($BF_3\cdot H_2O$; Fonari *et al.*, 1997) in the form of hydrogen-bonded molecular or ionic complexes. The Ge-containing species $GeF_4\cdot 2H_2O$ and $(GeF_5\cdot H_2O)^-$, which are similar to the Si-containing complexes, were obtained by direct reaction between GeO_2–HF solution and 18-crown-6 and diaza-18-crown-6 (Gelmboldt *et al.*, 1996). The general tendency is that partial replacement of O atoms by N atoms in the macrocyclic ring or the application of aza-macrocycles (Simonov, Fonari *et al.*, 1998; Simonov, Lipkowski *et al.*, 1998; Fonari *et al.*, 1998, 1999) provokes the extraction of charged species, *viz.* $(SiF_5\cdot H_2O)^-$, SiF_6^{2-}, $(GeF_5\cdot H_2O)^-$ and GeF_6^{2-}, from aqueous solutions of fluorosilicic acid, H_2SiF_6, or its germanium analog, H_2GeF_6.

We recently reported the single-crystal X-ray structure of triclinic *rac*-5,7,7,12,12,14-hexamethyl-1,4,8,11-tetraazoniacyclotetradecane bis(hexafluorogermanate) tetrahydrate (space group $P\overline{1}$; Fonari *et al.*, 1999), which shows extended intermolecular hydrogen bonding. As part of this study, we redetermined the structure of the title compound, (I), in order to improve on earlier structure determinations. Unexpectedly, the X-ray analysis revealed a new monoclinic (space group $P2_1/c$) polymorph of (I), which is the subject of the present communication.



(I)

The centrosymmetric formula unit of (I) is shown in Fig. 1. The slightly distorted $[GeF_6]^{2-}$ octahedron is characterized by Ge—F distances in the range 1.746 (1)–1.825 (1) Å and F—Ge—F angles that deviate slightly (3°) from 90 or 180° (Table 1); the geometry of the anion coincides with previously reported data (Fonari *et al.*, 1999; Simonov, Fonari *et al.*, 1998). The tetraprotonated macrocyclic tetraamine cation, $[H_4(C_{16}H_{36}N_4)]^{4+}$, resides on the inversion center, and the first coordination sphere of this cation is comprised of two $[GeF_6]^{2-}$ anions and two water molecules. Atom F4 bridges atoms N1 and N4 of the basic macrocycle *via* two N—H···F hydrogen bonds (N1···F4 and N4···F4; Table 2); the same N atoms are also bound *via* N1···F6 and N4···F2 interactions.

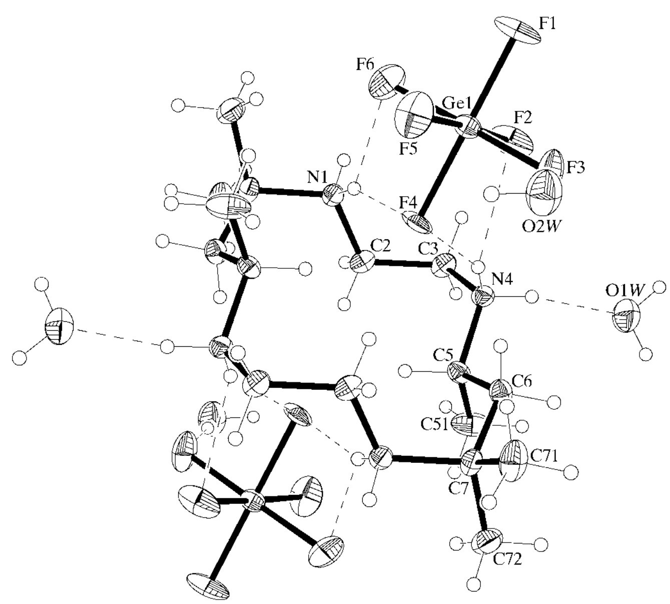


Figure 1
A view of the structure of (I). Displacement ellipsoids are drawn at the 50% probability level, and only the asymmetric unit is labelled.

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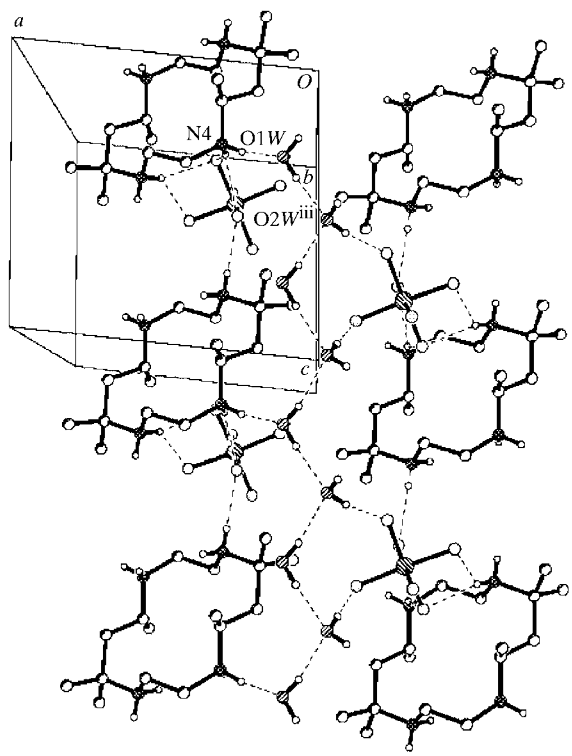

Figure 2
Part of the crystal structure of (I), showing the inorganic anionic chains, formed by hydrogen-bonded anions and water molecules, that alternate with macrocyclic cations. For the sake of clarity, H atoms bonded to C atoms have been omitted. [Symmetry code: (iii) $-x$, $1 - y$, $-z$.]

Atom F2 links two macrocycles translated along the *c* axis (*via* N—H···F interactions; see Table 2 for symmetry code).

Water molecule O2*W* has no direct contacts with the macrocycle but is involved in a negatively charged zigzag chain, which develops along the *c* direction in the unit cell and combines inorganic species, $[GeF_6]^{2-}$ anions and water molecules (Fig. 2). In this chain, O2*W* acts as a double hydrogen-bond donor and bridges two $[GeF_6]^{2-}$ anions that are related by the glide plane [O2*W*···F3 = 2.795 (2) Å and O2*W*···F1^{v} = 2.739 (2) Å; see Table 2 for symmetry code]. In the function of double acceptor, each O2*W* water molecule bridges two O1*W* molecule [O1*W*···O2*W*^{iii} = 2.911 (2) Å and O1*W*···O2*W*^{iv} = 2.820 (3) Å; see Table 2 for symmetry codes], and thus the alternating water molecules themselves form chains. These chains are further complicated by $[GeF_6]^{2-}$ anions, attached to O2*W* molecules in such a way that each anion and three water molecules form a ten-membered cage closed by four hydrogen bonds [$R_4^4(10)$ in graph-set notation; Etter, 1990]. The above-mentioned N—H···F and N—H···O hydrogen bonds between the negatively charged chains and positively charged macrocycles combine the components into a three-dimensional network, in which the inorganic chains alternate with the rows of macrocyclic cations (Fig. 2).

In the previously reported triclinic polymorph of the title compound (Fonari *et al.*, 1999), the immediate environment of the macrocyclic cation is the same as in (I), while the hydrogen-bonding motifs that consolidate the components into a three-dimensional network differ from those in (I) (Fig. 3). Two $[GeF_6]^{2-}$ anions and two O2*W* water molecules related by the inversion center are combined into heterotetramers [graph set $R_4^4(12)$]. These alternate with the macrocyclic cations in chains propagated along the *c* direction in the unit cell. These chains are further combined in layers arranged parallel to the *ac* plane *via* two O1*W* water molecules related by a center of symmetry. Water molecules are themselves organized into a four-membered chains that differ from the infinite water chains in (I). Along the *b* direction, the above-mentioned layers are joined into a three-dimensional network through N—H···O and N—H···F hydrogen bonds.

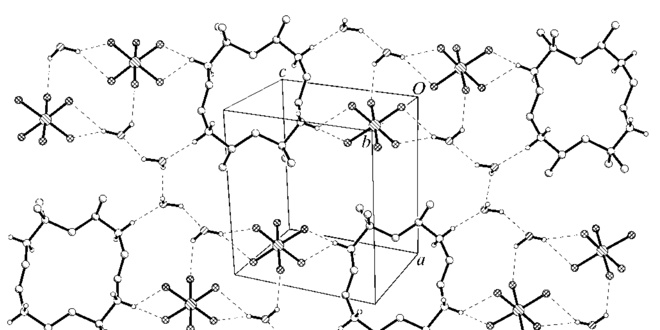

Figure 3
Part of the crystal packing for the triclinic polymorph. For the sake of clarity, H atoms bonded to C atoms have been omitted.

Experimental

To a solution of *rac*-5,7,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane (1 mmol) in methanol (10 ml), a solution of H_2GeF_6 (3 *M* in 1.5 ml) was added, and the mixture boiled on a water bath. The resulting clear solution was reduced slowly in volume by evaporating the solvent at room temperature [m.p. of (I) is 343 K]. Analysis found: C 24.39, H 6.28, F 36.01, N 7.26%; $C_{16}H_{48}F_{12}Ge_2N_4O_4$ requires: C 24.53, H 6.17, F 35.48, N 7.15%.

Crystal data

$(C_{16}H_{40}N_4)[GeF_6]_2 \cdot 4H_2O$
M_r = 733.76
Monoclinic, $P2_1/c$
a = 9.5650 (19) Å
b = 16.522 (3) Å
c = 9.0210 (18) Å
β = 96.28 (3)°
V = 1417.1 (5) Å^3
Z = 2
D_x = 1.720 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 24 reflections
θ = 5.6–16.2°
μ = 2.23 mm^{-1}
T = 293 (2) K
Plate, white
0.25 × 0.20 × 0.20 mm

Data collection

Phillips PW1100 four-circle diffractometer
ω–2θ scans
Absorption correction: empirical (North *et al.*, 1968)
T_{min} = 0.606, T_{max} = 0.664
4350 measured reflections
4137 independent reflections
3251 reflections with $I > 2\sigma(I)$
R_{int} = 0.015
θ_{max} = 30.0°
$h = 0 \rightarrow 13$
$k = -23 \rightarrow 0$
$l = -12 \rightarrow 12$
3 standard reflections every 100 reflections intensity decay: 0.1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.028$
$wR(F^2) = 0.072$
$S = 0.95$
4137 reflections
208 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0437P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 0.65$ e Å^{-3}
$\Delta\rho_{min} = -0.62$ e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.0035 (6)

The coordinates of the H atoms attached to atoms N1 and N4 and of the water H atoms were determined from a difference map and were refined isotropically, subject to a DFIX restraint. All other H atoms were treated as riding.

Data collection: Lehmann & Larsen (1974); cell refinement: *FEBO* (Belletti, 1996); data reduction: Lehmann & Larsen (1974); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 (Farrugia, 1997); software used to prepare material for publication: *SHELXL*97.

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Table 1
Selected geometric parameters (Å, °).

Ge1—F5	1.7459 (12)	Ge1—F6	1.7805 (15)
Ge1—F1	1.7703 (13)	Ge1—F2	1.8081 (12)
Ge1—F3	1.7708 (14)	Ge1—F4	1.8246 (11)
F5—Ge1—F1	94.30 (7)	F3—Ge1—F2	90.02 (7)
F5—Ge1—F3	90.76 (7)	F6—Ge1—F2	88.10 (7)
F1—Ge1—F3	92.34 (8)	F5—Ge1—F4	92.44 (6)
F5—Ge1—F6	90.98 (7)	F1—Ge1—F4	173.00 (6)
F1—Ge1—F6	91.75 (8)	F3—Ge1—F4	89.45 (7)
F3—Ge1—F6	175.42 (7)	F6—Ge1—F4	86.24 (7)
F5—Ge1—F2	177.94 (6)	F2—Ge1—F4	85.66 (6)
F1—Ge1—F2	87.58 (7)		
N1—C2—C3—N4	83.49 (18)	C5—C6—C7—N1^{i}	−48.63 (19)
C2—C3—N4—C5	54.5 (2)	C6—C7—N1^{i}—C2^{i}	−64.22 (18)
C3—N4—C5—C6	−172.17 (13)	C7—N1^{i}—C2^{i}—C3^{i}	176.76 (13)
N4—C5—C6—C7	163.92 (14)		

Symmetry code: (i) $1-x, 1-y, -z$.

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H2N···F4	0.85 (2)	2.26 (2)	3.061 (2)	157.2 (18)
N1—H2N···F6	0.85 (2)	2.31 (2)	2.988 (2)	137.0 (17)
N1—H1N···F2^{ii}	0.81 (2)	2.09 (2)	2.894 (2)	172 (2)
N4—H3N···O1*W*	0.92 (2)	1.86 (2)	2.764 (2)	169 (2)
N4—H4N···F4	0.80 (2)	2.03 (2)	2.771 (2)	154 (2)
N4—H4N···F2	0.80 (2)	2.33 (2)	2.948 (2)	135 (2)
O1*W*—H1*W*···O2*W*^{iii}	0.854 (16)	2.086 (18)	2.911 (2)	162 (2)
O1*W*—H2*W*···O2*W*^{iv}	0.814 (16)	2.017 (17)	2.820 (3)	169 (3)
O2*W*—H3*W*···F3	0.811 (17)	1.988 (17)	2.795 (2)	173 (3)
O2*W*—H4*W*···F1^{v}	0.835 (18)	1.921 (19)	2.739 (2)	166 (3)

Symmetry codes: (ii) $1-x, 1-y, 1-z$; (iii) $-x, y-\frac{1}{2}, \frac{1}{2}-z$; (iv) $-x, 1-y, -z$; (v) $x, \frac{3}{2}-y, z-\frac{1}{2}$.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: DN1019). Services for accessing these data are described at the back of the journal.

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