

A three-dimensional open-framework germanate containing four-, five- and six-coordinated germanium

Kai Sun, Mike S. Dadachov, Tony Conradsson and Xiaodong Zou*

Structural Chemistry, Stockholm University, S-106 91 Stockholm, Sweden

Correspondence e-mail: zou@struc.su.se

Received 17 April 2000

Accepted 23 June 2000

A new three-dimensional open-framework germanate, namely ethylenediamine bis(ethylenediammonium) tetrahydroxooctadecaaxononagermanate, $(C_2H_8N_2)(C_2H_{10}N_2)_2[Ge_9O_{18}(OH)_4]$, has been synthesized hydrothermally and its structure determined by single-crystal X-ray diffraction. The framework is built of $[Ge_9O_{22}(OH)_4]$ units formed by four-, five- and six-oxygen-coordinated germanium and templated by ethylenediamine. Three types of intersecting channels are formed in the framework, one by eight-membered rings running along the *b* axis and the other two by ten-membered rings running parallel to the *a* and *c* axes, respectively.

Comment

Microporous framework compounds, such as aluminium silicates, are of broad interest due to their applications as absorbents, ion-exchangers and catalysts. Great efforts have been made to synthesize new open-framework aluminium silicates and other zeolite-like compounds using organic molecules as structure-directing templates. Recently, several new open-framework germanates have been reported (Jones *et al.*, 1992; Tripathi *et al.*, 1999; Li *et al.*, 1999; Conradsson *et al.*, 2000). In contrast to silicon, which is usually tetrahedrally coordinated to O atoms, germanium can form not only GeO_4 tetrahedra, but also GeO_6 octahedra, and GeO_5 square pyramids and trigonal bipyramids. We report here the synthesis and crystal-structure determination of a novel ethylenediamine (en) templated mixed-framework germanate, $en(enH_2)_2[Ge_9O_{18}(OH)_4]$, with an open three-dimensional structure built of $[Ge_9O_{22}(OH)_4]$ units.

The asymmetric unit contains five unique Ge atoms, forming one regular GeO_6 octahedron around Ge1, two highly distorted $GeO_4(OH)$ trigonal bipyramids (Ge2 and Ge3), and two regular GeO_4 tetrahedra (Ge4 and Ge5) (Fig. 1). One pair of GeO_4 tetrahedra and one pair of distorted $GeO_4(OH)$ trigonal bipyramids are connected by their vertices to form a $[Ge_4O_{11}(OH)_2]$ unit, of which the Ge atoms form a square. Two such units are linked by the octahedrally coordinated Ge1 atom in such a way that they are related by an inversion center

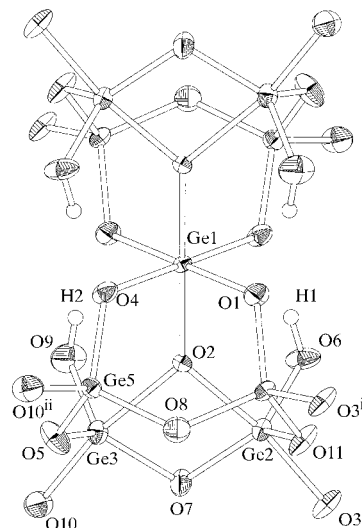


Figure 1

An ORTEP (Johnson, 1976) (50% probability ellipsoids) drawing of the secondary parallelepiped $[Ge_9O_{22}(OH)_4]$ unit of the title compound as seen nearly along the *b* axis with the atom-labeling scheme (the symmetry code is as in Table 1).

at the Ge1 position, forming a $[Ge_9O_{22}(OH)_4]$ unit of which the nine Ge atoms form a body-centered parallelepiped. Finally, the $[Ge_9O_{22}(OH)_4]$ parallelepiped units are corner-shared with each other in a body-centered manner such that an open three-dimensional framework results. Three types of intersecting channels are formed in the framework, one by ten-membered rings running along the *a* axis (Fig. 2), one by eight-membered rings along the *b* axis and the last by ten-membered rings running parallel to the *c* axis. The free diameters of the channels in the title compound are $3.6 \times 3.8 \text{ \AA}$ along the *a* axis, $4.2 \times 4.3 \text{ \AA}$ along the *b* axis and $3.6 \times$

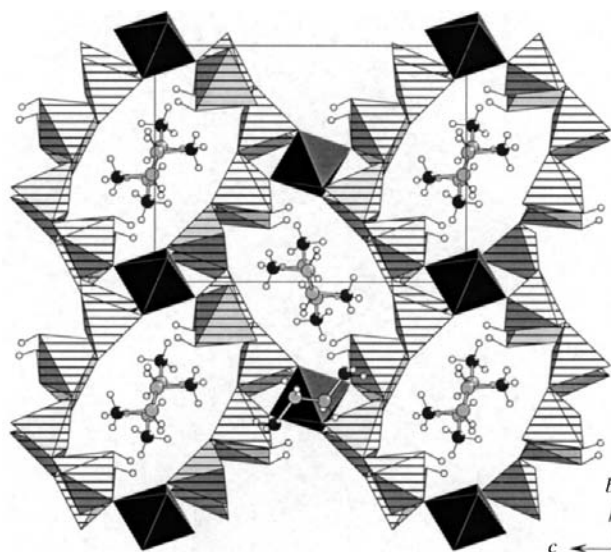


Figure 2

Polyhedral representation of the title structure viewed along the *a* axis. The GeO_6 octahedra are shown in black and the others in light grey. The two diprotonated ethylenediamine templates are in the middle of the ten-membered ring channels and the unprotonated one is shown on top of an octahedron.

5.8 Å along the *c* axis, measured by the O—O distances across the channels in each projection with a van der Waals radius of 1.4 Å subtracted.

As expected, the Ge—O distances are markedly longer [1.880 (3)–1.914 (3) Å] in the GeO₆ octahedron than in the GeO₄ tetrahedra [1.726 (3)–1.770 (3) Å] (Table 1). Two groups of Ge—O bonds are found in each of the GeO₅ trigonal bipyramids, *i.e.* three short equatorial bonds [1.770 (3)–1.790 (3) Å and two long axial bonds [1.810 (3) and 2.091 (3) Å]. Eight of the eleven unique O atoms are connected to two Ge atoms and one (O2) is connected to three Ge atoms. Finally, two O atoms (O6 and O9) are bound to one Ge atom and one H atom each, forming terminal hydroxyl groups. The presence of hydroxyl groups was confirmed independently by IR spectroscopy.

All three unique ethylenediamines are located across inversion centers. One of them is uncharged and the other two are diprotonated, acting as (enH₂)²⁺ counter-ions to the main framework. As expected, the diprotonated ethylenediamines (N1 and N2) are more strongly hydrogen bonded to the framework O atoms (Table 2). In the projection along each crystallographic axis, two different ethylenediamine molecules are located at the centers of the channels (Fig. 2).

The secondary building unit of the title compound, [Ge₉O₂₂(OH)₄], is similar to those found in the tetramethyl ammonium-templated [Ge₉O₁₄(OH)₁₂] (Tripathi *et al.*, 1999), en-templated [Ge₉O₁₉(OH)₂] (Jones *et al.*, 1992) and piperazine-templated [Ge₉O₁₈(OH)₄] (Li *et al.*, 1999) structures. All of the Ge₉ parallelepiped units are built by two pairs of tetrahedra, two pairs of trigonal bipyramids and one octahedron. Despite similarities in the gross composition, the secondary building units and framework charges among these germanates, there are several substantial geometrical and chemical differences. Only the tetramethylammonium-templated germanate is formed by isolated [Ge₉O₁₄(OH)₁₂] units (Tripathi *et al.*, 1999). The other three have corner-shared [Ge₉O₂₆H_{*n*}] units and contain one eight-ring and two ten-ring channels. Although the same template, ethylenediamine, was used in the syntheses of the title compound and an en-templated [Ge₉O₁₉(OH)₂] (Jones *et al.*, 1992), the geometrical arrangements of the tetrahedral pairs and the trigonal bipyramidal pairs within the parallelepiped Ge₉ units are quite different. In the title compound, the pairs sit in a *trans* position, related by an inversion center at a Ge1 octahedron, while in en-templated [Ge₉O₁₉(OH)₂], they sit in a *cis* position. On the other hand, the structure of the title compound is rather similar to that of the piperazine-templated [Ge₉O₁₈(OH)₄] (Li *et al.*, 1999), even though the structure-directing templates are different in these two compounds.

Thermogravimetric analysis showed a weight loss of 2.5% up to 548 K and 15% between 548 and 723 K. The latter weight loss is comparable with the loss of all the en molecules (15.6% wt). IR measurements of the compound heated to 723 K did not, in contrast to the fresh sample, show peaks attributable to amines. X-ray powder diffraction shows that the sample lost its crystallinity when heated to 723 K and GeO₂ was formed. The final experimental weight loss up

to 923 K was 21%, close to the calculated weight loss of 21.1%.

Experimental

The title compound was synthesized under hydrothermal conditions from a mixture of ethylenediamine (en), germanium dioxide, boric acid, pyridine, hydrofluoric acid and water in the molar ratio 12:1:0.5:40:2:0.5. GeO₂ (0.601 g) was first added to a mixture of distilled water (0.532 g) and pyridine (18.172 g). Ethylenediamine (4.139 g), then H₃BO₃ (0.180 g) and finally HF (0.233 g) were added slowly. The mixture was stirred continuously. The final pH was 10.6. The solution was sealed in a Teflon-lined autoclave (Parr) and heated at 443 K for 10 d under autogeneous pressure. The final product consisted of two distinct crystal morphologies, *i.e.* big prismatic crystals and spherical particles formed by small needle-like crystals. The large prismatic crystals (the title compound) were suitable for single-crystal X-ray diffraction. X-ray powder diffraction showed that the other compound, the small needle-like crystals, was monoclinic with space group *P*2₁/*n* and *a* = 13.605, *b* = 12.756, *c* = 9.687 Å, β = 92.258° and *V* = 1685 Å³.

Crystal data

(C ₂ H ₈ N ₂)(C ₂ H ₁₀ N ₂) ₂ [Ge ₉ O ₁₈ -(OH) ₄]	<i>D</i> _x = 2.961 Mg m ⁻³
<i>M</i> _r = 1193.68	Mo <i>K</i> α radiation
Monoclinic, <i>P</i> 2 ₁ / <i>n</i>	Cell parameters from 5000 reflections
<i>a</i> = 10.1958 (15) Å	<i>θ</i> = 2.86–25.98°
<i>b</i> = 9.9753 (10) Å	<i>μ</i> = 10.059 mm ⁻¹
<i>c</i> = 13.1655 (19) Å	<i>T</i> = 293 (2) K
β = 90.695 (17)°	Prism, colorless
<i>V</i> = 1338.9 (3) Å ³	0.060 × 0.040 × 0.038 mm
<i>Z</i> = 2	

Data collection

Stoe IPDS diffractometer	2077 reflections with <i>I</i> > 2σ(<i>I</i>)
Oscillation scans	<i>R</i> _{int} = 0.058
Absorption correction: numerical (<i>X</i> RED; Stoe & Cie, 1997a)	<i>θ</i> _{max} = 25.98°
<i>T</i> _{min} = 0.577, <i>T</i> _{max} = 0.721	<i>h</i> = -12 → 12
10 190 measured reflections	<i>k</i> = -11 → 12
2598 independent reflections	<i>l</i> = -16 → 16
	Intensity decay: none

Refinement

Refinement on <i>F</i> ²	<i>w</i> = 1/[σ ² (<i>F</i> _o ²) + (0.0315 <i>P</i>) ²]
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)] = 0.027	where <i>P</i> = (<i>F</i> _o ² + 2 <i>F</i> _c ²)/3
<i>wR</i> (<i>F</i> ²) = 0.058	(Δσ) _{max} = 0.041
<i>S</i> = 0.958	Δρ _{max} = 0.80 e Å ⁻³
2598 reflections	Δρ _{min} = -0.63 e Å ⁻³
204 parameters	Extinction correction: <i>SHELXL97</i> (Sheldrick, 1997)
H atoms treated by a mixture of independent and constrained refinement	Extinction coefficient: 0.00047 (18)

Table 1

Selected bond lengths (Å).

Ge1—O4	1.880 (3)	Ge3—O10	1.810 (3)
Ge1—O2	1.890 (3)	Ge3—O2	2.091 (3)
Ge1—O1	1.914 (3)	Ge4—O1	1.739 (3)
Ge2—O6	1.774 (3)	Ge4—O3 ⁱ	1.744 (3)
Ge2—O11	1.778 (3)	Ge4—O11 ⁱⁱ	1.752 (3)
Ge2—O7	1.790 (3)	Ge4—O8	1.770 (3)
Ge2—O3	1.874 (3)	Ge5—O10 ⁱⁱⁱ	1.726 (3)
Ge2—O2	1.957 (3)	Ge5—O4	1.743 (3)
Ge3—O9	1.770 (3)	Ge5—O5 ⁱⁱ	1.766 (3)
Ge3—O7	1.781 (3)	Ge5—O8	1.769 (3)
Ge3—O5	1.781 (3)		

Symmetry codes: (i) *x* - ½, ½ - *y*, *z* - ½; (ii) 1 - *x*, -*y*, -*z*; (iii) ½ + *x*, ½ - *y*, *z* - ½.

Table 2

Hydrogen-bonding geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O6—H1...O4	0.82	1.81	2.614 (4)	169
O9—H2...O1	0.82	1.83	2.641 (4)	170
N1—H1C...O3 ⁱ	0.89	1.87	2.750 (5)	172
N1—H1E...O9	0.89	2.27	2.965 (6)	135
N1—H1D...O6	0.89	1.96	2.828 (6)	166
N1—H1D...O11 ⁱ	0.89	2.45	2.826 (5)	106
N2—H2C...O9 ⁱⁱ	0.89	2.29	2.965 (7)	132
N2—H2D...N3	0.89	1.80	2.687 (9)	171
N2—H2E...O7 ⁱⁱⁱ	0.89	2.34	3.053 (6)	138
N2—H2E...O3 ⁱⁱⁱ	0.89	2.52	3.355 (6)	156
N3—H3C...O6 ^{iv}	0.90 (2)	2.23 (3)	3.081 (7)	158 (5)
N3—H3D...O5 ⁱⁱ	0.90 (2)	2.47 (4)	3.256 (7)	146 (5)

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

All H atoms could be located from the difference Fourier map and the two diprotonated ethylenediamines (N1 and N2) could be identified. The positions of all H atoms, except H3C and H3D whose positional parameters were refined (see Table 2 for distances) were then geometrically idealized and allowed to ride on their parent atoms (O—H = 0.82, C—H = 0.97 and N—H = 0.89 Å). The isotropic displacement parameters of all the H atoms were assigned to be 1.2 times of their parent atoms.

Data collection: *EXPOSE* (Stoe & Cie, 1997b); cell refinement: *CELL* (Stoe & Cie, 1997b); data reduction: *INTEGRATE* (Stoe & Cie, 1997b); program(s) used to solve structure: *SHELXS97* (Shel-

drick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Bergerhoff, 1996).

This project was supported by the Swedish Natural Science Research Council (NFR).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: OS1114). Services for accessing these data are described at the back of the journal.

References

- Bergerhoff, G. (1996). *DIAMOND*. Gerhard-Domagk Str. 1, 53121 Bonn, Germany.
- Conradsson, T., Zou, X.-D. & Dadachov, M. S. (2000). *Inorg. Chem.* **39**, 1716–1720.
- Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- Jones, R. H., Chen, J., Thomas, J. M., George, A., Hursthouse, M. B., Xu, R., Lu, S. & Yang, G. (1992). *Chem. Mater.* **4**, 808–812.
- Li, H., Eddaoudi, M. & Yaghi, O. M. (1999). *Angew. Chem. Int. Ed. Engl.* **38**, 653–655.
- Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
- Stoe & Cie (1997a). *XRED*. Version 1.09/Windows. Stoe & Cie GmbH, Darmstadt, Germany.
- Stoe & Cie (1997b). *Stoe IPDS Software Manual*. Stoe & Cie GmbH, Darmstadt, Germany.
- Tripathi, A., Young, V. G. Jr, Johnson, G. M., Cahill, C. L. & Parise, J. B. (1999). *Acta Cryst.* **C55**, 496–499.