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Lead germanium oxide

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The crystal structure of the title compound, $PbGeO_3$, shows a three-dimensional framework assembled by Pb_6 and Ge_6 structural building units. The Pb atom is coordinated by five O atoms in square-pyramidal coordination, while the Ge atom is tetrahedrally coordinated by four O atoms.

Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(Ge–O) = 0.019 Å
R factor = 0.050
wR factor = 0.164
Data-to-parameter ratio = 13.4

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

Over the past decades, the synthesis of new open-framework materials with either pure tetrahedral or mixed polyhedral microporous arrangements have received great attention due to their functional applications in catalysis, adsorption, ion-exchange and radioactive waste remediation. Not only aluminium and silicon, but also boron, gallium, phosphorus, germanium and transition metals have been choosen as open-framework building elements to synthesize new three-dimensional materials (Li *et al.*, 1998; Lin *et al.*, 2003; Plévert *et al.*, 2001; Xu, Fan, Chino *et al.*, 2004; Xu, Fan, Elangovan *et al.*, 2004). Compared with silicon, germanium not only adopts longer metal–oxygen distances (about 1.76 Å for Ge—O, 1.61 Å for Si—O), but also exhibits three types of coordination polyhedra, *viz.* GeO_4, GeO_5 and GeO_6. Therefore, the flexibility of the polyhedral model for germanium allows the formation of various open frameworks. In particular, germanium shows a great ability to form rings containing three metal atoms. Some germanates with such rings have already been reported (Bu *et al.*, 1998; Li *et al.*, 2000; Xu, Ogura & Okubo, 2004).

In this work, we have designed and synthesized the title compound, which features a three-dimensional framework derived from Pb_6 and Ge_6 structural building units. Both building units are connected by a new type of Ge_2Pb ring. The molecular structure of the title compound is shown in Fig. 1. The asymmetric unit of $PbGeO_3$ contains one formula unit. The O atoms in the open framework can be divided into three groups, *viz.* O_{2b}, O_{3b} and O_{4b}, where O_{2b} represents an O atom

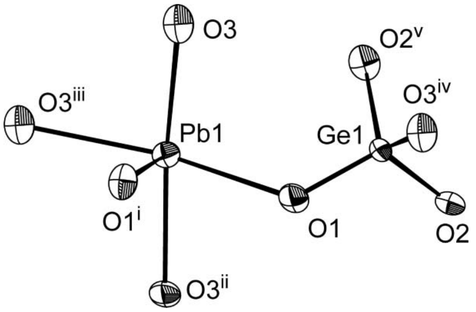

Figure 1
A fragment of the structure of the title compound. Displacement ellipsoids are drawn at the 70% probability level. Symmetry codes as in Table 1.

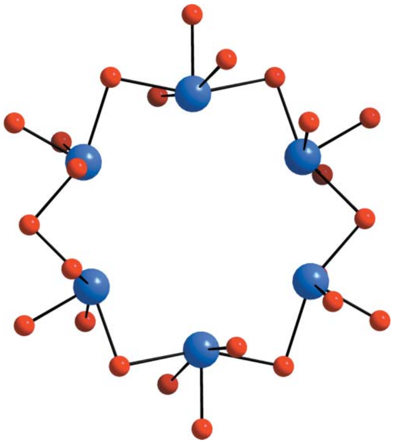

Figure 2
The structure of the Pb_6 building unit.

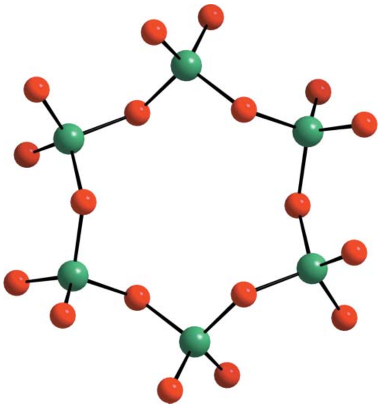

Figure 3
The structure of the Ge_6 building unit.

connected to two Ge atoms, O_{3b} is connected to one Ge and two Pb atoms, and O_{4b} to one Ge and three Pb atoms. The Pb atom is five-coordinated by two O_{3b} and three O_{4b} atoms.

As shown in Fig.2, six PbO_5 square pyramids form a Pb_6 ring structure by sharing corners, and six corner-sharing GeO_4 tetrahedra form a Ge_6 ring (Fig. 3). These two building units are connected by Ge_2Pb rings (two GeO_4 and one PbO_5), yielding a three-dimensional open framework with channels along the [111] direction (the rhombohedral symmetry axis) (Fig. 4).

The Pb—O and Ge—O bond lengths (Table 1) are in agreement with those found in previously reported lead and germanium compounds (Bu *et al.*, 1998; Shi *et al.*, 2002). The shortest Pb···Pb distance in the Pb_6 building unit is 3.6910 (8) Å, while Pb···Pb···Pb is 118.066 (12)°, which is very close to 120°.

Experimental

The title compound was hydrothermally synthesized from a mixture of GeO_2, H_3BO_3, $Pb(OAc)_2 \cdot 3H_2O$, diethylenetriamine, HF, pyridine and H_2O in the molar ratio 2:1:2:4:4:74:180. In a typical synthesis, GeO_2 (0.01 g) and H_3BO_3 (0.03 g) were dissolved in a mixed solvent of pyridine (2.84 g) and water (1.60 g), followed by the addition of $Pb(OAc)_2 \cdot 3H_2O$ (0.36 g) and diethylenetriamine (0.23 g) with constant stirring. Finally, hydrofluoric acid (0.1 ml, 40 wt %) was added to the above mixture. The mixture was kept in a 25 ml Teflon-lined steel autoclave at 443 K for 7 d. The autoclave was slowly cooled to room temperature, and then the product was filtered off, washed with distilled water and acetone, and dried at room temperature. Colourless block-shaped crystals were obtained. We have attempted to find crystals of better quality and to optimize the synthesis, but no better single crystals could be obtained.

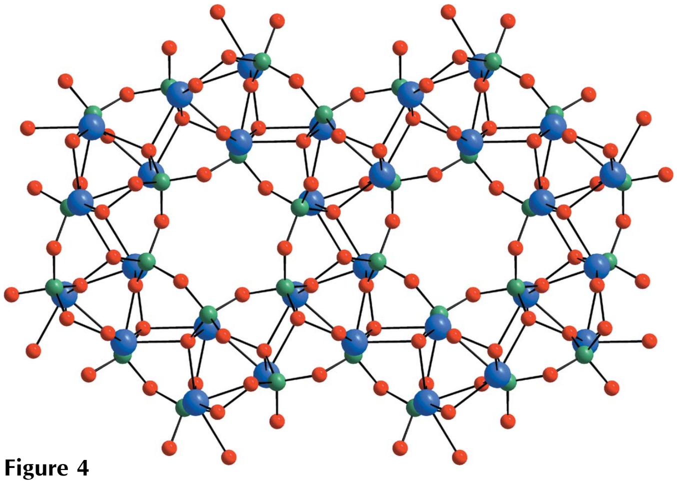

Figure 4
The three-dimensional open framework with channels, viewed along [111].

Crystal data

GeO_3Pb
$M_r = 327.78$
Rhombohedral, $R\bar{3}$
$a = 9.3282$ (2) Å
$\alpha = 113.4560$ (2)°
$V = 512.43$ (2) Å^3
$Z = 6$
$D_x = 6.373$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 57.82$ mm^{-1}
$T = 293$ (2) K
Block, colourless
0.04 × 0.03 × 0.03 mm

Data collection

Bruker APEX2 CCD diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
$T_{\min} = 0.206$, $T_{\max} = 0.276$ (expected range = 0.132–0.176)
2654 measured reflections
628 independent reflections
553 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.047$
$\theta_{\max} = 25.5°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.050$
$wR(F^2) = 0.164$
$S = 1.21$
628 reflections
47 parameters
$w = 1/[\sigma^2(F_o^2) + (0.1096P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 4.40$ e Å^{-3}
$\Delta\rho_{\min} = -3.49$ e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.0022 (8)

Table 1
Selected bond lengths (Å).

Pb1—O1$^{\rm i}$	2.270 (14)	Ge1—O1	1.723 (14)
Pb1—O3$^{\rm ii}$	2.416 (15)	Ge1—O3$^{\rm iv}$	1.725 (15)
Pb1—O1	2.458 (14)	Ge1—O2	1.779 (15)
Pb1—O3	2.551 (16)	Ge1—O2$^{\rm v}$	1.781 (15)
Pb1—O3$^{\rm iii}$	2.590 (15)		

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

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The highest peak in the difference map is located 1.08 (2) Å from Pb1, while the deepest hole is 1.13 (3) Å from Pb1.

Data collection: *APEX2* (Bruker, 2005); cell refinement: *SAINT* (Bruker, 2002); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997*a*); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997*a*); molecular graphics: *SHELXTL* (Sheldrick, 1997*b*); software used to prepare material for publication: *SHELXTL*.

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