$Z = 8$
$D_x = 3.967$ Mg m^{-3}

Room temperature
Cube
$0.25 \times 0.22 \times 0.22$ mm
Colourless

Data collection

Rigaku AFC-6*A* diffractometer
2θ-ω scans
Absorption correction: by integration from crystal shape
$T_{\min} = 0.453$, $T_{\max} = 0.521$
4608 measured reflections
134 independent observed reflections

134 observed reflections $[|F_o| \geq 3\sigma(|F_o|)]$
$R_{\text{int}} = 0.019$
$\theta_{\max} = 32.5°$
$h = -12 \rightarrow 12$
$k = -12 \rightarrow 12$
$l = 0 \rightarrow 12$
3 standard reflections
monitored every 100 reflections
intensity variation: $\leq 1.4\%$

Refinement

Refinement on F
$R = 0.031$
$wR = 0.045$
$S = 9.85$
134 reflections
17 parameters
$w = 1/\sigma^2(|F_o|)$
$(\Delta/\sigma)_{\max} = 0.44$
$\Delta\rho_{\max} = 1.3$ e Å^{-3}
$\Delta\rho_{\min} = -1.2$ e Å^{-3}

Extinction correction: Zachariasen (1968)
Extinction coefficient: $1.86\,(4) \times 10^{-4}$
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV) and Tokonami (1965) for O atoms

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{\text{eq}} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	Wyckoff position	x	y	z	U_{eq}
Nb	8(c)	0.14028 (3)	x	x	0.0074
O(1)	8(c)	−0.1090 (4)	x	x	0.0084
O(2)	24(g)	0.1247 (3)	x	0.3601 (3)	0.0112
Li	24(g)	0.3782 (5)	x	0.1046 (6)	0.017 (1)

Table 2. *Selected geometric parameters* (Å, °)

Nb—Nb$^{\text{iii}}$	3.3381 (7)	Nb—Li	2.846 (4)
Nb—O(1$^{\text{i}}$)	2.130 (4)	Nb—O(1$^{\text{ii}}$)	2.130 (4)
Nb—O(1$^{\text{iii}}$)	2.130 (4)	Nb—O(2)	1.858 (3)
Nb—O(2$^{\text{iv}}$)	1.858 (3)	Nb—O(2$^{\text{v}}$)	1.858 (3)
Li—O(2$^{\text{iv}}$)	2.145 (5)	Li—O(2$^{\text{v}}$)	2.145 (5)
Li—O(2$^{\text{ix}}$)	2.057 (6)	Li—O(1$^{\text{vi}}$)	2.414 (7)
Li—O(2$^{\text{vii}}$)	2.095 (5)	Li—O(2$^{\text{viii}}$)	2.095 (5)
O(1)—O(1$^{\text{iii}}$)	2.593 (5)		
O(1$^{\text{i}}$)—Nb—O(1$^{\text{ii}}$)	75.0 (1)	O(1$^{\text{i}}$)—Nb—O(2)	92.6 (1)
O(1$^{\text{i}}$)—Nb—O(2$^{\text{iv}}$)	164.2 (1)	O(1$^{\text{i}}$)—Nb—O(2$^{\text{v}}$)	92.6 (1)
O(2)—Nb—O(2$^{\text{iv}}$)	97.8 (1)	O(2$^{\text{iv}}$)—Li—O(2$^{\text{v}}$)	81.5 (2)
O(2$^{\text{iv}}$)—Li—O(2$^{\text{ix}}$)	93.8 (2)	O(2$^{\text{iv}}$)—Li—O(1$^{\text{vi}}$)	88.2 (2)
O(2$^{\text{iv}}$)—Li—O(2$^{\text{vii}}$)	92.7 (2)	O(2$^{\text{iv}}$)—Li—O(2$^{\text{viii}}$)	166.5 (3)
O(2$^{\text{ix}}$)—Li—O(1$^{\text{vi}}$)	177.3 (2)	O(2$^{\text{ix}}$)—Li—O(2$^{\text{vii}}$)	98.8 (2)
O(2$^{\text{vii}}$)—Li—O(1$^{\text{vi}}$)	79.3 (2)	O(2$^{\text{vii}}$)—Li—O(2$^{\text{viii}}$)	90.2 (2)
Nb—O(1$^{\text{i}}$)—Nb$^{\text{iii}}$	103.2 (2)		

Symmetry codes: (i) $x, -x, -x$; (ii) $-x, x, -x$; (iii) $-x, -x, x$; (iv) z, x, x; (v) x, z, x; (vi) $\frac{1}{2}+x, \frac{1}{2}+x, \frac{1}{2}+x$; (vii) $\frac{1}{2}+x, \frac{1}{2}-x, \frac{1}{2}-z$; (viii) $\frac{1}{2}-x, \frac{1}{2}+x, \frac{1}{2}-z$; (ix) $\frac{1}{2}-x, \frac{1}{2}-x, z-\frac{1}{2}$.

Among the 4608 measured reflections within the hemisphere, 2283 reflections were considered observed. Refinements by full-matrix least squares on these observed reflections were carried out with corrections for absorption and extinction. 134 reflections were obtained from the 2283 corrected reflections by averaging the equivalent reflections. The 134 independent reflections were used in the final refinement by full-matrix least squares on F. All calculations were carried out using the *UNICS*III program system (Sakurai & Kobayashi, 1979) and the full-matrix least-squares program *RADIEL* (Coppens, Guru Row, Leung, Stevens, Becker & Yang, 1979).

Lists of structure factors and anisotropic displacement parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71587 (4 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: OH1036]

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$Bi_{12}(Bi^{III}_{0.5}Tl^{III}_{0.5})O_{19.50}$

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Abstract

The structure of the sillenite-type title compound has been determined at room temperature by single-

crystal neutron diffraction. $Tl^{III}O_4$ tetrahedra are replaced statistically by $Bi^{III}O_3$ groups, statistically oriented with respect to the threefold axis. The distances in the TlO_4 tetrahedra and BiO_3 groups are 2.116 (9) and 2.02 (2) Å, respectively.

Comment

The present structure investigation was performed as part of a detailed study of sillenite-type crystals. Their general chemical formula is usually expressed as $Bi_{12}MO_{20}$, where M in stoichiometric sillenites represents tetravalent atoms, *e.g.* Si, Ge *etc.*, or statistically distributed atoms such as (Fe^{III},P^{V}). For non-stoichiometric sillenites, $Bi_{12}MO_{20\pm x}$, there are several structural models (Radaev, Simonov, Kargin & Skorikov, 1992) which depend on the type of M atom occupying the 2(*a*) tetrahedral sites of space group *I*23. It was established (Radaev, Muradyan, Kargin, Sarin, Rider & Simonov, 1989; Radaev, Muradyan & Simonov, 1991) that in Ga, Fe and Zn sillenites, all Bi atoms are trivalent. $Ga^{III}O_4$, $Fe^{III}O_4$ or $Zn^{II}O_4$ tetrahedra and $Bi^{III}O_3$ groups are statistically distributed over tetrahedral voids in the structure. When the effective valence of M exceeds four, for instance in V sillenite (Radaev, Muradyan, Sarin, Kanepit, Yudin, Marin & Simonov, 1989), the electroneutrality is achieved by additional O atoms in 6(*b*) sites of space group *I*23.

The title compound is a sillenite with one of the largest M atoms. Its crystal structure and the oxidation states of Tl and Bi were of interest to us.

Refinement of the standard structural model (Abrahams, Jamieson & Bernstein, 1967; Abrahams, Bernstein & Svensson, 1979) using anisotropoic displacement parameters [$T = \exp(-\sum_i\sum_j\beta_{ij}h_ih_j)$] led to $wR = 2.27$, $R = 2.42\%$ and $S = 2.29$. Checking atomic site occupancies revealed vacancies at the O(3) site only. These O atoms form coordination tetrahedra with M cations (Fig. 1). By refinement of the occupancy factor q of O(3) the agreement factors were reduced to $wR = 1.98$, $R = 2.21\%$ and $S = 1.99$ at $q[O(3)] = 0.88$ (2). This means that the chemical formula of the Tl sillenite is $Bi_{12}MO_{19.50}$. It results directly from valence balance that the valence of M = (Bi,Tl) is three. Moreover, the value of the occupancy factor q[O(3)] also indicates that only three and a half out of four O(3) atoms forming the tetrahedral environment of the M site are, in fact, present. In other words, half of all M tetrahedra lack one vertex. Similar results have been found for Ga and Fe sillenites (Radaev, Muradyan, Kargin, Rider & Simonov, 1989; Radaev, Muradyan & Simonov, 1991). Therefore, we propose that Tl^{III} atoms occupy half the 2(*a*) sites and are tetrahedrally coordinated by O(3) atoms, whereas Bi^{III} atoms in 2(*a*) sites have ψ-tetrahedral coordination, BiO_3E, with three O(3) atoms and a lone-electron pair, E, in one vertex. Because of the similar neutron-scattering lengths of Bi and Tl it is impossible to determine reliably the ratio of these atoms in 2(*a*). Therefore, the mean scattering length of M was assumed to be 8.655 fm, which corresponds to the aforementioned model with 50:50 population of 2(*a*) by Tl and Bi.

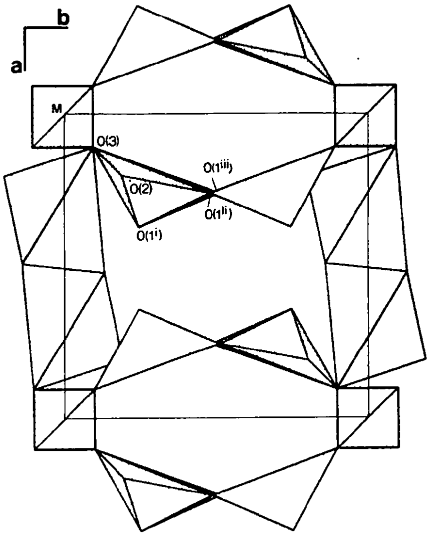

Fig. 1. A projection of the structure of an ideal sillenite on the (001) plane. BiO_5 polyhedra connect translationally identical $MO(3)_4$ tetrahedra.

The value of the isotropic displacement parameter of the M atom was rather large: $B_M = 2.22$ (7) Å^2. Besides, in residual nuclear-density maps near 2(*a*), positive peaks of 1.3 fm Å^{-3} (background value $|\Delta\rho| \geq 0.2$ fm Å^{-3}) were observed on the threefold axis in the direction towards the O(3) atoms. The peaks of positive residual nuclear density indicate that, as in Ga, Fe and Zn sillenites, the Bi_M atom is displaced from the origin towards the O-atom vacancy. It was also found that, unlike Ga, Fe and Zn sillenites, the displacement ellipsoid of O(3) is extended along the M—O(3) direction [$\sigma_{\parallel} = 0.185$ (4) and $\sigma_{\perp} = 0.139$ (5) Å]. The elongated shape of the ellipsoid may be accounted for by statistical occupation of two sites by oxygen depending on whether it forms TlO_4 tetrahedra or BiO_3 groups, which are of different sizes. Finally, the following model was refined: with Tl atoms occupying 50% of 2(*a*) sites, the atoms Bi_M, occupying the other 50% of tetrahedral M voids, are displaced from the origin towards the O-atom vacancy. O(3) is split into $O(3)_{Tl}$ and $O(3)_{Bi}$ which are thought to be coordinated to Tl and Bi_M, respectively. Each Tl atom has a tetrahedral environment formed by $O(3)_{Tl}$ atoms; the occupancy factor of $O(3)_{Tl}$ is fixed at 0.5. Bi_M atoms are coordinated by three $O(3)_{Bi}$ atoms; the occupancy factor of $O(3)_{Bi}$ is fixed at $0.88 - 0.5 = 0.38$.

The refinement of this model led to $wR = 1.45$, $R = 1.72\%$ and $S = 1.47$. The refinement of the positional parameters of Bi_M as well as those of $O(3)_{Tl}$ and $O(3)_{Bi}$ was carried out using the step-by-step scanning technique (Muradyan, Radaev & Simonov, 1989). It should be noted that the displacement parameters of Tl, Bi_M, $O(3)_{Tl}$ and $O(3)_{Bi}$ cannot be determined very precisely because of a strong correlation between them, and may contain larger errors than listed in Table 1.

The proposed structural model of Tl sillenite is very similar to that of the Ga and Fe sillenites. As in Ga, Fe and Zn sillenites, Bi_M atoms seem to be displaced towards O(3) vacancies which leave space for the lone-electron pairs of the Bi_M^{III} atoms. The mean M—O(3) interatomic distances in Ga, Fe and Zn sillenites are 1.879–1.947 Å. Refined interatomic distances Bi_M—O(3) in these sillenites are 2.018–2.091 Å with bonding angles O(3)—Bi_M—O(3) of 98.9°. In the Tl sillenite the mean M—O(3) distance is 2.066 (3) Å. Separately refined interatomic distances are $Bi_M—O(3)_{Bi} = 2.02\,(2)$ Å × 3 [angle $O(3)_{Bi}—Bi_M—O(3)_{Bi} = 100.0\,(2)°$] and $Tl—O(3)_{Tl} = 2.116\,(9)$ Å × 4.

Comparison of the interatomic distances of the ideal Ge sillenite (Radaev, Simonov, Kargin & Skorikov, 1992) and sillenites with O(3) vacancies (Table 2) indicates a remarkable shortening of the Bi—O(3) bond in the latter. The stability of sillenite structures results not only from changes in the anionic sublattice, but also from shifts of the Bi atoms in 24(f). Bi-atom disordering with respect to a mean position is compensated for by the displacement parameters of the Bi atom whose ellipsoid is extended along the O(3)—O(1^{ii}) direction (Table 3).

Experimental

Single crystals were obtained from α-Bi_2O_3 and Tl_2O_3 (99.5% pure) with 30 wt % NaOH as solvent by the hydrothermal method at 523-573 K and pressure of up to 1000 kg cm^{-2}. Crystallization was carried out by oriented seed of $Bi_{12}GeO_{20}$.

Crystal data

$Bi_{12}(Bi_{0.5}Tl_{0.5})O_{19.50}$
$M_r = 3026.4$
Cubic
$I23$
$a = 10.221\,(20)$ Å
$V = 1068\,(6)$ Å^3
$Z = 2$
$D_x = 9.41$ Mg m^{-3}

Neutron radiation
$\lambda = 1.167$ Å
Cell parameters from 15 reflections
$\theta = 20$-$30°$
$\mu = 0.0004$ mm^{-1}
$T = 293$ K
5.0 × 4.0 × 2.0 mm
Dark red

Data collection

Syntex $P\bar{1}$ diffractometer
$\theta/2\theta$ scans
Absorption correction: none
2806 measured reflections
333 independent reflections
306 observed reflections [$I \geq 3\sigma(I)$]

$R_{int} = 0.06$
$\theta_{max} = 67°$
$h = 0 \rightarrow 16$
$k = -16 \rightarrow 16$
$l = -16 \rightarrow 16$
1 standard reflection
frequency: 60 min
intensity variation: < 3%

Refinement

Refinement on F
$R = 0.0172$
$wR = 0.0145$
$S = 1.47$
306 reflections
32 parameters
$w = 1/\sigma^2(F_o)$
$(\Delta/\sigma)_{max} = 5$

$\Delta\rho_{max} = 0.2$ fm Å^{-3}
$\Delta\rho_{min} = -0.2$ fm Å^{-3}
Extinction correction: Becker & Coppens (1974) type II
Extinction coefficient: $r^* = 2.5 \times 10^{-7}$
Atomic scattering factors from Sears (1984)

Table 1. *Site occupancy factors, fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$B_{eq} = (4/3)\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	Multiplicity	Occupancy	x	y	z	B_{eq}
Bi	24(f)	1.0	0.17652 (5)	0.31921 (5)	0.01454 (5)	1.122 (8)
Tl	2(a)	0.5	0	0	0	0.93 (6)
Bi_M	8(c)	0.125	−0.0175 (5)	x	x	1.9 (2)
O(1)	24(f)	1.0	0.13490 (8)	0.24819 (8)	0.48821 (8)	1.12 (1)
O(2)	8(c)	1.0	0.1877 (1)	x	x	1.41 (2)
$O(3)_{Tl}$	8(c)	0.5	0.8805 (5)	x	x	1.05 (7)
$O(3)_{Bi}$	8(c)	0.38	0.8930 (9)	x	x	3.3 (2)

Note: Bi_M is Bi near M site 2(a); Tl is on M site; O(3) is split and thought to be coordinated to Bi_M and Tl, respectively.

Table 2. *Interatomic distances* (Å) *in* Bi *polyhedra of some sillenites*

	Ge	Fe	Tl
Bi—O(1^i)	2.072 (1)	2.0675 (8)	2.0645 (9)
Bi—O(1^{ii})	2.221 (1)	2.2434 (8)	2.244 (1)
Bi—O(1^{iii})	2.622 (1)	2.6230 (8)	2.597 (1)
Bi—O(2)	2.2146 (6)	2.2201 (5)	2.2254 (6)
Bi—O(3^{iv})	2.6241 (8)	2.5735 (7)	2.527 (3) for $O(3)_{Tl}$ 2.599 (6) for $O(3)_{Bi}$

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

Table 3. *Root-mean square displacements* (Å) *of the* Bi *atom in some sillenites*

Direction towards	Ge	Fe	Tl
O(1^i)	0.081	0.095	0.095
O(1^{ii})	0.099	0.148	0.142
O(1^{iii})	0.100	0.125	0.122
O(2)	0.095	0.109	0.115
O(3)	0.100	0.151	0.143

Neutron diffraction data were collected at the VVRC reactor of a branch of the L. Y. Karpov Institute of Physical Chemistry at Obninsk, Kaluga Region, Russia; $\lambda = 1.167$ Å, $(\sin\theta/\lambda)_{max} = 0.79$ Å^{-1}. The data were averaged in point group $m\bar{3}$. All calculations were performed with the *PROMETHEUS* program system (Zucker, Perenthaler, Kuhs, Bachman & Schulz, 1983). The atomic neutron-scattering lengths were $b_{Bi} = 8.5256$, $b_{Tl} = 8.785$ and $b_O = 5.805$ fm (Sears, 1984).

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Lists of structure factors and anisotropic displacement parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71748 (7 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: SH1073]

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P_2Se_5

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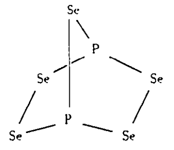
Abstract

The structure of 2,3,5,6,7-pentaselena-1,4-diphosphabicyclo[2.2.1]heptane is built from separate norbornane-like molecules with Se atoms in the bridging position. The P—Se bond lengths fall in the range 2.234 (2)–2.254 (2) Å and the Se—Se bond lengths are 2.387 (1) and 2.390 (1) Å.

Comment

A view of the molecule (I) is shown in Fig. 1. The X-ray structure analysis confirms the constitution of the molecule deduced from ^{31}P and ^{77}Se NMR data (Blachnik, Lönnecke & Tattershall, 1991) as 2,3,5,6,7-pentaselena-1,4-diphospabicyclo[2.2.1]heptane, a P—Se norbornane which consists of two nearly regular five-membered rings. A view of the structure along [100] is shown in Fig. 2. The P_2Se_5 molecules form approximately hexagonal close-packed layers parallel to (010). These layers are shifted successively by $\vec{a}/2$ or $\vec{b}/2$, leading to a coordination number of ten for each P_2Se_5 molecule. The corresponding interlayer distances are 5.02 and 5.10 Å, respectively.



(I)

The P—Se bond distances are found in the range 2.234 (2)–2.254 (2) Å and correspond to the single-

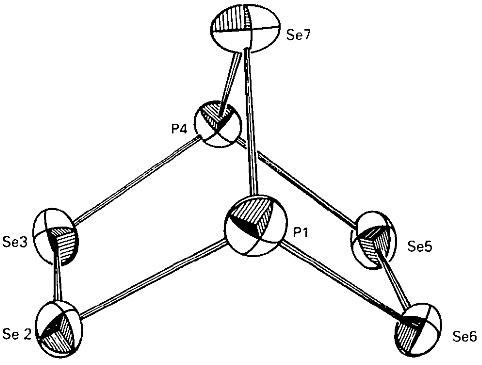


Fig. 1. Structure of the P_2Se_5 molecule.

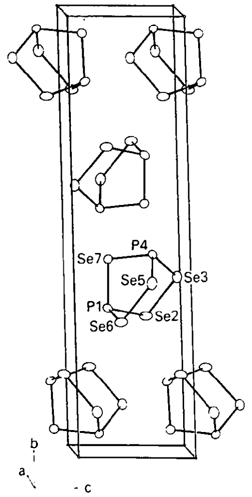


Fig. 2. Structure of P_2Se_5 viewed along [100].