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Natural monoclinic $AgPb(Bi_2Sb)_3S_6$, an Sb-rich gustavite

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The crystal structure of the Sb-rich variety of the mineral gustavite, silver lead tris(dibismuth/antimony) hexasulfide, $AgPb(Bi_2Sb)_3S_6$, consists of blocks of diagonal chains of four octahedra, *viz.* *M*1*a* (Bi), *M*2*a* (Sb/Bi), *M*2*b* (Bi/Sb) and *M*1*b* (Ag), separated by Pb atoms in a trigonal prismatic coordination. Two marginal octahedral sites, *M*1*a* and *M*1*b*, where the gustavite substitution $Ag^+ + Bi^{3+} = 2Pb^{2+}$ takes place, are formed by Bi and Ag, respectively. Two central octahedra, *M*2*a* and *M*2*b*, where the $Bi^{3+} = Sb^{3+}$ substitution takes place, are formed by two mixed Bi/Sb sites with different occupancies of Bi and Sb. The alternating occupation of the *M*1 site by Bi and Ag atoms (which thus creates two distinct sites *M*1*a* and *M*1*b*) results in the monoclinic space group $P2_1/c$. A statistical distribution of Ag/Bi in the *M*1 position (one mixed Ag/Bi site) was reported for synthetic gustavite, resulting in the orthorhombic space group *Cmcm*.

Comment

Gustavite, $AgPbBi_3S_6$, a member of the lillianite homologous series, was discovered in the cryolite deposit at Ivigtut, Greenland, and described and named by Karup-Møller (1970). The mineral crystallized in an orthorhombic centred cell with dimensions $a = 13.55$ (3) Å, $b = 19.44$ (3) Å and $c = 4.11$ (1) Å. Harris & Chen (1975) found that natural gustavite from Bernic Lake and Camsell River deposits in Canada was monoclinic; they reported a $P2_1/c$ cell with $a = 7.077$ (7) Å, $b = 19.566$ (12) Å, $c = 8.272$ (8) Å and $\beta = 107.18$ (9)°, and observed that if in this cell the relatively weak $l = 2n + 1$ reflections were ignored, the remaining reflections could be indexed in a pseudo-cell with space-group symmetry *Bbmm* and cell parameters almost identical to those of Karup-Møller. The geometric features of the lillianite structures and the crystal chemistry of the lillianite homologues were described in detail by Makovicky & Karup-Møller (1977*a*). They concluded that what was originally interpreted as a supercell of the centred orthorhombic cell described by Karup-Møller was a twin of the monoclinic true cell, identical to that described by Harris & Chen (1975). Attempts at the structure determination of monoclinic natural gustavite by Steins *et al.* (1991) were unsatisfactory. Later, Bente *et al.* (1993) published the structure of a synthetic gustavite which, unlike natural gustavite, is orthorhombic, space group *Cmcm*, with cell parameters $a = 4.077$ (2) Å, $b = 13.477$ (7) Å and $c = 19.88$ (2) Å.

The lillianite homologous series is an example of the accretional extensive series (Ferraris *et al.*, 2004). Members of this series are Pb–Bi–Ag sulfosalts with structures consisting of alternating layers of PbS (NaCl) archetype cut parallel to $(311)_{PbS}$. The overlapping octahedra of adjacent mirror-related layers are replaced by bicapped trigonal coordination prisms of PbS_{6+2}, with the Pb atoms positioned on the mirror planes (Otto & Strunz, 1968). Distinct homologues differ in the thickness of the PbS-like layers and this is expressed as the number of octahedra (*N*) in the chain that runs diagonally across an individual archetypal layer (block) (Makovicky & Karup-Møller, 1977*a*.) Each lillianite homologue can be denoted as $^{N1,N2}L$, where *N*1 and *N*2 are the values of *N* for two alternating (neighbouring) sets of layers (chains of octahedra) separated by trigonal prisms of Pb. Natural lillianite homologues start at $N = 4$. In the Ag-free subsystem Pb–Bi–S, $^{4,4}L$ ($Pb_3Bi_2S_5$, lillianite, xilingolite) and $^{7,7}L$ ($Pb_6Bi_2S_9$, heyrovskyite, aschalmamite) are known. With the $Ag^+ + Bi^{3+} = 2Pb^{2+}$ substitution in octahedral layers, apart from $^{4,4}L$ (gustavite), there are also $^{4,7}L$ (vikingite), $^{4,8}L$ (treasurite), $^{5,9}L$ (eskimoite) and $^{11,11}L$ (ourayite), as well as the disordered combination of different proportions of slabs ^4L and ^7L (a so-called schirmerite) (Makovicky & Karup-Møller, 1977*b*).

The structure of the gustavite reported here consists of 11 independent sites. The five metal positions include one Pb site (*M*3), one Ag site (*M*1*b*), one Bi site (*M*1*a*) and two mixed Bi/Sb sites (*M*2*a* with dominant Sb and *M*2*b* with dominant Bi), and there are six S sites (S1*a*, S1*b*, S2, S3, S4*a* and S4*b*). The numbering scheme of the sites used here is that used by Berlepsch *et al.* (2001) for the structure of xilingolite (monoclinic $Pb_3Bi_2S_6$) and by Pinto *et al.* (2006) for Ag-free lillianite (orthorhombic $Pb_3Bi_2S_6$). All of the atoms are in a general Wyckoff position 4*e* of the space group $P2_1/c$ (Fig. 1). The structure of gustavite is built of alternating slabs of PbS archetype cut parallel to $(311)_{PbS}$, and each layer is $N = 4$ octahedra thick (Fig. 2). Each layer contains the sequence of central atoms *M*1*a* (Bi), *M*2*a* (Sb/Bi), *M*2*b* (Bi/Sb) and *M*1*b* (Ag). The slabs are separated by rods of Pb atoms in a bicapped trigonal prismatic coordination approximately parallel to (010) at $y \simeq 0.25$ and 0.75.

The standing bicapped trigonal prism (site *M*3) is occupied by Pb and is situated on the plane of the unit-cell twinning of the PbS-type (octahedral) structure. It is characterized by Pb—S bond distances between 2.830 (5) and 3.311 (8) Å, typical of Pb (Table 1; atom symmetry codes in the following discussion correspond with those in Table 1). The shortest bonds of 2.830 (5) and 2.841 (7) Å are to two symmetry-related S3 atoms, which form the vertices of the marginal octahedral sites *M*1*a* and *M*2*b* where the Ag–Bi substitution takes place, and are similar to the equivalent distances in heyrovskyite, xilingolite and lillianite. The distances to the

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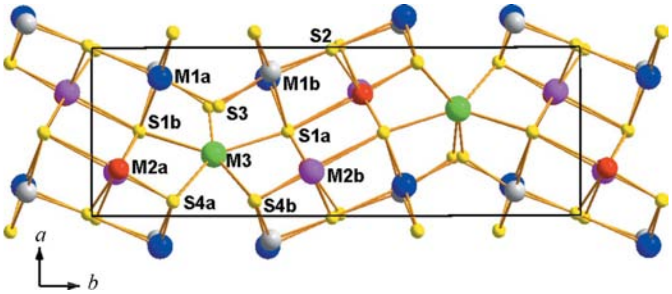

Figure 1
The crystal structure of gustavite, a monoclinic $^{4,4}L$ homologue of the lillianite homologous series, viewed along the *c* axis. *M*3 is Pb in a bicapped trigonal prismatic coordination, coordination number 8. *M*1*a* is Bi, *M*1*b* is Ag, *M*2*a* is Sb/Bi (Sb is the major component) and *M*2*b* is Bi/Sb (Bi is the major component), all in octahedral coordination, coordination number 6.

capping atoms S1*a* and S1*b*, which are also part of the marginal octahedra, are 3.101 (8) and 3.141 (8) Å, respectively, which are very similar to the same distances in xilingolite [3.093 (12) Å] but differ significantly from that in lillianite [3.416 (4) Å]. The longest distances [3.311 (8) and 3.307 (6) Å] are to the S4*a* and S4*b* atoms forming the base edge of the most distorted site *M*1*b* (Ag). The calculated bond valence (Brown & Altermatt, 1985) for this pure Pb site is 1.974 (15) v.u. The anisotropic displacement parameters attain the largest values along [010].

The remaining four *M* sites are all in a slightly distorted octahedral coordination. *M*1*a* and *M*1*b* are marginal octahedral sites closest to the plane of unit-cell twinning where the Ag–Bi substitution takes place. *M*1*a* is the least distorted octahedral site and is occupied by Bi, with *M*1*a*—S distances between 2.609 (8) and 3.177 (8) Å. The shortest distance is to atom S3, which is the vertex of the octahedron and coordinates to the Pb atom in the trigonal prismatic site, and the longest distance is to atom $\mathrm{S}2^{\mathrm{v}}$, which is the opposite vertex and coordinates to the Bi/Sb mixed site. The base of the octahedron, running parallel to (150), is almost rectangular, with two distances to atoms $\mathrm{S}4a^{\mathrm{iv}}$ and $\mathrm{S}4b^{\mathrm{ii}}$ of 2.725 (8) and 2.739 (6) Å, respectively, and two longer distances to atoms $\mathrm{S}1a^{\mathrm{iii}}$ and S1*b* of 2.975 (6) and 2.980 (8) Å, respectively, with the Bi atom displaced away from the centre of the base towards the S4 atoms. The angle between the central atom and the two S atoms at the vertices is 175.2 (2)°, much closer to 180° than in the case of the more distorted site *M*1*b*. The calculated bond valence for Bi is 2.89 (3) v.u. The atomic displacement parameters of the Bi atom show no positional disorder and are nearly isotropic, unlike the other marginal octahedral site *M*1*b*.

*M*1*b* is the most distorted octahedral site and is occupied by Ag. The *M*1*b*—S distances are between 2.495 (8) and 3.359 (8) Å. Similar to the *M*1*a* site, the shortest distance is to atom S3 at the vertex of the octahedron and coordinating to the Pb atom in the trigonal prismatic site (towards the margin of the slab of octahedra). The distance to atom S2 at the opposite vertex and coordinating to the Bi/Sb mixed site is 2.606 (9) Å. The base of the octahedron shows the largest distortion. It has a trapezoidal shape, with two shorter bonds of 2.708 (6) and 2.795 (9) Å to atoms $\mathrm{S}4a^{\mathrm{ii}}$ and $\mathrm{S}4b^{\mathrm{iv}}$, respectively, and two longer bonds of 3.359 (8) and 3.314 (6) Å to atoms S1*a* and $\mathrm{S}1b^{\mathrm{iii}}$, respectively, with the Ag atom displaced away from the centre of the base towards the S4 atoms. The angle between the central atom and the two S atoms at the vertices is 165.4 (2)°, significantly different from the ideal value of 180° and considerably less than in the case of the *M*1*a* site. The calculated bond valence for Ag is 1.162 (12) v.u. The atomic displacement parameters of the Ag atom are large (more than double those of Bi in the *M*1*a* site) and highly anisotropic, showing strong positional disorder, roughly along the line between atoms S1*a* and $\mathrm{S}4b^{\mathrm{iv}}$ across the base of the octahedron. Augmented atomic displacement parameters of Ag have been observed in other sulfosalt structures, such as diaphorite (Armbruster *et al.*, 2003).

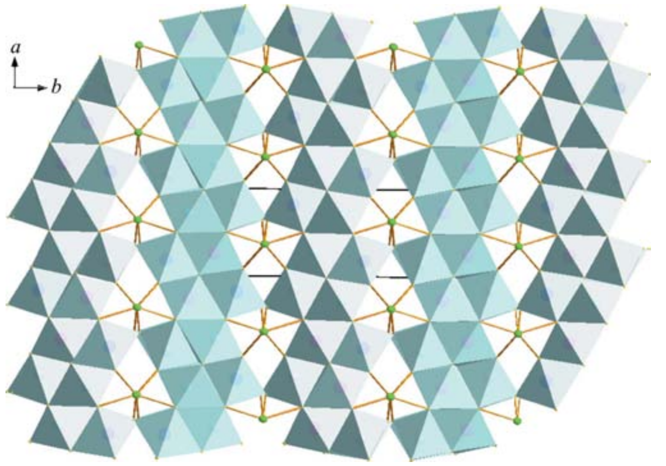

Figure 2
The arrangement of the parallel layers of diagonal chains of four octahedra in the structure of gustavite, viewed along the *c* axis. Neighbouring blocks of octahedral layers are separated by Pb atoms in trigonal prismatic coordination.

The octahedra in the central part of the octahedral layer are formed by two mixed Sb/Bi sites, *M*2*a* and *M*2*b*. The mixed Sb/Bi site *M*2*a*, in which the Sb fraction is 0.650 (10), has a slightly distorted Sb-like coordination with three short *M*1*a*—S bonds [2.540 (8), 2.579 (6) and 2.608 (8) Å] opposed by much longer *M*1*a*—S distances [3.139 (9), 3.159 (6) and 3.337 (8) Å], revealing an active and symmetrically placed lone electron pair. The shortest distance of 2.540 (8) Å to the vertex formed by atom S4*a* is counterbalanced across the lone electron pair micelle by the distance of 3.337 (8) Å to the opposite vertex formed by atom $\mathrm{S}1a^{\mathrm{ix}}$, which is the capping atom of the trigonal prismatic Pb atom. The base of the octahedron is nearly rectangular, with two distances of 2.579 (6) and 2.608 (8) Å to atoms S1*b* and $\mathrm{S}1a^{\mathrm{iii}}$, respectively, and two much longer distances of 3.139 (9) and 3.159 (6) Å to two symmetry-related S2 atoms, with the central atom displaced from the centre of the rectangle towards atoms $\mathrm{S}1a^{\mathrm{iii}}$ and S1*b*. The angle between the central atom and the two S atoms at the vertices is 174.56 (19)°. The calculated bond valence for Sb is 2.54 (2) v.u., for Bi it is 3.32 (3) v.u. and for this mixed site it is 2.93 v.u., which is close to the theoretical value of 3. The atomic displacement parameters of this Sb/Bi site show the smallest displacement of all the metal sites, with a slight anisotropy in the direction perpendicular to (010).

The last octahedral site, *M*2*b*, is a mixed Bi/Sb site, with a Bi fraction of 0.739 (12), and *M*2*b*—S distances between 2.563 (8) and 3.251 (8) Å. The lone electron pair of Bi is less active than that of Sb, which is reflected in the shorter bond of 3.251 (8) Å across the lone electron pair micelle to the vertex atom S1$b^{\rm vi}$, compared with 3.337 (8) Å to the equivalent S atom of the Sb-dominant *M*2*a* site. Accordingly, atom S4*b* at the opposite vertex shows the shortest distance of 2.563 Å. The base is nearly rectangular and the central atom is displaced from the centre, with two shorter bonds of 2.746 (7) and 2.776 (9) Å to two symmetry-related S2 atoms, and two longer bonds of 2.936 (6) and 2.931 (8) Å to atoms S1*a* and S1$b^{\rm iii}$, respectively. The angle between the central atom and the two S atoms at the vertices is 177.94 (19)°. The calculated bond valence for Bi is 2.96 (3) v.u., for Sb it is 2.26 (2) v.u. and the calculated valence of this mixed site is 2.78 v.u. This is less than the theoretical value of 3 and, similarly to other sulfosalt structures, this could mean that we are not dealing with a single position but with at least two overlapping fractional sites (Makovicky, 2007).

An attempt was made to bring the structural formula of the title compound closer to that obtained by microprobe analysis, especially with regard to the content of Ag and Pb. The occupancies of the mixed sites were adjusted to fit the chemical composition given by electron-probe microanalysis and then refined. All Ag content is found in the marginal octahedral sites. Thus, special attention was paid to the *M*1*a* site (Bi), which can be refined with the same *R* factors as a pure Bi site with occupancy 0.909 (4), resulting in the current structural formula, or as a mixed site with a Bi fraction of 0.81 and an Ag fraction of 0.19. The former model was chosen because: (i) an Ag content of 1.00 atom per formula unit (*apfu*) is closer to that established from the microprobe analysis (1.08 *apfu*, *c.f.* 1.22 *apfu* with the latter model); (ii) the sum of Bi + Sb from the refinement is closer to the measured value of 3.10 (2.91 *apfu* in the former model compared with 2.80 *apfu* in the latter); (iii) the charge balance of the cations is closer to the ideal value of 12 (11.77 in the former model and 11.69 in the latter); (iv) in the latter model, the bond valence of Bi in *M*1*a* attains an unreasonably high value of 3.62 (3). The *M*3 site is occupied only by Pb and the occupancy of the site does not refine below 100% of Pb.

In conclusion, comparison of the structures of natural monoclinic gustavite and synthetic orthorhombic gustavite shows that the main features of the two structures are very similar, with the same type of coordination. The main difference is in the octahedral sites. Monoclinic gustavite contains two symmetry-independent sites *M*1*a* and *M*1*b* and two symmetry-independent sites *M*2*a* and *M*2*b*, instead of one equivalent site *M*1 and one site *M*2 in synthetic orthorhombic gustavite. It is the occupancy of the octahedral sites *M*1 and *M*2 that results in a monoclinic or orthorhombic cell. The marginal octahedral site *M*1 in the orthorhombic structure, with a statistical occupancy of 50% Bi and 50% Ag, splits into two sites *M*1*a* and *M*1*b* in the monoclinic structure, with one site occupied by Ag and the other by Bi. The same applies to the *M*2 site. Thus, if there are approximately equal amounts of Bi and Sb in the formula, there is only one site *M*2 which always has equal occupancies of Bi and Sb, and there are no *M*2*a* and *M*2*b* sites with different occupancies of the two atoms, resulting in monoclinic symmetry.

Experimental

The sample containing the title mineral was found during mineralogical investigation of primary ores from mediaeval mine dumps in the Kutná Hora polymetallic deposit, Czech Republic. A crystal fragment (sample ST 63) was extracted from a polished section of a homogenous single-phase grain pre-analyzed by electron microprobe with the following composition in wt%: Ag 11.36, Pb 16.90, Fe 0.01, Cd 0.01, Bi 42.96, Sb 11.39, S 18.51, Se 0.08, Σ = 101.23. The gustavite fragment was found to be homogeneous within analytical error. The formula from the microprobe calculated to 11 atoms is $Ag_{1.08}Pb_{0.84}(Bi_{2.11}Sb_{0.96})_{\Sigma=3.07}(S_{5.93}Se_{0.01})_{\Sigma=5.94}$, $Z = 4$, $N_{\rm chem} = 4.02$, Bi/(Bi + Sb) = 0.69 and gustavite substitution $L = 107.2\%$.

The measured crystal was a strongly absorbing material with a linear absorption coefficient $\mu \sim 55$ mm^{-1}. The absorption correction was carried out in several steps. A highly redundant data set was collected with average redundancy 4.7 for *P*2/*m* symmetry. $R_{\rm int}$ for the space group $P2_1/c$ before absorption correction was 0.302 for all reflections. The crystal shape was indexed using the program *CrysAlis RED* (Oxford Diffraction, 2008), which lowered the $R_{\rm int}$ value to 0.253. The distances and angles of the indexed faces were then refined using the program *X-SHAPE* (Stoe & Cie, 1998), which lowered $R_{\rm int}$ to 0.169. The resulting shape was checked against the photographs of the sample used for the numerical absorption correction and followed by multi-scan correction. The resulting $R_{\rm int}$ was 0.1078. In the final step, 58 reflections were excluded for which the intensity differed by more than 20 estimated standard deviations from the average value in the relevant symmetry-equivalent group, and the final $R_{\rm int}$ for the space group $P2_1/c$ was 0.0918 for all reflections and 0.0747 for observed reflections.

Crystal data

$AgPb(Bi_2Sb)_3S_6$
$M_r = 1035.9$
Monoclinic, $P2_1/c$
$a = 7.0455$ (6) Å
$b = 19.5294$ (17) Å
$c = 8.3412$ (11) Å
$\beta = 107.446$ (10)°
$V = 1094.9$ (2) Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 54.58$ mm^{-1}
$T = 293$ K
0.25 × 0.2 × 0.1 mm

Data collection

Oxford Gemini CCD diffractometer
Absorption correction: numerical followed by multi-scan (both implemented in *CrysAlis RED*; Oxford Diffraction, 2008)
$T_{\rm min} = 0.022$, $T_{\rm max} = 0.159$
10947 measured reflections
2408 independent reflections
1290 reflections with $I > 3\sigma(I)$
$R_{\rm int} = 0.092$

Refinement

$R[F^2 > 3\sigma(F^2)] = 0.059$
$wR(F)[F^2 > 3\sigma(F^2)] = 0.060$
$S = 1.98$
2408 reflections
103 parameters
$\Delta\rho_{\rm max} = 3.80$ e Å^{-3}
$\Delta\rho_{\rm min} = -4.13$ e Å^{-3}

Bond valences were calculated using the formula $s = \exp[(r_0 - r)/B]$, where r_0 is an element-pair-specific bond-valence parameter, r is the bond distance and B is a constant equal to 0.37 (Brown &

Table 1
Selected geometric parameters (Å, °).

Pb3—S3	2.841 (7)	Ag1*b*—S1*a*	3.359 (8)
Pb3—S3$^{\rm i}$	2.830 (5)	Ag1*b*—S4*a*$^{\rm ii}$	2.708 (6)
Pb3—S4*b*	3.307 (6)	Ag1*b*—S1*b*$^{\rm iii}$	3.314 (6)
Pb3—S4*b*$^{\rm i}$	3.141 (8)	Ag1*b*—S2	2.606 (9)
Pb3—S1*a*	3.101 (8)	Bi2*b*—S4*b*	2.563 (8)
Pb3—S4*a*	3.224 (6)	Bi2*b*—S1*a*	2.936 (6)
Pb3—S4*a*$^{\rm i}$	3.311 (8)	Bi2*b*—S1*b*$^{\rm vi}$	3.251 (8)
Pb3—S1*b*	3.141 (8)	Bi2*b*—S1*b*$^{\rm iii}$	2.931 (8)
Bi1*a*—S3	2.609 (8)	Bi2*b*—S2$^{\rm vii}$	2.776 (9)
Bi1*a*—S4*b*$^{\rm ii}$	2.739 (6)	Bi2*b*—S2$^{\rm viii}$	2.746 (7)
Bi1*a*—S1*a*$^{\rm iii}$	2.975 (6)	Sb2*a*—S1*a*$^{\rm ix}$	3.337 (8)
Bi1*a*—S4*a*$^{\rm iv}$	2.725 (8)	Sb2*a*—S1*a*$^{\rm iii}$	2.608 (8)
Bi1*a*—S1*b*	2.980 (8)	Sb2*a*—S4*a*	2.540 (8)
Bi1*a*—S2$^{\rm v}$	3.177 (8)	Sb2*a*—S1*b*	2.579 (6)
Ag1*b*—S3	2.495 (8)	Sb2*a*—S2$^{\rm ix}$	3.139 (9)
Ag1*b*—S4*b*$^{\rm iv}$	2.795 (9)	Sb2*a*—S2$^{\rm x}$	3.159 (6)
S3—Bi1*a*—S2$^{\rm v}$	175.2 (2)	S4*b*—Bi2*b*—S1*b*$^{\rm vi}$	177.94 (19)
S3—Ag1*b*—S2	165.4 (2)	S1*a*$^{\rm ix}$—Sb2*a*—S4*a*	174.56 (19)

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

Altermatt, 1985). The atom sites are labelled as follows: *M*3 = Pb3, *M*1*a* = Bi1*a*, *M*1*b* = Ag1*b*, mixed site *M*2*a* = Sb2*a* + Bi2*a*, and mixed site *M*2*b* = Bi2*b* + Sb2*b*.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2008); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2008); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SUPERFLIP* (Palatinus & Chapuis, 2007); program(s) used to refine structure: *JANA2006* (Petříček *et al.*, 2006); molecular graphics: *DIAMOND* (Brandenburg & Putz, 2005); software used to prepare material for publication: *JANA2006*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FN3031). Services for accessing these data are described at the back of the journal.

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