

The crystal structure of baličžuničite, $\text{Bi}_2\text{O}(\text{SO}_4)_2$, a new natural bismuth oxide sulfate

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ABSTRACT

The crystal structure of baličžuničite, $\text{Bi}_2\text{O}(\text{SO}_4)_2$, a new mineral species from the La Fossa crater of Vulcano (Aeolian Islands, Italy), was solved from single-crystal X-ray diffraction data and refined to $R = 0.0507$. The structure is triclinic, space group $P\bar{1}$, with $a = 6.7386(3)$, $b = 11.1844(5)$, $c = 14.1754(7)$ Å, $\alpha = 80.082(2)^\circ$, $\beta = 88.462(2)^\circ$, $\gamma = 89.517(2)^\circ$, $V = 1052.01(8)$ Å³ and $Z = 6$. The crystal structure consists of six independent Bi sites, six S sites and 27 O sites of which three are oxo oxygen atoms not bonded to sulfur. Bismuth and S atoms are arranged close to a eutectic pattern parallel to the (100) plane. The planes are stacked atom on atom such that Bi always overlays S and *vice versa*. This structural feature is shared with the known structure of the high-temperature polymorph of the same compound, stable at $T > 535^\circ\text{C}$. However, the sequences of Bi and S atoms in the two structures are different and so are the arrangements of oxygen atoms. Characteristic building blocks in the structure of baličžuničite are clusters of five Bi atoms which form nearly planar trapezoidal Bi_5 groups with oxo oxygens located in the centres of the three Bi_3 triangles, which form the trapezoids. The trapezoidal $\text{Bi}_5\text{O}_3^{9+}$ ions are joined along [100] with SO_4^{2-} groups by means of strong bismuth-sulfate oxygen bonds, forming infinite [100] rods with composition $\text{Bi}_5\text{O}_3(\text{SO}_4)_5^-$. One sixth of the Bi atoms do not participate in trapezoids, but form, with additional SO_4^{2-} groups, rows of composition BiSO_4^+ , also parallel to [100]. $[\text{Bi}_5\text{O}_3(\text{SO}_4)_5^-]$ rods form infinite layers parallel to (010) with $[\text{BiSO}_4^+]$ rows located on the irregular surface of contact between adjacent layers. Bi atoms occur in four different coordination types, all showing the stereochemical influence of the Bi^{3+} lone electron pair. In this respect the crystal structure of baličžuničite shows greater variability than its high-temperature polymorph which has only two types of the Bi coordination spheres present in baličžuničite.

KEYWORDS: baličžuničite, bismuth oxide sulfate, single-crystal X-ray diffraction, crystal structure, lone electron pair.

Introduction

BISMUTH OXIDE phases containing sulfate groups are of interest in chemistry and materials science owing to their potential use as ionic conductors (Smirnov *et al.*, 2003; Crumpton and Greaves, 2004). To date more than ten different synthetic bismuth oxysulfates (Jones, 1984; Aurivillius, 1987, 1988; Francesconi *et al.*, 1998; Smirnov *et al.*, 2003; Crumpton and Greaves, 2004) have

been obtained in the laboratory, but the occurrence of these compounds in Nature is very rare. As a matter of fact, before the recent discovery of some new natural bismuth oxysulfates as sublimates from fumaroles of the La Fossa crater at Vulcano (Aeolian Islands, Italy), only two minerals of this group were known, cannonite, $\text{Bi}_2(\text{SO}_4)\text{O}(\text{OH})_2$ (Stanley *et al.*, 1992; Capitani *et al.*, 2013) and riomarinarite $\text{Bi}(\text{SO}_4)(\text{OH})\cdot\text{H}_2\text{O}$ (Rögner, 2005; Graunar and Lazarini, 1982). The oxysulfate assemblage recently discovered at Vulcano consists of two phases recently approved as new minerals by the

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IMA Commission on New Minerals, Nomenclature and Classification (CNMNC), baličžuničite, $\text{Bi}_2\text{O}(\text{SO}_4)_2$ (IMA2012-098; Pinto *et al.*, 2013, 2014) and leguernite, $\text{Bi}_{12.67}\text{O}_{14}(\text{SO}_4)_5$ (IMA2013-051; Garavelli *et al.*, 2013, 2014), and a third potentially new bismuth sulfate compound with composition $\text{Bi}_{14}\text{O}_{16}(\text{SO}_4)_5$, which is still under investigation.

Contrary to the cases of synthetic phases, which are often available only in the form of powder aggregates, the natural phases from Vulcano consist of prismatic or needle-like single crystals, large enough for accurate determination of the crystal structure by single-crystal X-ray diffraction (XRD) methods. Hence, the structural study of these natural phases represents an exceptional opportunity to improve our knowledge of the crystal chemistry of Bi-oxysulfate compounds.

In this paper we report a full and detailed description of the crystal structure of baličžuničite, $\text{Bi}_2\text{O}(\text{SO}_4)_2$, the first Bi oxysulfate discovered in the Vulcano fumarole assemblages (Pinto *et al.*, 2013). The description of this new mineral species was reported by Pinto *et al.* (2014). Baličžuničite is the first natural Bi oxysulfate completely lacking water molecules or OH groups. Synthetic $\text{Bi}_2\text{O}(\text{SO}_4)_2$ was investigated by Jones (1984) who identified from powder XRD data two different phases, α - $\text{Bi}_2\text{O}(\text{SO}_4)_2$, stable at low temperature and β - $\text{Bi}_2\text{O}(\text{SO}_4)_2$, which is stable above 535°C. No symmetry or unit-cell parameters were determined for these phases. Aurivillius (1988) synthesized and investigated the crystal structure of a compound with monoclinic symmetry and composition $\text{Bi}_2\text{O}(\text{SO}_4)_2$, but no relationships with the previously described α and β forms were reported. The investigation of baličžuničite (Pinto *et al.*, 2014) clarified the relationships among the previously reported synthetic phases. From comparison of the powder XRD patterns, Pinto *et al.* (2014) concluded that baličžuničite is the natural analogue of α - $\text{Bi}_2\text{O}(\text{SO}_4)_2$. Similarly, comparison of powder XRD data suggests a correspondence between the synthetic monoclinic $\text{Bi}_2\text{O}(\text{SO}_4)_2$ phase described by Aurivillius (1988) and β - $\text{Bi}_2\text{O}(\text{SO}_4)_2$ of Jones (1984) (Pinto *et al.*, 2014).

The detailed investigation of the baličžuničite crystal structure performed in the present study and its comparison with the monoclinic high-temperature polymorph investigated by Aurivillius (1988) give some insight into structural features and relationships among the low-

and high-temperature form of $\text{Bi}_2\text{O}(\text{SO}_4)_2$, clarifying the nature of the phase transition.

Various supplementary Tables and Figures (Tables 4 and 6, Figs 5 and 6) have been deposited with the Principal Editor of *Mineralogical Magazine* and can be downloaded from www.minersoc.org/pages/e_journals/dep_mat_mm.html.

Experimental

Single-crystal XRD data were collected from a selected crystal fragment (0.240 mm \times 0.104 mm \times 0.083 mm) using a Bruker AXS X8 APEX2 CCD automated diffractometer equipped with a k -geometry goniometer and graphite-monochromated $\text{MoK}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$, 50 kV, 30 mA). A Miracol fibre optics capillary collimator (0.3 mm) was used to enhance the intensity of the $\text{MoK}\alpha$ radiation and to reduce X-ray beam divergence. Five sets of 30 frames were used for initial cell determination, whereas complete data collection was accomplished by several φ and ω scans with 0.5° frame width, 60 s exposure time per frame and a crystal-to-detector distance of 40 mm. The collection strategy was optimized by the *Apex* suite of programs (Bruker, 2003a). Details of data collection and refinement are summarized in Table 1. Intensity integration, correction for Lorentz, polarization, background effects and scaling was done using the *SAINTRIX* package (Bruker, 2003b). A semi-empirical absorption correction (Blessing, 1995) was applied using the *SADABS* program (Sheldrick, 2008a). The estimated minimum and maximum X-ray transmission factors were 0.483 and 0.746, respectively. The data point to a triclinic cell with parameters $a = 6.7386(3)$, $b = 11.1844(5)$, $c = 14.1754(7) \text{ \AA}$, $\alpha = 80.082(2)$, $\beta = 88.462(2)$, $\gamma = 89.517(2)^\circ$, $V = 1052.01(8) \text{ \AA}^3$. The triclinic symmetry was validated with the software routine *AddSym* implemented in *PLATON* (Spek, 2005). Statistical tests on the distributions of $|E|$ values gave the mean $|E^2 - 1|$ value of 0.891, suggesting a centrosymmetric space group. In light of this and the absence of systematic extinctions, $P\bar{1}$ was selected as the space group.

The crystal structure of baličžuničite was solved by direct methods using the program *SHELXS-97* (Sheldrick, 1997a) and the subsequent structure refinement proceeded by means of the full-matrix least-squares program *SHELXL-97* (Sheldrick, 1997b). Neutral scattering factors for Bi, S and O were taken from the *International*

THE CRYSTAL STRUCTURE OF BALIČŽUNIČITE

TABLE 1. Summary of parameters describing data collection and refinement for baličžuničite.

Empirical structural formula	Bi ₂ O(SO ₄) ₂
Crystal dimensions (mm)	0.083 × 0.104 × 0.204
Crystal system, space group	Triclinic, <i>P</i> $\bar{1}$
<i>a</i> (Å)	6.7386(3)
<i>b</i> (Å)	11.1844(5)
<i>c</i> (Å)	14.1754(7)
α (°)	80.082(2)
β (°)	88.462(2)
γ (°)	89.517(2)
<i>V</i> (Å ³)	1052.01(8)
<i>Z</i>	6
Temperature (K)	293
<i>D</i> (g cm ⁻³)	5.929
X-ray conditions (kV, mA)	50, 30
Wavelength of radiation (Å)	0.71073
Detector-to-sample distance (mm)	40
Number of frames	2020
Rotation width per frame (°)	0.5
Measuring time (s)	60
Maximum covered 2 θ (°)	52.88 (<i>d</i> = 0.80 Å)
Independent reflections	4287
Reflections with <i>F</i> > 4 σ (<i>F</i>)	3856
<i>R</i> _{int}	0.0439
<i>R</i> _{σ}	0.0468
Ranges of <i>h</i> , <i>k</i> , <i>l</i>	-8 ≤ <i>h</i> ≤ 8 -13 ≤ <i>k</i> ≤ 13 -17 ≤ <i>l</i> ≤ 17
<i>R</i> [<i>F</i> > 4 σ (<i>F</i>)]	0.0507
<i>R</i> (all data)	0.0574
<i>wR</i> [<i>F</i> > 4 σ (<i>F</i>)]	0.1107
<i>wR</i> (all data)	0.1130
Goof	1.206
Refined parameters	217
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0158P)^2 + 117.505997P]$ where $P = [\max(F_o)^2 + 2(F_c)^2]/3$
ρ_{\min} , ρ_{\max} (e Å ⁻³)	-2.98, 3.47

Tables for X-ray Crystallography (Ibers and Hamilton, 1974). The structure was refined to a final *R* = 0.0507 for 3856 observed reflections with *I* > 2 σ (*I*), and *R* = 0.0574 for all the 4287 independent reflections. Bi and S atoms were refined anisotropically, whereas isotropic displacement parameters were applied for O atoms. An attempt to refine O atoms anisotropically resulted in several non-positive definite ellipsoid functions with marginally smaller *R* factors and was abandoned. Final coordinates and displacement parameters are reported in Table 2. Selected interatomic distances and angles are reported in Tables 3 and supplementary 4 (available from www.minersoc.org/pages/e_journals/dep_mat_mm.html), respectively, in comparison

with those of similar coordination types in the monoclinic structure of the synthetic Bi₂O(SO₄)₂ (Aurivillius 1988). The structure factors and CIF file for the baličžuničite crystal structure have been deposited with the Principal Editor of *Mineralogical Magazine* and are available from www.minersoc.org/pages/e_journals/dep_mat_mm.html.

Results and discussion

Description of the crystal structure

The crystal structure of baličžuničite consists of six independent Bi sites, six S sites and 27 O sites of which three are not sulfate oxygen atoms (O1, O2 and O3, Table 2). The resulting structural

TABLE 2. Fractional atomic coordinates and displacement parameters (\AA^2) for baličuničite.

Atom	x/a	y/b	z/c	$U_{\text{eq/iso}}$	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Bi(1)	0.32303(11)	0.26686(7)	0.08679(5)	0.01183(18)	0.0124(4)	0.0117(4)	0.0110(4)	-0.0006(3)	-0.0029(3)	0.0006(3)
Bi(2)	0.82886(11)	0.53970(7)	0.15591(5)	0.01036(17)	0.0098(4)	0.0093(4)	0.0124(4)	-0.0034(3)	-0.0001(3)	0.0015(3)
Bi(3)	0.76466(12)	0.86186(7)	0.13679(6)	0.01320(18)	0.0156(4)	0.0072(4)	0.0172(4)	-0.0028(3)	-0.0034(3)	0.0017(3)
Bi(4)	0.74596(11)	0.62711(7)	0.38112(5)	0.01086(17)	0.0115(4)	0.0109(4)	0.0107(4)	-0.0034(3)	-0.0009(3)	0.0023(3)
Bi(5)	0.32337(11)	0.70789(6)	0.62464(5)	0.00988(17)	0.0100(4)	0.0078(4)	0.0118(4)	-0.0014(3)	-0.0005(3)	0.0014(3)
Bi(6)	0.16084(12)	0.00838(7)	0.36111(9)	0.01279(18)	0.0146(4)	0.0110(4)	0.0128(4)	-0.0023(3)	-0.0004(3)	0.0032(3)
S(1)	0.8163(7)	0.1875(4)	0.1809(4)	0.0095(9)	0.006(2)	0.011(2)	0.011(2)	-0.0001(18)	-0.0019(17)	0.0020(18)
S(2)	0.3146(7)	0.5708(4)	0.0809(4)	0.0079(9)	0.004(2)	0.005(2)	0.014(2)	-0.0002(18)	-0.0009(17)	0.0022(17)
S(3)	0.2604(7)	0.9460(4)	0.1159(4)	0.0104(10)	0.009(2)	0.010(2)	0.012(2)	-0.0005(18)	0.0013(18)	0.0006(18)
S(4)	0.2536(7)	0.6655(5)	0.3996(4)	0.0104(10)	0.006(2)	0.012(2)	0.014(3)	-0.0023(19)	-0.0049(18)	0.0020(18)
S(5)	0.1985(7)	0.3136(4)	0.3323(4)	0.0104(10)	0.008(2)	0.011(2)	0.013(2)	0.0002(19)	-0.0008(18)	-0.0009(18)
S(6)	0.6634(7)	0.9222(4)	0.4137(4)	0.0094(9)	0.008(2)	0.011(2)	0.009(2)	-0.0028(18)	-0.0004(18)	0.0009(18)
O(1)	0.801(2)	0.6900(13)	0.2333(10)	0.014(3)						
O(2)	0.7427(19)	0.4715(12)	0.3143(9)	0.006(3)						
O(3)	0.762(2)	0.7219(12)	0.054(10)	0.010(3)						
O(4)	0.201(4)	0.983(2)	0.2043(18)	0.059(6)						
O(5)	0.158(2)	0.6251(13)	0.1337(10)	0.014(3)						
O(6)	0.221(2)	0.4637(13)	0.0443(11)	0.015(3)						
O(7)	0.478(2)	0.5267(13)	0.1463(10)	0.012(3)						
O(8)	0.617(2)	0.3439(13)	0.0045(10)	0.013(3)						
O(9)	0.701(2)	0.2948(13)	0.2060(10)	0.011(3)						
O(10)	0.106(3)	0.8710(15)	0.7262(12)	0.024(4)						
O(11)	0.678(2)	0.1127(14)	0.1408(11)	0.020(3)						
O(12)	0.977(2)	0.2380(15)	0.1093(12)	0.021(3)						
O(13)	0.127(2)	0.3788(14)	0.2426(11)	0.020(3)						
O(14)	0.038(2)	0.2873(13)	0.4032(11)	0.016(3)						
O(15)	0.637(2)	0.6202(13)	0.6321(10)	0.013(3)						
O(16)	0.290(2)	0.1957(13)	0.3117(11)	0.015(3)						
O(17)	0.095(3)	0.5963(16)	0.3706(13)	0.027(4)						
O(18)	0.419(2)	0.6739(13)	0.3291(11)	0.015(3)						
O(19)	0.325(2)	0.6019(14)	0.4967(11)	0.019(3)						
O(20)	0.185(2)	0.7878(14)	0.4111(12)	0.021(3)						
O(21)	0.784(2)	0.8724(13)	0.3406(11)	0.015(3)						
O(22)	0.199(2)	0.0026(14)	0.5385(11)	0.019(3)						
O(23)	0.507(2)	0.0044(12)	0.3677(10)	0.011(3)						
O(24)	0.583(2)	0.8218(14)	0.4846(11)	0.017(3)						
O(25)	0.096(3)	0.892(2)	0.0766(16)	0.046(5)						
O(26)	0.316(2)	0.0579(14)	0.0478(11)	0.018(3)						
O(27)	0.420(3)	0.8602(17)	0.1314(14)	0.033(4)						

formula is $\text{Bi}_2\text{O}(\text{SO}_4)_2$, in excellent agreement with chemical data (Pinto *et al.*, 2014). Bismuth atoms, the oxo oxygen atoms and sulfate tetrahedra are arranged in layers parallel to (100). Bismuth atoms and sulfate tetrahedra in (100) layers form rows along $[010]$, $[013]$ and $[01\bar{1}]$ in a quasi-close packed (eutactic) arrangement. Rows along $[01\bar{1}]$ are the most regular and consist of sequences formed by three subsequent rows: a row of sulfate tetrahedra, a row of Bi atoms and a row of alternating two sulfate tetrahedra and two Bi atoms. The two Bi atoms from the latter row form, with three Bi atoms from the Bi row, a nearly planar trapezoidal group consisting of three almost regular triangles (Fig. 1). The Bi–Bi distances within each trapezoidal group are smaller than the distances between Bi atoms from adjacent groups (Table 3). Each Bi_3 triangle from the trapezoidal group is centred by one of the oxo oxygen atoms [O(1), O(2) and O(3), Bi–O = 2.08–2.33 Å], thus forming nearly planar $\text{Bi}_5\text{O}_3^{9+}$ groups (Fig. 2). The Bi–O–Bi angles of these groups range from $105.6(5)^\circ$ to $135.3(7)^\circ$ (Table 4, supplementary) and are in good agreement with similar planar or slightly pyramidal three-coordinated oxo oxygens in a number of Bi and Sb compounds cited by Aurivillius (1988).

Adjacent (100) atomic layers are inverse to each other and positioned so that the rows of Bi atoms from one layer underlie the sulfate rows from the other one. In contrast, the mixed Bi– SO_4 rows underlie the mixed rows from the other one with Bi– SO_4 superpositions. In this arrangement, the Bi atoms which form trapezoids [Bi(1), Bi(2), Bi(3), Bi(4) and Bi(5)] are bonded to two sulfate groups along $[100]$ by strong Bi–O bonds, forming infinite $\text{SO}_4\text{–Bi–SO}_4\text{–Bi}$ chains with Bi–O distances ranging from 2.320(14) to 2.476(14) Å (Fig. 3). Planar trapezoidal-shaped $\text{Bi}_5\text{O}_3^{9+}$ groups with corresponding SO_4^{2-} ions form infinite $[100]$ rods with composition $\text{Bi}_5\text{O}_3(\text{SO}_4)_5^-$, which are arranged in pairs, displaced with respect to each other by $\frac{1}{2}$ along $[100]$ (Fig. 3). The rings formed by two Bi(6) and two S(6) O_4 groups are situated in the channels formed between these rods. The rings are interconnected along $[100]$ by longer Bi–O contacts (2.77 and 3.02 Å) into stripes with BiSO_4^+ composition.

Coordination polyhedra

Bismuth atoms in the structure of baličžuničite are characterized by asymmetric, one-sided coordination (Table 3 and Fig. 4*a–d*). They are generally formed by three to five close oxygen neighbours

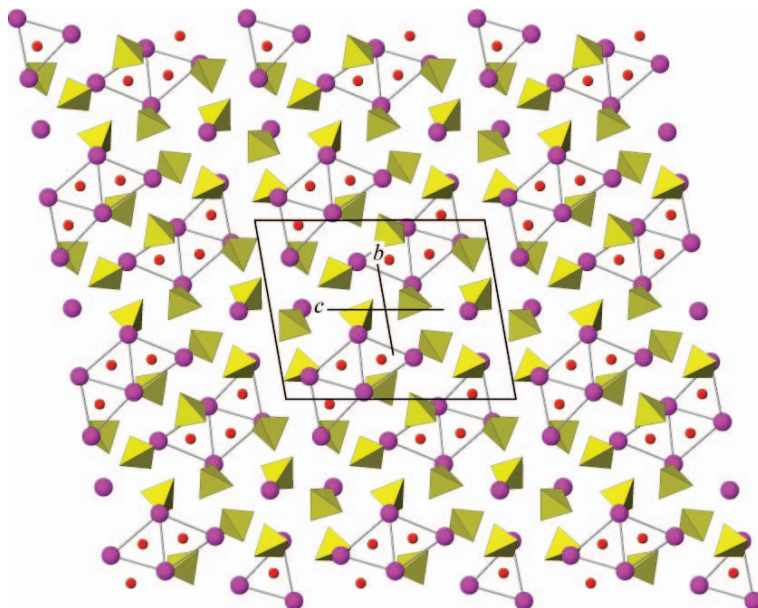


FIG. 1. The crystal structure of baličžuničite seen along $[100]$. SO_4 tetrahedra are yellow, large pink atoms are Bi, small red atoms are oxo oxygen atoms. Bi_3 triangles in Bi_5 trapezoidal groups are marked.

TABLE 3. Selected bond distances (Å) in the crystal structures of baličžuničite and in synthetic monoclinic $\text{Bi}_2\text{O}(\text{SO}_4)_2$ (Aurivillius, 1988).

Baličžuničite		Synthetic monoclinic $\text{Bi}_2\text{O}(\text{SO}_4)_2$	
Bi-Bi distances			
Bi(1)–Bi(3)	3.762(1)*	Bi(2)–Bi(3)	3.590(1)*
Bi(1)–Bi(2)	3.893(1)*	Bi(2)–Bi(5)	3.912(1)*
Bi(1)–Bi(6)	4.542(1)	Bi(2)–Bi(2)	5.140(1)
Bi(1)–Bi(2)	4.695(1)	Bi(3)–Bi(4)	3.969(1)*
Bi(1)–Bi(2)	4.824(1)	Bi(3)–Bi(6)	4.717(1)
Bi(1)–Bi(5)	4.840(1)	Bi(3)–Bi(3)	5.479(1)
Bi(1)–Bi(3)	5.353(1)	Bi(4)–Bi(5)	3.795(1)*
Bi(2)–Bi(4)	3.526(1)*	Bi(4)–Bi(5)	4.620(1)
Sulfate tetrahedra			
S(1)–O(11)	1.448(17)	S(3)–O(27)	1.431(20)
–O(10)	1.473(17)	–O(4)	1.432(27)
–O(12)	1.509(15)	–O(25)	1.436(23)
–O(9)	1.511(15)	–O(26)	1.487(15)
S(2)–O(5)	1.465(15)	S(4)–O(17)	1.439(21)
–O(8)	1.472(14)	–O(18)	1.470(15)
–O(7)	1.484(14)	–O(20)	1.474(17)
–O(6)	1.532(16)	–O(19)	1.525(15)
Bi bonded to one oxo oxygen			
Bi(1)–O(3)	2.081(14) A	Bi(5)–O(2)	2.090(13) A
–O(6)	2.285(14) E	–O(15)	2.320(14) E
–O(12)	2.362(14) E	–O(19)	2.331(17) E
–O(8)	2.363(13) E	–O(9)	2.400(14) E
–O(26)	2.494(16) E	–O(14)	2.476(14) E
–O(11)	2.976(14)	–O(24)	2.758(14)
–O(13)	2.993(16)	–O(10)	2.879(19)
Bi bonded to two oxo oxygens			
Bi(3)–O(3)	2.108(15) E	Bi(4)–O(25)	2.116(14) E
–O(1)	2.175(13) E	–O(2)	2.120(14) E
–O(27)	2.326(20) A	–O(18)	2.368(14) A
–O(25)	2.375(20) A	–O(17)	2.372(20) A
–O(26)	2.685(15)	–O(21)	2.717(14)
–O(11)	2.871(16)	–O(19)	2.870(14)
–O(21)	2.918(16)	–O(24)	3.012(16)
Baličžuničite			
Bi(1)–Bi(2)	3.801(5)**	Bi(1)–Bi(2)	3.801(5)**
Bi(1)–Bi(3)	3.808(4)**	Bi(1)–Bi(3)	3.808(4)**
Bi(1)–Bi(5)	4.597(4)	Bi(1)–Bi(5)	4.597(4)
Bi(2)–Bi(3)	3.495(5)	Bi(2)–Bi(3)	3.495(5)
Bi(2)–Bi(6)	3.834(4)**	Bi(2)–Bi(6)	3.834(4)**
Bi(2)–Bi(5)	4.960(5)	Bi(2)–Bi(5)	4.960(5)
Synthetic monoclinic $\text{Bi}_2\text{O}(\text{SO}_4)_2$			
Bi(3)–Bi(4)	3.839(5)**	Bi(3)–Bi(4)	3.839(5)**
Bi(3)–Bi(4)	4.960(4)	Bi(3)–Bi(4)	4.960(4)
Bi(4)–Bi(4)	4.611(6)	Bi(4)–Bi(4)	4.611(6)
Bi(5)–Bi(6)	3.798(4)**	Bi(5)–Bi(6)	3.798(4)**
Bi(5)–Bi(6)	3.826(5)**	Bi(5)–Bi(6)	3.826(5)**
Bi(6)–Bi(6)	3.512(7)	Bi(6)–Bi(6)	3.512(7)
Sulfate tetrahedra			
S(3)–O(31)	1.39(6)	S(3)–O(31)	1.46(6)
–O(32)	1.44(5)	–O(32)	1.48(6)
–O(33)	1.55(6)	–O(33)	1.52(6)
–O(34)	1.56(6)	–O(34)	1.54(4)
S(4)–O(43)	1.45(5)	S(4)–O(43)	1.51(5)
–O(41)	1.50(6)	–O(41)	1.52(5)
–O(44)	1.52(5)	–O(44)	1.53(5)
–O(42)	1.55(5)	–O(42)	1.56(5)
Sulfate tetrahedra			
Bi(4)–O(3)	2.12(6) A	Bi(4)–O(3)	2.06(6) A
–O(61)	2.32(5) E	–O(61)	2.29(5) E
–O(41)	2.38(4) E	–O(41)	2.38(4) E
–O(44)	2.40(5) E	–O(44)	2.40(5) E
–O(42)	2.58(4) E	–O(42)	2.58(4) E
–O(64)	2.70(5)	–O(64)	2.67(5)
–O(31)	2.97(8)	–O(31)	2.87(8)
Sulfate tetrahedra			
Bi(3)–O(2)	2.09(4) E	Bi(3)–O(2)	2.22(6) E
–O(3)	2.20(6) E	–O(3)	2.23(4) E
–O(24)	2.22(5) A	–O(33)	2.29(6) A
–O(21)	2.32(4) A	–O(34)	2.39(6) A
–O(53)	2.66(6)	–O(42)	2.64(6)
–O(61)	2.71(5)	–O(32)	2.68(5)
–O(52)	2.93(5)	–O(13)	2.86(6)
Sulfate tetrahedra			
S(5)–O(52)	1.34(5)	S(5)–O(52)	1.34(5)
–O(51)	1.46(4)	–O(51)	1.46(4)
–O(54)	1.53(6)	–O(54)	1.53(6)
–O(53)	1.58(5)	–O(53)	1.58(5)
S(6)–O(64)	1.41(6)	S(6)–O(64)	1.41(6)
–O(63)	1.42(5)	–O(63)	1.42(5)
–O(62)	1.50(6)	–O(62)	1.50(6)
–O(61)	1.56(4)	–O(61)	1.56(4)
Sulfate tetrahedra			
Bi(5)–O(1)	2.17(5) A	Bi(5)–O(1)	2.17(5) A
–O(23)	2.30(5) E	–O(23)	2.30(5) E
–O(51)	2.41(3) E	–O(51)	2.41(3) E
–O(54)	2.47(6) E	–O(54)	2.47(6) E
–O(14)	2.54(4) E	–O(14)	2.54(4) E
–O(22)	2.83(4)	–O(22)	2.83(4)
–O(22)	2.87(8)	–O(22)	2.87(8)
Sulfate tetrahedra			
Bi(6)–O(1)	2.09(5) E	Bi(6)–O(1)	2.09(5) E
–O(1)	2.18(3) E	–O(1)	2.18(3) E
–O(63)	2.35(5) A	–O(63)	2.35(5) A
–O(62)	2.35(6) A	–O(62)	2.35(6) A
–O(23)	2.72(6)	–O(23)	2.72(6)
–O(14)	2.73(6)	–O(14)	2.73(6)
–O(44)	3.32(5)	–O(44)	3.32(5)

Bi bonded to three oxo oxygens		Isolated Bi
Bi(2)—O(1)	2.164(16) A Bi(6)—O(16)	2.265(14)
—O(2)	2.304(12) E —O(4)	2.298(26)
—O(3)	2.331(13) E —O(23)	2.337(14)
—O(7)	2.379(14) E —O(20)	2.452(15)
—O(5)	2.414(14) E —O(10)	2.468(18)
—O(9)	2.843(13) —O(22)	2.524(16)
—O(13)	2.845(14) —O(22)	2.771(14)
—O(6)	2.874(16) —O(21)	3.017(14)

* Bi—Bi bonds inside Bi₅ trapezoids in the structure of baličžuničite.

** Bi—Bi bonds inside Bi₄ rhombi in the structure of synthetic monoclinic Bi₂O(SO₄)₂ (Aurivillius, 1988). E stands for equatorial, A for axial. Calculations were performed using the *ITON* software (Balič-Žunič and Vieković, 1996).

at distances of up to 2.5 Å plus additional weakly bonded oxygen atoms, which give very irregular overall coordination geometries. These types of asymmetrical coordination are common in Bi³⁺ compounds and indicate the presence of stereochemically active 6sp² lone-pair electrons (Aurivillius, 1988, and reference therein).

There are four coordination types of Bi atoms in the structure of baličžuničite: Bi atoms bonded to three oxo oxygens [Bi(2); Fig. 4a]; Bi atoms bonded to two oxo oxygen atoms [Bi(3) and Bi(4); Fig. 4b]; Bi in contact with only one oxo oxygen atom [Bi(1) and Bi(5); Fig. 4c]; Bi atoms not bonded with oxo oxygen atoms [Bi(6); Fig. 4d].

The closest coordination environment of Bi(2), residing in the middle of the Bi₅O₃⁹⁺ trapezoids, consists of five ligands, three oxo oxygens almost in the same plane with the Bi cation and two sulfate oxygens (O5 and O7) approximately on a line perpendicular to it (Fig. 4a). Coordination is completed by three more distant sulfate oxygens (O6, O9, O13) placed opposite to the oxo oxygens. The closest five oxygens form a distorted square pyramid. The arrangement of oxygens departs significantly from the ideal pyramids, 33% from the Archimedean and 44% from the maximum volume square pyramid (Makovicky and Balič-Žunič, 1998), mostly because the height of the pyramid is significantly short. A Bi atom is situated below the base of the pyramid. Taking all eight surrounding oxygens into account, their arrangement approximates a bicapped trigonal prism with only 5% volume distortion compared to the ideal maximum volume case (Makovicky and Balič-Žunič, 1998).

The second type of coordination is represented by Bi atoms forming the short base of the trapezoid, i.e. Bi(3) and Bi(4). Their coordination environment consists of two oxo oxygens at distances from 2.11 to 2.17 Å, two sulfate oxygens at somewhat longer distances of 2.33 to 2.38 Å lying approximately on a line perpendicular to the plane defined by the two oxo atoms and Bi, and the three much more distant sulfate oxygens approximately in the same plane with the oxo atoms and Bi (Fig. 4b). Including the latter, the coordination of Bi(3) and Bi(4) can be described as a distorted pentagonal bipyramid with the axis of the pyramid parallel to [100]. The volume distortions for the Bi(3) and Bi(4) coordinations compared to the ideal pentagonal bipyramid are 9% and 25%, respectively (Table 6, supplementary).

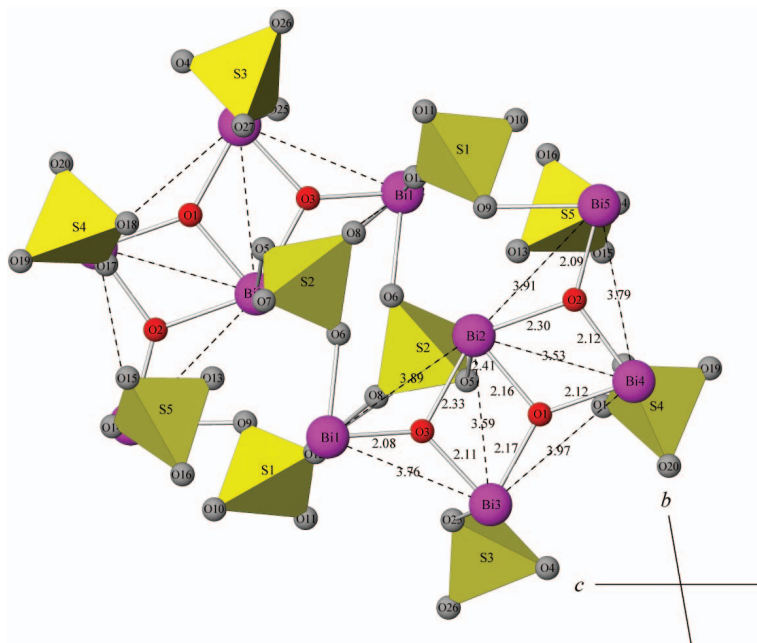


FIG. 2. A detail of $\text{Bi}_5\text{O}_3^{9+}$ trapezoidal groups with attached sulfate groups; Bi–Bi and Bi–oxo oxygen bond lengths are reported.

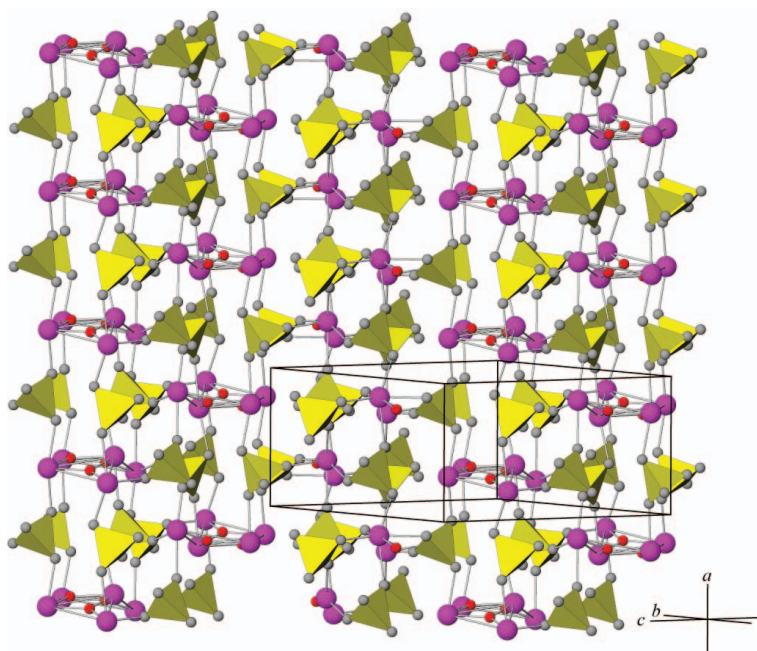


FIG. 3. A section of the crystal structure of baličžuničite parallel to $(01\bar{1})$ with the strong Bi–O bonds indicated. Infinite $\text{SO}_4\text{--Bi--SO}_4\text{--Bi}$ strings along $[100]$ can be seen in pairs of infinite columns of composition $\text{Bi}_5\text{O}_3(\text{SO}_4)_5^-$ displaced by $\frac{1}{2}$ along $[100]$ and in pairs of displaced BiSO_4 columns alternating with them.

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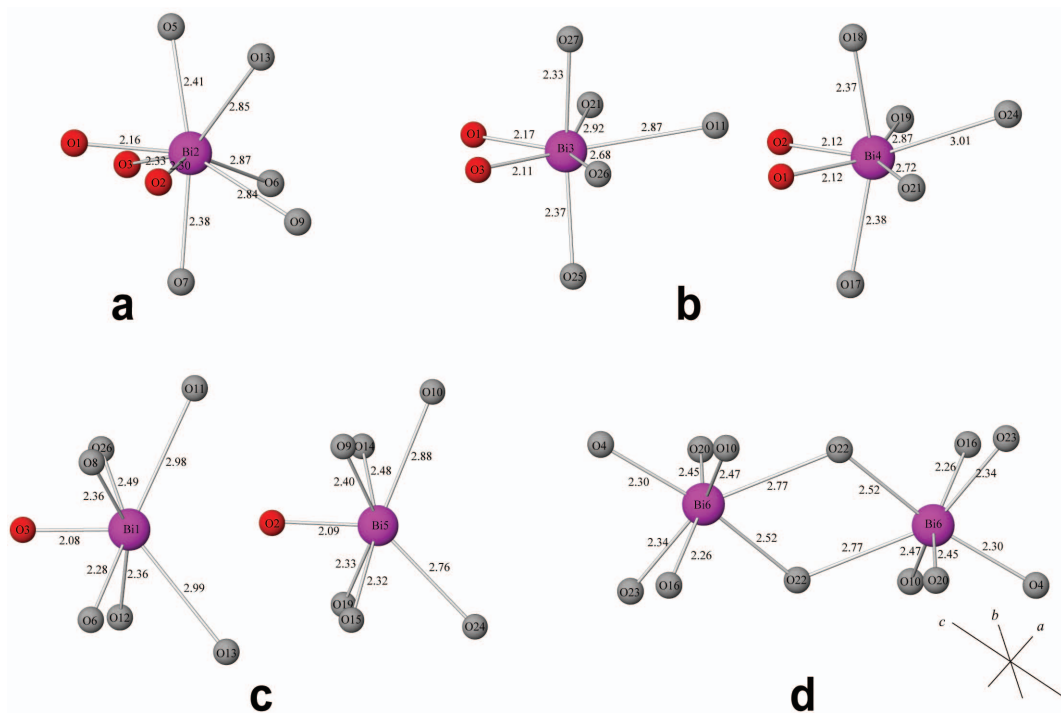


FIG. 4. Coordination environment of Bi atoms in the crystal structure of baličžuničite: (a) Bi(2); (b) Bi(3) and Bi(4); (c) Bi(1) and Bi(5); (d) a pair of Bi(6) atoms.

Bismuth atoms belonging to the third group are Bi(1) and Bi(5), which are located at the ends of the larger base of the Bi_5 trapezoids. These Bi atoms are bonded to one oxo oxygen at 2.08 and 2.09 Å, respectively, and an additional four sulfate oxygens at distances of 2.28 to 2.49 Å. Together, they form a square pyramid with the volume distortions compared to the maximum volume pyramid of 55% and 52%, respectively. Similar to the Bi(2) coordination, Bi(1) and Bi(5) atoms are situated below the base of the pyramid. The coordination is completed with two more distant oxygen atoms, at Bi–O distances of 2.98 and 2.99 Å in Bi(1), and 2.76 and 2.88 Å in Bi(5) (Fig. 4c). Considering these additional Bi–O bonds, the overall coordination of Bi(1) and Bi(5) can be described as a distorted monocapped trigonal prism often encountered in the structures of Bi and Sb-sulfosalts (Makovicky and Baličžunič, 1998; Berlepsch *et al.*, 2001). Compared to the maximum volume monocapped trigonal prism the volume distortions are 21% and 13%, respectively.

The Bi(6) atom, not belonging to the trapezoidal Bi_5 group, resides in a distorted

octahedral arrangement of oxygen atoms with three closer oxygens with bond lengths ranging from 2.26 to 2.34 Å and three on the opposite side of the Bi atom at distances of 2.45 to 2.52 Å. The volume distortion compared to the ideal octahedron is 18%. From the side of the three more distant oxygens, Bi is approached by two more oxygens at 2.77 and 3.02 Å (Fig. 4d).

Taking into account the general assumptions of the valence-shell electron-pair repulsion (VSEPR) model (Gillespie and Nyholm, 1957; Gillespie, 1963*a,b*, 2008 and references therein) and its extension by Andersson, Galy and coworkers (Andersson *et al.*, 1973; Galy *et al.*, 1975), Bi^{3+} ions occur in three different stereochemistries in the crystal structure of baličžuničite: distorted tetrahedral BiO_3E , distorted trigonal bipyramidal BiO_4E and distorted octahedral or square-bipyramidal BiO_5E (E denotes stereochemically active lone pair electrons).

The first type is represented by Bi(6). The three bonds are in the range 2.27 to 2.34 Å, average 2.30 Å, with O–Bi–O angles of 87°, 86° and 69° (Table 4, supplementary). The discrepancy from the ideal tetrahedral angle of 109.5° can be related

to the repulsion of the lone electron pair. Similar coordination types can also be observed for some Bi atoms in the crystal structures of leguermite (Garavelli *et al.*, 2014) and the synthetic phases $\text{Bi}_{26}\text{O}_{27}(\text{SO}_4)_{12}$ and $\text{Bi}_{14}\text{O}_{16}(\text{SO}_4)_5$ (Aurivillius, 1987).

The Bi atoms with trigonal bipyramidal BiO_4E coordinations are Bi(3) and Bi(4). They show two oxygen atoms in the axial positions and three equatorial positions occupied by two oxygens and a sterically active lone electron pair, respectively. It represents one of the most common oxygen coordinations of lone pair elements (Gillespie, 1963*b*) and occurs in several Bi and Sb minerals and synthetic compounds such as $\alpha\text{-Bi}_2\text{O}_3$ (Malmros, 1970), $\beta\text{-Bi}_2\text{O}_3$ (Blower and Greaves, 1988), $\text{Bi}_{14}\text{O}_{20}(\text{SO}_4)$ (Francesconi *et al.*, 1998), leguermite, $\text{Bi}_{12.67}\text{O}_{14}(\text{SO}_4)_5$ (Garavelli *et al.*, 2014), cannonite, $\text{Bi}_2(\text{SO}_4)\text{O}(\text{OH})_2$ (Capitani *et al.*, 2013), $\text{Sb}_4\text{O}_2(\text{OH})(\text{SO}_4)_4(\text{H}_5\text{O}_2)\cdot\text{H}_2\text{O}$ (Douglade and Mercer, 1980), SbPO_4 (Kinberger, 1970) and synthetic monoclinic $\text{Bi}_2\text{O}(\text{SO}_4)_2$ (Aurivillius, 1988).

The Bi–O equatorial bonds in Bi(3) and Bi(4) coordinations of baličžuničite are ~ 2.1 Å and are shorter than the axial bonds (Table 3) falling inside the ratio range of $r_{\text{ax}}/r_{\text{eq}} = 1.1\text{--}1.2$ observed in a number of similar coordination types (Gillespie, 1963*b*). The equatorial and axial O–Bi(3)–O and O–Bi(4)–O angles are presented in Table 4 (supplementary). The axial angles agree well with corresponding angles in other Bi and Sb compounds with similar coordination types (Table 5), whereas the equatorial angles are significantly smaller than those observed in the other compounds, which usually show values of $\sim 90^\circ$ (Aurivillius, 1988). Angles of $\sim 72^\circ$ are also present in Bi coordinations (Table 4, deposited) of the high-temperature monoclinic polymorph of $\text{Bi}_2\text{O}(\text{SO}_4)_2$ (Aurivillius, 1988), which shows the same types of Bi coordination spheres (see below).

The decrease of the equatorial angle below the ideal (120°) and lengthening of the axial bonds in trigonal bipyramidal BiO_4E coordinations are attributed to electron repulsion effects associated with the lone pair electrons on Bi^{3+} (Francesconi *et al.*, 1998). Aurivillius (1988) pointed out that owing to the large average M–O distances, the influence of the lone pair in Bi-oxide compounds may be less than it is for Sb in Sb-oxide compounds, so less rigid trigonal bipyramids can be expected in the former with respect to the latter. Taking into account this consideration we may suppose that the angles of $\sim 72^\circ$ observed

in BiO_4E coordinations of the baličžuničite structure and its high-temperature polymorph (Aurivillius, 1988) are not only due to electron repulsion effects associated with lone-pair electrons, but also by packing effects connected to the presence of strongly bonded groups $\text{Bi}_5\text{O}_3^{2+}$ ($\text{Bi}_4\text{O}_2^{8+}$ in $\beta\text{-Bi}_2\text{O}(\text{SO}_4)_2$; see below) with oxo oxygens in trigonal holes. Instead, the majority of the other known Bi oxysulfates [see for instance $\text{Bi}_{26}\text{O}_{27}(\text{SO}_4)_{12}$ and $\text{Bi}_{14}\text{O}_{16}(\text{SO}_4)_5$ (Aurivillius, 1987) and leguermite, $\text{Bi}_{12.67}\text{O}_{14}(\text{SO}_4)_5$ (Garavelli *et al.*, 2014)] are characterized by fluorite-like structural portions in which oxo oxygens occupy larger tetrahedral holes.

The Bi atoms in the baličžuničite structure showing distorted square bipyramidal BiO_5E coordination are Bi(1), Bi(2) and Bi(5). Their coordination polyhedra are characterized by five oxygen atoms in square pyramidal geometry and the lone electron pair under the base of the square pyramid. They are characterized by the significantly longer equatorial Bi–O bonds in the base of the pyramid compared to the axial bond (Table 3) and angles between the axial and the equatorial oxygen atoms of $<90^\circ$ (Table 4, supplementary), because the Bi atoms are situated below the base, as mentioned earlier. Similar coordination is observed in a number of halide and oxide compounds with active lone electron pair elements (Gillespie, 1963*a,b*; Robinson and Gillespie, 2003). Some examples are Sb atoms in SbCl_5 (Ohlberg, 1959), Bi2 in the structure of $\alpha\text{-Bi}_2\text{O}_3$ (Malmros, 1970), and Sb(2) and Sb(3) atoms in the structure of $\text{Sb}_4\text{O}_2(\text{OH})(\text{SO}_4)_4(\text{H}_5\text{O}_2)\cdot\text{H}_2\text{O}$ (Douglade and Mercer, 1980). As noted below, Bi(1), Bi(4) and Bi(5) in the structure of the high-temperature polymorph of baličžuničite also have the same type of coordination, with similar characteristics (Table 3 and supplementary Table 4).

To understand the stereochemical effect of the lone electron pair of Bi^{3+} it is not enough just to investigate the configuration of the short Bi–O bonds, because the pair not only repels the strong Bi–O bonds, reflected in the distortion of bond angles, but also influences the oxygen atoms on the side to which the lone electron pair is displaced from the atomic nucleus. It is this distortion of the total surrounding of the atoms with the lone electron pair that gives the strongest geometrical impression of the stereochemical activity. This forms the basis of the extended VSEPR model (Andersson *et al.*, 1973; Galy *et al.*, 1975) where the lone electron pair is treated as

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 TABLE 5. Selected angles (°) in tetrahedral BiO₃E, trigonal bipyramidal BiO₄E and square pyramidal BiO₅E coordinations of bismuth and antimony compounds.

Compound	Atom	Tetrahedral BiO ₃ E		Reference
		O–Bi–O		
Leguernite Bi _{12.67} O ₁₄ (SO ₄) ₅	Bi(3)	86(1), 83(1), 75(1)		Garavelli <i>et al.</i> (2014)
	Bi(4)	85(1), 80(1), 73(1)		
	Bi(5)	81(1), 81(1), 74(1)		
	Bi(6)	88(1), 83(1), 75(1)		
Compound	Atom	Trigonal bipyramids BiO ₄ E		Reference
		O _{eq} –M–O _{eq}	O _{ax} –M–O _{ax}	
α-Bi ₂ O ₃	Bi(1)	93(1)	153(1)	Malmros (1970)
β-Bi ₂ O ₃	Bi	82(1)	172(1)	Blower and Greaves (1988)
Bi ₁₄ O ₂₀ (SO ₄)	Bi(2)	92(1)	173(1)	Francesconi <i>et al.</i> (1998)
Leguernite Bi _{12.67} O ₁₄ (SO ₄) ₅	Bi(1)	90(1)	131(1)	Garavelli <i>et al.</i> (2014)
	Bi(2)	82(1)	131(1)	
Sb ₄ O ₂ (OH)(SO ₄) ₄ (H ₅ O ₂) H ₂ O	Sb(1)	84(1)	160(1)	Douglade and Mercier (1980)
	Sb(4)	93(1)	140(2)	
Compound	Atom	Square bipyramids BiO ₅ E		Reference
		O _{ax} –M–O _{eq}	O _{eq} –M–O _{eq}	
α-Bi ₂ O ₃	Bi(2)	96(1)	154(1)	Malmros (1970)
		78(1)		
		76(1)		
		82(1)		
Sb ₄ O ₂ (OH)(SO ₄) ₄ (H ₅ O ₂) H ₂ O	Sb(2)	71(1)	154(1)	Douglade and Mercier (1980)
		76(1)		
		80(1)		
	Sb(3)	73(1)	159(2)	
		71(1)		
		82(1)		
		77(1)		
		68(1)		

a sphere occupying a defined volume eccentric to the atomic nucleus. Moreover, the use of the total coordination of Bi³⁺ supports the calculation of both the centroid and the eccentricity of the full coordination (Balič-Žunić and Makovicky, 1996). The position of the former closely represents the mass centre of the lone electron pair (Olsen *et al.*, 2010) while the latter is a quantitative measure of its expression. The calculations made for the Bi sites in the crystal structure of baličžuničite using the program *IVTON* (Balič-Žunić and Vicković, 1996) reveal that for Bi(1), Bi(2), Bi(3), Bi(4) and Bi(5) the lone electron pair is displaced away from the shortest bonds, which in all cases involves the oxo oxygens. In the case of Bi(3)

and Bi(4), which have two short bonds to oxo oxygens each, the lone electron pair is displaced along the bisecting line of the bond angle. In the case of Bi(6), which is not bonded to any oxo ligand and sits in a distorted octahedral environment, the lone electron pair is displaced away from the octahedral face formed by the three oxygens that have the shortest bonds with Bi and towards the opposite face formed by the three oxygens at longer bond distances. Considering the eccentricities of coordinations, the strongest stereochemical activity is expressed by the lone electron pairs of Bi(1) and Bi(4), followed by the Bi(2), Bi(5), Bi(3), and the weakest by the Bi(6) lone electron pair (Table 6, supplementary).

The sulfate groups in baličžuničite give S–O distances that range from 1.43 to 1.53 Å (Table 3) with an average of 1.48 Å, which is the typical value observed for sulfate anions (Palmer *et al.*, 1972).

The oxo oxygens, which sit almost in the centres of planar OBi_3 fragments (with 0.1–0.2 Å displacements), each give bond-valence sums (Brese and O’Keeffe, 1991) of ~ 2.5 and appear overbonded. The same amount of ‘overbonding’ is obtained for the same type of oxo oxygen coordination in the high-temperature structure (Aurivillius, 1988), and the same effect can be observed for the OSb_3 planar coordination in $\text{Sb}_4\text{O}_2(\text{OH})(\text{SO}_4)_4(\text{H}_5\text{O}_2)(\text{H}_2\text{O})$ (Douglade and Mercier, 1980). The crystal-structure refinement does not suggest a deviation from planarity in a form of displacement parameters perpendicular to the coordination plane or even a split site of the oxo oxygens which could account for longer bonds. The ‘overbonding’ of oxo oxygens contributes to the corresponding enlarged bond-valence sums of Bi atoms which lie at ~ 3.1 to 3.2, compared to Bi(6) which is not bonded to oxo oxygens and has a valence sum of 2.99. In our opinion this is a sign that the bonds between oxo oxygen and Bi are significantly different to bonds between sulfate oxygen and Bi, the former being more shared in character, the latter with more closed shell interactions. However, only a detailed electron density study would be able to reveal such details.

Comparison with the synthetic monoclinic $\text{Bi}_2\text{O}(\text{SO}_4)_2$

As noted above, baličžuničite is the natural analogue of the low-temperature polymorph of $\text{Bi}_2\text{O}(\text{SO}_4)_2$ [described as $\alpha\text{-Bi}_2\text{O}(\text{SO}_4)_2$ by Jones (1984)], whereas the phase with the same composition synthesized and structurally investigated by Aurivillius (1988) represents the high-temperature polymorph [$\beta\text{-Bi}_2\text{O}(\text{SO}_4)_2$ in Jones (1984)]. Common to the crystal structures of both polymorphs is the arrangement of Bi atoms and sulfate groups in layers with a eutactic arrangement, and oxo oxygens in the same layers in trigonal planar coordination with Bi atoms (Fig. 1 and supplementary Fig. 5, available from www.minersoc.org/pages/e_journals/dep_mat_mm.html). These layers, which are parallel to (100) in baličžuničite (Fig. 3) and parallel to (010) in the high-temperature polymorph (Fig. 6, supplementary), are stacked in a

manner that the Bi atoms from one layer overlap with the sulfate groups from the neighbouring two layers and *vice versa*. In this way, Bi atoms alternating with sulfate groups form infinite rods which extend along [100] in the baličžuničite structure and along [010] in the monoclinic high-temperature structure (Aurivillius, 1988). The closest Bi atoms are arranged in a triangular manner around the oxo oxygens, but with different groupings in the two structures. In baličžuničite the groups consist of three triangles condensed in a trapezohedral fashion (Figs 1 and 2), whereas in the monoclinic high-temperature polymorph planar, rhomboidal $\text{Bi}_4\text{O}_2^{8+}$ groups are formed by the combination of two Bi triangles surrounding oxo oxygen atoms (Fig. 5, supplementary). The latter structure is, moreover, characterized by only one type of infinite rod with a rhombic section, in contrast to the baličžuničite structure in which stripes of separate Bi(6) coordination sites and sulfate groups occur together with rods formed of trapezohedral $\text{Bi}_5\text{O}_3^{9+}$ groups and sulfate groups.

In the rhomboidal $\text{Bi}_4\text{O}_2^{8+}$ groups of the crystal structure of the high-temperature polymorph, Bi atoms are bonded to one oxo oxygen [Bi(1), Bi(4), Bi(5)] or to two oxo oxygen atoms [Bi(2), Bi(3), Bi(6)]. In this respect, Bi atoms in the former group are similar to Bi(1) and Bi(5) in the baličžuničite structure, whereas those in the latter group resemble Bi(3) and Bi(4) in the baličžuničite structure. The similarity extends to the rest of the coordination sphere for these Bi atoms (Table 3). Compared to baličžuničite the crystal structure of the high-temperature polymorph shows less variation in the coordination types of Bi, because in the baličžuničite structure there are also Bi(2) and Bi(6) atoms, the former coordinated to three oxo oxygens, the latter not coordinated to any oxo oxygen with a specific arrangement of both closer and more distant oxygen ligands (see above). The stereochemical influences of the Bi^{3+} lone electron pairs are comparable for the equivalent coordination types in the two crystal structures. The eccentricities of the coordination modes where Bi are bonded to one oxo oxygen are somewhat larger in baličžuničite compared to $\beta\text{-Bi}_2\text{O}(\text{SO}_4)_2$ (50–60% vs. 40–45%), but it is the opposite for the coordination where Bi is bonded to two oxo oxygen atoms (45–55% vs. 40–60%). However, the quantitative differences should be taken with reservation, because the crystal-structure data of the high-temperature polymorph

may not be adequate for an accurate structure refinement (see below).

Sulfate groups in the crystal structure of the high-temperature polymorph contain S–O distances which deviate significantly from the expected value of 1.48 Å (Table 3). A comparison of coordination parameters for sulfate groups in the crystal structures of the two polymorphs is reported in Table 6 (supplementary). The values of the polyhedral distortion (v) and volume eccentricity (ECC v) are generally lower in the baličžuničite structure and thus indicate more regular and symmetrical coordination. According to Aurivillius (1988), the reason for the partly abnormal S–O distances in the structure of the β phase may be the presence of errors in the XRD data. The author mentions a “superstructure effect” arising from the fact that the data contain a restricted number of strong reflections among a very large number of weak or absent reflections, which might need longer measuring times in order to produce more reliable intensities and, consequently, more accurate oxygen coordinates. The anomalous S–O distances might also be related to a disordered orientation of the sulfate tetrahedra. Both effects would influence not only the calculated parameters of the S coordination sphere, but also those of Bi. In this light, a reinvestigation of the crystal structure of the high-temperature polymorph is desirable.

Aurivillius (1988) described the structure of β - $\text{Bi}_2\text{O}(\text{SO}_4)_2$ as built of infinite layers with strong internal bonds extending parallel to the (201) plane and joined by weaker Bi–O bonds (Fig. 6, supplementary). In the crystal structure of baličžuničite the strong Bi–O bonds make a three dimensional network with sulfate groups and no structural layering of this kind can be observed.

Unit-cell parameters of the β phase are $a = 32.160(9)$, $b = 6.706(25)$, $c = 22.612(16)$ Å and $\beta = 119.55(5)^\circ$. They appear related to those of baličžuničite by the crystal-lattice transformation [022], [100], [020] as pointed out in Pinto *et al.* (2014). However, comparison of the two structures shows that this crystal-lattice transformation is not caused by a close structural relationship between the two, but is enabled by some common metrical features. Both structures show an arrangement of the Bi atoms and sulfate groups in an almost eutactic pattern in layers with Bi–Bi, Bi–S and S–S distances of ~ 4 Å. The nearly perfect overlap of the layers [(100) in baličžuničite and (010) in the high-temperature monoclinic

form] in both structures produces an interlayer distance of ~ 3.35 Å and makes the a axis in baličžuničite nearly perpendicular to the (100) plane. Although the general pattern of the Bi and S atoms in the two structures is similar and allows for several types of lattice-transformation relations (one of them mentioned above), the sequence of the Bi and S atoms are different and the arrangement of oxygen atoms is not simply related in the two structures. We therefore conclude that the transformation from the low-temperature to the high-temperature structure modification of $\text{Bi}_2\text{O}(\text{SO}_4)_2$, which according to Jones (1984) occurs at $\sim 530^\circ\text{C}$, is not a displacive one and involves breaking of bonds. The slow rate of the transformation between the α and the β forms of $\text{Bi}_2\text{O}(\text{SO}_4)_2$, as well as the relatively large enthalpy changes reported for this phase transition (Jones, 1984), are also consistent with a reconstructive transformation.

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References

- Andersson, S., Åström, A., Galy, J. and Meunier, G. (1973) Simple calculations of bond lengths and bond angles in certain oxides, fluorides or oxide fluorides of Sb^{3+} , Te^{4+} and Pb^{2+} . *Journal of Solid State Chemistry*, **6**, 187–190.
- Aurivillius, B. (1987) Pyrolysis products of $\text{Bi}_2(\text{SO}_4)_3$. Crystal structure of $\text{Bi}_{26}\text{O}_{27}(\text{SO}_4)_{12}$ and $\text{Bi}_{14}\text{O}_{16}(\text{SO}_4)_5$. *Acta Chemica Scandinavica*, **A41**, 415–422.
- Aurivillius, B. (1988) Pyrolysis products of $\text{Bi}_4(\text{SO}_4)_3$. II. Crystal structure of $\text{Bi}_2\text{O}(\text{SO}_4)_2$. *Acta Chemica Scandinavica*, **A42**, 95–110.
- Balič-Žunič, T. and Makovicky, E. (1996) Determination of the centroid or “the best centre” of a coordination polyhedron. *Acta Crystallographica*, **B52**, 78–81.
- Balič-Žunič, T. and Vicković, I. (1996) IVTON program for the calculation of geometrical aspects of crystal structures and some crystal chemical applications. *Journal of Applied Crystallography*, **29**, 305–306.
- Berlepsch, P., Makovicky, E. and Balič-Žunič, T. (2001) Crystal chemistry of meneghinite homologues and related sulfosalts. *Neues Jahrbuch für Mineralogie, Monatshefte*, 115–135.

- Blessing, B. (1995) An empirical correction for absorption anisotropy. *Acta Crystallographica*, **A51**, 33–38.
- Blower, S.K. and Greaves, C. (1988) The structure of β - Bi_2O_3 from powder neutron diffraction data. *Acta Crystallographica*, **C44**, 587–589.
- Brese, N.E. and O’Keeffe, M. (1991) Bond-valence parameters for solids. *Acta Crystallographica*, **B47**, 192–197.
- Bruker (2003a) *APEX2*. Bruker Analytical X-ray Systems Inc., Madison, Wisconsin, USA.
- Bruker (2003b) *SAINT-IRIX*. Bruker Analytical X-ray Systems Inc., Madison, Wisconsin, USA.
- Capitani, G.C., Catelani, T., Gentile, P., Lucotti, A. and Zema, M. (2013) Cannonite $[\text{Bi}_2\text{O}(\text{SO}_4)(\text{OH})_2]$ from Alfenza (Crodo, Italy): crystal structure and morphology. *Mineralogical Magazine*, **77**, 3067–3079.
- Crumpton, T.E. and Greaves, C. (2004) The structural chemistry and oxide ion conducting properties of the new bismuth oxide sulfate, $\text{Bi}_8\text{O}_{11}(\text{SO}_4)$. *Journal of Materials Chemistry*, **14**, 2433–2437.
- Douglade, P.J. and Mercier, R. (1980) Structure du tétrasulfate d’hydroxodioxotétraantimoine(III) et de dioxonium monohydraté $\text{Sb}_4^{11}\text{O}_2(\text{OH})(\text{SO}_4)_4(\text{H}_5\text{O}_2)\cdot\text{H}_2\text{O}$ (ou $\text{Sb}_2\text{O}_3\text{SO}_3\cdot 2\text{H}_2\text{O}$). *Acta Crystallographica*, **B36**, 2919–2925.
- Francesconi, M.G., Kibyshire, A.L. and Greaves, C. (1998) Synthesis and structure of $\text{Bi}_{14}\text{O}_{20}(\text{SO}_4)$, A new bismuth oxide sulfate. *Chemistry of Materials*, **10**, 626–632.
- Galy, J., Meunier, G., Andersson, S. and Åström, A. (1975) Stéréochimie des éléments comportant des paires non liées: Ge(II), As(III), Se(IV), Br(V), Sn(II), Sb(III), Te(IV), I(V), Xe(VI), Tl(I), Pb(II), et Bi(III) (oxydes, fluorures et oxyfluorures). *Journal of Solid State Chemistry*, **13**, 142–159.
- Garavelli, A., Pinto, D., Bindi, L. and Mitolo, D. (2013) Leguermite, IMA 2013-051. CNMNC Newsletter No. 17, October 2013, page 3002; *Mineralogical Magazine*, **77**, 2997–3005.
- Garavelli, A., Pinto, D., Bindi, L. and Mitolo, D. (2014) Leguermite, $\text{Bi}_{12.67}\text{O}_{14}(\text{SO}_4)_5$, a new Bi-oxy sulfate from the fumarole deposit of “La Fossa” crater, Vulcano, Aeolian Islands, Italy. *Mineralogical Magazine*, **78**, 1629–1645.
- Gillespie, R.J. (1963a) The valence-shell electron-pair repulsion (VSEPR) theory of directed valency (Review). *Journal of Chemical Education*, **40**, 295–301.
- Gillespie, R.J. (1963b) The stereochemistry of five-coordination. Part I. Non-transition elements. *Journal of the Chemical Society*, 4672–4678.
- Gillespie, R.J. (2008) Fifty years of the VSEPR model. *Coordination Chemistry Reviews*, **252**, 1315–1327.
- Gillespie, R.J. and Nyholm, R.S. (1957) Inorganic stereochemistry. *Quarterly Review of the Chemical Society*, **11**, 339–380.
- Graunar, M. and Lazarini, F. (1982) Di- μ -hydroxo-bis[$\text{aqua}\text{sulfatobismuth(III)}$]. *Acta Crystallographica*, **B38**, 2879–2881.
- Ibers, J.A. and Hamilton, W.C. (1974) *International Tables for X-ray Crystallography*, **Vol. 4**. The Kynoch Press, Birmingham, UK.
- Jones, W.M. (1984) Equilibrium pressures over the systems bismuth trisulfate dibismuthmonoxydisulfate and dibismuthmonoxydisulfate dibismuthdioxymonosulfate. Slow transformation between two crystalline forms of dibismuthmonoxydisulfate. *Journal of Chemical Physics*, **80**, 3408.
- Kinberger, B. (1970) The crystal structure of SbPO_4 . *Acta Chemica Scandinavica*, **24**, 320–328.
- Malmros, G. (1970) The crystal structure of α - Bi_2O_3 . *Acta Chemica Scandinavica*, **24**, 384–396.
- Makovicky, E. and Balić-Zunić, T. (1998) New measure of distortion for coordination polyhedra. *Acta Crystallographica*, **B54**, 766–773.
- Ohlberg, S.M. (1959) The crystal structure of antimony pentachloride at -30°C . *Journal of the American Chemical Society*, **81**, 811–813.
- Olsen, L.A., Lopez-Solano, J., Garcia, A., Balic-Zunic, T. and Makovicky, E. (2010) Dependence of the lone pair of bismuth on coordination environment and pressure: an *ab initio* study on $\text{Cu}_4\text{Bi}_5\text{S}_{10}$ and Bi_2S_3 . *Journal of Solid State Chemistry*, **183**, 2133–2143.
- Palmer, K.J., Wong, R.Y. and Lee, K.S. (1972) The crystal structure of ferric ammonium sulfate trihydrate, $\text{FeNH}_4(\text{SO}_4)_2\cdot 3\text{H}_2\text{O}$. *Acta Crystallographica*, **B28**, 236–241.
- Pinto, D., Garavelli, A. and Mitolo, D. (2013) Balićzunićite, IMA 2012-098. CNMNC Newsletter No. 16, August 2013, page 2699; *Mineralogical Magazine*, **77**, 2695–2709.
- Pinto, D., Garavelli, A. and Mitolo, D. (2014) Balićzunićite, $\text{Bi}_2\text{O}(\text{SO}_4)_2$, a new fumarole mineral from the “La Fossa” crater at Vulcano, Aeolian Islands, Italy. *Mineralogical Magazine*, **78**, 1043–1055.
- Robinson, E.A. and Gillespie, R.J. (2003) Ligand close packing and the geometry of the fluorides of the nonmetals of periods 3, 4, and 5. *Inorganic Chemistry*, **42** 3865–3872.
- Rögner, P. (2005) Riominerale, ein neues Wismutmineral vom Abbau Falcacci, Rio Marina, Elba (Italien). *Aufschluss*, **56**, 53–60.
- Sheldrick, G.M. (2008a) *SADABS. Version 2008/1*. University of Göttingen, Germany.
- Sheldrick, G.M. (1997a) *SHELXS-97. A program for automatic solution of crystal structures*. University of Göttingen, Germany.
- Sheldrick, G.M. (1997b) *SHELXL-97. A program for crystal structure refinement*. University of Göttingen, Germany.

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- Smirnov, V.I., Ponomareva, V.G., Yuklin, Y.M. and Uvarov, N.F. (2003) Fluorite-related phases in the $\text{Bi}_2\text{O}_3\text{--SO}_3$ system. *Solid State Ionics*, **156**, 79–84.
- Spek, A.L. (2005) *PLATON, A Multipurpose Crystallographic Tool*. Utrecht University, Utrecht, The Netherlands.
- Stanley, C.J., Roberts, A.C., Harris, D.C., Criddle, A.J. and Szymański, J.T. (1992) Cannonite, $\text{Bi}_{20}(\text{OH})_2\text{SO}_4$, a new mineral from Marysvale, Utah, USA. *Mineralogical Magazine*, **56**, 605–609.

