



Article

Biagioniite, Tl_2SbS_2 , from the Hemlo gold deposit, Marathon, Ontario, Canada: occurrence and crystal structure

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Abstract

Biagioniite, ideally Tl_2SbS_2 , is a new mineral from the Hemlo gold deposit, Marathon, Ontario, Canada. It occurs as very rare anhedral crystals up to 65 μm across associated with aurostibite, stibarsen and native gold in a calcite matrix. Biagioniite is opaque with a metallic lustre and shows a black streak. In reflected light biagioniite is moderately birefractant and not pleochroic. Under crossed polars it is weakly anisotropic with blueish to light-blue rotation tints. Internal reflections are absent.

Reflectance percentages for the four standard wavelengths (R_{min} and R_{max}) are 35.9 and 37.5 (471.1 nm); 34.7 and 36.2 (548.3 nm); 33.8 and 35.3 (586.6 nm); and 31.5 and 33.7 (652.3 nm), respectively. A mean of four electron microprobe analyses gave: Tl 65.12(31), Ag 3.52(9), Sb 20.22(12), S 10.80(8), total 99.66 wt.%, corresponding, on the basis of a total of 5 atoms, to $(Tl_{1.87}Ag_{0.19})_{\Sigma 2.06}Sb_{0.97}S_{1.97}$. Biagioniite is monoclinic, space group Pc , with $a = 11.0895(9)$, $b = 14.3124(11)$, $c = 7.9352(6)$ Å, $\beta = 96.230(8)^\circ$, $V = 1252.02(17)$ Å³ and $Z = 8$. The four strongest powder-diffraction lines [d in Å (I/I_0) (hkl)] are: 3.56 (100) (310); 3.37 (75) ($\bar{2}31$); 3.79 (60) (012); 3.03 (60) (032). In the crystal structure [$R_1 = 0.024$ for 2655 reflections with $I > 2\sigma(I)$], thallium adopts various coordinations extending from quasi-linear to quasi-tetrahedral. Antimony forms Sb–Sb pairs, which lead to the formula $[Tl^{+1}]_4[Sb_2]^{4+}[S^{2-}]_4$. Biagioniite is isostructural with dervillite, Ag_2AsS_2 . The new mineral has been approved by the International Mineralogical Association Commission on New Minerals, Nomenclature and Classification (IMA2019–120) and named for Cristian Biagioni, Associate Professor of Mineralogy at the Department of Earth Sciences of the University of Pisa, Italy.

Keywords: biagioniite, new mineral, thallium, sulfosalt, Hemlo deposit, Canada

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Introduction

Several elements, having economic value or environmental concern, are hosted in sulfosalts, a group of complex minerals typically occurring in hydrothermal settings. Our ongoing effort in the last two decades (Bindi and Biagioni, 2018, and references therein) has been the study of these minerals from a structural point of view to try to: (1) elucidate the role played by minor components, which could give interesting insights into the physico-chemical conditions of the crystallisation environments, and (2) allow the potential description of unpredictable structures, unexpected crystallographic features, and new mineral species. Such a body of knowledge has been critical for assessing both the technological potentialities of sulfosalts as well as their geological significance.

In the course of this research project (i.e. Biagioni *et al.*, 2016; Bindi *et al.*, 2012a,b, 2015a,b), we examined a sample from the Hemlo gold deposit, Marathon, Ontario, Canada (Harris, 1989), belonging to the mineralogical collections of the Museo di Storia Naturale of the University of Florence. The sample consists of tiny criddleite grains associated closely with aurostibite, stibarsen and native gold in a calcite matrix. Among the stibarsen

fragments, a small unique grain that turned out to be biagioniite, Tl_2SbS_2 , was found.

Biagioniite was approved as a new mineral by the International Mineralogical Association – Commission on New Minerals, Nomenclature and Classification (IMA2019-120, Bindi and Moëlo, 2020). The mineral name honours Cristian Biagioni (b. 1981), Associate Professor of Mineralogy at the Department of Earth Sciences of the University of Pisa, Italy. He is the current Italian Member of the IMA-Commission of New Minerals, Nomenclature and Classification and he is co-author of the description of more than 50 new mineral species. In addition, he contributed to the discovery of the Tl-rich nature of pyrite ores from the Apuan Alps (northern Tuscany, Italy), promoting a new scientific investigations of these ore deposits both from a mineralogical and environmental point of view (e.g. Biagioni *et al.*, 2013, 2017). The holotype material is deposited in the mineralogical collection of the Museo di Storia Naturale of the University of Florence, Italy, under catalogue number 46582/G.

Here we report the description of the new mineral biagioniite, together with the determination of its crystal structure.

Material studied

The Museum sample containing biagioniite comes from the Hemlo gold deposit, which is located near the northeast shore of Lake Superior, 35 km east of Marathon, Ontario (Harris,

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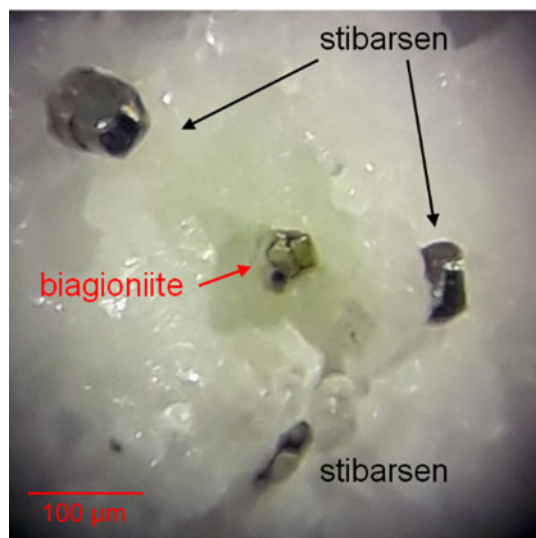


Fig. 1. Incident-light image of biagioniite associated with stibarsen on a calcite matrix. Museo di Storia Naturale of the University of Florence, catalogue number 46582/G.

1989; Tomkins *et al.*, 2004). The deposit, discovered in 1982, is of Archean age and occurs at the contact of felsic metavolcanics and pelitic metasediments. It consists of several mineralised zones, of which the main zone extends for a length of 2900 m, for a distance of 2500 m down-dip and ranges in thickness from 3 to 45 m. The ore minerals were formed from hydrothermal fluids that may in part be related to the shear zone.

Native gold is the principal gold mineral in the deposit (Harris, 1989). The gold ore is substantially enriched in Mo, V, As, Sb, Hg, Tl and Ba and contains a diverse assemblage of minerals. Interestingly, there is a close spatial association between the mercury and thallium minerals. In this regard, the realgar–cinnabar-rich quartz veins that occur within the central portion of the deposit are common hosts for the thallium minerals (Harris, 1989). Routhierite is the most common thallium mineral, parapirotite is less abundant, while vaughanite and criddleite are rare.

Physical and optical properties

Biagioniite occurs as very rare crystals grown on a calcite matrix (Fig. 1). The mineral exhibits a subhedral to anhedral grain morphology, and shows no inclusions of, or intergrowths with, other minerals. The maximum grain size of biagioniite is $\sim 65 \mu\text{m}$. It is black in colour and shows a black streak. The mineral is opaque in transmitted light and exhibits a metallic lustre. No cleavage is observed, and the fracture is uneven. The calculated density (for $Z = 8$) for the empirical formula (see below) is 6.192 g/cm^3 . Unfortunately, the density could not be measured here because of the small grain size. The Mohs hardness, estimated with respect to the surrounding calcite, is ~ 3 .

In plane-polarised incident light, biagioniite is creamy in colour, moderately bireflectant and not pleochroic. Between crossed polars, biagioniite is weakly anisotropic with blueish to light-blue rotation tints. Internal reflections are absent and there is no optical evidence of growth zonation.

Reflectance measurements were performed in air by means of a MPM-200 Zeiss microphotometer equipped with a MSP-20 system processor on a Zeiss Axioplan ore microscope. The filament temperature was $\sim 3350 \text{ K}$. An interference filter was adjusted, in

Table 1. Electron microprobe analysis results (four analytical spots, wt.% of elements) for biagioniite.

	Mean	Range
Ag	3.52(9)	3.35–3.77
Tl	65.12(31)	64.58–65.79
Sb	20.22(12)	19.65–21.08
S	10.80(8)	10.02–11.23
Total	99.66	99.09–100.16

turn, to select four wavelengths for measurement (471.1, 548.3, 586.6 and 652.3 nm). Readings were taken for specimen and standard (SiC) maintained under the same focus conditions. The diameter of the circular measuring area was 0.04 mm. Reflectance percentages for R_{min} and R_{max} are: 35.9 and 37.5 (471.1 nm); 34.7 and 36.2 (548.3 nm); 33.8 and 35.3 (586.6 nm); and 31.5 and 33.7 (652.3 nm), respectively.

Chemical composition

A preliminary chemical analysis using energy-dispersive spectrometry performed on the crystal fragment used for the structural study did not indicate the presence of elements ($Z > 9$) other than Tl, Sb, S and minor Ag. Analyses were carried out using a JEOL 8200 microprobe (wavelength dispersive

Table 2. Crystallographic data and experimental details for the selected biagioniite crystal.

Crystal data	
Formula	Tl_2SbS_2
Crystal size (mm)	$0.040 \times 0.050 \times 0.065$
Crystal system, space group	Monoclinic, Pc (#7)
Temperature (K)	293(3)
Form	blocky
Colour	black
a (Å)	11.0895(9)
b (Å)	14.3124(11)
c (Å)	7.9352(6)
β (°)	96.230(8)
V (Å ³)	1252.02(17)
Z	8
Calculated density (g/cm ³)	6.192
μ (mm ⁻¹)	56.16
Data collection	
Instrument	Bruker D8 Venture
Radiation type, wavelength (Å)	$\text{MoK}\alpha$, $\lambda = 0.71073$
Detector-to-sample distance (cm)	6
Number of frames	1248
Measuring time (s)	30
Maximum covered 2θ (°)	74.98
Absorption correction	Multi-scan
T_{min} , T_{max}	0.121, 0.155
Collected reflections	20,833
Unique reflections	4520
Reflections with $F_o > 4\sigma(F_o)$	2655
R_{int}	0.0321
R_σ	0.0424
Range of h, k, l	$-16 \leq h \leq 16$, $-21 \leq k \leq 21$, $-13 \leq l \leq 13$
Refinement	
Refinement	Full-matrix least squares on F^2
Final R_1 [$F_o > 4\sigma(F_o)$]	0.0243
Final R_1 (all data)	0.0315
GoF	0.939
Number refined parameters	182
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ ($e^- \text{Å}^{-3}$)	1.72, -1.57

Table 3. Atoms, fractional atom coordinates (Å), and atomic displacement parameters (Å²) for biagioniite.

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U_{eq}</i>
Tl1	0.23733(13)	0.59615(8)	0.42312(14)	0.0344(3)
Tl2	0.04141(14)	0.91367(9)	0.72629(15)	0.0437(4)
Tl3	0.69297(12)	0.90702(8)	0.12240(13)	0.0299(3)
Tl4	0.35736(13)	0.89299(8)	0.62921(17)	0.0356(3)
Tl5	0.56511(13)	0.60615(8)	0.89568(17)	0.0355(3)
Tl6	0.96143(15)	0.79027(10)	0.30728(18)	0.0526(4)
Tl7	0.8383(2)	0.49262(12)	0.6517(2)	0.0838(7)
Tl8	0.96092(16)	0.68618(11)	0.8476(2)	0.0713(5)
Sb1	0.31287(16)	0.68477(11)	0.9379(2)	0.0143(4)
Sb2	0.61774(17)	0.68126(12)	0.3516(2)	0.0167(4)
Sb3	0.30962(17)	0.83097(11)	0.1799(2)	0.0155(4)
Sb4	0.62590(17)	0.82160(12)	0.6039(2)	0.0157(4)
S1	0.1528(7)	0.5806(4)	0.0502(9)	0.0188(15)
S2	0.7909(7)	0.9183(5)	0.5002(8)	0.0177(14)
S3	0.1927(7)	0.7465(4)	0.6551(8)	0.0162(14)
S4	0.7352(8)	0.7510(5)	0.8912(8)	0.0229(17)
S5	0.8479(7)	0.6293(4)	0.4144(9)	0.0191(15)
S6	0.5150(7)	0.5673(5)	0.5200(9)	0.0237(17)
S7	0.0903(7)	0.8956(5)	0.1036(8)	0.0202(15)
S8	0.4270(7)	0.9350(4)	0.0130(9)	0.0179(14)

Table 4. Selected bond distances (Å) for biagioniite.

Tl1–S3	2.909(6)	Tl5–S6	2.750(7)	Sb1–S1	2.552(8)
Tl1–S1	2.916(7)	Tl5–S4	2.805(8)	Sb1–S3	2.635(6)
Tl1–S1	3.014(7)	Tl5–S6	3.024(7)	Sb1–Sb3	2.843(2)
Tl1–S6	3.119(8)	Tl5–Sb1	3.067(2)	<Sb1–S>	2.677
<Tl1–S>	2.990	<Tl5–S>	2.912		
Tl2–S7	2.967(7)	Tl6–S7	2.726(7)	Sb2–S6	2.465(8)
Tl2–S7	2.995(6)	Tl6–S5	2.802(7)	Sb2–S5	2.653(8)
Tl2–S3	3.011(6)	Tl6–S2	3.148(7)	Sb2–Sb4	2.830(3)
Tl2–S2	3.140(7)	<Tl6–S>	2.892	<Sb2–S>	2.649
<Tl2–S>	3.028				
Tl3–S2	2.932(7)	Tl7–S5	2.712(7)	Sb3–S8	2.458(7)
Tl3–S4	2.960(7)	Tl7–S5	2.725(7)	Sb3–S7	2.612(7)
Tl3–S8	3.010(7)	<Tl7–S>	2.719	Sb3–Sb1	2.843(2)
Tl3–S2	3.080(6)			<Sb3–S>	2.638
<Tl3–S>	2.996				
Tl4–S8	2.768(7)	Tl8–S4	2.726(9)	Sb4–S2	2.504(8)
Tl4–S3	2.802(7)	Tl8–S1	2.942(7)	Sb4–S4	2.663(7)
Tl4–S8	3.118(7)	Tl8–S3	3.246(7)	Sb4–Sb2	2.830(3)
<Tl4–S>	2.896	<Tl8–S>	2.971	<Sb4–S>	2.666

spectrometry mode, 25 kV, 20 nA, 1 μm beam size, counting times 20 s for peak and 10 s for background). The following lines were used: AgLα, TlMα, SbLβ and SKα. The standards employed were: synthetic TlI (Tl), pure element (Ag), synthetic Sb₂Te₃ (Sb) and pyrite (S). The crystal fragment was found to be homogeneous within analytical error. The average chemical compositions (four analyses on different spots) together with wt.% ranges of elements are reported in Table 1. On the basis of 5 atoms, the empirical formula of biagioniite is (Tl_{1.87}Ag_{0.19})Σ_{2.06}Sb_{0.97}S_{1.97}. The simplified ideal formula is (Tl, Ag)₂SbS₂, and the ideal formula is Tl₂SbS₂ (Z = 8), which requires Tl 68.74, Sb 20.48, S 10.78, total 100 wt.%.

X-ray crystallography and crystal-structure determination

The same crystal fragment (40 × 50 × 65 μm) used to obtain the chemical data was selected for X-ray single-crystal diffraction.

Table 5. Observed and calculated* powder X-ray diffraction data (*d* in Å) for biagioniite

<i>l_{est}</i>	<i>l_{calc}</i>	<i>d_{obs}</i>	<i>d_{calc}</i>	<i>h k l</i>
10	12	4.65	4.6463	121
	9		4.1219	211
20	23	3.98	3.9678	221
15	19	3.89	3.9002	131
20	22	3.85	3.8485	102
60	67	3.79	3.8024	012
15	23	3.75	3.7601	131
	14		3.6885	221
40	40	3.68	3.6747	300
	8		3.6073	230
	9		3.5921	102
20	18	3.58	3.5781	040
100	100	3.56	3.5592	310
40	47	3.48	3.4840	112
	26		3.4543	022
20	24	3.39	3.4033	140
	15		3.3894	122
	25		3.3862	202
75	81	3.37	3.3724	231
35	36	3.27	3.2689	320
20	23	3.24	3.2585	041
	19		3.2103	122
40	37	3.16	3.1637	141
	10		3.1286	321
40	39	3.08	3.0875	141
60	62	3.03	3.0398	032
	11		2.9873	212
	15		2.8618	241
	9		2.8093	222
20	19	2.795	2.7924	312
	8		2.7613	232
	19		2.7515	241
20	25	2.555	2.5539	302
	12		2.5216	421
20	17	2.515	2.5142	312
	9		2.3855	341
	8		2.3753	421
	14		2.3461	431
30	29	2.342	2.3434	223
	15		2.3167	052
	19		2.2582	350
30	26	2.228	2.2279	342
	14		2.2220	161
	17		2.2125	133
20	22	2.116	2.1153	143
30	31	2.089	2.0905	521
	8		2.0864	261
	14		2.0787	342
	15		2.0593	441
	9		2.0449	511
	9		1.9721	004
	15		1.9574	171
	9		1.9223	243
	12		1.8791	271
	9		1.8285	362
	9		1.7739	513
	9		1.7647	163
	8		1.4864	652

*Calculated diffraction pattern obtained with the atom coordinates and occupancies reported in Table 3 (only reflections with *I_{rel}* ≥ 8 are listed).

Data were collected using a Bruker D8 Venture diffractometer equipped with an Photon II CCD detector, with graphite-monochromatised MoKα radiation (λ = 0.71073 Å). Biagioniite was found to be monoclinic, with *a* = 11.0895(9), *b* = 14.3124(11), *c* = 7.9352(6) Å, β = 96.230(8)°, *V* = 1252.02(17) Å³ and *Z* = 8. The analysis of the systematic absences (*h0l*: *l* = 2*n* and *00l*: *l* = 2*n*)

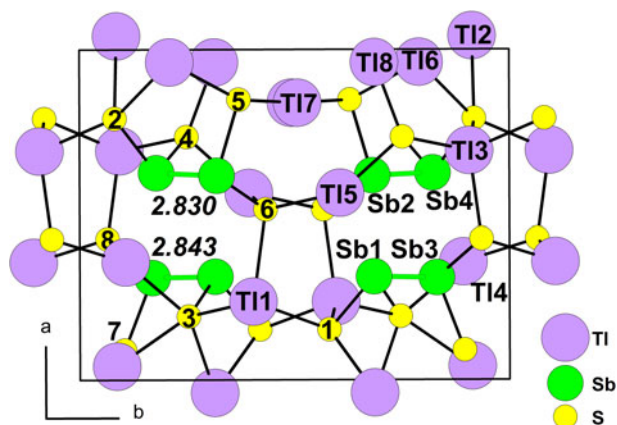


Fig. 2. The crystal structure of biagioniite down [001]: unit-cell content, atoms labels and Sb-Sb bond lengths (Å). Tl, Sb and S atoms are given as purple, green and yellow circles, respectively.

led to the choice of the space groups Pc and $P2_1/c$. Although the statistical tests on the distribution of $|E|$ values ($|E^2-1|=0.812$) indicated the absence of an inversion centre, suggesting the choice of the space group Pc , the structure was preliminarily solved in the $P2_1/c$ space group. A residual $R_1=0.18$ value was achieved quickly. However, the preliminary structural model obtained indicated a large atomic disorder. The structure model was subsequently optimised, and an ordered model was sought, but no improvement in R could be achieved. At this point, a thorough analysis of the structure (essentially based upon the observation of the very large atomic displacement parameters for particular atoms) suggested that some symmetry element of the $P2_1/c$ space group should be

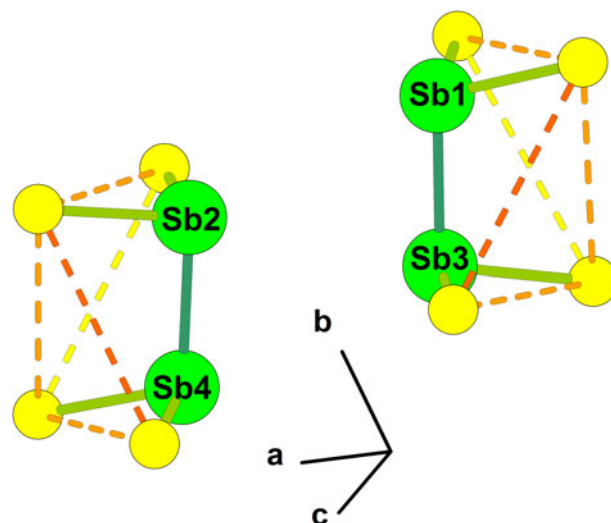


Fig. 4. Coordination of the Sb pairs with S atoms.

removed. The reflection and atomic position data sets were then adapted to the Pc space group (showing the same reflections conditions) and the structure refined. After several cycles, an ordered solution with full site occupancies was finally determined by carefully removing atoms with low site occupancies and/or non-realistic distances with neighbouring atoms and adding significant positions found in the difference-Fourier syntheses. The structure could be smoothly refined in Pc without any damping factor or restrictions by the program *SHELXL* (Sheldrick, 2008). The occupancy of all the sites was left free to vary (Tl vs. □; Sb vs. □; S vs. □,

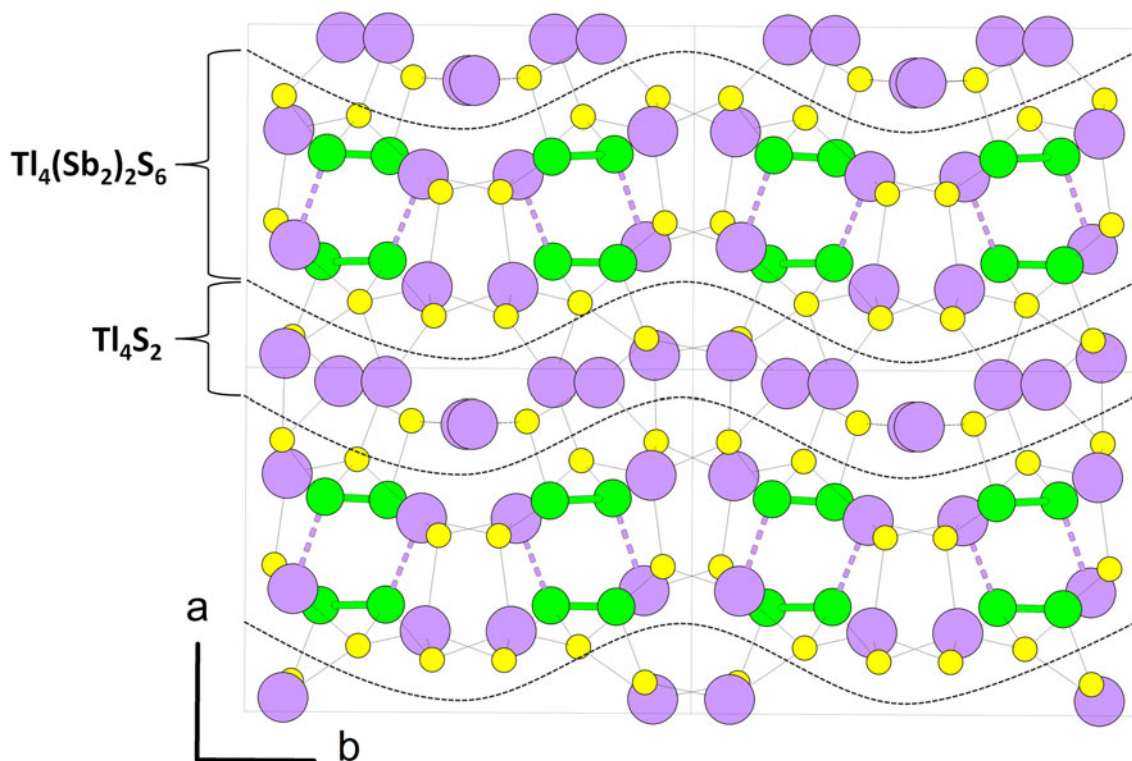


Fig. 3. Biagioniite: $2a \times 2b$ cell. $Tl_4(Sb_2)_2S_6$ ribbons parallel to [001], stacked along [010], form undulated layers along [100]. These layers are separated by a one-atom-thick layer of Tl_4S_2 .

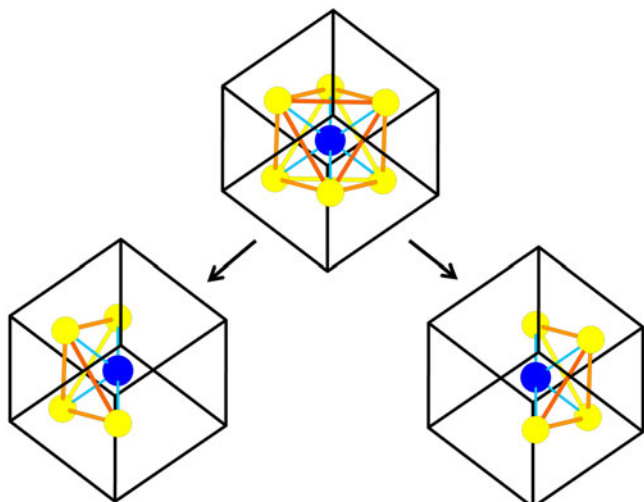


Fig. 5. Coordination of each Sb pair (down, reduced to a central blue atom) with four S atoms corresponding to a hemi-octahedron cut along a symmetry plane (through two opposite edges of the cube). Two neighbouring hemi-octahedra brought closer allow the rebuilding of the octahedron (above).

where \square = a vacancy) but all the positions were found to be fully occupied. Neutral scattering curves for Tl, As and S were taken from the *International Tables for X-ray Crystallography* (Wilson, 1992). At the last stage, with anisotropic atomic displacement parameters for all the atoms and no constraints, the residual value settled at $R_1 = 0.0243$ for 2655 observed reflections [$2\sigma(I)$ level] and 182 parameters and at $R_1 = 0.0315$ for all 4520 independent reflections.

Note that the acentric structural model we obtained does not show high values in the correlation matrix between pairs of atoms which are equivalent in the centrosymmetric space group $P2/c$. To test whether the acentric model is to be preferred to the centric one we also tested the presence of twinning by inversion in the non-centrosymmetric structure refinement. Indeed, as is well known, a centrosymmetric structure that is refined as non-centrosymmetric will show a twin scale factor, equivalent to the Flack parameter in the case of inversion twinning (Flack *et al.*, 2006; Müller *et al.*, 2006), that refines to 50% within analytical uncertainty. We found the racemic twin-component scale factor refined to 0.09(2), consistent with a highly asymmetrical

distribution of the enantiomorphic components and indicating the acentric model as the right choice.

Experimental details and R indices are given in Table 2. Fractional atomic coordinates and atomic displacement parameters are reported in Table 3. Bond distances are given in Table 4. The crystallographic information files have been deposited with the Principal Editor of *Mineralogical Magazine* and are available as Supplementary material (see below).

Powder X-ray diffraction data (Table 5) were collected with an Oxford Diffraction Excalibur PX Ultra diffractometer fitted with a 165 mm diagonal Onyx CCD detector and using copper radiation ($\text{CuK}\alpha$, $\lambda = 1.54138 \text{ \AA}$). The least squares refinement gave the following values: $a = 11.0999(9)$, $b = 14.273(1)$, $c = 7.9323(7) \text{ \AA}$, $\beta = 96.29(1)^\circ$ and $V = 1249.1(1) \text{ \AA}^3$.

Description of the structure and discussion

The structure of biagioniite projected down $[001]$ is reported in Fig. 2. It is isostructural with dervillite, Ag_2AsS_2 (Bindi *et al.*, 2013). An enlarged projection of the structure (Fig. 3) allows one to distinguish $\text{Tl}_4(\text{Sb}_2)_2\text{S}_6$ ribbons parallel to $[001]$, stacked along $[010]$, to form undulated layers along $[100]$. These layers are separated by a one-atom-thick Tl_4S_2 layer. It is noteworthy, there are two Sb–Sb pairs, Sb1–Sb3 (2.843 Å) and Sb2–Sb4 (2.830 Å).

The coordination of these pairs is represented in Fig. 4. Coordination of each pair with four S atoms corresponds to a hemi-octahedron cut along a symmetry plane (through two opposite edges of the cube – Fig. 5). Two neighbouring hemi-octahedra brought closer allow a single octahedron to be rebuilt.

In the $\text{Tl}_4(\text{Sb}_2)_2\text{S}_6$ ribbon layer, Tl1 and Tl3 exhibit a tetrahedral coordination with S, whereas the coordination is triangular for Tl4 and Tl5. Nevertheless, the coordination environment for Tl4 and Tl5 is completed by additional short Tl–Sb bonds (Tl5–Sb1 = 3.067 Å and Tl4–Sb4 = 3.175 Å).

The coordination of Tl atoms of the Tl_4S_2 layer is shown in Fig. 6. There is a central zig-zag row of tetrahedral Tl atoms, flanked by two stripes of triangular Tl, and then two stripes of linear Tl. Contrary to the $\text{Tl}_4(\text{Sb}_2)_2\text{S}_6$ ribbon-layer (see below), here there is linear Tl on one mirror position, and tetrahedral Tl along the second mirror position. It is worth noting the linear coordination of Tl7. To the best of our knowledge, biagioniite seems to be

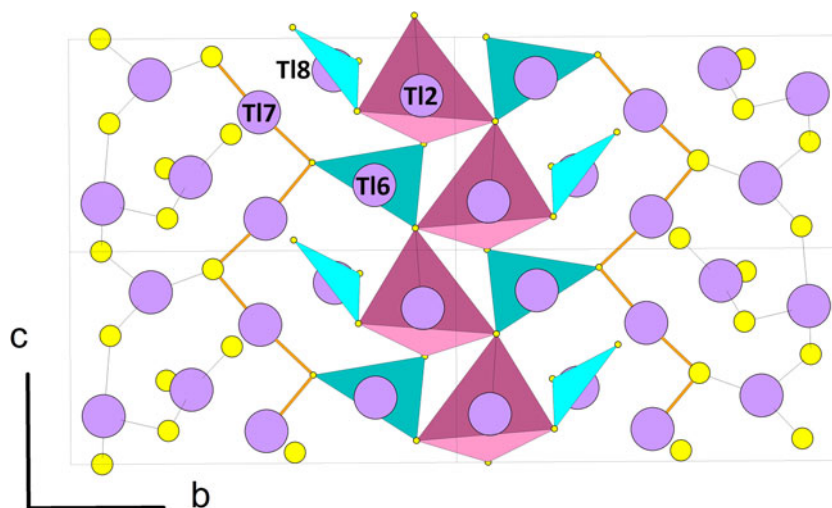


Fig. 6. Coordination of Tl atoms in the Tl_4S_2 layer in the structure of biagioniite. Tl2: tetrahedral; Tl6 and Tl8: triangular; Tl7: linear.

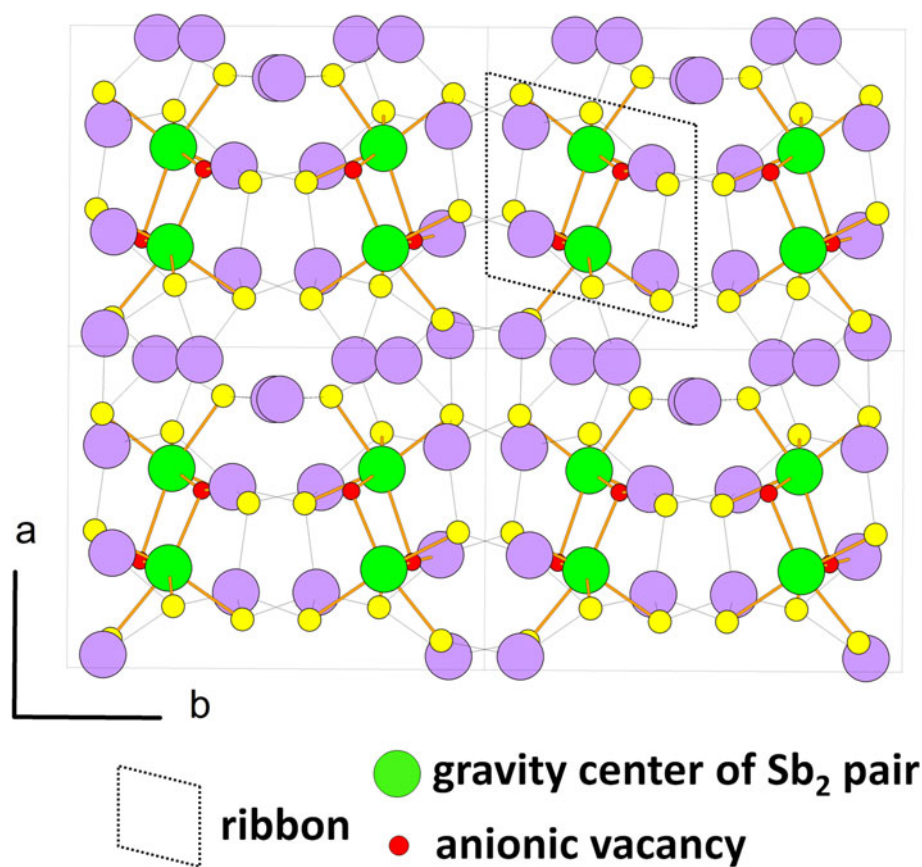


Fig. 7. Sb_2 pairs have been replaced by a single atom (G, green) at their gravity centre, and an anionic vacancy (●, red) has been added. One $Tl_4(Sb_2)_2S_6$ ribbon (now $Tl_4G_2S_6\square_2$) has been selected.

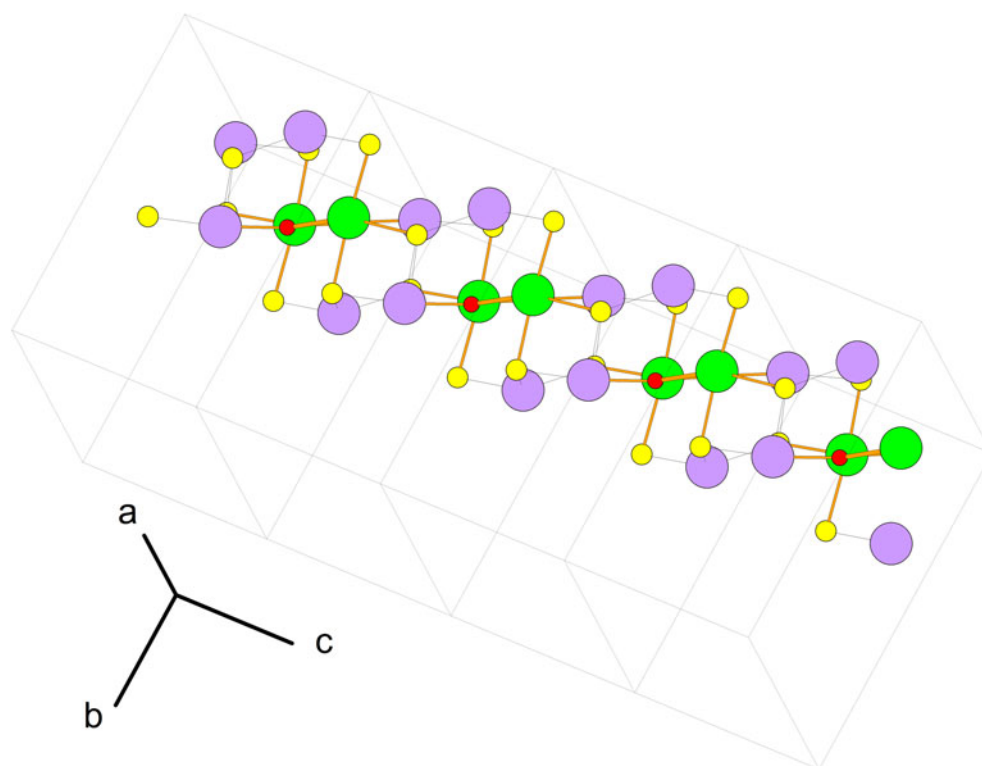


Fig. 8. One $Tl_4G_2S_6\square_2$ ribbon in the crystal structure of biagiioniite can be described as a distorted derivative of PbS structure.

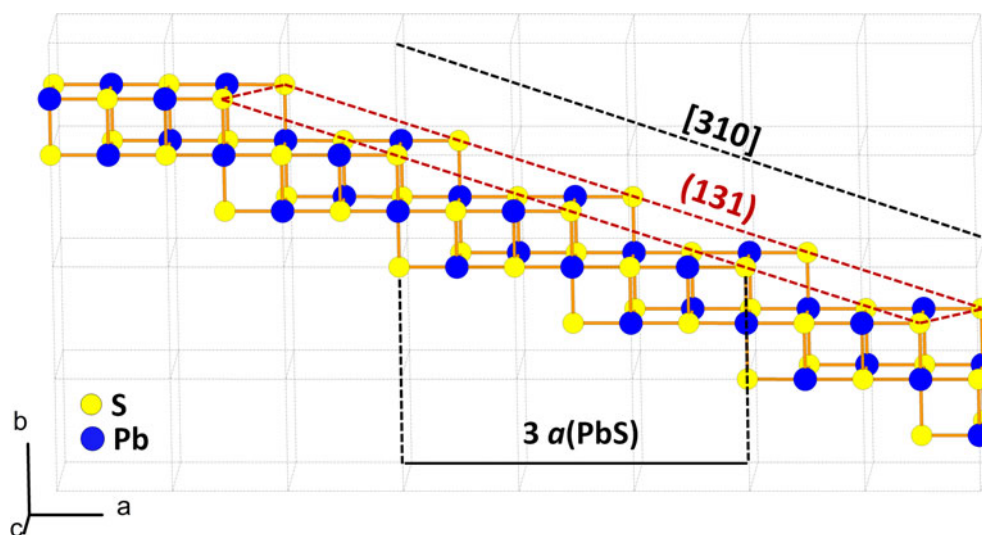


Fig. 9. A Pb_6S_8 ideal ribbon parallel to $[310]$, two-atoms-thick, and three-octahedra large. The junction between two ribbons in the structure of biagioniite along $[010]$ corresponds to (131) of PbS .

the first example of a natural chalcogenide showing Tl in linear coordination. For a review of Tl chalcogenides see Makovicky (2018).

In Fig. 7, the Sb_2 pairs have been replaced by a single atom (G) at their gravity centre, and an anionic vacancy (\square) has been added. One $\text{Tl}_4(\text{Sb}_2)_2\text{S}_6$ ribbon (now $\text{Tl}_4\text{G}_2\text{S}_6\square_2$) has been selected. Projection of this ribbon (Fig. 8) shows that it is a distorted derivative of the PbS structure. The Pb_6S_8 ideal ribbon (Fig. 9) is parallel to $[310]$, two-atoms-thick, and three-octahedra large. The junction between two ribbons along $[010]$ (mirror in the structure, with a shift along c , to preclude S–S short bond in the interface) corresponds to (131) of PbS . The two sides of such a junction (the two different mirror positions) have the same topology.

Bond-valence calculations (Table 6) have been computed on the basis of the following bond parameters: $R_{\text{Sb,S}} = 2.45$ (Brese and O’Keeffe, 1991), $R_{\text{Tl,S}} = 2.55$ (Biagioni *et al.*, 2014) and $R_{\text{Sb,Sb}} = 2.82$ (O’Keeffe and Brese, 1992). Tl atoms are overbonded (bond valence from 1.11 up to 1.36 valence units, vu), but we have not considered in the computation the presence of minor Ag disordered at the Tl positions, although it would be very minor. Sb–Sb bond lengths (2.830 and 2.843 Å) agree well with $R_{\text{Sb,Sb}}$ corresponding to one vu; nevertheless, Sb atoms are underbonded varying from 2.31 to 2.57 vu. This feature has also been observed in sartorite (Berlepsch *et al.* 2003) and in minerals such as dadsonite (Makovicky *et al.*, 2006), and was discussed in detail by Mills *et al.* (2009). The overall bond-valence sum of the eight S sites is 15.95, very close to the theoretical value (16 vu). These results may be due to uncertainty in the positions of some S atoms: a small shift closer to Sb atoms would reduce Sb underbonding together with Tl overbonding, without significant change of the S bond-valence sum.

The presence of dimeric $[\text{Sb}_2\text{S}_4]^{4-}$ ions with a central Sb–Sb bond in biagioniite means the formula could be written as $[\text{Tl}^{+1}]_4[\text{Sb}_2]^{4+}[\text{S}^{2-}]_4$. However, it is difficult to analyse such polycationic compounds in strict bond-valence terms, as the electronegativity of such elements lies between that of common cations and common anions. The weak Tl–Sb bonds in biagioniite are good examples of the ‘anionic’ behaviour, which could be explained through dative donation of the Sb lone pair to the

Table 6. Bond-valence sums (vu) for biagioniite.

Tl1	1.25	Sb1	2.31	S1	1.76
Tl2	1.11	Sb2	2.51	S2	1.86
Tl3	1.21	Sb3	2.57	S3	1.99
Tl4	1.28	Sb4	2.40	S4	2.02
Tl5	1.36			S5	2.35
Tl6	1.33			S6	2.04
Tl7	1.27			S7	1.89
Tl8	1.12			S8	2.04

closed-shell d^{10} Tl cations. On the contrary, in dervillite, short Ag–As bonds are lacking (Bindi *et al.*, 2013).

Tl_2SbS_2 has never been described either in Nature or as synthetic compound. Actually, the experimental TlSbS_2 –Tl section includes three ternary compounds, namely Tl_2SbS_2 , Tl_4SbS_2 and Tl_5SbS_2 . The former two compounds melt congruently at 613 and 683 K, whereas the latter one decomposes by peritectic reaction at 663 K (Jafarov *et al.*, 2016). But, in fact, the Tl_2SbS_2 compound has been found to be $\text{Tl}_3\text{SbS}_3 + \text{Sb}$ – a two-phase mixture instead of a single, independent chemical compound. Such a S-deficient formula for biagioniite indicates its formation at Hemlo at low f_{S_2} , in accordance to its association with stibarsen, SbAs, aurostibite, AuSb_2 , and criddleite, $\text{TlAg}_2\text{Au}_3\text{Sb}_{10}\text{S}_{10}$ (also S-deficient).

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