Oscarkempffite, Ag$_{10}$Pb$_4$(Sb$_{17}$Bi$_9$)$_{Σ26}$S$_{48}$, a new Sb-Bi member of the lillianite homologous series

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Oscarkempffite, ideally Ag$_{10}$Pb$_4$(Sb$_{17}$Bi$_9$)$_{Σ26}$S$_{48}$, is a new mineral species found in old material (1929–30) from the Colorado vein, Animas mine, Chocaya Province, Department of Potosi, Bolivia. It is associated with aramayoite, stannite, miargyrite, pyrargyrite and tetrahedrite. Oscarkempffite forms anhedral grains and grain aggregates up to 10 mm across. The mineral is opaque, greyish black with a metallic lustre; it is brittle without any discernible cleavage. In reflected light oscarkempffite is greyish white, pleochroism is distinct, white to dark grey. Internal reflections are absent. In crossed polars, anisotropism is distinct with rotation tints in shades of grey. The reflectance data (%, air) are: 39.9, 42.6 at 470 nm, 38.6, 41.7 at 546 nm, 38.1, 41.2 at 589 nm and 37.3, 40.6 at 650 nm. Mohs hardness is 3–3½, microhardness VHN$_{50}$ exhibits a range 189–208, with a mean value 200 kg mm$^{-2}$. The average results of four electron-microprobe analyses in a grain are: Cu 0.24(7), Ag 14.50(8), Pb 11.16(14), Sb 28.72(16), Bi 24.56(17), S 20.87(5), total 100.05(6) wt.%., corresponding to Cu$_{0.24}$Ag$_{9.92}$Pb$_{4.00}$Sb$_{17.36}$Bi$_{8.64}$S$_{47.84}$ (on the basis of Me + S = 88 apfu). The simplified formula, Ag$_{10}$Pb$_4$Sb$_{17}$Bi$_9$S$_{48}$, is in accordance with the results of a crystal-structure determination. The density, 5.8 g cm$^{-3}$, was calculated using the ideal formula. Oscarkempffite has an orthorhombic cell with $a$ = 13.199(2), $b$ = 19.332(3), $c$ = 8.249(1) Å, $V$ = 2116.3(5) Å$^3$, space group $Pnca$ and $Z$ = 1. The strongest eight lines in the (calculated) powder-diffraction pattern are [d in Å(1)hkl]: 3.66(35)(122), 3.37(70)(132), 3.34(100)(250), 2.982(55)(312), 2.882(86)(322), 2.733(29)(332), 2.073(27)(004) and 2.062(31)(182). Comparison with gustavite, andorite and roshchinite confirms its independence as a mineral species.

**Keywords:** oscarkempffite, sulfosalt, new mineral, lillianite homologous series, Animas mine, Chocaya Province, Bolivia.

**Introduction**

The lillianite homologous series (Makovicky and Karup-Møller, 1977a,b) was defined for Pb-Bi-Ag sulfosalts although it was noticed from the start that three antimony-based phases andorite, randothrite and fizelyte (Hellner, 1958) belonged to the same structural family. The andorite–ramdohrite branch of the lillianite series was subsequently studied in detail by Moøel et al. (1989). Phases belonging to the lillianite homologous series are composed of slabs of the slightly distorted PbS archetypal structure, cut and mirror-twinned on (113)$_{PbS}$. The octahedral coordinations present in the slabs are altered to bicapped prismatic coordinations on the composition plane between adjacent slabs. Slab thickness can vary by increments of one or more octahedra, measured diagonally across a slab. The number of octahedra along this diagonal determines the order $N$ of the

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homologue. Substitution \([\text{Ag} + (\text{Sb} + \text{Bi})] \)-for-2\(\text{Pb}\) is not present in the slabs but in most cases it does not involve the prismatic \(\text{Pb}\) positions. For \(N = 4\), relevant for the present study, this substitution spans compositions from \(\text{Pb}_3\text{Bi}_2\text{S}_6\) to \(\text{PbAg}(\text{Bi},\text{Sb})\) \(\text{S}_6\), expressed as the substitution percentage from 0 to 100%. The end-member composition \(\text{Pb}_3\text{Sb}_2\) \(\text{S}_6\) is unknown, both as a natural or a synthetic phase, and probably cannot exist as a lillianite homologue. Cases of ‘oversubstitution’, in which the prismatic position is also involved, are known, mostly for the \(\text{Sb}\)-based cases (Moëlo et al., 1989). For \(N = 4\), and a Bi-based case, an orthorhombic \(\text{Bi}n\text{m}n\text{m}\) structure exists for substitutions of up to \(~60\%\); whereas a monoclinic \(\text{P}2_1/\text{c}\) superstructure is present for substitutions close to 100% (Makovicky and Karup-Møller 1977b). The situation for the \(\text{Sb}\)-based phases is more complicated for the \(N = 4\) line, with two highly substituted-to-oversubstituted phases (complicated 6-fold and 4-fold superstructures of the basic lillianite scheme) and several moderately substituted cases present, commonly with other cations modifying the simple \(\text{PbAg-Sb}\) scheme.

Studies of the mixed antimony-bismuth members of the lillianite homologous series were first limited to a chemical characterization of them by means of electron microprobe analyses. It was established (Mozgova et al., 1987, Moëlo et al., 1989) that extensive Bi-Sb substitution may be present, straddling the 50:50 Sb:Bi divide, although typical gustavites and lillianites have low contents of antimony (e.g. Makovicky and Topa, 2011 and the numerous references in Moëlo et al., 1989). In a similar way, nearly all occurrences of andorite–ramdohrite homologues have only low contents of bismuth (Moëlo et al., 1989). Notable occurrences of mixed \(\text{Sb-Bi}\) phases are the Alyaskitovoye deposit (Yakutia, Russia) (Mozgova et al., 1987), Flat Head (Montana, USA) (Karup-Møller and Makovicky, unpublished), Julcani (Peru), El Mechero (Peru), Bazoges-en-Paillers (Vendee, France) (all three by Moëlo et al., 1987) and Kutná Hora (Central Bohemia, Czech Republic) (Pažout and Dušek, 2010). Investigations of mixed phases were hampered mostly by extreme variability of Sb:Bi ratios, commonly inside one aggregate or a needle-shaped grain, typical for nearly all investigated occurrences. In spite of it, a successful crystal structure investigation was performed by Pažout and Dušek (2009) on Sb-containing gustavite, \(\text{PbAgBi}_3\text{Sb}_6\), from the deposit of Kutná Hora, Czech Republic, with \(a = 7.0455\), \(b = 19.5294\), \(c = 8.3412\) Å and \(\beta = 107.446°\), space group \(\text{P}2_1/\text{c}\). Another published structure of this category from Kutná Hora is that of \(\text{Ag}_{0.71}\text{Pb}_{1.52}\text{Bi}_{1.32}\text{Sb}_{1.45}\text{S}_6\), with \(a = 4.254\), \(b = 13.309\), \(c = 19.625\) Å, space group \(\text{C}2\text{mc}\) (Pažout and Dušek, 2010). This orthorhombic phase has a substitution percentage of only 70.5%, according to the substitution scheme defined above (Makovicky and Karup-Møller, 1977a,b and Makovicky and Topa, 2014).

The new investigation of the old material from the Colorado vein, Animas mine, Chocaya Province, Department of Potosi, Bolivia (Ahlfeld and Reyes, 1938, Ahlfeld and Schneider-Scherbina, 1964,) offered a chance to extend further the chemical range of investigated Sb-Bi lillianite homologues with \(N = 4\) and led to the definition of oscarkempffite as a new species.

The mineral and its name have been approved by the CNMNC–IMA, under the number IMA-2011-029 (Topa et al., 2011). The name is in honour of Oscar Kempff Bacigalupo (1948–), eminent Bolivian mineralogist and economic geologist, who discovered several large mineral deposits in Bolivia (e.g. the deposit of Don Mario). The holotype specimen of oscarkempffite is deposited in the reference collection of the Naturhistorisches Museum Wien, Wien, Austria, with catalogue number N 9593. Cotyope material is deposited in the reference collection of the Natural History Museum, London, UK, with catalogue number BM 20, 3.

**Occurrence**

Oscarkempffite has been determined in old samples which originate from the expeditions of W. Vaux in 1929–30. The locality which is given on the labels associated with the two specimens of this mineral, is Animas mine, Colorado vein. Chocaya is a typical deposit of the Ag-Sn formation of Bolivia. Its geographical position is 66°33'W and 21°S. It is situated NW of Atocha in the province of Sur Chicas, department of Potosi, Southern Bolivia, and thus very close to the tectonic lineament which separates Paleozoic rocks of the Central Andes from the high planes (‘altiplano’) of Bolivia. The vein-type Ag-Sn deposits occur NE of a volcanic stock of dacitic rocks which has a diameter of 9 km and rises up against the Ordovician plane for more than 900 metres. The volcanic rocks are strongly altered and propylitization, silicification and pyritization are very common.

Colorado, which is the principal vein, follows a distinct fault zone for more than 1800 m along strike. Other veins which parallel the Colorado structure are Arturo and Animas towards the west.
and Burton and Judíos towards the east. The Colorada vein has been exploited downwards for almost 750 m in the northern part and 600 m in the Animas section in its southern part. In the upper part of this vein cassiterite was associated with freibergite and members of the stannite–késterite family. Textures which clearly indicated open space filling have very distinct banding, crustification and cockades.

At the Animas mine, some 70 m from the surface, an extremely rich ore shoot composed of various silver minerals was encountered during the exploitation of the mine. At a depth of 125 m, the ore shoot had a length of 30 m, a thickness of 2 m and the grade of silver was almost 3.5%. The principal silver mineral was freibergite. At the – 235 m level the high-grade zone contained the new mineral species aramayoite, Ag(Sb,Bi)S₂, accompanied by stannite, miargyrite, pyrargyrite and freibergite. Aramayoite has been described in detail by Spencer and Mountain (1926).

Oscarkempffite, the new sulfosalt species, is a typical associate of this assemblage containing aramayoite. Though no details about the exact level are given on the labels associated with the specimens, it can be assumed with certainty, that their origin is from the same level as the discovery of aramayoite (–235 m level). The last and more important exploitation at the Animas mine stopped in 1961, after significant amounts of Pb, Ag, Sn and Zn were mined. However, small-scale mining by local mining communities (‘cooperativas’) at the

![Fig. 1. (a) A BSE photograph of an aggregate of oscarkempffite showing differences in the contents of cations with high Z values as smooth zoning with a higher average Z in the centre. (b) The same aggregate in reflected light (crossed polars) displays an irregular mosaic character and pronounced anisotropy; associated with pyrite. (c) A large field of Ag-bearing tetrahedrite with another, still richer in silver (lighter) generation deposited in a void. Irregular grains of oscarkempffite penetrate into tetrahedrite on the boundary and enclose a small aramayoite grain. (d) A complex round sulfide aggregate interpreted as a replacement of an old unknown mineral aggregate. Oscarkempffite (a ‘wreath’ of light grains and a grain in the centre) is corroded and cemented by a later, large grain of Bi-rich aramayoite (lighter grey) and another grain of Bi-poorer aramayoite (slightly darker grey, left-hand parts). Small crystals of quartz and a grain of tetrahedrite with a ‘cap’ of Ag-enriched tetrahedrite (dark grey) are enclosed. At lower corners of the figure, dark semi-decomposed grains of stannite are present. See the text for interpretation.](image-url)
Mineral association

Oscarkempffite forms anhedral grains attaining a size of up to several mm and grain aggregates ranging up to 10 mm across. A back-scatter scanning electron (BSE) photograph (Fig. 1a) of such an aggregate shows differences in the contents of cations with high Z values as smooth zoning with a higher average Z in the centre. The same aggregate in reflected light (Fig. 1b) displays an irregular mosaic character and pronounced anisotropy. The surrounding association is not visible because of high contrast. Figure 1c shows a large field of Ag-bearing tetrahedrite with another, richer in silver (lighter on the BSE image), generation deposited in a void, along with irregular grains of oscarkempffite that penetrate into tetrahedrite on the boundary and enclose a small aramayoite grain. The complex round sulfide aggregate in Fig. 1d is interpreted as a replacement of an old unknown precursor mineral (aggregate) of approximately round shape by oscarkempffite (a ‘wreath’ of light grains and a grain in the centre) cemented by a large grain of bismuth-rich aramayoite (lighter grey) and another of less bismuthian aramayoite variety (slightly darker grey, lower left part). Small crystals of quartz and a grain of tetrahedrite with a ‘cap’ of Ag-enriched tetrahedrite variety (dark grey on the BSE image) are enclosed. Close to the lower corners of the figure, dark semi-decomposed grains of stannite are present. Oscarkempffite overgrew/replaced the original aggregate from the outside and later also the remaining old grain. Much of oscarkempffite was subsequently replaced by aramayoite. Stannite apparently predated aramayoite, as seen in the lower right-hand corner.

Physical properties

The colour of the mineral is greyish black, streak is dark grey; it is opaque with metallic lustre; and non-fluorescent. Hardness (Mohs) is 3–3½, microhardness, VHN₅₀, ranges between 189 and 208, with a mean value 200 kg mm⁻². The mineral is brittle with irregular fracture; no cleavage or parting are observed. Density could not be measured because of paucity of available material. Calculated density is 5.8 g cm⁻³ using the empirical formula. No crystal forms and twinning of the anhedral grains and aggregates were observed. The a:b:c ratio calculated from the unit-cell parameters (see below) is 0.683:1:0.429.

Optical properties

In reflected light (plane polars) the colour of oscarkempffite is greyish white. Pleochroism is distinct, white to dark grey; bireflectance is weak to distinct (in oil); no internal reflections were detected. With crossed polars, anisotropism is distinct with rotation tints in shades of grey. Reflectance values in air and oil, (The Natural History Museum, London, UK, WTiC standard, refractive index of oil: 1.515 at 23°C) are given in Table 1. A slight, fairly even decrease of reflectance with increasing wavelength is observed.

Chemical data

Chemical analyses of oscarkempffite (Table 2) were carried out using an electron microprobe JEOL JXA-8600, installed at University of

| Table 1. Reflectance values in air and oil (WTiC standard, refractive index of oil: 1.515 at 23°C) for oscarkempffite. |
|---|---|---|---|---|
| λ (nm) | Rₘₐₓ | Rₘᵢₙ | Rₘₐₓ | Rₘᵢₙ |
| 400 | 41.6 | 44.4 | 26.0 | 41.6 |
| 420 | 40.8 | 43.6 | 25.4 | 40.8 |
| 440 | 40.5 | 43.2 | 24.7 | 40.5 |
| 460 | 40.1 | 42.7 | 24.3 | 40.1 |
| 470 | 39.9 | 42.6 | 24.1 | 39.9 |
| 480 | 39.7 | 42.5 | 23.8 | 39.7 |
| 500 | 39.4 | 42.2 | 23.5 | 39.4 |
| 520 | 39.0 | 42.0 | 23.1 | 39.0 |
| 540 | 38.7 | 41.7 | 22.7 | 38.7 |
| 546 | 38.6 | 41.7 | 22.6 | 38.6 |
| 560 | 38.4 | 41.5 | 22.4 | 38.4 |
| 580 | 38.1 | 41.3 | 22.2 | 38.1 |
| 589 | 38.1 | 41.2 | 22.1 | 38.1 |
| 600 | 38.0 | 41.1 | 22.0 | 38.0 |
| 620 | 37.7 | 40.8 | 21.7 | 37.7 |
| 640 | 37.4 | 40.7 | 21.7 | 37.4 |
| 650 | 37.3 | 40.6 | 21.4 | 37.3 |
| 660 | 37.1 | 40.4 | 21.3 | 37.1 |
| 680 | 36.9 | 40.2 | 21.1 | 36.9 |
| 700 | 36.8 | 39.9 | 21.1 | 36.8 |

The reference wavelengths required by the Commission on Ore Mineralogy (COM) are given in bold.
| Nr. | Mineral    | NA | Cu       | Ag       | Fe       | Zn       | Pb       | Sb       | Bi       | S        | total    |
|-----|------------|----|----------|----------|----------|----------|----------|----------|----------|----------|----------|
| 1   | tetrahedrite | 16 | 23.99(30)| 19.97(20)| 5.64(12) | 0.87(13) | -        | 26.39(39)| -        | 23.00(14)| 99.86(30)|
| 2   | tetrahedrite | 3  | 17.38(24)| 28.63(01)| 4.98(31) | 1.34(19) | -        | 25.55(06)| -        | 22.18(12)| 100.06(04)|
| 3   | aramayoite  | 3  | -        | 34.26(23)| -        | -        | 27.70(33)| 17.50(44)| 20.06(09)| 99.52(21)|
| 4   | aramayoite  | 3  | -        | 35.26(28)| -        | -        | 30.55(19)| 13.48(25)| 20.53(03)| 99.82(11)|
| 5   | aramayoite  | 3  | 36.34(12)| -        | -        | -        | 36.83(68)| 5.45(56) | 21.05(07)| 99.67(11)|
| 6   | oscarkempffite | 5  | 0.35(07) | 13.98(19)| -        | -        | 12.56(77)| 30.13(49)| 21.41(20)| 21.33(12)| 99.76(13)|
| 7   | oscarkempffite | 4  | 0.24(03) | 14.50(08)| -        | -        | 11.16(14)| 28.72(16)| 24.56(17)| 20.87(05)| 100.05(06)|
| 8   | oscarkempffite | 4  | 0.29(04) | 14.48(08)| -        | -        | 10.03(36)| 27.12(40)| 26.73(37)| 21.04(15)| 99.96(32)|

The data are expressed in wt.%. NA = Number of analyses. Formulae are calculated on the basis of \(\Sigma (\text{Me} + \text{S}) = 29\) apfu for tetrahedrite, 24 apfu for aramayoite and 88 apfu for oscarkempffite, respectively. \(N_{\text{chemical}}\) and \(\text{Ag}_{\text{substr}}\) are calculated as described in Makovicky and Topa (2014).

1: \(\text{Cu}_{6.80}\text{Ag}_{3.33}\text{Fe}_{1.82}\text{Zn}_{0.24}\text{Sb}_{3.90}\text{S}_{12.91}\)
2: \(\text{Cu}_{5.12}\text{Ag}_{4.97}\text{Fe}_{1.67}\text{Zn}_{0.38}\text{Sb}_{3.93}\text{S}_{12.94}\)
3: \(\text{Ag}_{6.09}\text{Sb}_{4.35}\text{Bi}_{1.06}\text{S}_{11.97}\)
4: \(\text{Ag}_{6.12}\text{Sb}_{4.70}\text{Bi}_{1.21}\text{S}_{11.98}\)
5: \(\text{Ag}_{6.12}\text{Sb}_{4.84}\text{Bi}_{1.57}\text{S}_{11.92}\)
6: \(\text{Cu}_{6.80}\text{Ag}_{9.44}\text{Pb}_{1.68}\text{Sb}_{16.40}\text{Bi}_{7.44}\text{S}_{48.32}; \ N_{\text{chemical}} = 4.08, \text{Ag}_{\text{substr}} = 121\%\)
7: \(\text{Cu}_{0.24}\text{Ag}_{9.92}\text{Pb}_{0.00}\text{Sb}_{17.36}\text{Bi}_{8.64}\text{S}_{47.84}; \ N_{\text{chemical}} = 4.07, \text{Ag}_{\text{substr}} = 124\%\)
8: \(\text{Cu}_{0.33}\text{Ag}_{9.92}\text{Pb}_{3.68}\text{Sb}_{16.40}\text{Bi}_{9.44}\text{S}_{48.32}; \ N_{\text{chemical}} = 4.09, \text{Ag}_{\text{substr}} = 125\%\)
Salzburg, Austria, (WDS mode, 25 kV, 20 nA, 5 μm beam diameter, ZAF correction procedure). Other elements (Hg, Tl and As) were sought but not detected. The standards and wavelengths used are chalcopyrite (nat.) CuKα, FeKα, sphalerite (nat.) ZnKα, metal (syn.) AgLα, galena (nat.) PbLα, stibnite (nat.) SbLα and bismuthinite (syn.) BiLα and SKα. Data for oscarkempffite and associated minerals are presented in Table 2.

The empirical formula of oscarkempffite varies between (Ag,Cu)\(_{0.88}\)Pb\(_{4.40}\)Sb\(_{18.0}\)Bi\(_{7.44}\)S\(_{48.32}\) and (Ag,Cu)\(_{10.24}\)Pb\(_{3.68}\)Sb\(_{16.40}\)Bi\(_{9.44}\)S\(_{48.32}\). It is very close to the simplified formula Ag\(_{10}\)Pb\(_{4}\)(Sb\(_{17}\)Bi\(_{9}\))\(_{26}\)S\(_{48}\).

The crystal structure defines oscarkempffite as a lillianite homologue with the order \(N=4\). The cation ratios resulting from the chemical analysis confirm this assignment, yielding \(N=4.07–4.09\). With respect to the measure of \([\text{Ag}+(\text{Bi},\text{Sb})] \leftrightarrow 2\text{Pb}\) substitution, typical for the lillianite–gustavite and

### Table 3. Powder X-ray diffraction data for oscarkempffite.

| \(I_{rel.}\) | \(d_{meas}/\text{Å}\) | \(d_{calc}/\text{Å}\) | \(h\) | \(k\) | \(l\) |
|-----|----------------|----------------|-----|-----|-----|
| 5   | 6.292          | 6.263          | 2   | 1   | 0   |
| 5   | 5.463          | 5.463          | 2   | 2   | 0   |
| 20* | 3.904          | 3.904          | 2   | 4   | 0   |
| 30* | 3.663          | 3.672          | 1   | 2   | 2   |
| 100b| 3.354          | 3.340          | 2   | 5   | 0   |
| 20* | 3.264          | 3.263          | 4   | 1   | 0   |
| 5   | 3.053          | 3.068          | 1   | 4   | 2   |
| 40* | 2.988          | 2.991          | 3   | 1   | 2   |
| 80* | 2.889          | 2.889          | 3   | 2   | 2   |
| 30* | 2.741          | 2.740          | 3   | 3   | 2   |
| 10* | 2.551          | 2.550          | 2   | 7   | 0   |
| 5*  | 2.417          | 2.417          | 0   | 8   | 0   |
| 40* | 2.263          | 2.267          | 1   | 7   | 2   |
| 20* | 2.112          | 2.111          | 5   | 3   | 2   |
| 60  | 2.066          | 2.062          | 1   | 8   | 2   |
| 30* | 2.027          | 2.028          | 5   | 4   | 2   |
| 30* | 2.008          | 2.008          | 6   | 4   | 0   |
| 30  | 1.931          | 1.930          | 5   | 5   | 2   |
| 20* | 1.890          | 1.889          | 3   | 8   | 2   |
| 10* | 1.834          | 1.836          | 5   | 6   | 2   |
| 5*  | 1.803          | 1.802          | 4   | 9   | 0   |
| 50* | 1.766          | 1.766          | 2   | 5   | 4   |
| 10* | 1.722          | 1.722          | 7   | 0   | 2   |

*Lines used for unit-cell refinement. Indexed on \(a = 13.240(5), b = 19.339(7), c = 8.320(4)\) Å; refined on 17 reflections, between 3.904 and 1.772 Å, for which unambiguous indexing was possible, based on the calculated powder pattern derived from the successful determination of the crystal structure; intensities were estimated visually; b = broad line; the pattern was not corrected for shrinkage and no internal standard was used.

### Table 4. Calculated powder X-ray diffraction data for oscarkempffite.*

| \(I_{rel.}\) | \(d_{calc}/\text{Å}\) | \(h\) | \(k\) | \(l\) |
|-----|----------------|-----|-----|-----|
| 8   | 6.25           | 2   | 1   | 0   |
| 10  | 5.45           | 2   | 2   | 0   |
| 20  | 3.90           | 2   | 4   | 0   |
| 35  | 3.66           | 1   | 2   | 2   |
| 70  | 3.37           | 1   | 3   | 2   |
| 100 | 3.34           | 2   | 5   | 0   |
| 15  | 3.30           | 4   | 0   | 0   |
| 22  | 3.25           | 4   | 1   | 0   |
| 6   | 3.22           | 0   | 6   | 0   |
| 55  | 2.982          | 3   | 1   | 2   |
| 25  | 2.895          | 2   | 6   | 0   |
| 86  | 2.881          | 3   | 2   | 2   |
| 29  | 2.733          | 3   | 3   | 2   |
| 13  | 2.105          | 5   | 3   | 2   |
| 5   | 2.082          | 6   | 3   | 0   |
| 27  | 2.073          | 0   | 0   | 4   |
| 31  | 2.062          | 1   | 8   | 2   |
| 29  | 2.023          | 5   | 4   | 2   |
| 16  | 2.002          | 6   | 4   | 0   |
| 9   | 1.9332         | 0   | 10  | 0   |
| 9   | 1.9297         | 5   | 5   | 2   |
| 14  | 1.8863         | 3   | 8   | 2   |
| 8   | 1.8319         | 5   | 6   | 2   |
| 5   | 1.8002         | 4   | 9   | 0   |
| 24  | 1.7610         | 2   | 5   | 4   |
| 5   | 1.7556         | 4   | 0   | 4   |
| 5   | 1.7500         | 3   | 9   | 2   |
| 5   | 1.7484         | 4   | 1   | 4   |
| 6   | 1.7165         | 7   | 0   | 2   |
| 6   | 1.6858         | 2   | 6   | 4   |
| 6   | 1.6680         | 4   | 10  | 0   |
| 6   | 1.6264         | 8   | 2   | 0   |
| 7   | 1.4403         | 6   | 4   | 4   |
| 5   | 1.4140         | 0   | 10  | 4   |

*The theoretical pattern was calculated with PowderCell 2.3 software (Kraus and Nolze, 1999) in Debye-Scherrer configuration employing CuKα radiation (\(\lambda = 1.540598\) Å), a fixed slit and no anomalous dispersion. Cell parameters, space group, atom positions, site-occupancy factors and isotropic displacement factors from the crystal-structure determination were used. The strongest lines are given in bold.
fizelyite–andorite substitution lines (both $N = 4$), 
oscarkempffite is extensively oversubstituted, with 
a substitution percentage of 120–124%.

Chemical analyses (Table 2) of aggregates 
shown in Fig. 1d represent the three groups of 
oscarkempffite chemistries and two types of 
tetrahedrite illustrated, among which the one 
richest in Ag represents the minor later phase 
(Fig. 1c). Among the three analyses of aramayoite, 
os. 3 and 4 represent the aggregate in Fig. 1d, no. 5 
another aggregate. In conclusion, they show a 
substantial variability of the Sb/Bi ratio.

Crystallography

A diffractometer with an area detector system was 
used to perform the single-crystal study (University 
of Salzburg, Austria). Cell parameters refined from 
single-crystal data are as follows: orthorhombic 
system, space group $Pnca$, $a = 13.199(2)$, $b = 
19.332(3)$, $c = 8.294(1)$ Å, cell volume $V = 
2116.3(5)$ Å$^3$ and $Z = 1$ for the above formula unit.

Powder X-ray data were collected using a 
114.6 mm diameter Debye-Scherrer camera (Cu 
radiation, Ni filter, CuKα = 1.54178 Å). Data are 
presented in Table 3. The calculated powder data 
from results of the single-crystal study are shown in 
Table 4. Cell parameters refined from the powder 
data are as follows: $a = 13.240(5)$, $b = 19.339(7)$, 
c = 8.320(4) Å and $V = 2130(2)$ Å$^3$, in fair agreement 
with the single-crystal data.

Crystal structure

A fragment with irregular shape and 0.15 mm × 
0.05 mm × 0.05 mm in size was mounted and 
analyzed on a Bruker AXS three-circle diffractom-
eter equipped with a CCD area detector.

The structure of oscarkempffite contains five 
distinct coordination polyhedra of cations and 
seven of anions. It contains a mixed (Pb,Bi) site 
with a trigonal prismatic coordination, a silver site 
with a distorted tetrahedral coordination in an 
octahedral arrangement of ligands, which 
alters along the 8 Å direction with a mixed 
(Sb$_{0.88}$Bi$_{0.12}$) site called Sb1, and a string of 
alternating Sb2 and a mixed (Sb$_{0.59}$Bi$_{0.41}$) sites, 
the latter called Sb3, in the central parts of PbS- 
like slabs. When proceeding along [100], the 
arrangement of consecutive atomic planes differs 
from that in the monoclinic gustavite structure, 
resulting in orthorhombic symmetry and in –Sb– 
Sb–Ag–Ag–Sb–Sb– zig-zag [010] chains of 
coordination octahedra instead of the Ag–Bi– 
Ag–Bi– chains present in gustavite. The crystal 
structure is shown in Fig. 2.

![Fig. 2. Cation and anion sites in the crystal structure of oscarkempffite. The unit cell is projected on (001). In the order of decreasing size spheres indicate: S, (Pb,Bi) (grey), (Sb,Bi) (white) and Ag (black). The (311)$_{PbS}$ slabs of the PbS-like arrangement are perpendicular to [010]; they are separated by [010] planes occupied by trigonal coordination prisms of (Pb,Bi).](image-url)
Details of the crystal structure and the interesting geometric relationships between the structures of orthorhombic oscarkempffite and monoclinic gustavite PbAgBi₃S₆ will be treated in another paper.

Relation to other species

Oscarkempffite is essentially a pure Ag-(Sb, Bi)-Pb sulfosalt with only trace amounts of copper and without As. It is a lillianite homologue \( N = 4 \) as confirmed by the \( N \) value calculated from the chemical analysis. With respect to the measure of \( (\text{Ag} + \text{Bi}) \leftrightarrow 2\text{Pb} \) substitution, typical of the lillianite–gustavite and fizelyite–andorite substitution lines, oscarkempffite is extensively oversubstituted, with a substitution percentage of 124\%, far beyond the 100\% value of gustavite, PbAgBi₃S₆ (Makovicky and Karup-Møller, 1977a, b) and the \( \sim 100\% \) value of senandorite (andorite VI; Sawada et al. (1987); [4]: Spiridonov et al. (1990); [5]: Petrova et al. (1986)).

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**Table 5. Comparative data for oscarkempffite and related minerals.**

| Mineral      | oscarkempffite | gustavite | andorite VI | roshchinite |
|--------------|----------------|-----------|-------------|-------------|
| Formula      | Ag₁₀Pb₂₋₁Sb₁₋₁Bi₄S₄₈ | Ag₄Pb₄Bi₉S₃S₂₄ | Ag₆Pb₆Sb₁₈S₃₆ | Ag₉.₃Pb₃Sb₂₅.₃S₄₈ |
| Substitution (%) | 124       | 100       | 100         | 120         |
| Crystal system | orthorhombic | monoclinic | orthorhombic | orthorhombic |
| Space group  | \( Pnca \)  | \( P₂₁/c \) | \( Pn₂,a \) | \( Pnma \)   |
| Cell parameters (Å) | | | | |
| \( a \) | 13.199     | 7.046     | 13.005      | 12.946      |
| \( b \) | 19.332     | 19.529    | 19.155      | 19.048      |
| \( c \) | 8.294      | 8.342     | 25.622      | 16.932      |
| \( \alpha, \beta, \gamma \) (°) | 90, 90, 90 | 90, 107.45, 90 | 90, 90, 90 | 90, 90, 90 |
| \( Z \) | 1           | 1         | 1           | 2           |
| \( R₁ \) factor (%) | 3.7        | 5.88      | 4.89        | -           |
| Ref⁴ | 1           | 2         | 3           | 4, 5        |

1 Also gustavite with less Sb substitution, \( \text{Ag}_4\text{Pb}_{11.2}\text{Sb}_{0.8}\text{S}_{24}, \) with \( a = 7.056, b = 9.691, c = 8.222 \, \text{Å}, \beta = 106.9°,\) space group \( P₂₁/c, R₁ = 2.76\%, \) by Makovicky and Topa (2011). ² Or senandorite. ³ Tentative crystal structure refinement of Petrova et al. (1986). [1]: this study; [2]: Pažout & Dušek (2010); [3]: Sawada et al. (1987); [4]: Spiridonov et al. (1990); [5]: Petrova et al. (1986).
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