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STEROPESITE, Tl_3BiCl_6, A NEW THALLIUM BISMUTH CHLORIDE FROM LA FOSSA CRATER, VULCANO, AEOLIAN ISLANDS, ITALY

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Abstract

Steropesite, Tl_3BiCl_6, a new thallium bismuth chloride, was found in an active high-temperature fumarole (~450°C) on the rim at La Fossa crater, Vulcano, Aeolian Islands, Sicily, Italy. The mineral occurs as tabular or stout lemon-yellow crystals up to 0.20 mm in length in association with bismuthinite and lafossaite. The mineral is monoclinic, space group *Cc* (no. 9), with Z = 16; the unit-cell parameters are *a* 26.686(5), *b* 15.127(3), *c* 13.014(3) Å, β 108.11(2)°, and *V* 4993(2) Å^3. The strongest six reflections in the X-ray powder-diffraction pattern [d_{obs} in Å(*I*)(*hkl)*] are: 3.773(100)(040), 2.113(93)($\underline{12}$00), 3.846(40)($\bar{3}$32), 2.710(35)(442), 3.884(30)(402), and 2.745(30)(513). Chemical analyses obtained with an electron microprobe in wavelength dispersion gave, on average, Tl 54.57, Bi 23.40, Cl 17.42, Br 4.13, Na 0.02, K 0.01, for a total of 99.55 wt.%, corresponding to the empirical formula: $(Tl_{2.89}Na_{0.01})_{\Sigma 2.90}Bi_{1.21}(Cl_{5.32}Br_{0.56})_{\Sigma 5.88}$. The calculated density for the compound with the above empirical formula is 5.737 g/cm^3. The average index of refraction *n* is 1.97(2) (λ = 589 nm). The structure was refined from single-crystal X-ray-diffraction data to a final *R* of 0.052 for 6232 independent observed reflections [$I > 2\sigma(I)$]. The asymmetric unit contains 4 Bi, 12 Tl and 24 Cl atoms. The bismuth atoms display a distorted octahedral coordination, with Bi–Cl distances in the range 2.618–2.789 Å. Considering a maximum value of 3.6 Å for the Tl–Cl distances, five of the twelve independent Tl atoms are six-coordinated (Tl–Cl in the range 3.023–3.596 Å), six are seven-coordinated (Tl–Cl between 3.106 and 3.558 Å), and one is eight-coordinated (Tl–Cl in the range 3.229–3.511 Å). The structure can be compared with those of other hexachlorobismuthates[III], such as $(NH_4)_3BiCl_6$, Cs_3BiCl_6 and CsK_2BiCl_6.

Keywords: steropesite, new mineral species, crystal structure, thallium bismuth chloride, hexachlorobismuthates(III), thallium minerals, Vulcano Island, Italy.

Sommaire

La steropesite, Tl_3BiCl_6, une espèce nouvelle, chlorure de thallium et de bismuth, a été découverte en bordure d'une fumerolle active à haute température (~450°C) au cratère La Fossa, à Vulcano, dans les îles Éoliennes, Sicile, Italie. Le minéral se présente en cristaux tabulaires plus ou moins trappus jaune-citron atteignant une longueur de 0.20 mm, en association avec bismuthinite et lafossaïte. C'est un minéral monoclinique, groupe spatial *Cc* (no. 9), avec Z = 16; les paramètres réticulaires sont *a* 26.686(5), *b* 15.127(3), *c* 13.014(3) Å, β 108.11(2)°, et *V* 4993(2) Å^3. Les six réflexions les plus intenses du spectre de diffraction X, méthode des poudres [d_{obs} en Å(*I*)(*hkl)*] sont: 3.773(100)(040), 2.113(93)($\underline{12}$00), 3.846(40)($\bar{3}$32), 2.710(35)(442), 3.884(30)(402), et 2.745(30)(513). Les analyses chimiques obtenues avec une microsonde électronique en dispersion d'énergie ont donné, en moyenne, Tl 54.57, Bi 23.40, Cl 17.42, Br 4.13, Na 0.02, K 0.01, pour un total de 99.55% (poids), ce qui correspond à la formule empirique: $(Tl_{2.89}Na_{0.01})_{\Sigma 2.90}Bi_{1.21}(Cl_{5.32}Br_{0.56})_{\Sigma 5.88}$. La densité calculée du composé ayant une telle composition serait 5.737 g/cm^3. L'indice de réfraction moyen *n* est 1.97(2) (λ = 589 nm). Nous en avons affiné la structure à partir de données obtenues sur monocristal jusqu'à un résidu final *R* de 0.052 pour 6232 réflexions indépendantes observées [$I > 2\sigma(I)$]. L'unité assymétrique contient quatre atomes de Bi, 12 de Tl et 24 de Cl. Les atomes de bismuth sont en coordinence octaédrique difforme, avec des distances Bi–Cl dans l'intervalle 2.618–2.789 Å. Avec une valeur maximale de 3.6 Å pour les distances Tl–Cl, cinq des douze atomes indépendants de Tl ont une coordinence six (Tl–Cl entre 3.023 et 3.596 Å), six ont une coordinence sept (Tl–Cl entre 3.106 et 3.558 Å), et un atome possède une coordinence huit (Tl–Cl entre 3.229 et 3.511 Å). Nous comparons la structure avec celle d'autres hexachlorobismuthates[III], par exemple $(NH_4)_3BiCl_6$, Cs_3BiCl_6 et CsK_2BiCl_6.

(Traduit par la Rédaction)

Mots-clés: steropesite, nouvelle espèce minérale, structure cristalline, chlorure de thallium et bismuth, hexachlorobismuthates(III), minéraux de thallium, île de Vulcano, Italie.

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INTRODUCTION

The island of Vulcano, a part of the Aeolian Archipelago, is located near the northern coast of Sicily. Its interesting geological features have long been known; recently, in connection with the increased activity of the fumaroles, results of further investigations have been published in the fields of volcanology and geochemistry (Campostrini *et al.* 2008, and references therein).

Concerning mineralogy, there has also been a renewed interest in the rare minerals occurring in the fumarole system of La Fossa crater, leading to the discovery of additional lead–bismuth sulfosalts, among which the new species mozgovaite, $PbBi_4(S,Se)_7$, and vurroite, $Pb_{20}Sn_2(Bi,As)_{22}S_{54}Cl_6$ (Vurro *et al.* 1999, Garavelli *et al.* 2005, and references therein). A substantial set of new halides have also been discovered, such as barberiite NH_4BF_4 (Garavelli & Vurro 1994), lafossaite TlCl (Roberts *et al.* 2006), demartinite, a hexagonal polymorph of the potassium hexafluorosilicate K_2SiF_6 (Gramaccioli & Campostrini 2007), and thermessaite, a new complex fluoride and sulfate, $K_2[AlF_3|SO_4]$ (Demartin *et al.* 2008a). Recent additions to this list also include a very unusual hexafluorosilicate–tetrafluoroborate, knasibfite $K_3Na_4[SiF_6]_3[BF_4]$ (Demartin *et al.* 2008c), hephaistosite $TlPb_2Cl_5$, a thallium and lead chloride isostructural with challacolloite KPb_2Cl_5 (Campostrini *et al.* 2008, Mitolo *et al.* 2008), and panichiite $(NH_4)_2Sn^{4+}Cl_6$, ammonium hexachlorostannate(IV), a unique example of a natural Sn^{4+} chloride (Demartin *et al.* 2009); there are also two new sulfohalides, *i.e.*, demicheleite-(Br) BiSBr (Demartin *et al.* 2008b), and BiSCl (IMA 2008–020). Here, we describe the new species steropesite, Tl_3BiCl_6 [thallium bismuth chloride or thallium hexachlorobismuthate(III)], which was also found in an active fumarole at La Fossa crater.

The mineral was approved as a new species by the IMA Commission on New Minerals, Nomenclature and Classification (No. 2008–014). The name is after Steropes (Στερόπης), one of the three Cyclops (κύκλωπες) and a son of Uranus. These mythological half-gods were helpers of Hephaistos (Hephaestus, Ηφαιστος), the ancient Greek god of fire, whose workshops were alleged to be located at Vulcano. The holotype is deposited (no. 2008–02) in the Reference Collection of Dipartimento di Chimica Strutturale e Stereochimica Inorganica of Università degli Studi di Milano.

OCCURRENCE, CHEMICAL DATA AND PHYSICAL PROPERTIES

In 2006, the presence of a rare chloride in an active high-temperature fumarole (~450°C) on a pyroclastic breccia collected at the rim of La Fossa crater, Vulcano Island, Aeolian archipelago, Sicily, Italy, was noticed by one of us (I.C.). On the basis of preliminary tests carried out using an EDS-equipped JEOL JSM5500 LV scanning electron microscope, it was found to contain essential thallium and bismuth, with no oxygen.

The mineral occurs in close association with bismuthinite and lafossaite, and forms aggregates of pale lemon-yellow crystals up to 0.2 mm in length. The habit is tabular on {100} or stout and more complex; the most common forms are {100}, {121}, {001}, $\{\bar{1}21\}$ and {010} (Figs. 1, 2); no twinning is apparent. The *a:b:c* proportions calculated from the unit-cell parameters are: 1.7641:1:0.8603. The mineral is not hygroscopic and seems stable in the open air. The streak is white; the luster is vitreous to adamantine. Cleavage and fracture were not observed. We did not observe any fluorescence both under SW and LW ultraviolet radiation.

The calculated density corresponding to the empirical formula and to the X-ray data is 5.737 g/cm^3. Owing to the reactive nature of the mineral with respect to all liquids of very high index of refraction, the mean $n = 1.97(2)$ was obtained from a measurement of the Brewster angle on grains in polished mounts; the corresponding Gladstone–Dale constant calculated using Mandarino's values (1981) is 1.922, leading to a compatibility index $[1 - (K_P/K_C)] = 0.025$.

Chemical analyses were carried out by means of a JEOL JXA 8200 electron microprobe under the following conditions: excitation voltage 15 kV, beam current 4×10^{-9} A, beam diameter 10 μm. Element concentrations were measured in wavelength-dispersive spectrometry (WDS) using $K\alpha$ lines for Na, K and Cl, the $L\alpha$ line for Br, and $M\alpha$ lines for Bi and Tl; no iodine was detected. The mean analytical results (average of results at 11 analyzed points) are reported in Table 1. The empirical formula obtained (based on 10 atoms *pfu*) is: $(Tl_{2.89}Na_{0.01})_{\Sigma 2.90}Bi_{1.21}(Cl_{5.32}Br_{0.56})_{\Sigma 5.88}$. The idealized formula is Tl_3BiCl_6, which requires: Tl 59.25, Bi 20.19, Cl 20.56, for a total of 100.00 wt.%. This content is in accordance with the result of the crystal-structure refinement (see below).

The overestimation of Bi and the underestimation of Tl and halogens in the electron-microprobe results derive from the partial and unavoidable volatilization of thallium halides from the sample and the standards under the electron beam, as is clearly indicated from the scars left on the polished samples after the measurements.

X-RAY DATA

X-ray powder-diffraction data have been obtained using a Rigaku DMAX-II diffractometer, with Cu$K\alpha$ radiation (Table 2). A least-squares fit of these data provided the unit-cell parameters *a* 26.719(4), *b* 15.125(2), *c* 12.998(2) Å, β 108.18(1)°, and *V* 4990(1) Å^3. Single-crystal diffraction data for structure determination were collected from a crystal measuring 0.05 × 0.04 × 0.02 mm with Mo$K\alpha$ radiation (λ = 0.71073 Å), using a Bruker Apex II diffractometer equipped with a 2K CCD detector. A one-minute frame-time and a frame width of 0.5° were used. A total of 21907 reflections, corresponding to a complete scan of the reciprocal lattice up to $2\theta_{max} = 65.6°$, were measured; of these, 14258 were found to be unique (R_{int} = 0.081). The unit-cell parameters obtained from 5540 single-crystal reflections with $I > 5\sigma(I)$ are reported in Table 3, together with other details concerning the data collection and refinement. The intensity data were reduced using the program SAINT (Bruker 2001), and corrected for Lorentz, polarization, and background. An absorption correction was applied using the SADABS program (Sheldrick 2000). The structure was solved by direct methods and refined using SHELXL97 program (Sheldrick 1997) implemented in the WINGX suite (Farrugia 1999). For some chlorine atoms, the values of anisotropic U were non-positive definite, confirming the non-negligible substitution of Cl by Br observed in the chemical analysis. Therefore, in view of the superabundant number of reflections (6232 *versus* 387

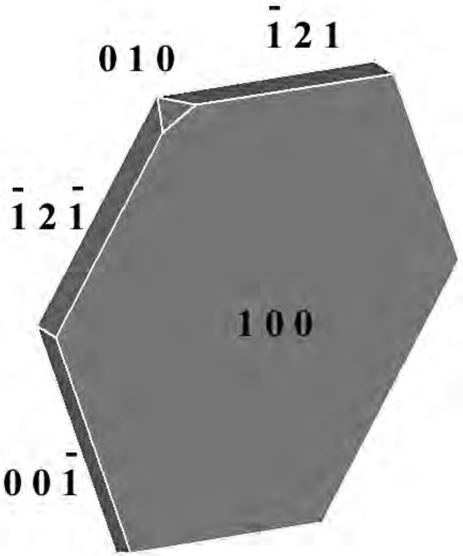

FIG. 1. A drawing of a crystal of steropesite. The indices of the forms have been obtained from optical measurements.

TABLE 1. CHEMICAL COMPOSITION OF STEROPESITE

Constituent	wt.%	Range	Probe standard
Tl	54.57	52.68 – 55.22	TlBr
Bi	23.40	22.34 – 24.44	Bi_2Se_3
Cl	17.42	16.64 – 19.26	Scapolite
Br	4.13	3.40 – 4.81	TlBr
Na	0.02	0 – 0.07	Scapolite
K	0.01	0 – 0.03	K-feldspar
Total	99.55		

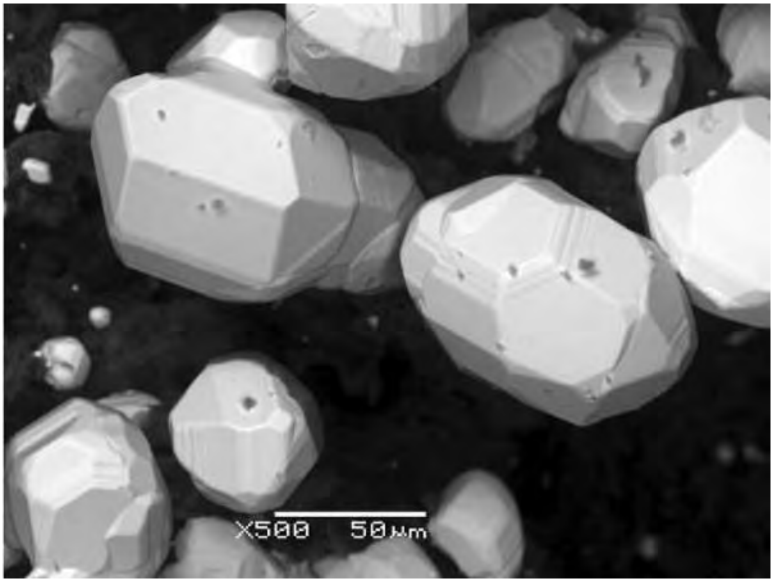

FIG. 2. SEM–BSE image of steropesite showing a more complex habit of some crystals.

refined parameters), the occupancies at each Cl site were also refined, resulting in reasonable values for all the thermal ellipsoids and the atomic Br:Cl ratio (the X_{Br} molar fractions are reported in Table 4); a different distribution of Br in the various sites is also evident. The average of such values is 0.16, which is reasonably near the corresponding result (0.10) of the chemical analysis, especially considering that the analysis was made on a different sample. The atomic displacement parameters (ADPs) of the Tl atoms are on average

TABLE 2. X-RAY POWDER-DIFFRACTION DATA FOR STEROPESITE

I/Io	*d* (Å) obs.	*d* (Å) calc.*	*h k l*	I/Io	*d* (Å) obs.	*d* (Å) calc.*	*h k l*
4	5.420	5.405	2 2 1	30	2.745	2.752	5 1 3
6	4.927	4.944	$\bar{4}$ 2 1	35	2.710	2.703	4 4 2
29	4.241	4.231	6 0 0	23	2.675	2.667	$\bar{8}$ 0 4
30	3.884	3.864	4 0 2	24	2.665	2.657	$\overline{10}$ 0 2
40	3.846	3.846	$\bar{3}$ 3 2	5	2.477	2.486	8 1 2
100	3.773	3.781	0 4 0	7	2.253	2.253	2 4 4
7	3.626	3.624	2 4 0	17	2.206	2.212	$\bar{9}$ 1 5
17	3.034	3.039	$\bar{5}$ 1 4	19	2.185	2.18	$\bar{8}$ 4 4
8	3.014	3.011	2 4 2	93	2.113	2.115	12 0 0
17	2.991	2.979	$\bar{2}$ 2 4	7	2.062	2.057	$\bar{6}$ 6 3
7	2.887	2.894	1 5 1	7	2.037	2.042	$\bar{8}$ 0 6
18	2.832	2.837	5 3 2	6	1.998	1.992	3 5 4
16	2.819	2.816	6 4 0	9	1.886	1.891	0 8 0
27	2.801	2.793	$\bar{6}$ 4 2	9	1.585	1.587	$\bar{8}$ 6 6

* Calculated from the unit cell: *a* 26.719(4), *b* 15.125(2), *c* 12.998(2) Å, β 108.18(1)°, obtained from least-squares refinement from the above data using the program UNITCELL (Holland & Redfern 1997).

TABLE 3. SINGLE-CRYSTAL DATA AND REFINEMENT PARAMETERS FOR STEROPESITE

Crystal system	monoclinic	Space group	*Cc* (no. 9)
a (Å)	26.686(5)	*V* (Å^3)	4993(2)
b (Å)	15.127(3)	Z	16
c (Å)	13.014(3)	Radiation	Mo*K*α
β (°)	108.11(2)	D_{calc} (g/cm^3)	5.506
F_{000}	6848	μ (mm^{-1})	53.887
Measured reflections	21907	Independent reflections	14258
Observed reflections [$I > 2\sigma(I)$]	7125	Parameters refined	387
Final *R* and w*R*2	0.052, 0.109		
Residual electron-density (e/Å^3)	-2.9 – 2.9	S	0.793

Notes: $R = \Sigma||Fo| - |Fc|| / \Sigma|Fo|$; $wR2 = \{\Sigma[w(Fo^2 - Fc^2)^2] / \Sigma[w(Fo^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(Fo^2) + (0.030q)^2]$, where $q = (Fo^2 + 2Fc^2)/3$; $S = \{\Sigma[w(Fo^2 - Fc^2)] / (n - p)\}^{1/2}$, where n is the number of reflections, and p is the number of refined parameters.

TABLE 4. COORDINATES AND DISPLACEMENT PARAMETERS [*Ueq*/*U(i,j)*] OF ATOMS IN STEROPESITE

Atom	*X/a*	*Y/b*	*Z/c*	*Ueq*	X_{Br}	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Bi(1)	-0.00830(5)	-0.12480(9)	0.36968(11)	0.0250(2)		0.0260(6)	0.0274(4)	0.0223(5)	0.0024(4)	0.0086(5)	0.0044(4)
Bi(2)	0.24734(6)	-0.37303(10)	0.37604(12)	0.0238(2)		0.0199(3)	0.0269(4)	0.0236(4)	-0.0015(4)	0.0054(3)	-0.0018(3)
Bi(3)	0.00352(5)	-0.37326(9)	-0.11938(11)	0.0243(2)		0.0242(6)	0.0279(4)	0.0205(5)	-0.0015(4)	0.0064(5)	-0.0011(4)
Bi(4)	-0.25202(6)	0.37855(10)	-0.13153(12)	0.0281(2)		0.0210(4)	0.0312(5)	0.0297(5)	-0.0021(4)	0.0048(3)	-0.0001(4)
Tl(1)	-0.03318(6)	-0. 36844(10)	-0.48112(13)	0.0602(4)		0.0463(9)	0.0612(8)	0.0668(10)	0.0125(8)	0.0087(7)	-0.0022(7)
Tl(2)	-0.16074(5)	-0.36256(10)	-0.20010(12)	0.0572(4)		0.0386(7)	0.0753(10)	0.0549(9)	-0.0127(7)	0.0104(6)	-0.0019(7)
Tl(3)	-0.05407(8)	0.15439(11)	0.52552(14)	0.0775(5)		0.0842(12)	0.0958(12)	0.0637(10)	0.0330(9)	0.0393(9)	0.0309(10)
Tl(4)	0.33229(5)	-0.66856(9)	0.25163(11)	0.0500(4)		0.0367(7)	0.0610(9)	0.0492(8)	0.0011(6)	0.0092(6)	-0.0072(6)
Tl(5)	0.15839(5)	-0.33754(9)	0. 63392(12)	0.0515(4)		0.0385(8)	0.0491(8)	0.0663(10)	0.0157(7)	0.0152(7)	0.0093(6)
Tl(6)	-0.33490(5)	0.11361(10)	-0.02024(12)	0.0597(5)		0.0315(7)	0.0729(10)	0.0690(10)	-0.0175(8)	0.0072(7)	-0.0003(6)
Tl(7)	0.05579(7)	-0.38652(13)	0.23997(14)	0.0875(6)		0.0540(11)	0.1358(14)	0.0741(12)	0.0478(11)	0.0220(9)	0.0099(10)
Tl(8)	0.02533(6)	-0.10958(10)	-0.28359(13)	0.0632(4)		0.0541(10)	0.0735(10)	0.0624(10)	-0.0186(8)	0.0184(8)	-0.0106(7)
Tl(9)	-0.34696(5)	0.42358(9)	-0.53056(11)	0.0510(4)		0.0396(7)	0.0547(8)	0.0557(8)	-0.0050(7)	0.0104(6)	0.0002(6)
Tl(10)	0.15184(6)	-0.13637(11)	0.14403(14)	0.0674(5)		0.0467 (9)	0.0626(10)	0.0929(13)	-0.0173(9)	0.0216(8)	-0.0148(7)
Tl(11)	-0.16214(5)	0.10996(10)	0.11014(13)	0.0550(4)		0.0323 (7)	0.0588(9)	0.0714(11)	0.0131(8)	0.0127(7)	0.0081(6)
Tl(12)	-0.15739(6)	-0.58543(10)	-0.38805(14)	0.0666(5)		0.0514(9)	0.0589(10)	0.0918(13)	-0.0370(9)	0.0256(8)	-0.0154(7)
Cl(1)	-0.0495(2)	-0.2766(4)	0.2645(5)	0.049(2)	0.30	0.061(4)	0.032(3)	0.054(4)	-0.016(3)	0.017(3)	-0.004(3)
Cl(2)	0.0566(3)	-0.1091(6)	0.2496(6)	0.052(2)	0.06	0.038(4)	0.089(6)	0.036(4)	0.009(4)	0.019(3)	0.013(4)
Cl(3)	0.0362(2)	0.0259(4)	0.4751(5)	0.051(2)	0.25	0.052(4)	0.045(4)	0.055(4)	-0.021(3)	0.014(3)	-0.004(3)
Cl(4)	-0.0741(3)	-0.1512(5)	0.4940(5)	0.047(2)	0.11	0.041(4)	0.073(5)	0.035(4)	0.002(3)	0.024(3)	0.007(3)
Cl(5)	-0.0797(3)	-0.0315(5)	0.2079(6)	0.055(2)	0.12	0.035(4)	0.071(5)	0.054 (5)	0.028(4)	0.007(3)	0.018(3)
Cl(6)	0.0626(3)	-0.2147(6)	0.5197(7)	0.057(2)	0.06	0.044(4)	0.063(5)	0.066(6)	0.038(4)	0.022(4)	0.029(4)
Cl(7)	0.2456(3)	-0.2892(4)	0.1925(5)	0.042(2)	0.11	0.057(4)	0.038(4)	0.033(4)	0.009(3)	0.015(3)	-0.002(3)
Cl(8)	0.1624(2)	-0. 2678 (4)	0.3816(5)	0.049(2)	0.24	0.053(4)	0.036(3)	0.061(4)	-0.002(3)	0.020(3)	0.014(3)
Cl(9)	0.2485(3)	-0.4548(4)	0.5676(5)	0.043(2)	0.14	0.036(3)	0.052(4)	0.037(4)	-0.002(3)	0.007(3)	-0.003(3)
Cl(10)	0.3296(2)	-0.4767(3)	0.3657 (4)	0.046(1)	0.32	0.046(3)	0.042(3)	0.051(4)	-0.014(3)	0.017(3)	0.013(2)
Cl(11)	0. 3274(3)	-0.2629(4)	0.4941 (5)	0.041(2)	0.03	0.039(4)	0.043(4)	0.036(4)	-0.005(3)	0.005(3)	-0.007(3)
Cl(12)	0.1725(3)	-0.4835(4)	0.2661(6)	0.053(2)	0.11	0.048(4)	0.039(4)	0.069(5)	-0.021(3)	0.015(4)	-0.013(3)
Cl(13)	-0.0561(3)	-0. 3965(5)	0.0096(6)	0.048(2)	0.09	0.045(4)	0.061(4)	0.041(4)	0.008(3)	0.020(3)	0.003(3)
Cl(14)	0.0647(2)	-0.5176(4)	-0.0211(5)	0.047(2)	0.28	0.042(3)	0.041(3)	0.052(4)	0.011(3)	0.007(3)	-0.003(3)
Cl(15)	0.0650(3)	-0.3522(5)	-0.2471(6)	0.056(2)	0.17	0.035(3)	0.094(5)	0.043(4)	-0.001(4)	0.020(3)	0.007(4)
Cl(16)	-0.0605(2)	-0.2329(4)	-0.2169 (5)	0.051(2)	0.29	0.048(4)	0.044(3)	0.060(4)	0.015(3)	0.016(3)	0.007(3)
Cl(17)	0.0684(3)	-0. 2725(5)	0.0408(7)	0.050(2)	0.02	0.058(5)	0.044(4)	0.045(5)	-0.013(4)	0.015(4)	-0.017(4)
Cl(18)	-0.0590(4)	-0.4767(6)	-0.2649(7)	0.071(3)	0.08	0.071(6)	0.080(6)	0.065(6)	-0.036(5)	0.028(5)	-0.016(5)
Cl(19)	-0.3546 (3)	0.3652(6)	-0.1549 (9)	0.016(5)	0.35	0.017(3)	0.151(8)	0.280(13)	-0.098(8)	0.015(5)	0.000(4)
Cl(20)	-0.2389 (4)	0.4212(6)	0.0757(7)	0.066(3)	0.00	0.094(8)	0.064(6)	0.038(5)	0.007(4)	0.017(5)	-0.013(5)
Cl(21)	-0.1497(3)	0.4086(5)	-0.1122(7)	0.064(2)	0.05	0.026(4)	0.070(5)	0.091(7)	0.013(4)	0.014(4)	-0.003(3)
Cl(22)	-0.2622(3)	0.3312(5)	-0.3408(6)	0.054(2)	0.04	0.070(6)	0.058(5)	0.030(4)	0.008(4)	0.010(4)	0.003(4)
Cl(23)	-0.2618(4)	0.5571(5)	-0.1552(7)	0.074(2)	0.09	0.097(7)	0.058(5)	0.078(6)	0.018(4)	0.044(5)	0.020(5)
Cl(24)	-0.2437(3)	0.2002(4)	-0.1012(6)	0.055(2)	0.08	0.082(6)	0.037(4)	0.059(5)	0.012(3)	0.042(5)	0.010(4)

X_{Br} is the molar fraction of bromine replacing Cl, as derived from the occupancy of the site in the structure refinement. The exponent of the anisotropic displacement factor takes the form: $-2\pi^2[U_{11}h^2(a^*)^2 + ... + 2U_{12}hka^*b^* + ...]$; $Ueq = ⅓(U_{11} + U_{22} + U_{33})$.

larger than those of the Bi atoms, a point that might suggest partial replacement of Tl by lighter atoms or groups not detectable by electron-microprobe analysis, among which especially ammonium. This possibility, however, was taken into account by refining the population of the Tl sites, but no significant deviation from unity was encountered at all sites, thereby excluding a significant replacement, in agreement with the total in the chemical analysis, which is close to 100%. Such an absence is also consistent with the lack of isotypism between the corresponding $Tl^+$and NH_4^+ compounds. The difference in the ADPs of atoms of nearly equal weight occurs because such parameters do not depend on the atomic mass exclusively, but they also depend on the nature, strength and network of the chemical bonds (see Gramaccioli 2002). Here, the set of bonds around the bismuth atoms is decidedly more covalent and more strongly connected than the corresponding set around the Tl^+ ions.

As the presence of twinning was suggested by the SHELXL97 program during the refinement, a twin matrix [$\bar{1}$ 0 0 / 0 $\bar{1}$ 0 / 0 0 $\bar{1}$] was also introduced; the relative percentages of the twins were refined to 0.73(1) and 0.27(1). The final R is 0.052 for 6232 observed reflections [$I > 2\sigma(I)$].

The final coordinates and displacement parameters of the atoms are reported in Table 4. A table of observed and calculated structure-factors may be obtained from The Depository of Unpublished Data, on the MAC website [document Steropesite CM47_373].

RESULTS AND DISCUSSION

Notwithstanding the relative similarity in the ionic radii of NH_4^+ and Tl^+, steropesite is not isostructural with the corresponding compound $(NH_4)_3BiCl_6$ or ammonium hexachlorobismuthate(III) (Belkyal *et al.* 1997). However, in spite of the greater difference in the ionic radii between Cs^+ and Tl^+ (1.70 *versus* 1.55) than that between NH_4^+ and Tl^+ (1.47 *versus* 1.55 Å, respectively), the structure of steropesite is more closely related to those of the corresponding cesium–potassium bismuth chlorides such as Cs_3BiCl_6 and CsK_2BiCl_6 (Benanchenhou *et al.* 1986), which can also be more properly considered as hexachlorobismuthates(III) (Figs. 3, 4). Such a phenomenon is interesting and can be explained on grounds that Tl–Cl bonds show a much more covalent character than those of the alkali metals, so that the concept of ionic radius cannot be entirely and unquestionably applied. For these two last compounds, which show $C2/c$ instead of Cc symmetry, the unit-cell volume (2883 and 2542 Å^3, respectively) is about one half that observed for our mineral (4993 Å^3). This difference in volume is essentially due to the doubling of the b parameter occurring in steropesite, leading to a Z value of 16 instead of 8, whereas the a and c parameters are comparable. Apart from this doubling and the different space-groups, the value of the β angle (about 108° for steropesite *versus* 99° for the other two compounds) indicates a further important difference. The lack of a center of symmetry in our mineral was definitively confirmed by using the MISSYM algorithm in the PLATON program (Le Page 1987, 1988, Spek 2003) and, in any case, by the geometrical non-equivalence of any possible couple of Bi and Tl atoms (see Table 5 and below). As is obvious in Figure 3, the structural relationships between our mineral and Cs_3BiCl_6 are clear: apart from the different orientation of the $BiCl_6^{3-}$ octahedra, which is best shown in Figure 4, an important difference is that one row of these octahedra along c is shifted by c/4. The asymmetric unit contains four Bi, twelve Tl and 24 Cl atoms. For $(NH_4)_3BiCl_6$,

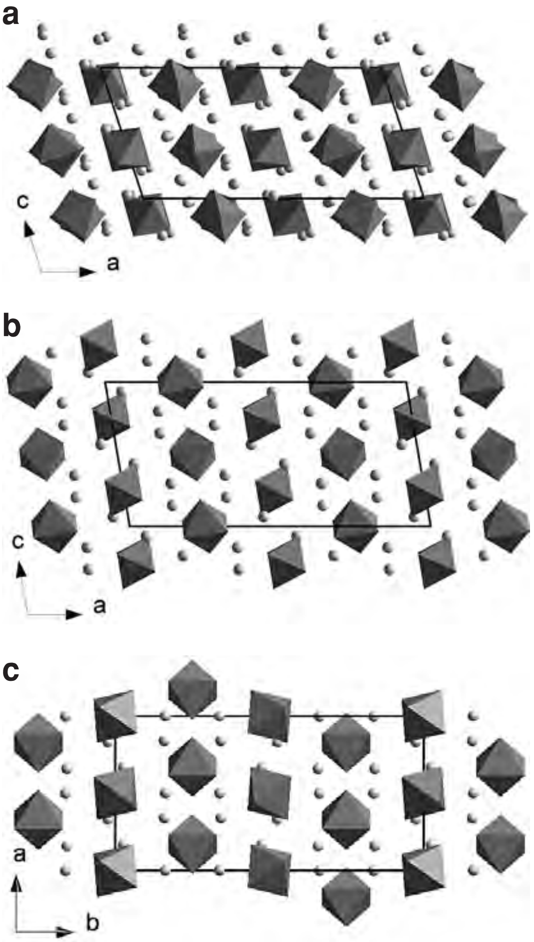

FIG. 3. A comparison of the crystal structures of steropesite (a), of Cs_3BiCl_6 (b) along [0 1 0], and that of the corresponding projection of $(NH_4)_3BiCl_6$ (c) along [0 0 1]. The octahedra represent the $BiCl_6^{3-}$ ions; the Tl^+, Cs^+ and the N atoms of the ammonium ions are shown as light gray spheres.

which is orthorhombic, space group *Pnma*, the most important difference with respect to Cs_3BiCl_6 is the structural distortion of the unit cell of the latter in the plane represented in Figure 3c.

The bismuth atoms display a distorted octahedral coordination, with Bi–Cl distances in the range 2.618–2.789 Å. Considering a maximum value of 3.6 Å for the Tl–Cl distances, five of the twelve independent Tl atoms are six-coordinated (Tl–Cl in the range 3.023–3.596 Å), six are seven-coordinated (Tl–Cl in the range 3.106–3.558 Å), and one is eight-coordinated (Tl–Cl in the range 3.229–3.511 Å).

In this mineral, as in a number of bismuth chlorides, the $6s^2$ non-bonding pair of the metal atom does not induce a substantial distortion of the $BiCl_6^{3-}$ octahedra. The average Bi–Cl distance ranges from 2.708 to 2.735 Å for each octahedron; the overall average for the Bi–Cl distances in this mineral is 2.717 Å, a value slightly larger than the corresponding values in other hexachlorobismuthates(III) such as Cs_3BiCl_6 (2.702 Å), CsK_2BiCl_6 (2.697 Å), $Cs_2NaBiCl_6$ (2.676 Å), and $(NH_4)_3BiCl_6$ (2.708 Å), respectively (Benachenhou *et al.* 1986, Pelle *et al.* 1984, Belkyal *et al.* 1997). The corresponding Bi–Cl distance in the *molecular* compound $BiCl_3$ is in comparison much shorter

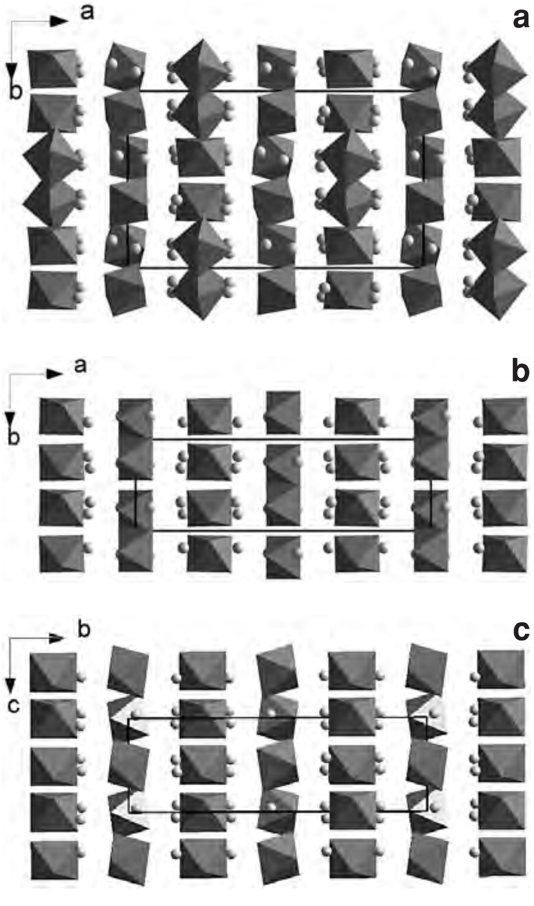

FIG. 4. Projections of the structures represented in Figure 3.

TABLE 5. INTERATOMIC DISTANCES (Å) IN STEROPESITE

Bi(1)-Cl(1)	2.724(6)	Bi(3)-Cl(13)	2.671(9)
Bi(1)-Cl(2)	2.680(9)	Bi(3)-Cl(14)	2.788(6)
Bi(1)-Cl(3)	2.735(6)	Bi(3)-Cl(15)	2.694(8)
Bi(1)-Cl(4)	2.760(8)	Bi(3)-Cl(16)	2.772(6)
Bi(1)-Cl(5)	2.750(7)	Bi(3)-Cl(17)	2.725(8)
Bi(1)-Cl(6)	2.636(8)	Bi(3)-Cl(18)	2.618(8)
<Bi(1)-Cl>	2.714	<Bi(3)-Cl>	2.711
Bi(2)-Cl(7)	2.692(7)	Bi(4)-Cl(19)	2.667(8)
Bi(2)-Cl(8)	2.789(6)	Bi(4)-Cl(20)	2.688(9)
Bi(2)-Cl(9)	2.774(7)	Bi(4)-Cl(21)	2.702(8)
Bi(2)-Cl(10)	2.734(6)	Bi(4)-Cl(22)	2.747(8)
Bi(2)-Cl(11)	2.767(6)	Bi(4)-Cl(23)	2.721(8)
Bi(2)-Cl(12)	2.656(6)	Bi(4)-Cl(24)	2.726(7)
<Bi(2)-Cl >	2.735	<Bi(4)-Cl>	2.708
Tl(1)-Cl(1)^a	3.491(7)	Tl(2)-Cl(13)	3.282(7)
Tl(1)-Cl(4)^a	3.446(8)	Tl(2)-Cl(16)	3.379(7)
Tl(1)-Cl(6)^a	3.454(9)	Tl(2)-Cl(18)	3.534(10)
Tl(1)-Cl(15)	3.353(6)	Tl(2)-Cl(7)^d	3.361(7)
Tl(1)-Cl(18)	3.504(10)	Tl(2)-Cl(11)^d	3.254(7)
Tl(1)-Cl(14)^b	3.303(7)	Tl(2)-Cl(20)^m	3.141(8)
Tl(1)-Cl(21)^m	3.106(7)	Tl(2)-Cl(23)^e	3.174(10)
<Tl(1)-Cl>	3.38	<Tl(2)-Cl>	3.304
Tl(3)-Cl(3)	3.315(7)	Tl(4)-Cl(10)	3.271(6)
Tl(3)-Cl(1)^c	3.587(7)	Tl(4)-Cl(1)^g	3.511(7)
Tl(3)-Cl(2)^c	3.514(7)	Tl(4)-Cl(4)^g	3.371(6)
Tl(3)-Cl(5)^c	3.251(9)	Tl(4)-Cl(5)^g	3.312(8)
Tl(3)-Cl(11)^f	3.307(7)	Tl(4)-Cl(9)^b	3.300(6)
Tl(3)-Cl(16)^c	3.325(7)	Tl(4)-Cl(11)^b	3.471(7)
		Tl(4)-Cl(22)^h	3.459(8)
		Tl(4)-Cl(24)^h	3.229(9)
<Tl(3)-Cl>	3.383	<Tl(4)-Cl>	3.366
Tl(5)-Cl(6)	3.135(8)	Tl(6)-Cl(24)	3.216(9)
Tl(5)-Cl(8)	3.482(7)	Tl(6)-Cl(7)^f	3.278(6)
Tl(5)-Cl(9)	3.311(8)	Tl(6)-Cl(9)^d	3.233(6)
Tl(5)-Cl(12)^i	3.167(7)	Tl(6)-Cl(12)^d	3.462(8)
Tl(5)-Cl(14)^i	3.462(6)	Tl(6)-Cl(14)^d	3.332(7)
Tl(5)-Cl(15)^j	3.324(8)	Tl(6)-Cl(15)^d	3.348(6)
Tl(5)-Cl(22)^k	3.268(8)	Tl(6)-Cl(17)^d	3.395(10)
<Tl(5)-Cl>	3.307	<Tl(6)-Cl>	3.323
Tl(7)-Cl(1)	3.363(7)	Tl(8)-Cl(16)	3.273(7)
Tl(7)-Cl(8)	3.386(6)	Tl(8)-Cl(2)^m	3.406(9)
Tl(7)-Cl(12)	3.362(7)	Tl(8)-Cl(3)^m	3.524(7)
Tl(7)-Cl(13)	3.516(7)	Tl(8)-Cl(4)^a	3.322(6)
Tl(7)-Cl(17)	3.217(9)	Tl(8)-Cl(5)^m	3.498(8)
Tl(7)-Cl(14)^i	3.372(7)	Tl(8)-Cl(6)^a	3.414(10)
		Tl(8)-Cl(19)^g	3.143(7)
<Tl(7)-Cl>	3.369	<Tl(8)-Cl>	3.369
Tl(9)-Cl(22)	3.114(7)	Tl(10)-Cl(2)	3.268(9)
Tl(9)-Cl(2)^l	3.236(7)	Tl(10)-Cl(7)	3.320(7)
Tl(9)-Cl(3)^l	3.503(7)	Tl(10)-Cl(17)	3.023(8)
Tl(9)-Cl(6)^l	3.407(9)	Tl(10)-Cl(3)^m	3.596(6)
Tl(9)-Cl(8)^l	3.150(6)	Tl(10)-Cl(20)^o	3.415(11)
Tl(9)-Cl(19)^n	3.558(10)	Tl(10)-Cl(23)^p	3.136(8)
Tl(9)-Cl(23)^n	3.189(11)		
<Tl(9)-Cl>	3.308	<Tl(10)-Cl>	3.293
Tl(11)-Cl(5)	3.048(7)	Tl(12)-Cl(18)	3.090(9)
Tl(11)-Cl(24)	3.231(7)	Tl(12)-Cl(11)^q	3.056(7)
Tl(11)-Cl(4)^m	3.226(8)	Tl(12)-Cl(13)^b	3.375(9)
Tl(11)-Cl(7)^f	3.344(8)	Tl(12)-Cl(20)^m	3.238(10)
Tl(11)-Cl(9)^d	3.269(7)	Tl(12)-Cl(21)^e	3.533(10)
Tl(11)-Cl(16)^c	3.477(6)	Tl(12)-Cl(22)^c	3.295(10)
<Tl(11)-Cl>	3.266	<Tl(12)-Cl>	3.265

Symmetry codes: a = x, y, z – 1; **b** = x, –y – 1, z – ½; **c** = x, –y, z + ½; **d** = x – ½, –y – ½ , z – ½; **e** = x, y – 1, z; **f** = x – ½ , y + ½, z; **g** = x + ½, y – ½, z; **h** = x + ½, –y – ½, z + ½; **i** = x, –y – 1, z + ½; **j** = x, y, z + 1; **k** = x + ½, y – ½, z + 1; **l** = x – ½, y + ½, z – 1; **m** = x, –y, z – ½; **n** = x, –y + 1, z – ½; **o** = x + ½, y – ½, z; **p** = x + ½, –y + ½, z +½; **q** = x – ½, y – ½, z – 1.

[2.424(5) Å], according to an accurate spectroscopic study by Töke & Hargittai (1995).

The coordination polyhedra around the thallium atoms are much more irregular, in line with the more ionic character of Tl(I)–Cl bonds. The overall average Tl–Cl distance is 3.328 Å, a value almost identical with the corresponding average for synthetic Tl_3PbCl_5 (3.326 Å: Keller 1977) and for the cubic phase of synthetic TlCl (3.328 Å: Smakula & Kalnajs 1955).

The mineral is a unique example of a natural compound in which the bismuth atoms are exclusively bound to halogen atoms. In contrast, in most other natural bismuth halides and in agreement with the tendency of Bi^{3+} to be subject to at least partial hydrolysis, the metal is also bonded to oxygen atoms, the best known example being bismoclite BiOCl (Keramides *et al*. 1993).

In the fumaroles at La Fossa crater, the abundance of bismuth sulfides or sulfosalts has long been known (Zambonini *et al*. 1924, Garavelli *et al*. 1997, and references therein); instead, the presence of bismuth halides as "true" minerals deposited around the fumaroles had never been reported so far; there are instead sulfohalides such as demicheleite-(Br) BiSBr, or its equivalent BiSCl [IMA 2008–020 (Demartin *et al*. 2008b)], or halogen-containing sulfosalts, such as in particular vurroite $Pb_{20}Sn_2(Bi,As)_{22}S_{54}Cl_6$ (Garavelli *et al*. 2005). In addition to the presence of all these halogen-bearing minerals, the discovery of steropesite and bismoclite in good crystals in a nearby fumarole emphasizes the role of halides in the origin of all the bismuth minerals at Vulcano; such a possibility is further confirmed by the discovery of bismuth halides and sulfohalides in quartz tubes inserted in these fumaroles (Garavelli *et al*. 1997, and references therein), and at Mutnovski, Kamchatka (Zelenski & Bortnikova 2005). The formation of all these minerals is very probably connected with the relatively high volatility of $BiCl_3$ (b.p. 447°C), followed by that of TlCl (b.p. 720°C) and $PbCl_2$ (b.p. 950°C) (Sigma-Aldrich 2006); the presence of sulfur (or H_2S) involves the presence of complex equilibria leading to chlorosulfides, sulfides and sulfosalts.

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