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Routhierite, Tl(Cu,Ag)(Hg,Zn)$_2$(As,Sb)$_2$S$_6$

Luca Bindi

Museo di Storia Naturale, Sezione di Mineralogia, Universitá di Firenze, Via La Pira 4, I-50121 Firenze, Italy
Correspondence e-mail: luca.bindi@unifi.it

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The crystal structure of the mineral routhierite, Tl(Cu,Ag)(Hg,Zn)$_2$(As,Sb)$_2$S$_6$, was solved and refined for the first time by means of single-crystal X-ray diffraction. The crystal structure consists of (Cu,Ag)S$_4$ and (Hg,Zn)S$_4$ tetrahedra, which share corners to form a framework with channels parallel to [001]. These channels contain TlS$_6$ and (As,Sb)S$_3$ polyhedra that share corners and edges with the tetrahedra. The crystal–chemical relationships with other Tl–Hg sulfosalts are outlined. The structure determination reported in this study definitively confirms that routhierite and stalderite possess the same crystal structure.

Comment

Routhierite, Tl(Cu,Ag)(Hg,Zn)$_2$(As,Sb)$_2$S$_6$, is a rare mineral first described by Johan *et al.* (1974) to occur with pierrotite, stibnite, smithite, sphalerite, realgar, orpiment, pyrite and barite in Jas Roux (Hautes-Alpes), France. By means of an X-ray single-crystal study (Weissenberg photographs), these authors pointed out that routhierite is tetragonal [possible space groups $I4mm$, $I\bar{4}2m$, $I\bar{4}m2$ and $I4/mmm$, with a = 9.977 (2) Å and c = 11.290 (3) Å]. However, Johan *et al.* (1974) were not able to proceed to a crystal structure determination of routhierite at that time. More recently, Graeser *et al.* (1995), during the structural description of the new Tl sulfosalt mineral stalderite, Tl(Cu,Ag)(Zn,Fe,Hg)$_2$(As,Sb)$_2$S$_6$, pointed out close relationships between stalderite and routhierite. They concluded that stalderite represents the Zn equivalent of routhierite. Similar conclusions were reached by Moelo *et al.* (2008) during a review of sulfosalt systematics. These authors considered routhierite as isotypic with stalderite. To help resolve the concerns relating to the structure of routhierite and to investigate the similarity in X-ray patterns for routhierite and stalderite, new crystal structure data for routhierite from its type locality, Jas Roux, are presented.

In the crystal structure of routhierite, (Cu,Ag)S$_4$ and (Hg,Zn)S$_4$ tetrahedra share corners to form a framework with channels parallel to [001] (Fig. 1). These channels contain TlS$_6$ and (As,Sb)S$_3$ polyhedra that share corners and edges with the tetrahedra (Fig. 2). In detail, the Tl atom is coordinated by (2+4) S atoms in the form of an orthorhombic pyramid with a split apex. Although there are two symmetry-independent and quite different Tl—S bond distances (Table 1), the mean Tl—S bond distance (*i.e.* 3.29 Å) is nearly identical to that observed in stalderite (*i.e.* 3.32 Å; Graeser *et al.*, 1995). The (Cu,Ag) and (Hg,Zn) atoms are surrounded by four S atoms to form slightly distorted tetrahedra. The (Cu,Ag)—S1 distance of 2.4325 (11) Å is greater than that observed in stalderite (*i.e.* 2.36 Å) because of the presence of minor amounts of silver replacing copper at this position. The mean (Hg,Zn)—S distance of 2.51 Å is in fair agreement with those observed for christite, TlHgAsS$_3$ (*i.e.* 2.56 Å; Brown & Dickson, 1976), and laffittite, AgHgAsS$_3$ (*i.e.* 2.59 Å; Nakai & Appleman, 1983). The shortening of the (Hg,Zn)—S distance in routhierite,

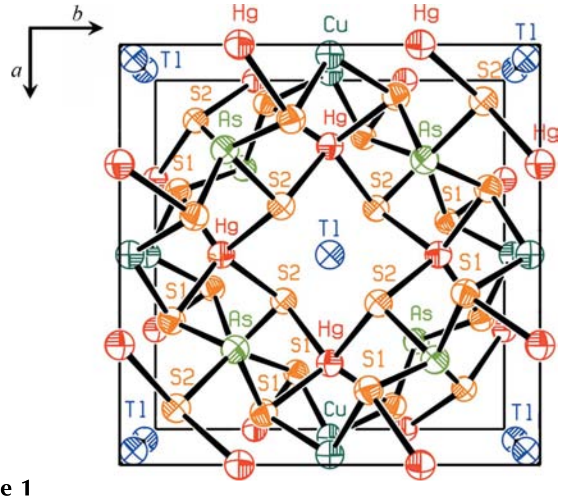

Figure 1
The crystal structure of routhierite, viewed down [001]. Displacement ellipsoids are drawn at the 50% probability level. The unit cell is outlined. The atom labels are generic and represent all of the symmetry-related atoms of each type in the unit cell. Mixed Cu/Ag, Hg/Zn and As/Sb sites are labelled as Cu, Hg and As, respectively.

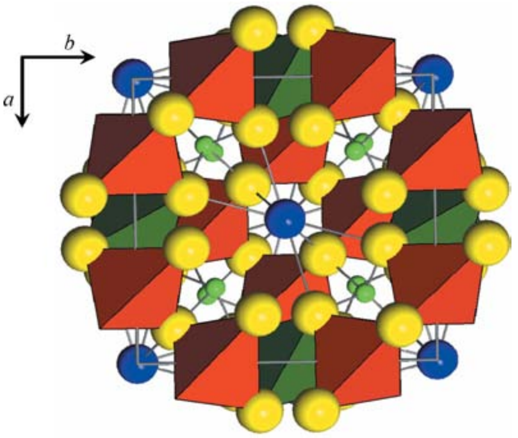

Figure 2
The crystal structure of routhierite, showing the linking of (Cu,Ag)S$_4$ and (Hg,Zn)S$_4$ tetrahedra (in dark green and red, respectively, in the electronic version of the paper), which share corners to form a framework with channels hosting Tl and (As,Sb) atoms. (In the electronic version of the paper, blue, light-green and yellow spheres indicate Tl, As and S atoms, respectively.) The unit cell is outlined.

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however, is due to the minor amount of Zn substituting for Hg. In stalderite, where only Zn is present at this position, the mean bond distance is 2.41 Å (Graeser *et al.*, 1995). Finally, the (As,Sb) atoms form a trigonal pyramid with three S atoms, with (As,Sb) at the apex [mean (As,Sb)—S = 2.34 Å], as is typical for sulfosalts. It is worth noting that a relatively short Tl—Tl distance of 3.4707 (6) Å was observed. This value is similar to the Tl—Tl distance found in elemental thallium (3.40 Å; Wells, 1962) and could indicate some Tl—Tl interactions in the structure. The same feature was also observed in stalderite (Graeser *et al.*, 1995).

The structure determination reported here confirms that routhierite and stalderite possess the same crystal structure.

Experimental

A crystal was selected from a natural specimen from the type locality (*i.e.* Jas Roux, France) belonging to the Mineralogical Collection of the Natural History Museum of Florence (catalogue No. 45164/G). 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 S, Cu, Zn, As, Ag, Sb, Hg and Tl, with a very minor amount of Fe. The chemical composition was then determined using wavelength dispersive analysis. The routhierite fragment was found to be homogeneous within analytical error. On the basis of 12 atoms, the chemical formula can be written as $\mathrm{Tl(Cu_{0.65}Ag_{0.35})_{\Sigma=1.00}(Hg_{1.70}Zn_{0.30})_{\Sigma=2.00}(As_{1.70}Sb_{0.30})_{\Sigma=2.00}S_{6.00}}$.

Crystal data

$\mathrm{Tl(Cu,Ag)(Hg,Zn)_2(As,Sb)_2S_6}$
$M_r = 1000.29$
Tetragonal, $I\bar{4}2m$
$a = 9.9821\ (11)$ Å
$c = 11.3122\ (12)$ Å
$V = 1127.2\ (2)$ Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 46.48$ mm^{-1}
$T = 298\ (2)$ K
0.12 × 0.10 × 0.07 mm

Data collection

Oxford Xcalibur-3 diffractometer
Absorption correction: Gaussian (*ABSPACK*; Oxford Diffraction, 2006)
$T_{\min} = 0.006$, $T_{\max} = 0.041$
2692 measured reflections
673 independent reflections
586 reflections with $I > 2\sigma(I)$
$R_{\mathrm{int}} = 0.029$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.011$
$wR(F^2) = 0.011$
$S = 0.88$
673 reflections
37 parameters
$\Delta\rho_{\max} = 0.76$ e Å^{-3}
$\Delta\rho_{\min} = -0.99$ e Å^{-3}
Absolute structure: Flack (1983), 388 Friedel pairs
Flack parameter: 0.223 (14)

Table 1
Selected bond lengths (Å).

Tl—S1	3.4526 (8)	Hg—S1	2.4808 (11)
Tl—S2	2.961 (2)	Hg—S2$^{\mathrm{iii}}$	2.5428 (15)
Tl—Tl$^{\mathrm{i}}$	3.4707 (6)	As—S1	2.3350 (14)
Tl—Sb$^{\mathrm{ii}}$	3.5226 (9)	As—S2	2.3387 (19)
Cu—S1	2.4325 (11)	S2—Zn$^{\mathrm{iv}}$	2.5428 (15)

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

The crystal structure of routhierite was solved and refined starting from the atomic coordinates reported for stalderite by Graeser *et al.* (1995). Convergence was rapidly attained for an anisotropic model of the structure. In the final cycles, the structure was refined as an inversion twin.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2006); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2006); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *XtalDraw* (Downs & Hall-Wallace, 2003); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FN3007). Services for accessing these data are described at the back of the journal.

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