

# Coquandite, $\text{Sb}_{6+x}\text{O}_{8+x}(\text{SO}_4)(\text{OH})_x \cdot (\text{H}_2\text{O})_{1-x}$ ( $x = 0.3$ ), from the Cetine mine, Tuscany, Italy: crystal structure and revision of the chemical formula

L. BINDI<sup>1,2,\*</sup>, C. BIAGIONI<sup>3</sup>, L. CECCANTINI<sup>4</sup>, M. BATONI<sup>4</sup> AND S. MENCHETTI<sup>1</sup>

<sup>1</sup> Dipartimento di Scienze della Terra, Università degli Studi di Firenze, Via G. La Pira 4, I-50121 Florence, Italy

<sup>2</sup> CNR – Istituto di Geoscienze e Georisorse, Sezione di Firenze, Via G. La Pira 4, I-50121 Florence, Italy

<sup>3</sup> Dipartimento di Scienze della Terra, Università di Pisa, Via S. Maria 53, I-56126 Pisa, Italy

<sup>4</sup> Gruppo Mineralogico Fiorentino, Via Poggio Bracciolini 23, I-56126 Florence, Italy

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## ABSTRACT

The crystal structure of the mineral coquandite, a rare Sb oxy-sulfate hydrate, was solved using intensity data collected from a crystal from the Cetine mine, Tuscany, Italy. This study revealed that the structure is triclinic, space group  $P\bar{1}$ , with  $a = 11.4292(5)$ ,  $b = 29.772(1)$ ,  $c = 11.2989(5)$  Å,  $\alpha = 91.152(3)$ ,  $\beta = 119.266(4)$ ,  $\gamma = 92.624(3)^\circ$  and  $V = 3346.4(2)$  Å<sup>3</sup>. The refinement of an anisotropic model led to an  $R$  index of 0.0347 for 21,061 independent reflections. Thirty-two Sb sites, five S sites and 67 oxygen sites occur in the crystal structure of coquandite. Sb atoms display the characteristic  $\text{SbO}_3E$  and  $\text{SbO}_4E$  coordinations whereas S fills  $(\text{SO}_4)$  tetrahedral groups. These atoms are arranged in five symmetry-independent layers perpendicular to  $\mathbf{b}^*$ . Four of them and their centrosymmetrical counterparts form complex modules stacked along  $\mathbf{b}^*$  and bonded through two Sb atoms and H bonds. The complex H bonding system in the structure is discussed. On the basis of information gained from this characterization, the crystal-chemical formula was revised according to the structural results, yielding  $\text{Sb}_{6+x}\text{O}_{8+x}(\text{SO}_4)(\text{OH})_x \cdot (\text{H}_2\text{O})_{1-x}$  ( $Z = 10$ ) with  $x = 0.3$  instead of  $\text{Sb}_6\text{O}_8(\text{SO}_4) \cdot \text{H}_2\text{O}$  ( $Z = 12$ ) as reported previously. A recalculation of the chemical data listed in the scientific literature for coquandite according to the structural results obtained here leads to a satisfactory agreement.

**KEYWORDS:** coquandite, Sb-sulfates, structure solution, crystal-structure refinement, Cetine mine.

## Introduction

COQUANDITE,  $\text{Sb}_6\text{O}_8(\text{SO}_4) \cdot \text{H}_2\text{O}$  (with  $Z = 12$ ), was established as a mineral species by Sabelli *et al.* (1992) during a study of oxidation minerals collected in the 1970s in the abandoned Pereta stibnite mine, Tuscany, Italy. Those authors supplied a detailed chemical and physical characterization of the mineral and described it as the third  $\text{Sb}^{3+}$ -oxy-sulfate known, the others being peretaite,  $\text{CaSb}_4\text{O}_4(\text{OH})_2(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$

(Cipriani *et al.*, 1980a; Menchetti and Sabelli, 1980a) and klebelsbergite,  $\text{Sb}_4\text{O}_4(\text{OH})_2(\text{SO}_4)$  (Cipriani *et al.*, 1980b; Menchetti and Sabelli, 1980b). Sabelli *et al.* (1992) were able to identify the correct triclinic unit-cell parameters for coquandite and understand the layered nature of the structure. However, the full structural details remained unknown because it was not possible to detect the whole set of atoms owing to pervasive twinning and/or structural disorder.

To help resolve the concerns relating to the mineral coquandite, a new X-ray single-crystal data collection for the mineral on a specimen from the Cetine mine, Tuscany, Italy, has been undertaken and the results are presented here.

\* E-mail: luca.bindi@unifi.it

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## Crystal-structure solution and refinement

A small {010}-tabular crystal fragment (0.010 mm × 0.130 mm × 0.260 mm) was hand-picked from a rock sample (Fig. 1) collected by one of us (LC) at the Cetine mine, Tuscany, Italy. In this sample, coquandite is associated with stibnite and quartz.

The selected crystal was preliminarily examined with a Bruker-Enraf MACH3 single-crystal diffractometer using graphite-monochromatized MoK $\alpha$  radiation. The data collection was then performed using an Oxford Diffraction Xcalibur 3 diffractometer (X-ray MoK $\alpha$  radiation,  $\lambda = 0.71073$  Å) fitted with a Sapphire 2 CCD detector (see Table 1 for details). Intensity integration and standard Lorentz-polarization corrections were undertaken with the *CrysAlis RED* (Oxford Diffraction, 2006) software package. Crystal shape and dimension optimization were performed with *X-shape* (Stoe and Cie, 1996), based on the *Habitus* program (Herrendorf, 1993). The set of reflections was corrected for absorption via a Gaussian analytical method and averaged according to the  $\bar{1}$  point group. The merging  $R$  for the data set decreased from 0.0608 before absorption correction to 0.0114 after this correction. No systematic absences were observed and the statistical tests on the distribution of  $|E|$  values strongly indicated the presence of an inversion centre ( $|E^2 - 1| = 0.988$ ). The structure solution was then initiated in the space group  $P\bar{1}$ .

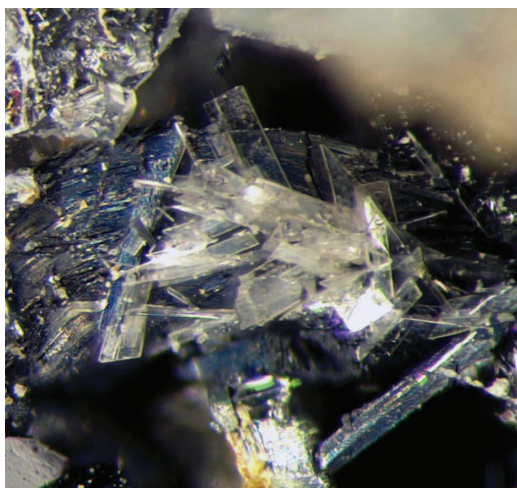


FIG. 1. Tabular transparent crystals of coquandite in the rock sample from the Cetine mine (field of view: 3 mm).

The position of most of the atoms was determined from the three-dimensional Patterson synthesis (Sheldrick, 2008). A least-squares refinement using these heavy-atom positions and isotropic temperature factors yielded an  $R$  factor of 15.35%. Three-dimensional difference-Fourier synthesis yielded the position of the remaining Sb and O atoms. The full-matrix least-squares program *SHELXL-97* (Sheldrick, 2008) was used for the refinement of the structure. The Sb30 position was split into two partially occupied (50%) positions (i.e. Sb30a and Sb30b) and the Sb32 and O63 positions were found to be partially occupied (50%). All the other Sb, S and O positions were found fully occupied by Sb, S and O, respectively, in agreement with the crystal-chemical environment observed (see below), giving rise to an overall stoichiometry of Sb<sub>63</sub>S<sub>10</sub>O<sub>133</sub> (see below for charge-balance considerations). At the last stage, with anisotropic atomic displacement parameters for all non-H atoms and no constraints, the residual value settled at  $R_1 = 0.0314$  ( $wR_2 = 0.0741$ ) for 12,343 independent observed reflections [ $2\sigma(I)$  level] and 946 parameters and at  $R_1 = 0.0347$  ( $wR_2 = 0.0744$ ) for all 21,061 independent reflections. Neutral scattering curves for Sb, S and O were taken from the *International Tables for X-ray Crystallography* (Ibers and Hamilton, 1974). Inspection of the difference-Fourier map revealed that maximum positive and negative peaks were 3.19 and 5.61  $e^-/\text{Å}^3$ , respectively.

Experimental details and  $R$  indices are given in Table 1. Fractional atomic coordinates and isotropic displacement parameters are reported in Table 2 and anisotropic displacement parameters in Table 3. The calculated X-ray powder-diffraction pattern, computed with the atom coordinates and occupancies reported in Table 2, is given in Table 4 together with that reported originally by Sabelli *et al.* (1992). Structure factors (Table 5) have been deposited with the Principal Editor of *Mineralogical Magazine* and are available from [www.minersoc.org/pages/e\\_journals/dep\\_mat\\_mm.html](http://www.minersoc.org/pages/e_journals/dep_mat_mm.html).

## Chemical composition

Unfortunately, the uniqueness of the coquandite crystal available for this study did not allow new chemical data to be obtained. However, if the electron microprobe analyses of coquandite reported by Sabelli *et al.* (1992) from the three occurrences (Pereta, Cetine and Lucky Knock;

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TABLE 1. Crystallographic data and refinement parameters for the selected coquandite crystal.

<b>Crystal data</b>	
Ideal formula	Sb <sub>6.3</sub> O <sub>8.3</sub> (SO <sub>4</sub> )(OH) <sub>0.3</sub> ·0.7H <sub>2</sub> O
Crystal system	triclinic
Space group	$P\bar{1}$
Unit-cell parameters (Å, °)	11.4292(5) 29.772(1) 11.2989(5) 91.152(3) 119.266(4) 92.624(3)
Unit-cell volume (Å <sup>3</sup> )	3346.4(2)
Z	10
Crystal size (mm)	0.010 × 0.130 × 0.260
<b>Data collection</b>	
Diffractometer	Oxford Diffraction Xcalibur 3
Temperature (K)	298(3)
Radiation, wavelength (Å)	MoK $\alpha$ , 0.71073
2 $\theta$ max for data collection (°)	64.71
Crystal-detector dist. (mm)	50
<i>h</i> , <i>k</i> , <i>l</i> ranges	−16−16, −44−44, −15−15
Axis, frames, width (°), time per frame (s)	$\omega$ , 2314, 1.00, 70
Total reflections collected	42,018
Unique reflections ( <i>R</i> <sub>int</sub> )	21,061 (0.011)
Unique reflections <i>I</i> > 2 $\sigma$ ( <i>I</i> )	12,343
Data completeness to $\theta_{\max}$ (%)	99.6
Absorption correction method	Gaussian
<b>Structure refinement</b>	
Refinement method	Full-matrix least-squares on <i>F</i> <sup>2</sup>
Data/restraints/parameters	21,061/0/946
<i>R</i> <sub>1</sub> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )], <i>wR</i> <sub>2</sub> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	0.0314, 0.0741
<i>R</i> <sub>1</sub> all, <i>wR</i> <sub>2</sub> all	0.0347, 0.0744
Gof on <i>F</i> <sup>2</sup>	0.653
Largest diff. peak and hole (e <sup>−</sup> /Å <sup>3</sup> )	3.19, −5.61

$$R_{\text{int}} = (n/n - 1)^{1/2} [F_o^2 - F_o(\text{mean})^2] / \Sigma F_o^2$$

$$R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|; wR_2 = \{ \Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2] \}^{1/2};$$

$$* w = 1 / [ \sigma^2(F_o^2) + (aP)^2 + bP ], \text{ where } P = (\max(F_o^2, 0) + 2F_c^2) / 3;$$

$$\text{GooF} = \{ \Sigma [w(F_o^2 - F_c^2)^2] / (n - p) \}^{1/2}$$

where *n* is the number of reflections and *p* is the number of refined parameters.

Table 6) are taken into account and normalized on the basis of  $\Sigma(\text{Sb}+\text{S}) = 7.3$  a.p.f.u. (as indicated by the structure determination), the values obtained are in keeping with the revised chemical formula proposed in the present study (see below).

## Results and discussion

### Description of the crystal structure

In the crystal structure of coquandite (Fig. 2) there are 32 independent Sb sites, five S sites and 67 oxygen sites. As reported above, one Sb site (Sb30) is split into two sub-positions, whereas one Sb (Sb32) and one O (O63) are half-occupied. Selected bond distances are given in Table 7.

Taking into account the lone pairs of electrons *E*, Sb sites show either an SbO<sub>4</sub>*E* or SbO<sub>3</sub>*E* coordination usual for Sb(III)–O compounds (Fig. 3), because of the repulsion by the stereoactive lone pair on Sb(III). Actually, intermediate arrangements between these two types are possible, with three short bond distances and one definitely longer. Among the 32 independent Sb positions, three kinds of coordination can be recognized: (1) pure SbO<sub>3</sub>*E*; (2) pure SbO<sub>4</sub>*E*; and (3) intermediate SbO<sub>3</sub>*E*/SbO<sub>4</sub>*E* coordinations. Assuming a cut-off distance for the long Sb–O bonds at 3.50 Å (according to Mills *et al.*, 2009), the coordination of Sb atoms is completed by additional ligands at distances

TABLE 2. Atom labels, site occupancy factors (s.o.f.), fractional atom coordinates, and equivalent isotropic displacement parameters ( $\text{\AA}^2$ ) for the selected coquandite crystal.

Atom	s.o.f.	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}$
Sb1	Sb <sub>1.00</sub>	0.79855(6)	0.05344(2)	0.57964(6)	0.0249(1)
Sb2	Sb <sub>1.00</sub>	0.47237(6)	0.05297(2)	0.27550(6)	0.0249(1)
Sb3	Sb <sub>1.00</sub>	0.43496(6)	0.06298(2)	0.92130(6)	0.0264(1)
Sb4	Sb <sub>1.00</sub>	0.08071(6)	0.06620(2)	0.24726(6)	0.0266(1)
Sb5	Sb <sub>1.00</sub>	0.77062(6)	0.07329(2)	0.91580(6)	0.0282(1)
Sb6	Sb <sub>1.00</sub>	0.73778(6)	0.06416(2)	0.20723(6)	0.0266(1)
Sb7	Sb <sub>1.00</sub>	0.08464(6)	0.05013(2)	0.56753(5)	0.0219(1)
Sb8	Sb <sub>1.00</sub>	0.35068(6)	0.16394(2)	0.03202(5)	0.0210(1)
Sb9	Sb <sub>1.00</sub>	0.31797(6)	0.16912(2)	0.37710(5)	0.0226(1)
Sb10	Sb <sub>1.00</sub>	0.69723(6)	0.17244(2)	0.71694(5)	0.0222(1)
Sb11	Sb <sub>1.00</sub>	0.72270(6)	0.18742(2)	0.03575(5)	0.0224(1)
Sb12	Sb <sub>1.00</sub>	0.03938(6)	0.17742(2)	0.07858(6)	0.0234(1)
Sb13	Sb <sub>1.00</sub>	0.98371(6)	0.15290(2)	0.71995(5)	0.0228(1)
Sb14	Sb <sub>1.00</sub>	0.63954(6)	0.15770(2)	0.32996(6)	0.0244(1)
Sb15	Sb <sub>1.00</sub>	0.03785(6)	0.16962(2)	0.44655(5)	0.0229(1)
Sb16	Sb <sub>1.00</sub>	0.34543(6)	0.18622(2)	0.71256(6)	0.0248(1)
Sb17	Sb <sub>1.00</sub>	0.27806(6)	0.27115(2)	0.88901(6)	0.0268(1)
Sb18	Sb <sub>1.00</sub>	0.89645(6)	0.25541(2)	0.51073(6)	0.0281(1)
Sb19	Sb <sub>1.00</sub>	0.63086(6)	0.27205(2)	0.21556(6)	0.0283(1)
Sb20	Sb <sub>1.00</sub>	0.20795(6)	0.27929(2)	0.51048(6)	0.0234(1)
Sb21	Sb <sub>1.00</sub>	0.95548(6)	0.27089(2)	0.83956(6)	0.0273(1)
Sb22	Sb <sub>1.00</sub>	0.63467(6)	0.28567(2)	0.89309(6)	0.0285(1)
Sb23	Sb <sub>1.00</sub>	0.22172(6)	0.27846(2)	0.16132(5)	0.0211(1)
Sb24	Sb <sub>1.00</sub>	0.49569(5)	0.38869(2)	0.64627(5)	0.0201(1)
Sb25	Sb <sub>1.00</sub>	0.14373(6)	0.38357(2)	0.63175(5)	0.0217(1)
Sb26	Sb <sub>1.00</sub>	0.82635(6)	0.38804(2)	0.96463(6)	0.0273(1)
Sb27	Sb <sub>1.00</sub>	0.81693(6)	0.37931(2)	0.32088(5)	0.0215(1)
Sb28	Sb <sub>1.00</sub>	0.49639(6)	0.39326(2)	0.31382(5)	0.0206(1)
Sb29	Sb <sub>1.00</sub>	0.14634(6)	0.38466(2)	0.96155(5)	0.0231(1)
Sb30a	Sb <sub>0.50</sub>	0.7791(1)	0.38202(4)	0.6368(1)	0.0285(3)
Sb30b	Sb <sub>0.50</sub>	0.8655(1)	0.37848(4)	0.6623(1)	0.0233(2)
Sb31	Sb <sub>1.00</sub>	0.49500(6)	0.50471(2)	0.18228(6)	0.0267(1)
Sb32	Sb <sub>0.50</sub>	0.4790(1)	0.48284(4)	0.4832(1)	0.0267(3)
S1	S <sub>1.00</sub>	0.1305(2)	0.04252(7)	0.9391(2)	0.0255(4)
S2	S <sub>1.00</sub>	0.4312(2)	0.06938(7)	0.5734(2)	0.0246(4)
S3	S <sub>1.00</sub>	0.5603(2)	0.27283(8)	0.5180(2)	0.0309(5)
S4	S <sub>1.00</sub>	0.5004(2)	0.38608(7)	0.9922(2)	0.0265(5)
S5	S <sub>1.00</sub>	0.1421(2)	0.40027(7)	0.2941(2)	0.0289(5)
O1	O <sub>1.00</sub>	0.2500(7)	0.0691(2)	0.9522(7)	0.049(2)
O2	O <sub>1.00</sub>	0.0432(7)	0.0726(2)	0.9596(6)	0.042(2)
O3	O <sub>1.00</sub>	0.0604(7)	0.0195(2)	0.8033(7)	0.049(2)
O4	O <sub>1.00</sub>	0.1790(7)	0.0092(2)	0.0411(7)	0.047(2)
O5	O <sub>1.00</sub>	0.5096(6)	0.0832(2)	0.7140(6)	0.036(2)
O6	O <sub>1.00</sub>	0.3194(6)	0.0985(2)	0.5039(6)	0.036(2)
O7	O <sub>1.00</sub>	0.3762(7)	0.0238(2)	0.5650(6)	0.044(2)
O8	O <sub>1.00</sub>	0.5154(6)	0.0740(2)	0.5066(6)	0.038(2)
O9	O <sub>1.00</sub>	0.6133(7)	0.2913(2)	0.6566(7)	0.052(2)
O10	O <sub>1.00</sub>	0.4364(7)	0.2443(2)	0.4811(7)	0.049(2)
O11	O <sub>1.00</sub>	0.5304(7)	0.3092(2)	0.4250(7)	0.050(2)
O12	O <sub>1.00</sub>	0.6629(7)	0.2460(2)	0.5139(6)	0.045(2)
O13	O <sub>1.00</sub>	0.5778(7)	0.3467(2)	0.0517(7)	0.049(2)
O14	O <sub>1.00</sub>	0.3578(7)	0.3752(2)	0.9111(6)	0.041(2)
O15	O <sub>1.00</sub>	0.5281(7)	0.4205(2)	0.0963(7)	0.049(2)

## CRYSTAL STRUCTURE OF COQUANDITE

Table 2 (*contd.*).

Atom	s.o.f.	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>iso</sub>
O16	O <sub>1.00</sub>	0.5454(7)	0.4044(2)	0.8981(7)	0.052(2)
O17	O <sub>1.00</sub>	0.0807(7)	0.3724(2)	0.1673(7)	0.053(2)
O18	O <sub>1.00</sub>	0.0748(7)	0.4419(2)	0.2794(6)	0.045(2)
O19	O <sub>1.00</sub>	0.1055(7)	0.3770(2)	0.3855(7)	0.051(2)
O20	O <sub>1.00</sub>	0.2884(7)	0.3999(2)	0.3735(7)	0.044(2)
O21	O <sub>1.00</sub>	0.0403(6)	0.2403(2)	0.4622(6)	0.041(2)
O22	O <sub>1.00</sub>	0.3085(6)	0.2496(2)	0.0719(6)	0.040(2)
O23	O <sub>1.00</sub>	0.9466(7)	0.3852(2)	0.8876(6)	0.044(2)
O24	O <sub>1.00</sub>	0.7288(7)	0.1283(2)	0.2376(6)	0.043(2)
O25	O <sub>1.00</sub>	0.4581(7)	0.1165(2)	0.2381(6)	0.044(2)
O26	O <sub>1.00</sub>	0.0771(7)	0.3720(2)	0.7645(6)	0.036(2)
O27	O <sub>1.00</sub>	0.9197(7)	0.1856(2)	0.5512(7)	0.049(2)
O28	O <sub>1.00</sub>	0.6908(7)	0.3878(2)	0.7633(6)	0.041(2)
O29	O <sub>1.00</sub>	0.9493(7)	0.3867(2)	0.5144(7)	0.046(2)
O30	O <sub>1.00</sub>	0.6901(7)	0.3913(2)	0.3880(6)	0.042(2)
O31	O <sub>1.00</sub>	0.7051(7)	0.2256(2)	0.8796(6)	0.040(2)
O32	O <sub>1.00</sub>	0.2326(7)	0.1910(2)	0.4807(6)	0.041(2)
O33	O <sub>1.00</sub>	0.1634(7)	0.1577(2)	0.6427(6)	0.044(2)
O34	O <sub>1.00</sub>	0.9212(7)	0.1951(2)	0.1490(6)	0.041(2)
O35	O <sub>1.00</sub>	0.7972(6)	0.3123(2)	0.3325(6)	0.040(2)
O36	O <sub>1.00</sub>	0.8741(7)	0.2048(2)	0.7763(6)	0.042(2)
O37	O <sub>1.00</sub>	0.2059(7)	0.2105(2)	0.2253(6)	0.044(2)
O38	O <sub>1.00</sub>	0.6691(6)	0.0661(2)	0.3831(6)	0.041(2)
O39	O <sub>1.00</sub>	0.1361(7)	0.3192(2)	0.6002(7)	0.047(2)
O40	O <sub>1.00</sub>	0.8022(7)	0.3213(2)	0.9618(6)	0.042(2)
O41	O <sub>1.00</sub>	0.4995(7)	0.4594(2)	0.3111(7)	0.048(2)
O42	O <sub>1.00</sub>	0.0261(7)	0.0749(2)	0.3877(6)	0.037(2)
O43	O <sub>1.00</sub>	0.3049(7)	0.2506(2)	0.6896(7)	0.045(2)
O44	O <sub>1.00</sub>	0.8534(7)	0.4456(2)	0.6643(7)	0.047(2)
O45	O <sub>1.00</sub>	0.6435(7)	0.0692(2)	0.9930(6)	0.046(2)
O46	O <sub>1.00</sub>	0.0876(7)	0.2469(2)	0.7930(6)	0.043(2)
O47	O <sub>1.00</sub>	0.6856(7)	0.2591(2)	0.0773(6)	0.046(2)
O48	O <sub>1.00</sub>	0.9019(6)	0.0852(2)	0.1159(6)	0.040(2)
O49	O <sub>1.00</sub>	0.1422(6)	0.1315(2)	0.2511(6)	0.040(2)
O50	O <sub>1.00</sub>	0.5394(7)	0.4045(2)	0.5044(6)	0.041(2)
O51	O <sub>1.00</sub>	0.3469(7)	0.2059(2)	0.8905(6)	0.041(2)
O52	O <sub>1.00</sub>	0.9452(7)	0.0960(2)	0.5874(6)	0.044(2)
O53	O <sub>1.00</sub>	0.4321(7)	0.1278(2)	0.9439(6)	0.043(2)
O54	O <sub>1.00</sub>	0.7587(7)	0.2270(2)	0.3299(7)	0.046(2)
O55	O <sub>1.00</sub>	0.5245(7)	0.0481(2)	0.1238(6)	0.038(2)
O56	O <sub>1.00</sub>	0.7951(6)	0.1260(2)	0.6725(6)	0.038(2)
O57	O <sub>1.00</sub>	0.7577(6)	0.1419(2)	0.8981(6)	0.040(2)
O58	O <sub>1.00</sub>	0.5274(7)	0.1934(2)	0.1676(7)	0.047(2)
O59	O <sub>1.00</sub>	0.0377(7)	0.2467(2)	0.0231(6)	0.041(2)
O60	O <sub>1.00</sub>	0.9071(7)	0.0153(2)	0.5136(7)	0.050(2)
O61	O <sub>1.00</sub>	0.1465(7)	0.3189(2)	0.9795(7)	0.046(2)
O62	O <sub>1.00</sub>	0.4884(7)	0.4532(2)	0.6694(7)	0.045(2)
O63	O <sub>0.50</sub>	0.341(1)	0.5063(4)	0.413(1)	0.050(4)
O64	O <sub>1.00</sub>	0.3217(7)	0.4899(2)	0.7653(7)	0.049(2)
O65W	O <sub>1.00</sub>	0.8730(7)	0.5052(2)	0.4935(7)	0.047(2)
O66W	O <sub>1.00</sub>	0.8371(7)	0.4870(2)	0.8988(7)	0.050(2)
O67W	O <sub>1.00</sub>	0.0122(7)	0.2882(2)	0.2483(6)	0.046(2)

TABLE 3. Anisotropic displacement parameters of the atoms for the selected coquandite crystal.

Atom	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Sb1	0.0255(3)	0.0262(3)	0.0238(3)	0.0017(2)	0.0128(3)	0.0016(2)
Sb2	0.0261(3)	0.0264(3)	0.0235(3)	0.0015(2)	0.0130(3)	0.0014(2)
Sb3	0.0273(3)	0.0279(3)	0.0251(3)	0.0018(2)	0.0138(3)	0.0015(2)
Sb4	0.0278(3)	0.0280(3)	0.0249(3)	0.0017(2)	0.0137(3)	0.0016(2)
Sb5	0.0294(3)	0.0299(3)	0.0264(3)	0.0019(3)	0.0145(3)	0.0020(2)
Sb6	0.0276(3)	0.0284(3)	0.0252(3)	0.0017(2)	0.0139(3)	0.0018(2)
Sb7	0.0228(3)	0.0234(3)	0.0208(3)	0.0015(2)	0.0116(3)	0.0014(2)
Sb8	0.0218(3)	0.0223(3)	0.0195(3)	0.0015(2)	0.0106(2)	0.0010(2)
Sb9	0.0236(3)	0.0239(3)	0.0207(3)	0.0016(2)	0.0113(3)	0.0008(2)
Sb10	0.0231(3)	0.0236(3)	0.0210(3)	0.0016(2)	0.0116(3)	0.0011(2)
Sb11	0.0236(3)	0.0240(3)	0.0207(3)	0.0014(2)	0.0117(3)	0.0010(2)
Sb12	0.0244(3)	0.0245(3)	0.0223(3)	0.0018(2)	0.0122(3)	0.0008(2)
Sb13	0.0241(3)	0.0245(3)	0.0214(3)	0.0018(2)	0.0123(3)	0.0017(2)
Sb14	0.0254(3)	0.0255(3)	0.0234(3)	0.0018(2)	0.0128(3)	0.0013(2)
Sb15	0.0244(3)	0.0244(3)	0.0211(3)	0.0016(2)	0.0121(3)	0.0011(2)
Sb16	0.0260(3)	0.0262(3)	0.0231(3)	0.0019(2)	0.0128(3)	0.0011(2)
Sb17	0.0277(3)	0.0283(3)	0.0247(3)	0.0017(2)	0.0139(3)	0.0015(2)
Sb18	0.0294(3)	0.0299(3)	0.0260(3)	0.0020(3)	0.0143(3)	0.0015(2)
Sb19	0.0297(3)	0.0296(3)	0.0267(3)	0.0019(3)	0.0148(3)	0.0015(2)
Sb20	0.0245(3)	0.0248(3)	0.0219(3)	0.0015(2)	0.0121(3)	0.0008(2)
Sb21	0.0287(3)	0.0289(3)	0.0257(3)	0.0018(2)	0.0144(3)	0.0011(2)
Sb22	0.0300(3)	0.0301(3)	0.0272(3)	0.0020(3)	0.0153(3)	0.0017(2)
Sb23	0.0222(3)	0.0224(3)	0.0198(3)	0.0014(2)	0.0113(3)	0.0009(2)
Sb24	0.0209(3)	0.0211(2)	0.0192(3)	0.0015(2)	0.0106(2)	0.0013(2)
Sb25	0.0230(3)	0.0227(3)	0.0207(3)	0.0015(2)	0.0117(3)	0.0013(2)
Sb26	0.0283(3)	0.0287(3)	0.0258(3)	0.0018(2)	0.0140(3)	0.0009(2)
Sb27	0.0224(3)	0.0225(3)	0.0202(3)	0.0014(2)	0.0110(2)	0.0008(2)
Sb28	0.0217(3)	0.0218(3)	0.0194(3)	0.0014(2)	0.0109(2)	0.0012(2)
Sb29	0.0244(3)	0.0241(3)	0.0217(3)	0.0017(2)	0.0119(3)	0.0013(2)
Sb30a	0.0301(7)	0.0304(6)	0.0257(7)	0.0022(5)	0.0142(6)	0.0015(5)
Sb30b	0.0243(6)	0.0248(6)	0.0220(6)	0.0013(5)	0.0122(6)	0.0014(4)
Sb31	0.0283(3)	0.0281(3)	0.0251(3)	0.0019(2)	0.0141(3)	0.0014(2)
Sb32	0.0287(7)	0.0280(6)	0.0253(6)	0.0014(5)	0.0146(6)	0.0004(5)
S1	0.026(1)	0.026(1)	0.026(1)	0.0015(9)	0.013(1)	0.0006(8)
S2	0.024(1)	0.025(1)	0.025(1)	0.0007(9)	0.012(1)	-0.0004(8)
S3	0.033(1)	0.032(1)	0.031(1)	0.002(1)	0.017(1)	0.0019(9)
S4	0.028(1)	0.026(1)	0.027(1)	0.0018(9)	0.015(1)	0.0013(9)
S5	0.030(1)	0.029(1)	0.028(1)	0.0008(9)	0.015(1)	0.0014(9)
O1	0.048(5)	0.046(4)	0.058(5)	0.004(4)	0.030(4)	0.007(4)
O2	0.047(4)	0.049(4)	0.033(4)	0.009(3)	0.022(4)	0.012(3)
O3	0.049(5)	0.049(4)	0.048(5)	0.003(4)	0.023(4)	0.004(3)
O4	0.049(5)	0.047(4)	0.047(4)	0.003(4)	0.025(4)	0.003(3)
O5	0.039(4)	0.036(3)	0.037(4)	0.002(3)	0.020(3)	0.007(3)
O6	0.037(4)	0.038(4)	0.030(4)	0.003(3)	0.015(3)	0.003(3)
O7	0.043(4)	0.049(4)	0.039(4)	0.002(3)	0.021(4)	0.001(3)
O8	0.044(4)	0.040(4)	0.038(4)	0.006(3)	0.024(4)	0.011(3)
O9	0.054(5)	0.044(4)	0.061(5)	0.005(4)	0.030(4)	-0.007(4)
O10	0.048(5)	0.056(4)	0.046(5)	0.002(4)	0.027(4)	-0.001(4)
O11	0.053(5)	0.053(4)	0.042(4)	0.001(4)	0.022(4)	0.000(4)
O12	0.052(5)	0.044(4)	0.042(4)	0.002(4)	0.025(4)	-0.004(3)
O13	0.048(5)	0.050(4)	0.052(5)	0.003(4)	0.026(4)	0.007(4)
O14	0.048(4)	0.037(4)	0.045(4)	0.002(3)	0.029(4)	0.000(3)
O15	0.056(5)	0.044(4)	0.046(4)	0.002(4)	0.026(4)	0.008(3)
O16	0.054(5)	0.054(4)	0.057(5)	-0.006(4)	0.035(4)	0.010(4)



## CRYSTAL STRUCTURE OF COQUANDITE

Table 3 (contd.).

Atom	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
O17	0.062(5)	0.056(5)	0.048(5)	-0.012(4)	0.032(4)	-0.003(4)
O18	0.050(5)	0.048(4)	0.034(4)	0.002(4)	0.020(4)	0.003(3)
O19	0.050(5)	0.058(5)	0.057(5)	-0.004(4)	0.035(4)	0.004(4)
O20	0.048(5)	0.043(4)	0.048(4)	0.001(4)	0.030(4)	0.001(3)
O21	0.040(4)	0.051(4)	0.032(4)	0.002(3)	0.018(3)	-0.002(3)
O22	0.043(4)	0.051(4)	0.031(4)	-0.002(3)	0.022(4)	-0.002(3)
O23	0.049(5)	0.045(4)	0.047(4)	0.002(3)	0.031(4)	0.003(3)
O24	0.045(4)	0.047(4)	0.039(4)	0.003(3)	0.021(4)	-0.006(3)
O25	0.046(4)	0.050(4)	0.038(4)	0.004(4)	0.022(4)	0.002(3)
O26	0.052(4)	0.039(4)	0.023(3)	0.009(3)	0.023(3)	0.004(3)
O27	0.066(5)	0.048(4)	0.041(4)	-0.002(4)	0.033(4)	-0.002(3)
O28	0.043(4)	0.043(4)	0.038(4)	-0.001(3)	0.021(4)	0.000(3)
O29	0.045(4)	0.049(4)	0.042(4)	0.003(4)	0.019(4)	-0.002(3)
O30	0.042(4)	0.043(4)	0.048(4)	0.004(3)	0.026(4)	-0.005(3)
O31	0.043(4)	0.043(4)	0.032(4)	0.002(3)	0.018(3)	0.004(3)
O32	0.046(4)	0.042(4)	0.039(4)	-0.001(3)	0.025(4)	-0.008(3)
O33	0.051(5)	0.044(4)	0.038(4)	0.006(4)	0.023(4)	0.011(3)
O34	0.043(4)	0.039(4)	0.047(4)	0.005(3)	0.026(4)	0.000(3)
O35	0.039(4)	0.044(4)	0.037(4)	-0.001(3)	0.020(4)	-0.001(3)
O36	0.043(4)	0.044(4)	0.045(4)	0.002(3)	0.027(4)	0.002(3)
O37	0.048(4)	0.044(4)	0.041(4)	0.002(3)	0.023(4)	0.000(3)
O38	0.034(4)	0.044(4)	0.032(4)	0.002(3)	0.006(3)	0.001(3)
O39	0.046(5)	0.047(4)	0.054(5)	0.007(4)	0.029(4)	0.000(4)
O40	0.041(4)	0.042(4)	0.040(4)	0.004(3)	0.019(4)	0.004(3)
O41	0.048(5)	0.054(4)	0.044(4)	0.003(4)	0.025(4)	0.011(3)
O42	0.053(4)	0.040(4)	0.029(4)	-0.002(3)	0.028(4)	0.002(3)
O43	0.041(4)	0.040(4)	0.045(4)	0.009(3)	0.013(4)	0.019(3)
O44	0.049(5)	0.050(4)	0.044(4)	0.003(4)	0.023(4)	0.003(3)
O45	0.060(5)	0.049(4)	0.031(4)	0.002(4)	0.024(4)	0.003(3)
O46	0.045(4)	0.050(4)	0.042(4)	0.008(3)	0.028(4)	0.002(3)
O47	0.063(5)	0.052(4)	0.031(4)	-0.004(4)	0.031(4)	0.002(3)
O48	0.042(4)	0.045(4)	0.036(4)	0.002(3)	0.021(4)	0.005(3)
O49	0.040(4)	0.039(4)	0.046(4)	0.004(3)	0.024(4)	0.006(3)
O50	0.058(5)	0.051(4)	0.027(4)	0.015(4)	0.029(4)	0.010(3)
O51	0.044(4)	0.050(4)	0.031(4)	0.000(3)	0.020(4)	0.011(3)
O52	0.050(5)	0.046(4)	0.043(4)	0.002(4)	0.028(4)	0.006(3)
O53	0.045(4)	0.044(4)	0.043(4)	0.002(3)	0.025(4)	0.001(3)
O54	0.049(5)	0.046(4)	0.046(4)	0.002(4)	0.026(4)	0.000(3)
O55	0.056(5)	0.039(4)	0.016(3)	-0.001(3)	0.015(3)	0.004(3)
O56	0.035(4)	0.043(4)	0.034(4)	0.000(3)	0.016(3)	-0.003(3)
O57	0.041(4)	0.043(4)	0.038(4)	0.000(3)	0.022(4)	0.002(3)
O58	0.049(5)	0.047(4)	0.048(5)	0.003(4)	0.027(4)	0.001(3)
O59	0.046(4)	0.046(4)	0.029(4)	0.000(3)	0.016(4)	0.005(3)
O60	0.047(5)	0.048(4)	0.048(5)	0.004(4)	0.017(4)	0.002(4)
O61	0.049(5)	0.049(4)	0.043(4)	0.006(4)	0.023(4)	0.002(3)
O62	0.042(4)	0.053(4)	0.046(4)	0.001(4)	0.026(4)	-0.006(3)
O63	0.045(9)	0.045(8)	0.06(1)	0.000(7)	0.021(8)	-0.005(7)
O64	0.049(5)	0.045(4)	0.046(4)	0.002(4)	0.019(4)	0.006(3)
O65W	0.053(5)	0.043(4)	0.051(5)	0.005(4)	0.030(4)	0.006(3)
O66W	0.055(5)	0.054(4)	0.039(4)	0.008(4)	0.021(4)	0.007(3)
O67W	0.052(5)	0.045(4)	0.041(4)	0.001(4)	0.023(4)	0.001(3)

TABLE 4. X-ray powder diffraction patterns for coquandite.

1*			2**		
<i>hkl</i>	<i>d</i> <sub>calc</sub> (Å)	<i>I</i> / <i>I</i> <sub>0</sub>	<i>hkl</i>	<i>d</i> <sub>obs</sub> (Å)	<i>I</i> / <i>I</i> <sub>0</sub>
020	14.8527	64	020	14.84	50
111	9.2700	9	111, 110	9.27	41
110	9.2588	8	—	—	—
120	8.5216	7	120	8.59	25
120	8.0331	5	—	—	—
021	8.0277	8	021, 120	8.01	34
040	7.4264	8	—	—	—
130	6.8051	11	130	6.81	67
050	5.9411	8	—	—	—
111	5.6981	7	111	5.70	14
102	5.6482	5	—	—	—
231	5.0440	5	—	—	—
060	4.9509	5	—	—	—
220	4.8107	3	—	—	—
220	4.6294	11	220	4.63	14
201	3.7597	7	201	3.765	19
113	3.6607	4	203, 311	3.690	15
321	3.5889	3	321	3.580	14
233	3.4561	3	181, 331	3.440	20
310	3.3196	9	—	—	—
090	3.3006	100	090	3.304	93
310	3.2733	7	—	—	—
023	3.2378	4	—	—	—
323	3.2010	27	323, 320	3.200	39
320	3.1939	28	—	—	—
153	3.1878	3	—	—	—
033	3.1614	9	—	—	—
191	3.1417	7	—	—	—
333	3.1164	51	191	3.138	24
191	3.1147	5	—	—	—
330	3.0863	45	330	3.092	100
033	3.0707	4	—	—	—
043	3.0573	76	043	3.052	16
343	3.0068	15	—	—	—
263	2.9727	3	—	—	—
353	2.8461	6	—	—	—
360	2.8405	26	360	2.842	32
053	2.8151	40	053	2.813	16
363	2.7095	25	363	2.712	32
370	2.6980	12	—	—	—
063	2.6759	4	—	—	—
373	2.5714	11	373	2.575	13
380	2.5559	6	—	—	—
073	2.5368	4	—	—	—
3.10.0	2.2864	3	390, 473	2.268	6
3.11.3	2.0964	5	292	2.097	4
3.11.0	2.0317	4	—	—	—
3.12.3	1.9869	10	582	1.989	5
3.12.0	1.9258	8	—	—	—
013.3	1.9196	14	035	1.918	16
313	1.9149	10	—	—	—
603	1.9026	9	—	—	—
3.13.3	1.8853	4	—	—	—



## CRYSTAL STRUCTURE OF COQUANDITE

Table 4 (contd.).

1*			2**		
<i>hkl</i>	<i>d</i> <sub>calc</sub> (Å)	<i>I</i> / <i>I</i> <sub>o</sub>	<i>hkl</i>	<i>d</i> <sub>obs</sub> (Å)	<i>I</i> / <i>I</i> <sub>o</sub>
$\bar{3}\bar{1}6$	1.8813	14	$\bar{6}43, \bar{5}91$	1.865	4
$\bar{3}.15.0$	1.7502	4	254	1.754	3
0.14.3	1.7435	4	—	—	—
$\bar{3}\bar{1}\bar{5}.3$	1.6830	3	$\bar{6}93$	1.685	4
$\bar{6}93$	1.6813	4	—	—	—
$\bar{3}86$	1.6660	6	—	—	—
$3\bar{1}0.3$	1.6569	4	383	1.655	5
383	1.6558	4	—	—	—
0.18.0	1.6503	4	—	—	—
$\bar{6}\bar{9}3$	1.6172	4	026	1.626	2
$\bar{3}\bar{1}0.6$	1.6046	5	—	—	—
$\bar{6}\bar{4}6$	1.5909	3	$6\bar{4}\bar{6}$	1.590	6

Note: 1\* = calculated powder pattern and indexing for the coquandite used in this study. The *d* values and intensities are calculated on the basis of *a* = 11.4292(5) Å, *b* = 29.772(1) Å, *c* = 11.2989(5) Å,  $\alpha$  = 91.152(3),  $\beta$  = 119.266(4),  $\gamma$  = 92.624(3)° and with the atomic coordinates reported in Table 2. The *XPOW* software version 2.0 (Downs *et al.*, 1993) was used.

2\*\* = observed powder pattern and indexing originally reported by Sabelli *et al.* (1992).

corresponding to small bond strengths. Consequently, the coordination sphere of Sb in coquandite ranges from 5 (Sb25 and Sb29) to 10 (Sb15).

A pure SbO<sub>3</sub>*E* coordination (Fig. 3a) is shown by 14 sites; they present three short distances, ranging between 1.875(7) Å (Sb31–O64) and 2.062(6) Å (Sb9–O49), with an average bond

distance of 1.99 Å. Additional bonds occur at distances longer than 2.5 Å.

A pure SbO<sub>4</sub>*E* coordination (Fig. 3b) is assumed by four Sb sites only, namely Sb7, Sb11, Sb12 and Sb23. This type of coordination polyhedron can be described as a trigonal bipyramid, with two axial and two equatorial Sb–O bonds. Galy *et al.* (1975) calculated the

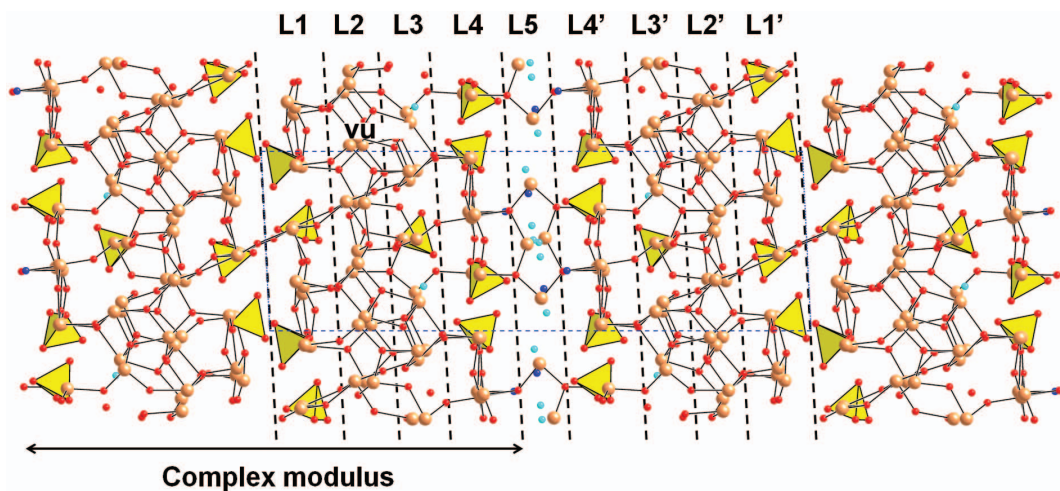


FIG. 2. Crystal structure of coquandite, as seen down *a*\* (*b* horizontal, *c* vertical). Cation layers are indicated, as well as the complex modulus (see text for explanations). Circles: orange = Sb sites; red = O sites; blue = O or mixed (O,OH) sites; light blue = H<sub>2</sub>O groups. Polyhedra: yellow = S sites.

TABLE 6. Chemical data from the literature (wt.% of oxides; Sabelli *et al.*, 1992) and atomic ratios [on the basis of  $\Sigma(\text{Sb}+\text{S}) = 7.3$ ] for coquandite from different localities.

	Pereta	Cetine	Lucky Knock	Ideal
Sb <sub>2</sub> O <sub>3</sub>	88.25	88.53	89.96	90.59
SO <sub>3</sub>	8.35	8.33	8.38	7.90
CaO	0.04	0.04	0.04	0.00
Na <sub>2</sub> O	0.02	0.02	0.05	0.00
H <sub>2</sub> O			1.43	1.51
Total	96.66	96.92	98.43	
Sb	6.23	6.23	6.24	6.3
S	1.07	1.07	1.06	1.0
Ca	0.01	0.01	0.01	0.0
Na	0.01	0.01	0.02	0.0

theoretically axial and equatorial bond and angle values. Axial and equatorial ideal distances are 2.27 and 2.02 Å, respectively, whereas axial and equatorial angles are 151.5 and 92.2°, respectively. The axial distances observed in coquandite range between 2.163(6) Å (Sb7–O60) and 2.278(6) Å (Sb11–O47), with an average value of 2.22 Å; the average axial angle is 143.4°, ranging from 142.0(2)° (O37–Sb23–O61) to 145.4(2)° (O57–Sb11–O47). Average equatorial bond distances and angles are 2.00 Å and 94.8°, respectively, with values ranging between 1.941(6) Å (Sb23–O22) and 2.074(6) Å

(Sb23–O59) for bond distances and between 91.0(2)° (O22–Sb23–O59) and 97.2(3)° (O34–Sb11–O31) for angles.

The remaining Sb sites display coordination environments intermediate between the SbO<sub>3</sub>E and SbO<sub>4</sub>E types, with three short distances and an additional one shorter than 2.5 Å. Moreover, the coordinations of the split site Sb30 and the half-occupied Sb32 site deserve further discussion. The two sub-positions Sb30a and Sb30b display a different bonding environment: Sb30a has two distances shorter than 2.50 Å and three distances between 2.50 and 2.53 Å (Fig. 3c),

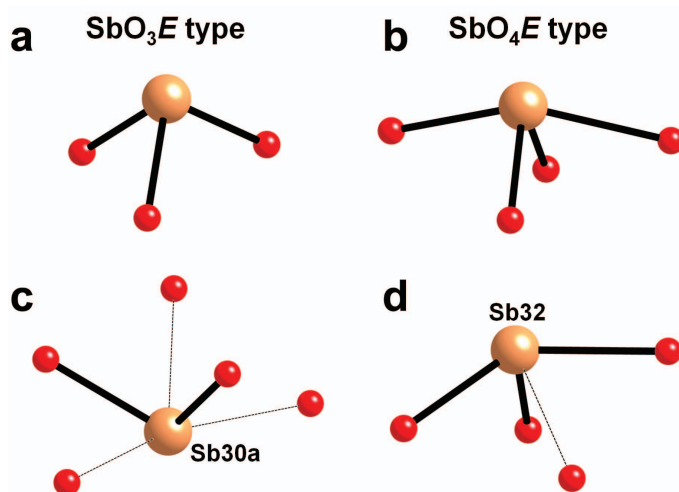


FIG. 3. Bonding environments of Sb atoms in coquandite. Thick lines = distances shorter than 2.40 Å; dashed lines = distances longer than 2.40 Å.

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whereas Sb30b has a coordination intermediate between  $\text{SbO}_3E$  and  $\text{SbO}_4E$  types. The Sb32 site is at too short a distance from the O63 site, i.e. 1.58(1) Å. Actually, owing to the half-occupancy of O63, this unrealistic short Sb–O contact can be excluded, suggesting a more reasonable bonding environment for the Sb32 site (Fig. 3*d*), with a coordination characterized by a very short Sb–O distance [1.81(1) Å], two longer ones, i.e. 2.175(6) Å and 2.254(7) Å and a long distance, at 2.446(6) Å.

The bond-valence sums (BVS), in valence units (vu) for the Sb sites, calculated using the parameters proposed by Mills *et al.* (2009), are given in Table 7. The BVS values are in good agreement with the ideal values, ranging between 2.86 vu for Sb6 and 3.21 vu for Sb24. The BVS of the split Sb30 sub-sites and for the half-occupied

Sb32 site are also in fair agreement with the expected values.

The Sb coordinations in coquandite are in excellent agreement with those described by Menchetti and Sabelli (1980*a,b*) for peretaite and klebelsbergite. In the former, Sb shows both  $\text{SbO}_3E$  and  $\text{SbO}_4E$  type coordinations, whereas in the latter the bond arrangement is intermediate between the two types, with one out of the four independent sites resembling an  $\text{SbO}_3E$  polyhedron and the remaining three being more similar to an  $\text{SbO}_4E$  polyhedron.

Sulfur is hosted in tetrahedral coordination. Average bond distances for the five independent S-centred tetrahedra range between 1.459 Å (S2 site) and 1.469 Å (S1 site), with individual distances varying from 1.431(6) Å (S2–O5) to 1.491(6) Å (S4–O16). Table 7 reports the BVS

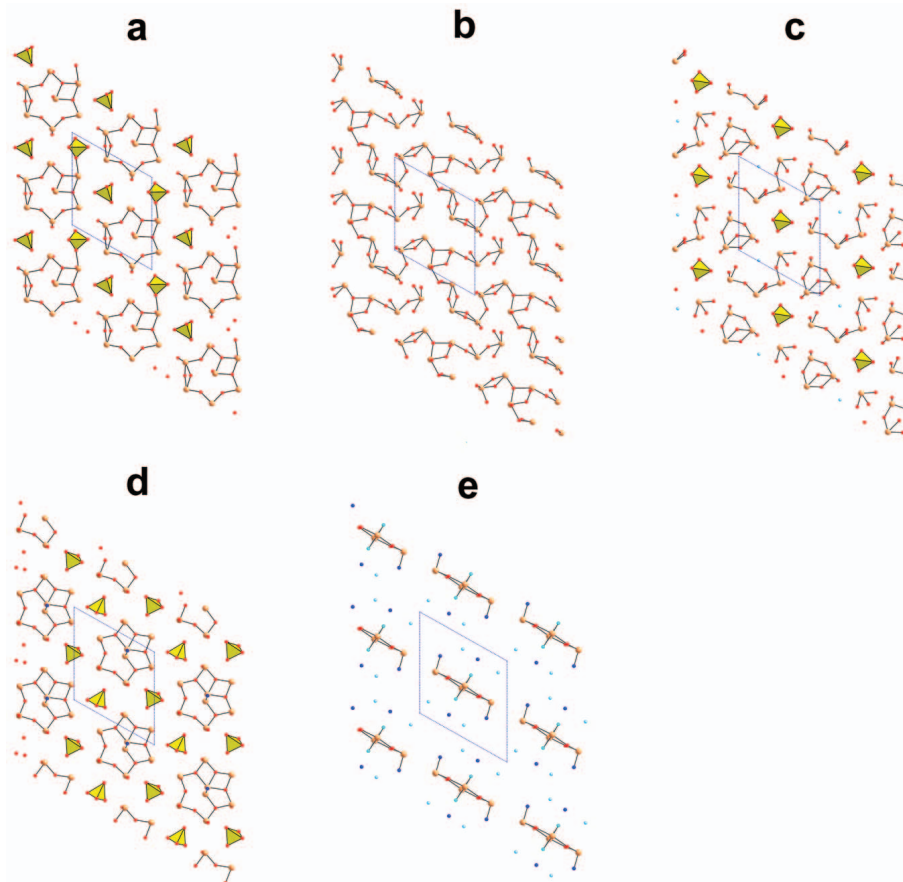


FIG. 4. The layers constituting the crystal structure of coquandite, as seen down  $b^*$ ,  $a$  vertical. L1 (a), L2 (b), L3 (c), L4 (d) and L5 (e).

TABLE 7. Selected bond distances (in Å) and bond-valence sums (BVS, in vu), for cations in coquandite. BVS are calculated by taking into account the site occupancy.

Sb1	-052	2.020(6)	Sb2	-025	1.943(7)	Sb3	-053	1.945(6)	Sb4	-048	1.968(7)	Sb5	-048	2.023(6)
	-038	2.033(6)		-038	1.978(6)		-055	2.067(6)		-042	1.984(5)		-045	2.028(6)
	-060	2.093(6)		-055	2.076(5)		-045	2.106(7)		-049	2.030(6)		-057	2.062(6)
	-056	2.393(6)		-08	2.471(6)		-01	2.319(6)		-03	2.845(6)		-04	2.551(7)
	-07	2.861(6)		-07	2.992(7)		-05	2.922(6)		-06	2.948(6)		-05	2.764(6)
	-08	3.020(6)		-04	3.276(7)		-055	3.422(6)		-02	3.074(6)		-02	2.906(6)
	-03	3.058(7)		-01	3.337(7)		BVS	2.93		-04	3.484(6)		-036	3.315(6)
	BVS	2.96		BVS	3.06		BVS	2.93		BVS	2.93		BVS	2.92
Sb6	-024	1.949(6)	Sb7	-042	1.974(6)	Sb8	-058	1.988(7)	Sb9	-032	1.973(6)	Sb10	-036	1.984(6)
	-045	2.127(6)		-060	2.034(6)		-053	1.992(6)		-037	2.045(7)		-056	2.019(6)
	-055	2.165(6)		-060	2.163(6)		-051	2.034(6)		-049	2.062(6)		-057	2.059(6)
	-038	2.469(6)		-052	2.234(6)		-025	2.534(7)		-010	2.507(6)		-031	2.367(6)
	-048	2.605(6)		-03	2.967(6)		-022	2.688(6)		-06	2.566(6)		-012	3.101(7)
	-042	2.903(7)		-033	3.265(6)		-01	2.950(6)		-025	3.175(6)		-05	3.326(6)
	-060	3.428(7)		-06	3.370(6)		BVS	3.08		BVS	3.00		BVS	2.94
	BVS	2.86		-07	3.471(6)		BVS	3.01		BVS	3.00		BVS	2.94
Sb11	-034	1.985(7)	Sb12	-034	1.958(6)	Sb13	-027	1.974(7)	Sb14	-024	1.996(6)	Sb15	-033	2.017(6)
	-031	2.050(6)		-037	2.004(6)		-056	2.066(6)		-058	2.010(7)		-021	2.107(6)
	-057	2.233(6)		-059	2.167(6)		-052	2.120(6)		-025	2.120(6)		-032	2.128(6)
	-047	2.278(6)		-049	2.249(7)		-036	2.299(6)		-054	2.419(6)		-027	2.246(6)
	-024	2.885(6)		-057	2.970(6)		-033	2.594(6)		-038	2.806(6)		-042	2.868(6)
	-058	3.242(6)		-036	3.138(7)		-046	2.926(6)		-027	3.006(7)		-034	3.077(6)
	-054	3.326(6)		-048	3.238(6)		-02	3.481(6)		-012	3.236(6)		-052	3.168(6)
	-053	3.358(6)		-02	3.382(6)		BVS	3.10		BVS	2.97		-049	3.192(6)
	BVS	2.87		BVS	3.12		BVS	3.10		BVS	2.97		-024	3.301(6)
Sb16	-033	1.969(6)	Sb17	-046	1.988(6)	Sb18	-054	2.008(6)	Sb19	-047	1.984(5)	Sb20	-039	1.992(6)
	-043	1.984(6)		-022	2.042(6)		-021	2.036(6)		-054	2.002(7)		-043	2.005(6)
	-051	2.075(6)		-051	2.126(7)		-027	2.138(7)		-035	2.017(6)		-021	2.015(6)
	-032	2.297(6)		-043	2.487(6)		-035	2.508(7)		-058	2.500(6)		-032	2.687(6)
	-053	2.941(7)		-061	2.639(6)		-012	2.688(6)		-013	2.815(7)		-067W	2.731(7)
	-06	3.386(6)		-014	3.159(6)		-046	2.877(7)		-022	3.246(6)		-010	3.016(6)
	BVS	3.10		-039	3.248(7)		-039	2.977(6)		-011	3.288(6)		-019	3.271(7)
	BVS	3.10		BVS	2.91		-036	3.498(6)		-012	3.320(6)		BVS	3.02
	BVS	3.10		BVS	2.96		BVS	2.96		BVS	3.12		BVS	3.02

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Sb21	-O59 -O46 -O36 -O61 -O40 -O31 -O23 BVS	1.980(6) 1.982(6) 2.090(6) 2.357(7) 3.124(6) 3.339(6) 3.448(6) 3.00	Sb22	-O40 -O31 -O47 -O9 -O13 -O43 BVS	1.930(6) 2.026(6) 2.054(6) 2.571(7) 2.837(6) 3.414(7) 2.96	Sb23	-O22 -O59 -O37 -O61 -O67W -O17 -O11 -O10 BVS	1.941(6) 2.074(6) 2.192(6) 2.208(7) 3.023(6) 3.307(7) 3.388(7) 3.438(7) 2.99	Sb24	-O62 -O50 -O28 -O16 -O20 BVS	1.942(6) 1.957(5) 1.961(7) 2.641(6) 2.863(7) 3.232(7) 3.21	Sb25	-O39 -O29 -O26 -O19 -O14 BVS	1.933(6) 1.962(7) 2.016(5) 2.599(6) 2.924(7) 3.06
Sb26	-O23 -O40 -O28 -O17 -O16 -O66W BVS	1.957(6) 1.989(6) 2.031(6) 2.751(8) 2.984(7) 3.065(7) 2.93	Sb27	-O29 -O30 -O35 -O19 -O13 -O15 BVS	1.958(7) 1.978(6) 2.012(6) 3.014(7) 3.029(7) 3.338(8) 2.87	Sb28	-O30 -O41 -O50 -O11 -O20 -O15 BVS	1.952(6) 1.968(7) 1.978(5) 2.781(7) 2.784(6) 2.784(6) 3.20	Sb29	-O61 -O26 -O23 -O14 -O17 BVS	1.973(7) 1.985(5) 2.012(7) 2.766(6) 2.796(6) 2.91	Sb30a	-O44 -O28 -O30 -O23 -O50 -O29 -O26 -O9 -O11 BVS	1.994(6) 2.125(6) 2.503(6) 2.525(7) 2.529(7) 2.885(6) 3.012(7) 3.304(7) 3.329(7) 1.31
Sb30b	-O44 -O26 -O23 -O29 -O28 -O30 -O50 BVS	2.010(7) 2.130(7) 2.244(6) 2.308(6) 2.764(6) 2.795(7) 3.391(7) 1.37	Sb31	-O64 -O41 -O62 -O15 -O16 -O66W BVS	1.875(7) 1.989(6) 2.001(6) 2.780(6) 2.858(7) 3.464(7) 3.15	Sb32	-O63W -O41 -O62 -O50 -O62 -O41 -O20 BVS	1.810(14) 2.175(6) 2.254(7) 2.446(6) 2.727(7) 2.767(6) 3.022(6) 3.375(6) 1.56	S1	-O4 -O2 -O3 -O1 BVS	1.446(7) 1.468(6) 1.475(7) 1.487(6) 6.09	S2	-O5 -O7 -O6 -O8 BVS	1.431(6) 1.450(6) 1.465(7) 1.489(6) 6.26
S3	-O11 -O9 -O12 -O10 BVS	1.457(7) 1.459(7) 1.469(7) 1.482(6) 6.12	S4	-O14 -O15 -O13 -O16 BVS	1.442(7) 1.445(6) 1.468(7) 1.491(6) 6.21	S5	-O18 -O20 -O19 -O17 BVS	1.458(7) 1.462(7) 1.464(6) 1.466(6) 6.19						

for S sites, calculated according to Brese and O'Keeffe (1991). All the S sites calculate to larger values than nominal, with BVS varying from 6.09 vu to 6.26 vu.

An alternative way to describe the crystal structure of coquandite is based upon anion-centred polyhedra (e.g. Krivovichev, 2009); this approach can be useful in the description of crystal structures containing additional anions, i.e. anions not involved in polyhedra of high-valence cations. In coquandite these anions are represented by the O atoms not bonded to S atoms, i.e. those hosted at the O21–O62 sites. The O63 site, being partially occupied and the sites occupied by water and hydroxyl groups (O64–O67W sites), should not be considered. In this respect, the coordination of the additional O atoms can be subdivided into two groups, forming OSb<sub>3</sub> triangles and OSb<sub>2</sub> dimeric groups, connected through edge- and corner-sharing. Such types of building units can be found in synthetic Sb oxy-sulfates [e.g. Sb<sub>2</sub>O(SO<sub>4</sub>)<sub>2</sub>, based on OSb<sub>2</sub> dimers and SO<sub>4</sub> groups, Mercier *et al.*, 1975; Sb<sub>6</sub>O<sub>7</sub>(SO<sub>4</sub>)<sub>2</sub>, formed by OSb<sub>3</sub>, OSb<sub>4</sub> and SO<sub>4</sub> groups, Bovin, 1976; Sb<sub>6</sub>O<sub>7</sub>(SO<sub>4</sub>)<sub>2</sub>, composed by OSb<sub>2</sub>, OSb<sub>3</sub>, OSb<sub>4</sub> and SO<sub>4</sub> groups, Fei *et al.*, 2012], as well as in peretaite and klebelsbergite (Menchetti and Sabelli, 1980*a,b*).

On the whole, nine layers perpendicular to **b**\* can be seen in the coquandite structure (Fig. 2), in agreement with what was hypothesized by Sabelli *et al.* (1992). The layered structure is formed by five symmetry-independent layers, namely L1, L2, L3, L4 and L5. Layer L1 (Fig. 4*a*) has chemical composition [Sb<sub>7</sub>(SO<sub>4</sub>)<sub>2</sub>O<sub>9.5</sub>]<sup>2-</sup>; it consists of pseudo-hexagonal rings of Sb-centred polyhedra, with an additional Sb site at the centre of the rings and two independent sulfate tetrahedra (S1 and S2). This arrangement is similar to that hypothesized by Sabelli *et al.* (1992), with groups of seven Sb-polyhedra linked closely to each other forming centred hexagons surrounded by (SO<sub>4</sub>) tetrahedra. Layer L2 (Fig. 4*b*) consists of branched chains of Sb-centred polyhedra, running along [001], having composition [Sb<sub>9</sub>O<sub>12.5</sub>]<sup>2+</sup>. The third layer L3 (Fig. 4*c*) shows trigonal [Sb<sub>3</sub>O<sub>4.5</sub>]<sup>0</sup> rings and finite [Sb<sub>4</sub>O<sub>4.5</sub>]<sup>3+</sup> polymers; an H<sub>2</sub>O group (i.e. O67W) occurs between alternating rings and polymers. The layer is completed by a sulfate group (S3), giving the chemical composition [Sb<sub>7</sub>(SO<sub>4</sub>)O<sub>9</sub>·H<sub>2</sub>O]<sup>1+</sup>. The fourth layer L4 (Fig. 4*d*) has a general topology similar to that shown by layer L1, with pseudo-hexagonal rings

of Sb-centred polyhedra, surrounding a central Sb-polyhedron and two independent sulfate groups, S4 and S5. The only difference is related to the presence of a minor amount of OH<sup>-</sup> groups substituting partially for O<sup>2-</sup> at the O44 site, giving the stoichiometry [Sb<sub>7</sub>(SO<sub>4</sub>)<sub>2</sub>O<sub>9.25</sub>(OH)<sub>0.25</sub>]<sup>-1.75</sup>.

The layers L1 to L4 and their centrosymmetrical counterparts, belonging to a preceding cell along **b**, form a complex modulus with composition [Sb<sub>60</sub>(SO<sub>4</sub>)<sub>10</sub>O<sub>80.5</sub>(OH)<sub>0.5</sub>·2H<sub>2</sub>O]<sup>-1.5</sup> (Fig. 2). Successive complex modules are separated by the L5 layer at the level **b** = ½ (Fig. 4*e*). This layer has the chemical composition [Sb<sub>3</sub>O<sub>2.5</sub>(OH)<sub>2.5</sub>·5H<sub>2</sub>O]<sup>+1.5</sup> and it is formed by a finite chain [Sb<sub>3</sub>O<sub>2</sub>(OH)<sub>2</sub>·H<sub>2</sub>O]<sup>+3</sup>, four H<sub>2</sub>O groups and the O44 site, which has a mixed (O<sub>0.5</sub>OH<sub>0.5</sub>)<sup>-1.5</sup> occupancy. Successive complex modules are connected through two Sb atoms (i.e. Sb31 and Sb32) and H bonds (see below) involving the L5 layer.

The nine layers result in the chemical formula Sb<sub>6.3</sub>(SO<sub>4</sub>)<sub>1.0</sub>O<sub>8.3</sub>(OH)<sub>3</sub>·7H<sub>2</sub>O or simply Sb<sub>6+x</sub>O<sub>8+x</sub>(SO<sub>4</sub>)(OH)<sub>x</sub>·(H<sub>2</sub>O)<sub>1-x</sub> (*x* = 0.3), with *Z* = 10. This layered structure is in keeping with the tabular morphology of coquandite, with crystals flattened on {010}.

### Hydrogen-bonding system

Table 8 reports the BVS for the O atoms calculated from the bonds to Sb and S. Whereas the majority of these atoms display good values of BVS, some of them are undersaturated, with BVS ranging from 0 vu (O65W) to 1.57 vu (O18). The occurrence of some O sites having very low BVS values suggests their occupancy by H<sub>2</sub>O groups, i.e. O65W, O66W and O67W. O65W and O66W belong to the L5 layer, whereas O67W belongs to the L3 layer. The examination of O...O contacts shorter than 3.0 Å (Table 9), which are not edges of coordination polyhedra, suggests the occurrence of H bonds.

O65W is at H-bond distances from O18, O44, O64 and the symmetry-related O65W. Through the O65W...O18 hydrogen bond, the undersaturation of the latter site is reduced; by applying the equation proposed by Ferraris and Ivaldi (1988), its BVS increases up to 1.76 vu, confirming its population by an O atom.

O65W is the acceptor in the O65W...O64 hydrogen bond; this latter site hosts an OH<sup>-</sup> group, as indicated by its BVS of 0.89 vu.

A more complex situation involves O44 that is bonded only to the split Sb30 site, receiving

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TABLE 8. Bond-valence calculation for O atoms (in vu) in coquandite.

O1	1.97	<b>O18</b>	<b>1.57</b>	O35	1.92	O52	2.03
O2	1.72	O19	1.91	O36	2.05	O53	1.97
O3	1.81	O20	1.87	O37	2.17	O54	2.06
O4	1.96	O21	2.27	O38	2.13	O55	2.08
O5	2.00	O22	1.98	O39	2.00	O56	1.95
O6	2.00	O23	2.17	O40	1.93	O57	2.09
O7	1.86	O24	1.97	O41	2.14	O58	2.04
O8	1.83	O25	1.94	O42	2.02	O59	2.19
O9	1.88	O26	2.06	O43	2.05	O60	2.11
O10	1.98	O27	2.11	<b>O44</b>	<b>0.84</b>	O61	2.03
O11	1.84	O28	2.12	O45	2.11	O62	2.14
O12	1.83	O29	2.13	O46	1.99	<b>O63W</b>	<b>0.64</b>
O13	1.89	O30	2.05	O47	2.09	<b>O64</b>	<b>1.12</b>
O14	1.97	O31	1.98	O48	2.00	<b>O65W</b>	<b>0.00</b>
O15	1.97	O32	2.17	O49	2.09	<b>O66W</b>	<b>0.12</b>
O16	1.87	O33	2.01	O50	2.15	<b>O67W</b>	<b>0.26</b>
O17	1.89	O34	1.89	O51	2.15		

Bold = undersaturated O atoms.

0.84 vu. The scrutiny of its O...O distances shorter than 3.0 Å suggests its involvement in a system of H bonds. Indeed, O44 is at a very short O...O distance to the half-occupied O63W, indicating a strong H bond; in addition, it is at H-bond distance with two other sites, i.e. O65W and O66W. If O63 is occupied, O44 could be the acceptor of three H bonds, from O63W, O65W and O66W. In this way, its BVS increases up to 1.56 vu, hosting an O atom; this value is actually too small for an O atom but, considering the disorder affecting the sites

involved in these H bonds, it could be acceptably retained. If O63W is empty, two possible H-bonding models can be hypothesized: (1) O44 is an acceptor of both H bonds with O65W and O66W (its BVS increases up to 1.18 vu); or (2) O44 is an acceptor in the O44...O66W bond and a donor in the O44...O65W bond (its BVS decreases down to 0.76 vu). In both cases, O44 could host an OH<sup>-</sup> group. Consequently a mixed (O<sub>0.5</sub>OH<sub>0.5</sub>) site occupancy is proposed for O44. The H-bonding system described is shown in Fig. 5a.

TABLE 9. O...O distances shorter than 3 Å and corresponding bond-valence strengths for acceptors (in vu) calculated according to Ferraris and Ivaldi (1988). BVS of oxygen atoms are reported before and after the correction for H bonds (indicated by the symbol \*).

O...O bonds donor → acceptor	<i>d</i> (Å)	vu	vu	vu*	vu	vu*		
O63W → O44	2.49(2)	0.38	O18	1.56	1.75	O17	1.89	2.05 <sup>5</sup>
O64 → O65W	2.685(10)	0.23	O44	0.84	0.76 <sup>1</sup>	O19	1.91	2.06 <sup>5</sup>
O44 → O65W	2.728(2)	0.21	O63W	0.64	1.56 <sup>2</sup>	O34	1.89	2.04
O65W → O18	2.771(8)	0.19	O64	1.12	0.26	O67W	0.26	-0.05
O65W → O65W	2.865(13)	0.16	O65W	0.00	0.89			
O66W → O44	2.991(9)	0.13	O66W	0.12	0.09 <sup>3</sup>			
O67W → O17	2.890(9)	0.16			-0.01 <sup>4</sup>			
O67W → O34	2.914(8)	0.15			-0.01			
O67W → O19	2.916(9)	0.15						

<sup>1</sup> if donor to O65W, O63 is empty; <sup>2</sup> if acceptor from O65W, O63 is full; <sup>3</sup> if acceptor from O44, donor to O65W; <sup>4</sup> if acceptor from O65W, donor to O44; <sup>5</sup> if acceptor from O67W.



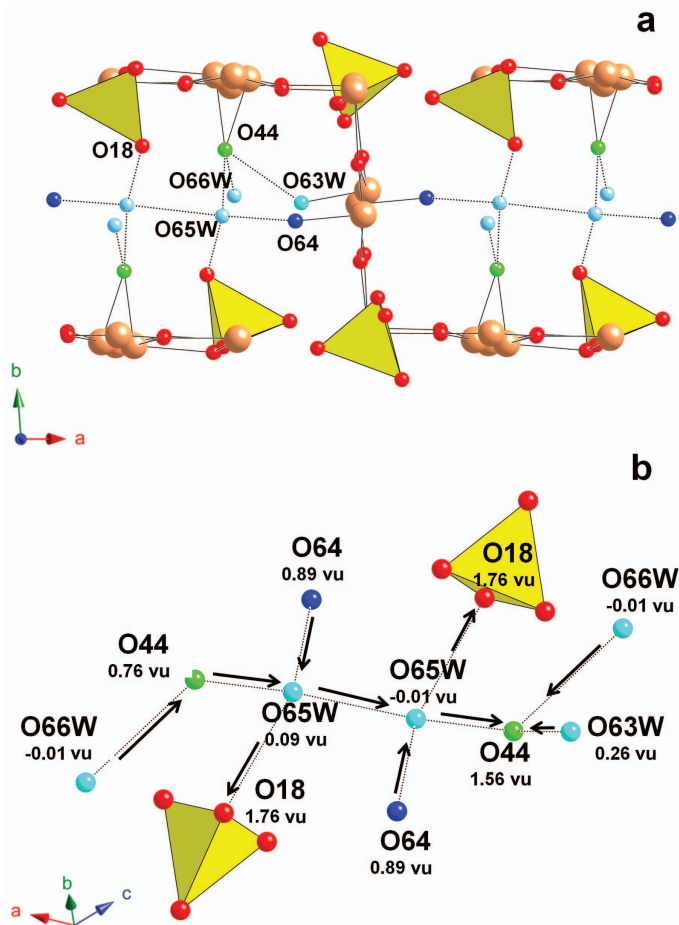


FIG. 5. Hydrogen bonds involving the L4 and L5 layers, as seen down  $c^*$  (a). In (b), a possible H-bonding system is shown. Circles: red = oxygen sites; green = mixed (O,OH) sites; blue = OH groups; light blue =  $H_2O$  groups; orange = Sb sites. Polyhedra: yellow = S sites.

By also considering the  $O65W \cdots O65W$  hydrogen bond, the second model results in a better BVS for O65W. In fact, taking the first model into account, O65W achieves a final BVS of  $-0.01$  vu if it is an acceptor in the  $O65W \cdots O65W$  hydrogen bond and a very small BVS of  $-0.33$  vu if it is a donor in the same bond. On the contrary, assuming the second model, O65W would achieve a BVS of 0.09 and  $-0.01$  vu if a donor and an acceptor in the  $O65W \cdots O65W$  hydrogen bond. This second model of an H-bonding system is illustrated in Fig. 5b.

Additional H bonds may involve O67W in the L3 layer. O67W is bonded weakly to Sb20 [ $Sb20-O67W = 2.731(7)$  Å] and Sb23

[ $Sb23-O67W = 3.023(6)$  Å], achieving a total BVS of 0.26 vu. Its bonding environment is shown in Fig. 6: O67W is at H-bond distances from O17 and O19, belonging to S5 and from O34. O67W may be involved in  $O34 \cdots O67W \cdots O17$  or  $O34 \cdots O67W \cdots O19$  bonds. In these H bonds, O67W could be donor of two H bonds, achieving a final BVS of  $-0.05$  vu, increasing those of O17, O19 and O34 up to 2.05, 2.06 and 2.04 vu, respectively.

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## CRYSTAL STRUCTURE OF COQUANDITE

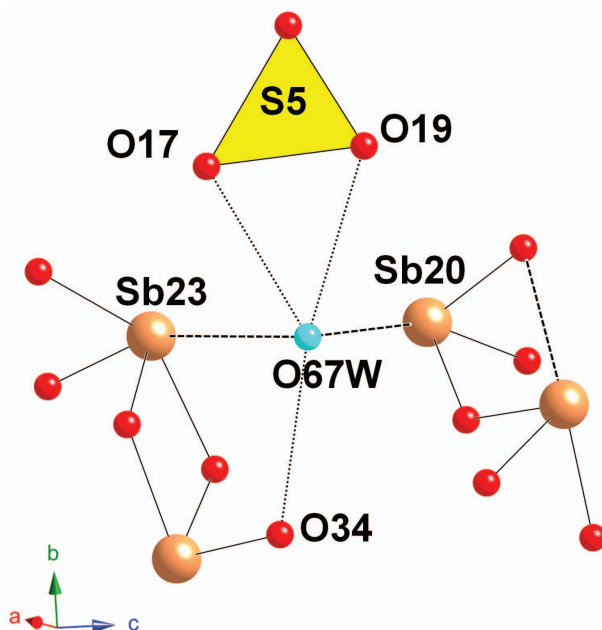


Fig. 6. Hydrogen bonds involving the O67W site. Dotted lines = O...O distances shorter than 3.0 Å; dashed lines = Sb–O bond distances longer than 2.50 Å.

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