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Steverustite, $Pb_5^{2+}(OH)_5[Cu^+(S^{6+}O_3S^{2-})_3](H_2O)_2$, a new thiosulphate mineral from the Frongoch Mine Dump, Devils Bridge, Ceredigion, Wales: description and crystal structure

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ABSTRACT

Steverustite, ideally $Pb_5^{2+}(OH)_5[Cu^+(S^{6+}O_3S^{2-})_3](H_2O)_2$, is a new supergene mineral from the Frongoch mine dump, Devils Bridge, Ceredigion, Wales. It generally forms fibrous fan-like bundles that occur in small cavities in quartz veins with other supergene species. Crystals are fibrous to acicular, elongated along [010], and are bounded by (*h*0*l*) faces too small to index reliably. It is transparent, colourless to white with a white streak, has a vitreous lustre, does not fluoresce under ultraviolet light and is brittle with a splintery fracture. The calculated density is 5.150 g/cm^3, and the calculated mean refractive index is 1.94. The mineral is monoclinic, $P2_1/n$, a 12.5631(7), b 8.8963(5), c 18.0132(11) Å, β 96.459(1)º, V 2000.5(3) Å^3, Z = 4, a:b:c = 1.41217:1:2.02480. The seven strongest lines in the X-ray powder diffraction pattern are as follows: d (Å), I, (h k l): 3.934, 10, ($\bar{1}14$); 3.934, 8, ($\bar{1}11$); 3.348, 7, ($\bar{3}13$); 6.211, 6, (200); 4.797, 6, (211); 3.026, 6, ($\bar{3}14$); 2.837, 5, (016). Chemical analysis by electron microprobe gave PbO 72.59, SO_3 15.78, Cu_2O 4.47, S^{2-} 6.32, H_2O 4.83, O=S^{2-} −3.15, total 100.84 wt.% where the amount of H_2O was determined by crystal-structure analysis. The resulting empirical formula is $Pb_{4.99}^{2+}Cu_{0.96}^{+}(S^{6+}O_3S^{2-})_{3.03}(OH)_{4.88}(H_2O)_{1.67}$, based on O + OH + H_2O + S^{2-} = 18.67 a.p.f.u. (atoms per formula unit) with H_2O = 1.67 a.p.f.u. (from crystal-structure solution and refinement).

The crystal structure of steverustite was solved by direct methods and refined to R_1 = 2.7% for 3366 unique ($F_o > 4\sigma F$) reflections. There are five distinct Pb^{2+} cations with coordination numbers from [8] to [11], all of which show stereoactive lone-pair behaviour and which form a strongly bonded cluster of composition $[Pb_5(OH)_5]$. There is one Cu^+ cation triangularly coordinated by three S^{2-} atoms that belong to three thiosulphate groups, forming a $Cu^+(S^{6+}O_3S^{2-})_3$ group. The $[Pb_5(OH)_5]$ units and $[Cu(S_2O_3)_3]$ groups occur at the vertices of interpenetrating 3^6 nets to form layers of composition $[Pb_5(OH)_5Cu(S_2O_3)_3]$ parallel to (010) which are linked by weaker bonds. Examination of the stereochemistry of thiosulphate and thionate structures shows that the combination of <S−O> and S−S distances are distinct for these two types of structures.

KEYWORDS: steverustite, new mineral, thiosulphate, Wales, UK.

Introduction

FRONGOCH is an abandoned lead-zinc mine at Pontrhydygroes, Upper Llanfihangell-y-Creuddyn, Ceredigion, Wales, and is located ~15 km east-south-east of Aberystwyth (UK OS Grid Reference: SN722744, Map Reference: 52º21′8″N , 3º52′35″W). The mine itself was operating from at least the late 1750s to 1903 (Bick *et al.*, 1996); since then, there has been sporadic working of the dumps for lead-zinc ore and hardcore (roadstone) (http://www.mindat.org/loc.php? loc=4724). Although the mining activity is relatively recent, the site is quite important from an archaeological perspective, and the

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buildings are classed as an Ancient Monument. The principal ore minerals are galena and sphalerite that occur in a discontinuous series of veins associated with WSW–ENE faults that cut Silurian mudstones/shales and arenites of the Devils Bridge formation (Llandovery age). Frongoch is well known for producing excellent specimens of brown pyromorphite and cerussite, and there are many secondary hydroxy-hydrated Pb- and Cu-sulphate minerals on the dump (Green *et al.*, 1996). In addition, the local drainage system has been the focus of many environmental studies concerning the transport and bio-absorption of heavy metals.

The mineral is named steverustite after Stephen Andrew Rust (born August 23rd, 1952, at Bushy, near Watford, Hertfordshire, UK), a long-time collector of UK minerals who discovered this mineral on the dumps of the Frongoch mine. Both the mineral and the name have been approved by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association (IMA2008-021). The holotype specimen of steverustite has been deposited in the mineral collection of the Canadian Museum of Nature, catalogue number CMNMC 86053.

Physical properties

Steverustite consists of laths <0.75 mm long that generally form fibrous fan-like bundles <1.5 mm across, but also occur as single laths, perched on a quartz-sulphide matrix (Fig. 1). It forms in small cavities (up to a few mm across) in quartz veins and is associated with sphalerite, galena, covellite, cerussite, anglesite, hemimorphite, sussannite, bechererite and caledonite. It is late in the paragenesis, forming after caledonite and bechererite by late-stage oxidation of galena. Individual crystals are fibrous to acicular, are elongated along [010], and bounded by (*h*0*l*) faces too small to index reliably. The mineral is transparent, colourless to white, and has a white streak, a vitreous lustre, and does not fluoresce under ultraviolet light. Individual crystals are too small to observe any cleavage or parting. Steverustite is brittle with a splintery fracture. The calculated density is 5.150 g/cm^3 and the calculated mean refractive index (n) is 1.94. As was the case with sidpietersite (Cooper and Hawthorne, 1999), where n ~ 2, steverustite shows intense internal reflections which prevented us from obtaining adequate reflectance data.

Chemical composition

Crystals were analysed using a Cameca SX100 electron microprobe operating in wavelength-dispersive mode with an accelerating voltage of 15 kV, a probe current of 10 nA, and a probe diameter of 5 μm. The following standards and X-ray lines were used: galena for Pb-*M*α and S-*K*α; chalcopyrite for Cu-*K*α, with peak count times of 20 s and background count times of 10 s. Raw intensities were converted to concentrations using the *PAP* approach of Pouchou and Pichoir (1985). The results expressed in terms of elements are given in Table 1. Conversion to oxides and calculation of the formula was more complicated than usual because of the presence of S in two valence states: (1) Pb and Cu were converted to PbO and Cu_2O, the valence states having been determined from the stereochemistry of the crystal structure; (2) S was expressed as S^{6+} and S^{2-} in a 1:1 ratio, as indicated by the crystal structure; S^{6+} was then converted to SO_3; (3) H_2O was calculated to give 5 (OH) and 1⅔ (H_2O) as indicated by the crystal structure; (4) the formula

FIG. 1. Aggregates of lath-like to acicular crystals of steverustite on a matrix. The field of view is 2.5 mm wide (photograph by David Green).

TABLE 1. Chemical composition (wt.%) of steverustite.

Constituent	EMP values	Constituent	Observed	Ideal
Pb	67.39	PbO	72.59	71.95
S	12.64	SO_3	15.78	15.49
Cu	3.97	Cu_2O	4.47	4.61
		S^{2-}	6.32	6.20
		H_2O	4.83	4.84
		$O \equiv S^{2-}$	−3.15	−3.09
Total	84.00		100.84	100

was normalized on O + (OH) + (H_2O) + S^{2-} = 18.67 a.p.f.u. (from crystal-structure solution). In addition, infrared spectroscopy (see below) indicated the presence of both (OH) and (H_2O). The empirical formula for steverustite is $Pb^{2+}_{4.99}Cu^{+}_{0.96}(S^{6+}O_3S^{2-})_{3.03}(OH)_{4.88}(H_2O)_{1.67}$ and the end-member formula is $Pb^{2+}_5(OH)_5[Cu^+(S^{6+}O_3S^{2-})_3](H_2O)_2$.

Infrared absorption spectroscopy

The infrared (IR) powder absorption spectrum of steverustite was recorded using a Nicolet FTIR 740 spectrophotometer in the range 4000−400 cm^{-1} (Fig. 2). In the principal (OH)-stretching region (3800−3000 cm^{-1}), the spectrum shows prominent sharp absorptions at 3587 and 3507 cm^{-1}, indicating the presence of (OH) groups in the structure. The broad band at 3368 cm^{-1} and the prominent H-O-H bend at 1646 cm^{-1} indicate the presence of (H_2O) in the structure. The strong bands at 1120−1140 and 988 cm^{-1} are characteristic of tetrahedrally coordinated S^{6+}, and the lower-energy ‘lattice’ bands are due to complex motions involving other polyhedra.

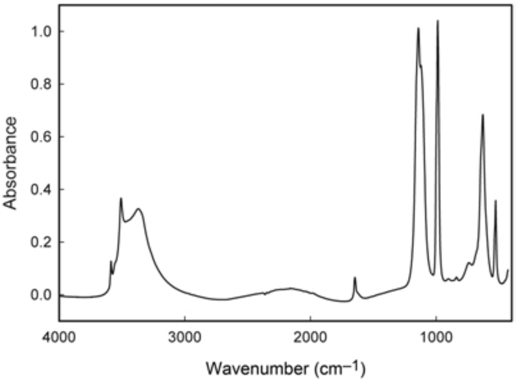

FIG. 2. The IR spectrum of steverustite.

X-ray powder diffraction

The powder-diffraction pattern (Table 2) was recorded with Cu-$K\alpha$ X-radiation on a Debye-Scherrer camera with a diameter of 114.6 mm and equipped with a Gandolfi attachment. Refinement of the unit-cell parameters gave the following values: a = 12.51(3), b = 8.859(16), c = 18.08(4) Å, β = 96.33(19)º, V = 1992(5) Å^3. Unit-cell dimensions were also determined on a single crystal with a Bruker diffractometer using graphite-monochromated Mo-$K\alpha$ X-radiation and the resulting values are close to the above values.

Other localities for steverustite

It seemed to us that steverustite should be a fairly common mineral. Mr Stephen Rust forwarded to us from other localities some specimens that are very similar in appearance. Three of these had crystals of sufficient quality that we were able to confirm their identity as steverustite by single-crystal X-ray (XRD) diffraction. All samples were also examined by electron microprobe analysis. Fragments from each sample were laid on the surface of a plexiglas disc and anchored with a minute drop of epoxy, carbon coated and examined with EDS and WDS spectrometry. In each sample, the EDS spectrum showed an intense peak assigned to Pb and a weak peak assigned to Cu; the S peak could not be resolved from the Pb peak. In addition, WDS scans were acquired in the vicinities of the Pb, Cu and S peaks. All spectra were compared with the spectra of one sample identified as steverustite by single-crystal XRD, and were extremely similar, indicating that they

TABLE 2. X-ray powder diffraction data for steverustite.

I_{est}	d_{meas} (Å)	d_{calc} (Å)	*h k l*	I_{est}	d_{meas} (Å)	d_{calc} (Å)	*h k l*
<1	9.025	8.986	0 0 2	2	3.482	3.494	2 2 1
8	6.897	6.849	$\bar{1}$ 1 1			3.465	2 0 4
1	6.527	6.552	1 1 1	7	3.348	3.335	$\bar{3}$ 1 3
6	6.211	6.218	2 0 0	2	3.178	3.182	$\bar{2}$ 2 3
1	5.689	5.646	$\bar{1}$ 0 3	6	3.026	3.034	$\bar{3}$ 1 4
1	5.463	5.458	1 1 2	1	2.920	2.914	0 3 1
6	4.797	4.785	2 1 1	5	2.837	2.837	0 1 6
1	4.078	4.064	$\bar{2}$ 1 3	1	2.622	2.632	$\bar{2}$ 2 5
10	3.934	3.928	$\bar{1}$ 1 4	1	2.483	2.489	4 2 1
2	3.741	3.732	1 2 2	1	2.295	2.287	3 3 2
2	3.556	3.561	0 2 3	1	2.211	2.217	1 3 5

114.6 mm Debye-Scherrer powder camera with Gandolfi attachment, Cu radiation and Ni filter (λ Cu-*K*α = 1.54178); intensities estimated visually. Not corrected for shrinkage and no internal standard.
a 12.51(3), *b* 8.859(16), *c* 18.08(4) Å, β 96.33(19)º, *V* 1992(5) Å^3

are chemically identical to steverustite. The list of localities is given in Table 3.

Crystal structure: X-ray data collection and structure refinement

Single-crystal XRD data were collected using a Bruker *P*4 diffractometer equipped with a 4K CCD detector (Mo-*K*α radiation) from a single crystal with dimensions 180 μm × 40 μm × 6 μm. The intensities of 54,698 reflections were collected to 50º2θ using 60 s per 0.2º frame. An empirical absorption correction (*SADABS*, Sheldrick, 1998) was applied, and the data were corrected for Lorentz, polarization and background effects. The refined unit-cell parameters were obtained from 7395 reflections with $I > 10\sigma I$. The structure was solved by direct methods and refined to R_1 = 2.7% and a Go*F* value of 1.222 for 3366 independent observed ($|F_o| > 4\sigma|F|$ reflections with the *SHELXTL* version 5.1 system of programs (Bruker, 1997). Details of the data collection and structure refinement are given in Table 4, final atomic parameters in Table 5, selected interatomic distances and angles in Table 6, and bond-valence values in Table 7. A CIF file has been deposited with the Principal Editor of *Mineralogical Magazine* and is available from www.minersoc.org/pages/e_journals/dep_mat_mm.html

TABLE 3. Other localities at which steverustite was identified.

Nantycar Mine dump, Rhayader, Powys, Wales (four samples known)
Bwlch Glas Mine, Talybont, Ceredigion, Wales (17 samples known, collected from the vein in the upper adit level)
Llangynog Mine dump, Llangynog, Powys, Wales (associated with bechererite, one of only two samples known)
Hendre Felen Mine dump. Ysbyty Ystwyth Ceredigion, Wales (six samples known)
Esgair Hir Mine dump, Talybont, Ceredigion, Wales (six samples known)
Penybach Mine dump, Talybont, Ceredigion, Wales (three samples known)
Llechwedd Helyg Mine dump, Bontgoch, Ceredigion, Wales (38 samples known)
Horners Vein dump, Leadhills, Strathclyde, Scotland (five samples known)
Lady Anne Hopetoun Shaft dump, Leadhills, Strathclyde, Scotland (ten samples known)
Susanna Mine dump, Leadhills, Strathclyde, Scotland (23 samples known)

TABLE 4. Details of data collection and crystal-structure refinement of steverustite.

a (Å)	12.5631(7)	Crystal size (μm)	6 × 40 × 180
b (Å)	8.8963(5)	Radiation	Mo-$K\alpha$
c (Å)	18.0132(11)	No. of reflections	54698
β (°)	96.459(1)	No. in Ewald sphere	13597
V (Å^3)	2000.5(3)	No. unique reflections	3530
Space group	$P2_1/n$	No. $\|F_o\| > 4\sigma\|F\|$	3366
Z	4	R_{merge} %	1.8
		R_1 %	2.7
		wR_2 %	6.1

Cell content: $4[Pb_5^{2+}(OH)_5[Cu^+(S^{6+}O_3S^{2-})_3](H_2O)_{1.67}]$

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

Description of the structure

Pb sites

There are five Pb sites with coordination numbers from [8] to [11] (Fig. 3). Pb(1), Pb(3), Pb(4) and Pb(5) each have three short bonds on one side (2.318–2.441 Å) of their coordination polyhedra and long bonds (2.684–3.358 Å to O; 3.288–3.681 Å to S) on the other side of their coordination polyhedra. As seen in Fig. 3, the short bonds are all to (OH) groups. The bonds to S^{2-} are extremely long, but the bond valences (Table 7) show that these interactions are significant. Ignoring these long Pb–S^{2-} bonds gives incident bond-valence sums of 1.66, 1.67 and 1.59 v.u. at S(4), S(5) and S(6), respectively. For Pb(2), there is one very short bond (2.230 Å) (Fig. 3b) and Pb(2) does not bond to an S^{2-} anion.

$Cu^+(S^{6+}O_3S^{2-})_3$ group

The Cu^+ atom is coordinated by three S^{2-} atoms [S(4), S(5), S(6)] that belong to three thiosulphate groups in a triangular arrangement (Fig. 4). The Cu^+ and S^{6+} atoms are close to the S^{2-} [S(4), S(5), S(6)] plane. Various geometrical details of this group are given in Table 6.

(OH) groups

The O atoms [O(10)–O(14)] belong to the five (OH) groups in steverustite, and form strong bonds to the Pb atoms (Table 7). The H atoms were located in difference-Fourier maps and inserted into the refinement model with the soft constraint that the H atom remain ~0.98 Å from the respective donor O atom. The associated hydrogen bonds are directed towards various S^{2-} and O^{2-} atoms of the thiosulphate groups, and towards the O atom of the (H_2O) groups (Tables 6, 7).

(H_2O) groups

The O atoms at O(15) and O(16) are (H_2O) groups as indicated by their incident bond-valence sums from the cations in the structure (Table 7). Site-scattering refinement showed that O(15) is fully occupied by (H_2O), and O(16) is occupied by $(H_2O)_{0.67}\square_{0.33}$. This gives steverustite a total (H_2O) content of 1.67 a.p.f.u. Although the H atoms associated with the (H_2O) groups could not be located in difference-Fourier maps, both stereochemistry and incident bond-valence requirements indicate that their associated hydrogen bonds are directed towards the O^{2-} and S^{2-} anions of the thiosulphate groups (Tables 6, 7).

Structure topology

In steverustite, all O atoms that form strong bonds (i.e. >0.35 v.u.) to Pb atoms are (OH) groups, and the resulting strongly bonded cluster has the composition $[Pb_5(OH)_5]$ (Table 6, Fig. 5). This $[Pb_5(OH)_5]$ cluster can be regarded as a structural unit, as the strong bonding is terminated at each O atom by the presence of a H atom (Hawthorne, 1992). At its core, the $Pb_5(OH)_5$ unit contains a tetrahedron of Pb^{2+} cations [Pb(1), Pb(3), Pb(4), Pb(5)], and one additional Pb^{2+} [Pb(2)] attaches to the Pb(1) corner of the tetrahedron through a strong bond to the (OH) group at O(14) (Fig. 3). These $[Pb_5(OH)_5]$ units and $[Cu(S_2O_3)_3]$ groups occur at the vertices of interpenetrating 3^6 nets

TABLE 5. Atomic positions and displacement parameters (Å^2) for steverustite.

	x	*y*	*z*	U_{eq}	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Pb(1)*	0.65998(3)	0.09839(5)	0.54396(2)	0.02733(11)	0.0301(2)	0.0261(2)	0.0265(2)	0.00290(17)	0.00625(17)	−0.00422(17)
Pb(2)	0.28510(3)	0.09642(5)	0.21832(2)	0.02820(11)	0.0325(2)	0.0288(2)	0.0227(2)	−0.00006(17)	0.00053(17)	−0.00231(17)
Pb(3)	0.85984(3)	0.37204(5)	0.49493(3)	0.03122(11)	0.0261(2)	0.0307(2)	0.0354(2)	−0.00109(18)	−0.00346(18)	−0.00299(17)
Pb(4)	0.57981(3)	0.36011(4)	0.37496(2)	0.02494(10)	0.0233(2)	0.0250(2)	0.0260(2)	0.00113(16)	0.00082(16)	0.00163(16)
Pb(5)	0.78717(4)	0.06441(5)	0.35321(2)	0.03227(11)	0.0403(2)	0.0320(2)	0.0255(2)	−0.00092(17)	0.00810(18)	0.00996(19)
Cu	0.30114(10)	0.28737(15)	0.58767(7)	0.0267(3)	0.0260(6)	0.0331(7)	0.0211(6)	0.0006(5)	0.0029(5)	0.0008(5)
S(1)	0.29060(19)	0.2829(3)	0.40072(13)	0.0204(5)	0.0224(12)	0.0202(12)	0.0178(12)	−0.0005(10)	−0.0013(10)	0.0000(10)
S(2)	0.53847(19)	0.2457(3)	0.69203(14)	0.0233(5)	0.0194(12)	0.0323(14)	0.0182(12)	−0.0017(11)	0.0020(10)	0.0000(10)
S(3)	0.0825(2)	0.3395(3)	0.68340(15)	0.0276(6)	0.0278(13)	0.0307(14)	0.0258(14)	0.0055(11)	0.0098(11)	0.0052(11)
S(4)S^{2-}	0.4014(2)	0.2870(3)	0.49234(14)	0.0244(5)	0.0208(12)	0.0320(14)	0.0196(12)	−0.0002(11)	−0.0009(10)	0.0005(11)
S(5)S^{2-}	0.3837(2)	0.2972(4)	0.70413(15)	0.0299(6)	0.0208(13)	0.0486(17)	0.0206(13)	−0.0003(12)	0.0033(10)	0.0018(12)
S(6)S^{2-}	0.1226(2)	0.2913(3)	0.57811(15)	0.0308(6)	0.0242(13)	0.0445(17)	0.0234(14)	0.0012(12)	0.0017(11)	0.0034(12)
O(1)	0.3503(6)	0.2731(10)	0.3351(4)	0.0333(18)	0.030(4)	0.049(5)	0.020(4)	−0.013(4)	0.001(3)	−0.003(4)
O(2)	0.2298(6)	0.4238(8)	0.3982(4)	0.0261(16)	0.031(4)	0.027(4)	0.019(4)	−0.001(3)	0.000(3)	0.009(3)
O(3)	0.2210(6)	0.1525(9)	0.4077(5)	0.0351(19)	0.032(4)	0.033(4)	0.036(5)	0.012(4)	−0.013(4)	−0.006(3)
O(4)	0.5760(7)	0.3441(10)	0.6357(5)	0.045(2)	0.032(4)	0.055(6)	0.055(6)	0.020(5)	0.027(4)	0.007(4)
O(5)	0.5442(7)	0.0874(10)	0.6699(5)	0.044(2)	0.032(4)	0.038(5)	0.062(6)	−0.009(4)	0.011(4)	−0.002(4)
O(6)	0.6033(6)	0.2677(13)	0.7632(5)	0.052(3)	0.029(4)	0.099(8)	0.027(4)	−0.023(5)	−0.006(4)	0.006(5)
O(7)	−0.0241(7)	0.4031(11)	0.6714(5)	0.046(2)	0.034(5)	0.058(6)	0.048(5)	−0.010(5)	0.010(4)	0.006(4)
O(8)	0.0841(9)	0.1994(10)	0.7250(5)	0.057(3)	0.104(8)	0.038(5)	0.033(5)	0.004(4)	0.030(5)	0.000(5)
O(9)	0.1602(7)	0.4443(10)	0.7198(4)	0.0371(19)	0.042(5)	0.047(5)	0.022(4)	0.003(4)	0.003(4)	−0.009(4)
O(10)(OH)	0.6727(5)	0.3453(8)	0.4968(4)	0.0222(15)	0.026(4)	0.025(4)	0.015(3)	−0.001(3)	0.001(3)	0.004(3)
O(11)(OH)	0.8243(6)	0.1101(8)	0.4860(4)	0.0282(17)	0.032(4)	0.029(4)	0.025(4)	0.003(3)	0.007(3)	0.012(3)
O(12)(OH)	0.7683(5)	0.3260(8)	0.3702(4)	0.0238(15)	0.026(4)	0.029(4)	0.018(4)	−0.005(3)	0.007(3)	−0.004(3)
O(13)(OH)	0.6198(6)	0.1052(8)	0.3920(4)	0.0271(16)	0.032(4)	0.024(4)	0.026(4)	−0.004(3)	0.008(3)	−0.003(3)
O(14)(OH)	0.7839(6)	0.2106(11)	0.6392(5)	0.047(2)	0.029(4)	0.053(6)	0.057(6)	−0.024(5)	−0.008(4)	0.014(4)
O(15)(H_2O)	−0.0013(7)	0.2895(16)	0.3997(6)	0.074(4)	0.030(5)	0.152(12)	0.043(6)	0.020(7)	0.012(4)	0.017(6)
O(16)(H_2O)	0.4551(11)	0.4840(15)	0.1400(10)	0.071(6)	0.053(9)	0.043(8)	0.109(14)	−0.022(8)	−0.023(8)	0.007(6)
H(1)	0.665(9)	0.435(8)	0.527(6)	0.038(16)**						
H(2)	0.883(6)	0.040(10)	0.500(7)	0.038(16)**						
H(3)	0.800(9)	0.383(12)	0.332(5)	0.038(16)**						
H(4)	0.570(7)	0.034(10)	0.365(6)	0.038(16)**						
H(5)	0.844(6)	0.148(11)	0.660(6)	0.038(16)**						

* all atoms were set to full occupancy except O(16) which refined to 0.67(3) occupancy.

** constrained to be equal during refinement.

(Fig. 6) to form a layer of composition $[Pb_5(OH)_5Cu(S_2O_3)_3]$ parallel to (010) and centred about the *n* glide at $y = ¼, ¾$. Note that the weaker bonds (i.e. <0.3 v.u.) are not shown in Fig. 6 in order to highlight the alternating pattern of $[Pb_5(OH)_5]$ and $[Cu(S_2O_3)_3]$ groups. When the (010) layers are viewed edge-on down [100] (Fig. 7), the $[Cu(S_2O_3)_3]$ groups overlie the $[Pb_5(OH)_5]$ groups (and *vice versa*) along [010].

Comparison with other thiosulphate minerals

Other thiosulphate minerals are bazhenovite (Chesnokov *et al*., 1987), viaeneite (Kucha *et al*., 1996) and sidpietersite (Roberts *et al*., 1999). However, the status of some of these minerals as thiosulphates is not clear. Bindi *et al*. (2005) investigated a bazhenovite-like crystal from the type locality for bazhenovite by single-crystal XRD and IR spectroscopy, and showed that it does not contain a thiosulphate group. However, the authors state that it is unknown as to whether a less altered form of bazhenovite containing a thiosulphate group may exist. The only other thiosulphate mineral with its structure adequately characterized is sidpietersite, $Pb_4^{2+}O_2(OH)_2\ (S^{6+}O_3S^{2-})$ (Cooper and Hawthorne, 1999). In sidpietersite, there are two O atoms that form four strong bonds (~0.5 v.u.) each to Pb atoms, resulting in strongly bonded Pb−O ladders flanked by additional Pb and O atoms [(OH)] that form ribbons along the *a* axis, with composition $[Pb_4O_2(OH)_2]$; these ribbons are cross-linked by thiosulphate groups. Sidpietersite has a cation:(S_2O_3) ratio of 4:1, and contains strongly bonded and polymerized ladders of the PbO structure. Steverustite, $Pb_5^{2+}(OH)_5[Cu^+(S^{6+}O_3S^{2-})_3](H_2O)_{1.67}$, has a cation:$(S_2O_3)$ ratio of 2:1 and contains isolated Pb(OH) units. Synthetic thio-sulphate compounds from the Inorganic Crystal Structure Database (ICSD)

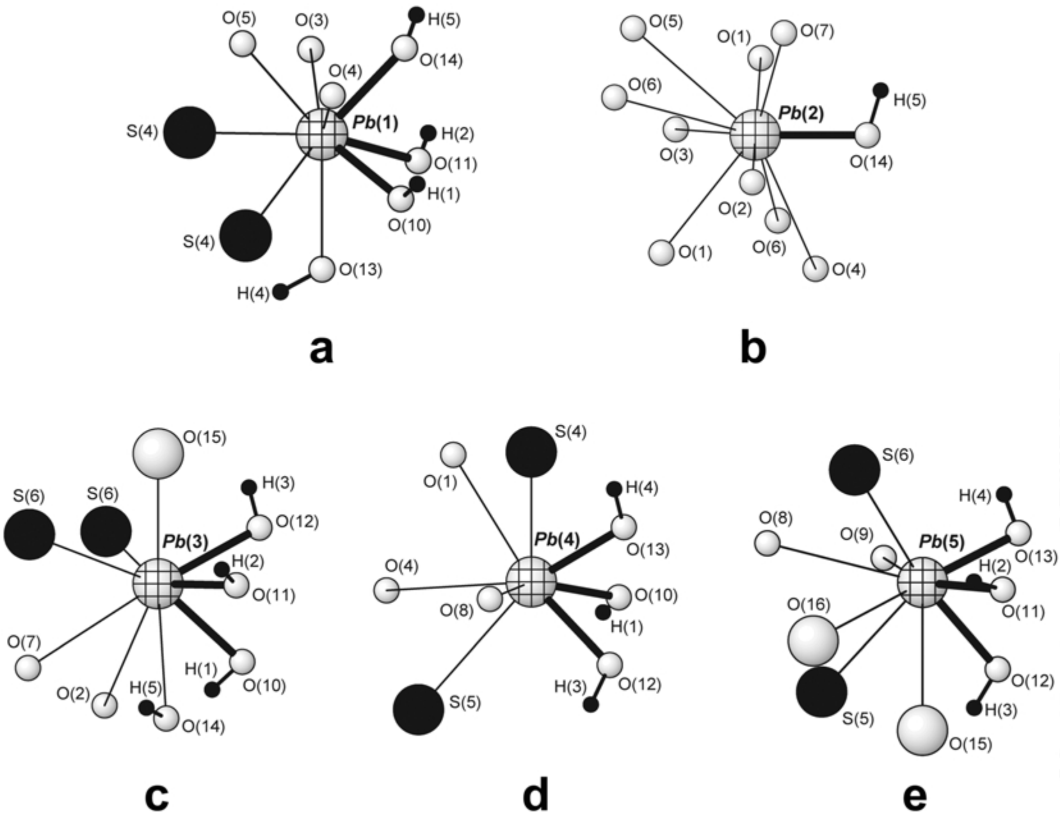

FIG. 3. The coordination of the *Pb* sites in steverustite; large cross-hatched circles: *Pb*, large black circles: S^{2-}, large shaded circles: H_2O, medium shaded circles: (OH), small black circles: H, heavy lines: short bonds ($\leqslant$2.44 Å), thin lines: long bonds ($\geqslant$2.59 Å).

TABLE 6. Selected interatomic distances (Å) and angles (º) for steverustite.

Pb(1)–O(3)a	2.772(8)	*Pb*(2)–O(1)	2.679(7)
Pb(1)–O(4)	3.002(9)	*Pb*(2)–O(1)e	3.424(8)
Pb(1)–O(5)	2.831(9)	*Pb*(2)–O(2)e	2.591(7)
Pb(1)–O(10)	2.367(7)	*Pb*(2)–O(3)	3.627(9)
Pb(1)–O(11)	2.418(7)	*Pb*(2)–O(4)f	2.918(9)
Pb(1)–O(13)	2.727(7)	*Pb*(2)–O(5)a	3.219(9)
Pb(1)–O14)	2.401(8)	*Pb*(2)–O(6)a	3.531(11)
Pb(1)–S(4)	3.681(3)	*Pb*(2)–O(6)f	2.783(10)
Pb(1)–S(4)a	3.559(3)	*Pb*(2)–O(7)c	2.630(8)
		Pb(2)–O(14)f	2.230(9)
Pb(3)–O(2)b	2.960(7)		
Pb(3)–O(7)d	3.356(9)	*Pb*(4)–O(1)	2.994(7)
Pb(3)–O(10)	2.367(7)	*Pb*(4)–O(4)b	3.272(9)
Pb(3)–O(11)	2.375(8)	*Pb*(4)–O(8)c	2.759(9)
Pb(3)–O(12)	2.441(7)	*Pb*(4)–O(10)	2.371(7)
Pb(3)–O(14)	3.207(11)	*Pb*(4)–O(12)	2.398(7)
Pb(3)–O(15)d	2.684(10)	*Pb*(4)–O(13)	2.336(7)
Pb(3)–S(6)b	3.288(3)	*Pb*(4)–S(4)	3.314(3)
Pb(3)–S(6)d	3.542(3)	*Pb*(4)–S(5)b	3.417(3)
Pb(5)–O(8)a	3.259(9)	*S*(1)–O(1)	1.472(8)
Pb(5)–O(9)c	2.732(8)	*S*(1)–O(2)	1.466(7)
Pb(5)–O(11)	2.420(7)	*S*(1)–O(3)	1.466(8)
Pb(5)–O(12)	2.362(7)	*S*(1)–S(4)	2.036(4)
Pb(5)–O(13)	2.318(7)		
Pb(5)–O(15)d	3.358(12)	*S*(2)–O(4)	1.458(8)
Pb(5)–O(16)g	3.304(14)	*S*(2)–O(5)	1.468(9)
Pb(5)–S(5)c	3.306(3)	*S*(2)–O(6)	1.452(8)
Pb(5)–S(6)a	3.538(3)	*S*(2)–S(5)	2.033(4)
Cu–S(4)	2.241(3)	*S*(3)–O(7)	1.448(9)
Cu–S(5)	2.235(3)	*S*(3)–O(8)	1.453(9)
Cu–S(6)	2.231(3)	*S*(3)–O(9)	1.452(9)
<*Cu*–S>	2.236	*S*(3)–S(6)	2.061(4)

Table 6 (*contd.*)

H-bonding							
O(10)–H(1)	0.98	H(1)....S(4)b	2.62(8)	O(10)....S(4)b	3.413(7)	O(10)–H(1)–S(4)b	138(9)
O(11)–H(2)	0.98	H(2)....O(16)h	2.59(11)	O(11)....O(16)h	3.173(16)	O(11)–H(2)–O(16)h	118(8)
O(12)–H(3)	0.98	H(3)....O(9)b	1.89(5)	O(12)....O(9)b	2.818(11)	O(12)–H(3)–O(9)b	157(10)
O(13)–H(4)	0.98	H(4)....O(5)a	1.85(3)	O(13)....O(5)a	2.811(11)	O(13)–H(4)–O(5)a	166(10)
O(14)–H(5)	0.98	H(5)....O(16)h	1.89(7)	O(14)....O(16)h	2.761(16)	O(14)–H(5)–O(16)h	146(10)
O(15)....O(6)f	2.960(13)			O(6)f–O(15)–S(6)	125.9(3)		
O(15)....S(6)	3.410(11)						
O(16)....O(3)i	2.730(15)			O(3)i–O(16)–S(5)b	107.2(4)		
O(16)....S(5)b	3.807(14)						
Details of the $Cu^{1+}(S^{6+}O_3S^{2-})_3$ group							
S(4)–*Cu*–S(5)	118.54(11)			*Cu*–S(4)–*S*(1)	103.24(13)		
S(4)–*Cu*–S(6)	126.01(11)			*Cu*–S(5)–*S*(2)	103.83(13)		
S(5)–*Cu*–S(6)	115.37(11)			*Cu*–S(6)–*S*(3)	106.24(14)		
<S^{2-}–*Cu*–S^{2-}>	119.97			<*Cu*–S^{2-}–S^{6+}>	104.44		
S(4)–*S*(1)–O(1)	106.8(3)			S(5)–*S*(2)–O(4)	109.1(4)		
S(4)–*S*(1)–O(2)	108.4(3)			S(5)–*S*(2)–O(5)	108.8(4)		
S(4)–*S*(1)–O(3)	107.7(3)			S(5)–*S*(2)–O(6)	108.9(4)		
O(1)–*S*(1)–O(2)	109.7(5)			O(4)–*S*(2)–O(5)	110.9(6)		
O(1)–*S*(1)–O(3)	112.6(5)			O(4)–*S*(2)–O(6)	109.9(6)		
O(2)–*S*(1)–O(3)	111.4(5)			O(5)–*S*(2)–O(6)	109.2(6)		
<φ–*S*(1)–φ>	109.4			<φ–*S*(2)–φ>	109.5		
S(6)–*S*(3)–O(7)	105.1(4)			*Cu*–ΔS(4)–S(5)–S(6)	−0.038(2)		
S(6)–*S*(3)–O(8)	107.8(4)			*S*(1)–ΔS(4)–S(5)–S(6)	0.002(5)		
S(6)–*S*(3)–O(9)	109.1(3)			*S*(2)–ΔS(4)–S(5)–S(6)	−0.452(5)		
O(7)–*S*(3)–O(8)	111.8(6)			*S*(3)–ΔS(4)–S(5)–S(6)	0.383(5)		
O(7)–*S*(3)–O(9)	112.4(5)						
O(8)–*S*(3)–O(9)	110.4(6)			S(4)–S(5)	3.847(4)		
<φ–*S*(3)–φ>	109.4			S(5)–S(6)	3.774(4)		
				S(4)–S(6)	3.985(4)		

a: $\bar{x}+1, \bar{y}, \bar{z}+1$; b: $\bar{x}+1, \bar{y}+1, \bar{z}+1$; c: $x+½, \bar{y}+½, \bar{z}-½$; d: $x+1, y, z$; e: $\bar{x}+½, y-½, \bar{z}+½$; f: $x-½, \bar{y}+½, z-½$; g: $\bar{x}+1½, y-½, \bar{z}+½$; h: $x+½, \bar{y}+½, z+½$; i: $\bar{x}+½, y+½, \bar{z}+½$

TABLE 7. Bond-valence* (v.u.) table for steverustite.

	Pb(1)	*Pb*(2)	*Pb*(3)	*Pb*(4)	*Pb*(5)	*Cu*	*S*(1)	*S*(2)	*S*(3)	Σ	H(1)	H(2)	H(3)	H(4)	H(5)	H(6)N′	H(7)N′	H(8)N′	H(9)N′	Σ
O(1)		0.23 0.06		0.12			1.51			1.92										1.92
O(2)		0.27	0.13				1.53			1.93										1.93
O(3)	0.19	0.04					1.53			1.76								0.20		1.96
O(4)	0.12	0.14		0.08				1.57		1.91										1.91
O(5)	0.17	0.08						1.52		1.77				0.20						1.97
O(6)		0.18 0.05						1.59		1.82						0.20				2.02
O(7)		0.25	0.07						1.61	1.93										1.93
O(8)				0.19	0.08				1.59	1.86										1.86
O(9)					0.20				1.59	1.79			0.20							1.99
O(10)	0.45		0.45	0.44						1.34	0.80									2.14
O(11)	0.40		0.44		0.40					1.24		0.80								2.04
O(12)			0.38	0.42	0.45					1.25			0.80							2.05
O(13)	0.20			0.48	0.50					1.18				0.80						1.98
O(14)	0.41	0.62	0.08							1.11					0.80					1.91
O(15)			0.22		0.07					0.29						0.80	0.80			1.89
O(16)					0.07					0.07		0.20			0.20			0.80	0.80	2.07
S(4)	0.07 0.05			0.13		0.36	1.10			1.71	0.20									1.91
S(5)				0.10	0.13	0.36		1.11		1.70									0.20	1.90
S(6)			0.14 0.07		0.07	0.37			1.02	1.67							0.20			1.87
Σ	2.06	1.92	1.98	1.96	1.97	1.09	5.67	5.79	5.81		1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	

* calculated from the curves of Brown (1981): Pb–O, and Brese and O'Keefe (1991): Pb–S, S–O and S–S.

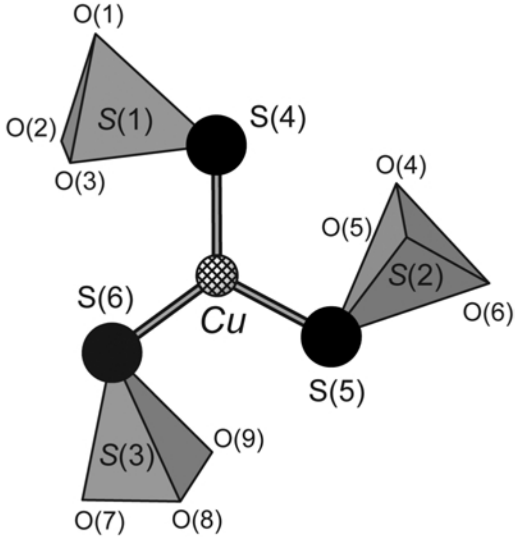

FIG. 4. The $Cu(S_2O_3)_3$ group in steverustite, shown with the three S^{2-} sites [S(4), S(5), S(6)] in the plane of the page. Legend as in Fig. 3, with a medium-sized diagonally cross-hatched circle as the *Cu* site.

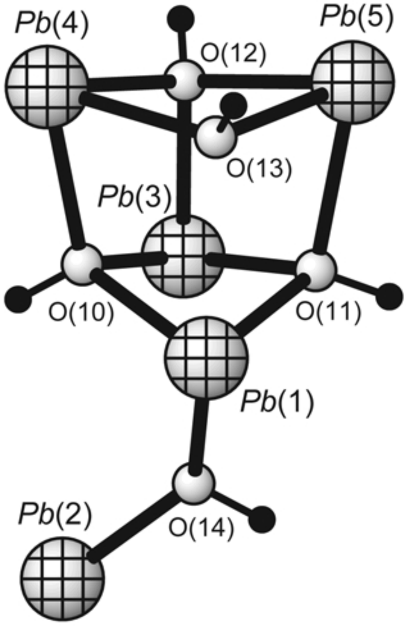

FIG. 5. The strongly bonded $Pb_5(OH)_5$ unit in steverustite. Legend as in Fig. 3.

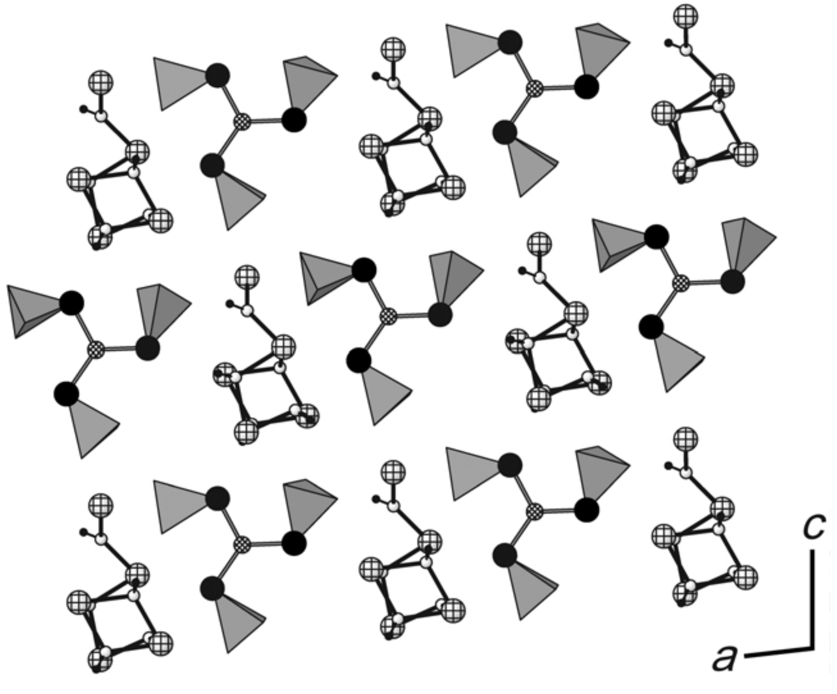

FIG. 6. The (010) layer of alternating $Pb_5(OH)_5$ and $Cu(S_2O_3)_3$ groups in steverustite. Legend as in Figs 3 and 4. Note that the longer Pb−φ bonds are not drawn.

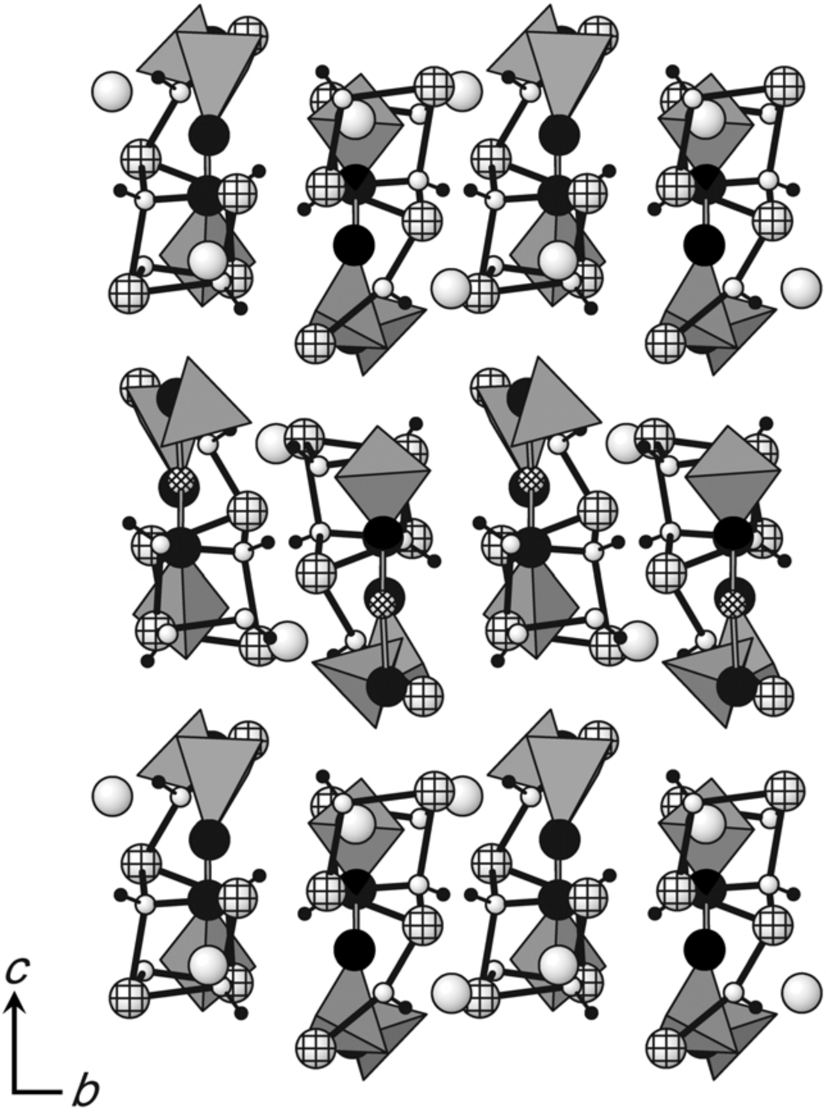

FIG. 7. Edge-on view of the (010) layers of $Pb_5(OH)_5$ and $Cu(S_2O_3)_3$ groups in steverustite projected down [100]. Legend as in Figs 3 and 4. Note that the longer Pb−φ bonds are not drawn.

contain cation:(S_2O_3) ratios of 1:1 or 2:1. Alhough steverustite has the same cation: (S_2O_3) ratio (2:1) as some of the synthetic thiosulphates, the steverustite structure is unique in that it contains strongly bonded units [i.e. Pb(OH)] in addition to the (S_2O_3) groups]. This difference is evident in the formula of steverustite, in which five additional anions [other than (S_2O_3) or (H_2O) groups] are present. None of the synthetic non-ammonium thiosulphates contains similar additional anions, and therefore lack these strongly bonded structural fragments or polymerized units. There is another thiosulphate compound, $Ba_2F_2(S_2O_3)$, formed from weathering of ancient slags, that also contains additional anions in its formula (Braithwaite *et al.*, 1993). Kampf (2009, pers. comm.) has solved the structure of this material, and has shown that it consists of condensed large-cation polyhedra linked by thiosulphate groups. In this regard, it is similar to steverustite and sidpietersite, and unlike synthetic thiosulphate compounds synthesized to date.

Comparison with other structures

We reviewed the crystal structures on the ICSD in which one S atom bonds to three O atoms and one S atom. These compounds are generally referred to as thionates or thiosulphates. Bond distances were obtained from single-crystal X-ray structure refinements of more modern (post-1972), well refined (R <8%) and well-ordered structures (40 structures, including steverustite). Dithionates, trithionates and thiosulphates contain $[S_2O_6]^{2-}$, $[S_3O_6]^{2-}$ and $[S_2O_3]^{2-}$ groups, respectively (Fig. 8) and typically form weaker bonds with group I and II metals in simple 1:2 and 1:1 ratios, and additional (H_2O) groups are often present. Dithionates, trithionates and thiosulphates also form compounds with transition-metal–$(NH_3)_n$ complexes. Additionally, there are more complex thionates of the form $[S_2A_xO_6]^{2-}$, where A = S, Se, Te and $x \leqslant 4$.

Thiosulphates

The S atoms of the thiosulphate group are normally assigned formal valences of 6+ and 2−, and this matter was discussed by Cooper and Hawthorne (1999). The $[S_2O_3]^{2-}$ groups form weak bonds to neighbouring cations at both the O atoms and S^{2-} anion. Here, we further subdivide the thiosulphates into two types based on the coordination of the large cation (X) adjacent to the S^{2-} anion. Cation X [X = H {(H_2O),NH_3,NH_4}, Na, K, Co, Ni, Ag, Cd, Ba, La, Pb] may bond, (1) to one or more S^{2-} atoms, in addition to one or more O or N atoms (Fig. 8*c*), or (2) entirely to S^{2-} anions of two-to-four thiosulphate groups [X = Cu, Ag, Au] (Fig. 8*d*). The latter coordination varies from linear [CN = 2] in $Na_3Au(S_2O_3)_2(H_2O)_2$ (Ruben *et al.*, 1974) (Fig. 9*a*), to triangular [CN = 3] in steverustite (Fig. 9*b*) to tetrahedral [CN = 4] in $(NH_4)_9Br_2[Ag(S_2O_3)_4]$ (El Bali *et al.*, 2002), $Na_4Cu(NH_3)_4[Cu(S_2O_3)_2]_2(NH_3)$ (Morosin and Larson, 1969), and $Na_4Ni(NH_3)_4[Ag(S_2O_3)_2]_2(NH_3)$ (Stomberg *et al.*, 1973) (Fig. 9*c*). Steverustite is the first occurrence of the $[Cu(S_2O_3)_3]^{5-}$ cluster and the coordination of a cation solely by three thiosulphate groups.

The <S−O> distances in thionate and thiosulphate groups are shown as a function of the corresponding S−S distance for the group in the 40 structures examined (Fig. 10). For the thionates, we have averaged the S−O and S−S distances that occur at both ends of the group, so

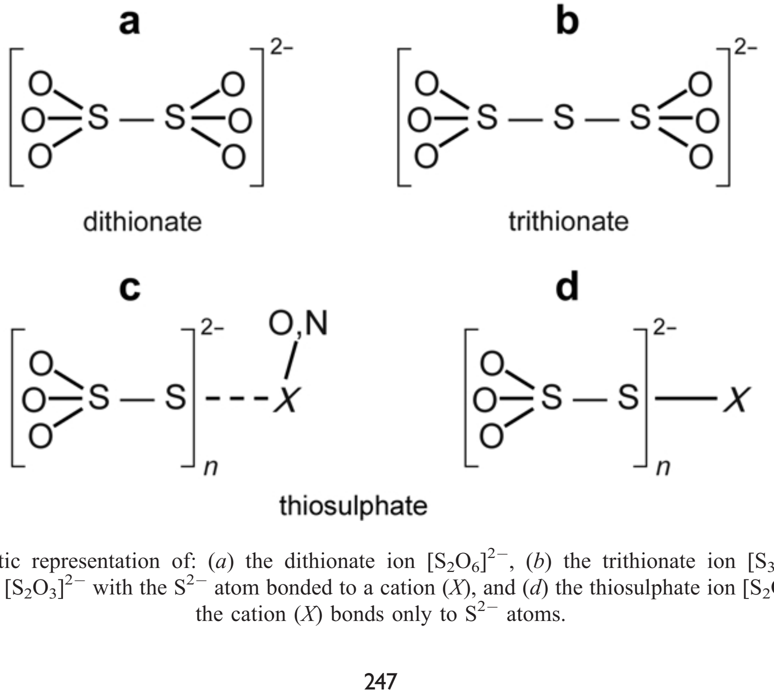

FIG. 8. Schematic representation of: (*a*) the dithionate ion $[S_2O_6]^{2-}$, (*b*) the trithionate ion $[S_3O_6]^{2-}$, (*c*) the thiosulphate ion $[S_2O_3]^{2-}$ with the S^{2-} atom bonded to a cation (X), and (*d*) the thiosulphate ion $[S_2O_3]^{2-}$ in which the cation (X) bonds only to S^{2-} atoms.

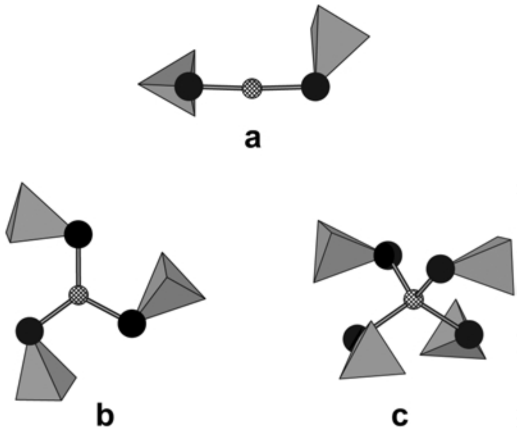

FIG. 9. Known $[(S_2O_3)_n{-}X]$ groups in crystal structures: (*a*) the linear $[Au(S_2O_3)_2]^{3-}$ group in $Na_3Au(S_2O_3)_2(H_2O)_2$, (*b*) the triangular $[Cu(S_2O_3)_3]^{5-}$ group in steverustite, and (c) the tetrahedral $[X(S_2O_3)_4]^{7-}$ group in $(NH_4)_9Br_2[Ag(S_2O_3)_4]$ and $Na_4Ni(NH_3)_4[Ag(S_2O_3)_2]_2(NH_3)$ with [X = Ag], and $Na_4Cu(NH_3)_4[Cu(S_2O_3)_2]_2(NH_3)$ with [X = Cu]. Legend as in Fig. 4, with the X cation diagonally cross-hatched.

that only one data point is shown per group; note that the individual S–O and S–S distances (not shown) fall within the field shown for the thionates (i.e. $1.429 \leqslant$ S–O $\leqslant 1.464$, $2.067 \leqslant$ S–S $\leqslant 2.153$ Å). The thionates and thiosulphates clearly fall into two distinct fields on Fig. 10, with a boundary at an S–S distance of ~2.07 Å separating the two fields. The thiosulphate groups that belong to minerals are also labelled on Fig. 10: [1] steverustite, [2] sidpietersite.

Conditions of formation

In oxidizing surface waters, thiosulphate forms complexes with Au^+ and Ag^+ ions (Webster, 1987; Benedetti and Boulegue, 1991). The $[Cu(S_2O_3)_3]^{5-}$ group in steverustite also contains a Group 1B cation (Cu^+) and may be present in near-surface waters under certain conditions. Steverustite, sidpietersite and $Ba_2F_2(S_2O_3)$ are all naturally occurring thiosulphates, and also contain accessory anions [O, (OH), F], resulting in stronger cation-anion, (Pb, Ba)-[O, (OH), F] interactions than in synthetic thiosulphates with alkali cations and only divalent anions. This feature of the naturally occurring thiosulphates distinguishes them from their synthetic cousins, which lack these more strongly bonded interactions. Moreover, the occurrence of monovalent anions suggests basic conditions of formation for

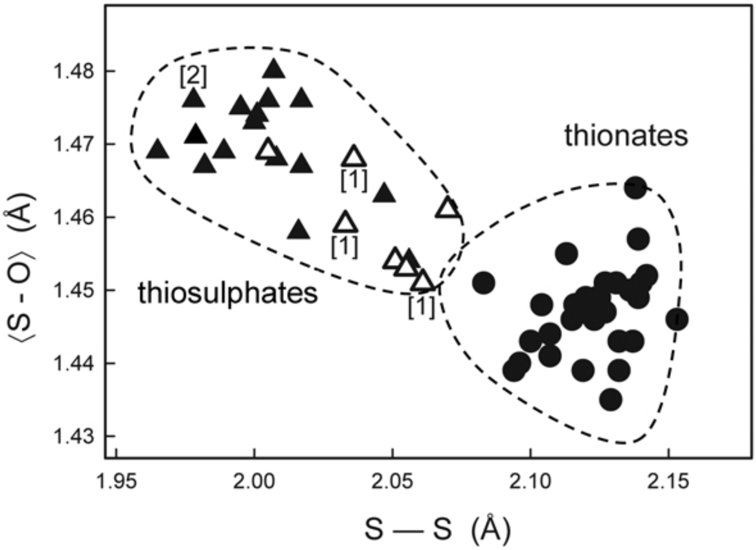

FIG. 10. The $\langle S^{6+}{-}O\rangle$ distance as a function of S–S distance for the compounds listed in Appendix A (available for download from www.minersoc.org/pages/e_journals/dep_mat_mm.html); black circles: thionate groups; black triangles: thiosulphate groups in which the S^{2-} atom bonds to cation (X) – (O,N) (cf. Fig. 8*c*); open triangles: thiosulphate groups in which the cation (X) bonds only to S^{2-} atoms (cf. Fig. 8*d*). Data belonging to steverustite and sidpietersite are labelled [1] and [2], respectively.

steverustite and sidpietersite, in accord with the suggestion of Braithwaite *et al*. (1993) that alkaline ($11 \leqslant pH \leqslant 13$) and mildly oxidizing conditions will favour the formation of natural $Ba_2F_2(S_2O_3)$.

Relationship with other species

Steverustite is chemically similar to sidpietersite, Pb_4^{2+} $(S^{6+}O_3S^{2-})O_2(OH)_2$ (Roberts *et al*., 1999), the only other thiosulphate mineral with a known structure at present. In steverustite, thiosulphate tetrahedra form $[Cu^{+}(S^{6+}O_3S^{2-})_3]$ clusters that link by weak bonds to $[Pb_5(OH)_5]$ clusters. In sidpietersite, isolated thiosulphate tetrahedra link to strongly bonded ribbons of Pb and O that resemble fragments of the PbO structure (Cooper and Hawthorne, 1999). As noted by Cooper and Hawthorne (1999), all synthetic thiosulphate compounds have thiosulphate tetrahedra floating in a network of weak cation–oxygen bonds usually involving H or alkali cations, and do not show the strongly bonded clusters found in these two thiosulphate minerals.

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