# THE STRUCTURE TOPOLOGY OF SIDPIETERSITE, $Pb^{2+}_4$ $(S^{6+}O_3S^{2-})$ $O_2$ $(OH)_2$, A NOVEL THIOSULFATE STRUCTURE

MARK A. COOPER AND FRANK C. HAWTHORNE§

*Department of Geological Sciences, University of Manitoba, Winnipeg, Manitoba R3T 2N2, Canada*

## ABSTRACT

The crystal structure of sidpietersite, $Pb^{2+}_4$ $(S^{6+}O_3S^{2-})$ $O_2$ $(OH)_2$, triclinic, $a$ 7.455(2), $b$ 6.496(2), $c$ 11.207(4) Å, $\alpha$ 114.33(2), $\beta$ 89.65(2), $\gamma$ 88.69(2)°, $V$ 494.3(3) Å³, $Z = 2$, space group $P\bar{1}$, has been solved by direct methods and refined to an $R$ index of 3.0% for 1292 observed ($| F_o | > 5\sigma | F_o |$) reflections measured with MoK$\alpha$ X-radiation. There are four symmetrically distinct $Pb$ sites occupied by $Pb^{2+}$ in very asymmetric coordinations typical of stereoactive lone-pair behavior. Sidpietersite contains a thiosulfate group, $(S^{6+}O_3S^{2-})$, and is the first thiosulfate mineral to be characterized structurally. The $<S^{6+}–O>$ distance is 1.48 Å, the $S^{6+}–S^{2-}$ distance is 1.98 Å, and the four anions form a distorted tetrahedral arrangement about the central cation. A ladder of $Pb^{2+}$ and O atoms (a motif from the structure of PbO) extends along the $a$ axis; this ladder is decorated by peripheral Pb atoms, and the resultant ribbons are cross-linked by thiosulfate groups to form a thick slab orthogonal to [001]. These slabs are linked along the $c$ axis by weak Pb–$S^{2-}$ bonds. The structure of sidpietersite is unrelated to any synthetic thiosulfate structures. The latter have cation:thiosulfate ratios between 1:1 and 2:1, and the structures consist of thiosulfate groups linked by weak bonds. In sidpietersite, the cation:thiosulfate ratio is 4:1, and the cations form extended polymerized arrays that are cross-linked by thiosulfate groups. There seems no intrinsic reason why more complex structures such as sidpietersite should not occur, at least as synthetic materials.

*Keywords*: sidpietersite, thiosulfate, crystal structure, Pb mineral, Tsumeb, Namibia.

## SOMMAIRE

Nous avons résolu la structure cristalline de la sidpietersite, $Pb^{2+}_4$ $(S^{6+}O_3S^{2-})$ $O_2$ $(OH)_2$, triclinique, $a$ 7.455(2), $b$ 6.496(2), $c$ 11.207(4) Å, $\alpha$ 114.33(2), $\beta$ 89.65(2), $\gamma$ 88.69(2)°, $V$ 494.3(3) Å³, $Z = 2$, groupe spatial $P\bar{1}$, par méthodes directes et affinement jusqu'à un résidu $R$ de 3.0% pour 1292 réflexions observées ($| F_o | > 5\sigma | F_o |$) et mesurées avec rayonnement MoK$\alpha$. La structure contient quatre sites $Pb$ symétriquement distincts, où sont logés les atomes $Pb^{2+}$ dans une coordinence assymétrique typique d'un comportement impliquant une paire d'électrons isolés stéréoactifs. La sidpietersite contient un groupe thiosulfate, $(S^{6+}O_3S^{2-})$, et en serait le premier exemple dans le règne minéral à être structuralement décrit. La distance $<S^{6+}–O>$ est 1.48 Å, la distance $S^{6+}$–$S^{2-}$ est 1.98 Å, et les quatre anions sont disposés dans un agencement tétraédrique difforme autour du cation central. Une échelle d'atomes $Pb^{2+}$ et O (motif retrouvé dans la structure de PbO) longe l'axe $a$, et est décoré par des atomes périphériques de Pb, et les rubans qui en résultent sont interliés par des groupes thiosulfatés pour former une épaisse couche perpendiculaire à [001]. Ces couches sont liées le long de l'axe $c$ par de faibles liaisons Pb–$S^{2-}$. Du point de vue structural, la sidpietersite ne ressemble à aucun composé thiosulfaté synthétique. Ce groupe de composés possède un rapport cation:thiosulfate entre 1:1 et 2:1, et leurs structures comportent des agencements de groupes thiosulfate liés par de faibles liaisons. Dans la sidpietersite, le rapport cation:thiosulfate est 4:1, et les cations forment des agencements allongés polymérisés, interliés par des groupes thiosulfatés. Il ne semble pas y avoir une raison intrinsèque pour empêcher la formation de structures plus complexes, comme celle de la sidpietersite, au moins parmi les matériaux synthétiques.

(Traduit par la Rédaction)

*Mots-clés*: sidpietersite, thiosulfate, structure cristalline, minéral de plomb, Tsumeb, Namibie.

§ *E-mail address*: frank_hawthorne@umanitoba.ca

## INTRODUCTION

Sidpietersite is a new mineral described by Roberts *et al.* (1999) from the Tsumeb mine, Namibia. It occurs in three different habits, one of which is as free-standing to radiating bladed-crystal aggregates and hence susceptible to crystal-structure analysis. Sidpietersite was the last mineral to crystallize in an assemblage of smithsonite, zincite, galena, sphalerite, minor quartz and greenockite. The mineral species was identified as "new" by determination of its unit cell (which did not correspond to any known species) and solution and refinement of the crystal structure; the results are presented here.

## EXPERIMENTAL

The crystals used in this work are from the type locality. The crystal used for collection of the intensity data is a thin plate, flattened on (001). It was attached to a sharpened glass fiber and mounted on a Siemens $P4$ automated four-circle diffractometer equipped with monochromated Mo$K\alpha$ X-radiation. Thirty-four reflections were detected on a 3 h rotation photograph ($6 < 2\theta < 25°$) and centered, and the unit-cell dimensions (Table 1) and orientation matrix were determined from the resulting setting angles. Intensity data were collected in $\theta$:2$\theta$ scan-mode at a fixed scan-rate of 1°2$\theta$/min. A total of 3044 reflections was collected over the range $4 \leq 2\theta \leq 60°$, with index ranges $\overline{10} \leq h < 10$, $\overline{9} < k < 9$, $\overline{9} < l < 15$. Two standard reflections were monitored every fifty-eight reflections; there were no significant changes in their intensities during data collection. Data for an empirical absorption-correction were collected in psi-scan mode at intervals of 5° for eight reflections distributed over the range 4 to 60°2$\theta$. The crystal was modeled as a plate, and all reflections with a plate-glancing angle less than 15° were discarded, reducing $R$(azimuthal) from 11.7 to 2.2%; the same model was then used to correct the $\theta$–2$\theta$ data, the standard corrections were done, and intensities were reduced to structure factors; of the 1974 unique reflections, 1292 were considered as observed ($|F_o| > 5\sigma |F_o|$).

### TABLE 1. MISCELLANEOUS INFORMATION FOR SIDPIETERSITE

| | | | |
|---|---|---|---|
| $a$ (Å) | 7.455(2) | crystal size (mm) | 0.015 x 0.04 x 0.04 |
| $b$ | 6.496(2) | Radiation | Mo$K\alpha$/Graphite |
| $c$ | 11.207(4) | Total no. of I | 3044 |
| $\alpha$ (°) | 114.33(2) | No. of I after 15° | 2118 |
| $\beta$ | 89.65(2) | glancing-angle correction | |
| $\gamma$ | 88.69(2) | No.of $|F|$ | 1974 |
| $V$ (Å³) | 494.3(3) | No. of $|F_o| > 5\sigma$ | 1292 |
| Sp Gr. | P1 | $R$ (azimuthal) % | 11.7 – 2.2 |
| $Z$ | 2 | $R$ (merge) % | 1.3 |
| $D_{calc.}$ (g.cm⁻³) | 6.765 | $R$ (obs) % | 3.0 |
| $\mu_m$ (mm⁻¹) | 68.3 | $wR$ (obs) % | 3.2 |

Unit cell contents: 2 [Pb$_4$ (S$^{6+}$O$_3$S$^{2-}$) O$_2$ (OH)$_2$]

$R = \Sigma(|F_o|-|F_c|)/\Sigma|F_o|$

$wR = [\Sigma w(|F_o|-|F_c|)^2/\Sigma F_o^2]^{1/2}$, $w = 1$

## STRUCTURE SOLUTION AND REFINEMENT

Scattering curves for neutral atoms were taken from the International Tables for X-ray Crystallography (1992); $R$ indices are of the form given in Table 1, and are expressed as percentages. The Siemens SHELXTL PLUS (PC version) system of programs was used for this work.

The structure was solved by direct methods, the solution with the highest figure-of-merit resulting in the correct structure. All atom locations and identities were derived by successive cycles of least-squares refinement and difference-Fourier synthesis. The $S(1)$ site was interpreted as being occupied by S$^{6+}$, and the surrounding (tetrahedral arrangement of) sites were assigned to O atoms. However, least-squares refinement resulted in one very inappropriate $S(1)$–O distance, a displacement factor of zero and a large negative residual in the difference-Fourier map at the anomalous O site. Careful electron-microprobe analysis revealed no constituents apart from Pb and S (and hence Cl⁻ could not be assigned to the anomalous O site); thus S$^{2-}$ was the only possible constituent of this site. Insertion of the S scattering factor at this site resulted in a stable refinement and a sensible solution consisting of two fully occupied $S$ sites with stereochemistry consistent with $S(1) = $ S$^{6+}$ and

### TABLE 2. ATOMIC POSITIONS AND DISPLACEMENT FACTORS (x 10⁴) FOR SIDPIETERSITE

| Site | $x$ | $y$ | $z$ | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ | $U_{eq}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| $Pb(1)$ | 0.1221(1) | 0.7483(1) | 0.0063(1) | 159(3) | 152(3) | 255(5) | 79(3) | −2(4) | 7(3) | 191(3) |
| $Pb(2)$ | 0.6198(1) | 0.5932(1) | 0.3116(1) | 168(4) | 311(4) | 219(5) | 104(4) | 22(4) | 0(3) | 235(3) |
| $Pb(3)$ | 0.1030(1) | 0.6262(1) | 0.3048(1) | 180(4) | 309(4) | 200(5) | 94(4) | −11(4) | −30(3) | 233(3) |
| $Pb(4)$ | 0.6275(1) | 0.7487(1) | 0.0275(1) | 146(3) | 155(3) | 239(5) | 77(3) | 16(4) | −3(3) | 182(3) |
| $S(1)$ | 0.3704(7) | 0.1253(8) | 0.3160(6) | 236(22) | 135(18) | 181(31) | 38(20) | −26(23) | −19(16) | 193(18) |
| $S(2)$ | 0.1509(9) | 0.204(1) | 0.4275(8) | 289(28) | 422(31) | 314(41) | 130(30) | 56(30) | 33(25) | 350(25) |
| $O(1)$ | 0.530(2) | 0.185(3) | 0.390(3) | 262(87) | 580(112) | 607(189) | 292(125) | 142(108) | 13(86) | 469(102) |
| $O(2)$ | 0.352(3) | 0.246(3) | 0.229(2) | 542(114) | 259(75) | 438(155) | 180(93) | 55(108) | −79(77) | 400(85) |
| $O(3)$ | 0.373(2) | −0.127(2) | 0.231(2) | 376(89) | 103(55) | 227(103) | −85(62) | −75(83) | −69(58) | 285(59) |
| $O(4)$ | 0.128(2) | 0.475(2) | 0.085(1) | 245(70) | 223(63) | 57(76) | 15(58) | 52(64) | 86(56) | 191(50) |
| $O(5)$ | 0.615(2) | 0.450(2) | 0.084(2) | 250(70) | 130(55) | 326(114) | 88(67) | 31(73) | 74(53) | 238(60) |
| $OH(1)$ | 0.874(2) | 0.357(3) | 0.245(2) | 198(66) | 397(79) | 132(84) | 154(70) | 41(67) | 21(62) | 228(56) |
| $OH(2)$ | 0.841(2) | 0.796(3) | 0.256(2) | 340(83) | 339(75) | 108(79) | 122(64) | −104(74) | −95(66) | 251(56) |

TABLE 3. SELECTED INTERATOMIC DISTANCES (Å) AND ANGLES (°) FOR SIDPIETERSITE

| | | | |
|---|---|---|---|
| Pb(1)–O(3)a | 2.99(2) | Pb(2)–O(1) | 3.20(3) |
| Pb(1)–O(4) | 2.28(2) | Pb(2)–O(1)b | 3.23(3) |
| Pb(1)–O(4)e | 2.35(1) | Pb(2)–O(2) | 2.91(2) |
| Pb(1)–O(5)d | 2.31(1) | Pb(2)–O(3)a | 2.95(2) |
| Pb(1)–OH(1)d | 2.61(2) | Pb(2)–O(5) | 2.33(2) |
| <Pb(1)–φ> | 2.51 | Pb(2)–OH(1) | 2.33(1) |
| | | Pb(2)–OH(2) | 2.37(2) |
| Pb(3)–O(2) | 2.88(2) | Pb(2)–S(2)b | 3.194(8) |
| Pb(3)–O(3)a | 2.92(2) | <Pb(2)–φ> | 2.81 |
| Pb(3)–O(4) | 2.25(2) | | |
| Pb(3)–OH(1)f | 2.37(2) | Pb(4)–O(2)d | 2.89(3) |
| Pb(3)–OH(2)f | 2.40(2) | Pb(4)–O(3)a | 2.80(2) |
| Pb(3)–S(2)c | 3.303(8) | Pb(4)–O(4)d | 2.32(1) |
| Pb(3)–S(2)a | 3.451(7) | Pb(4)–O(5) | 2.28(2) |
| Pb(3)–S(2) | 3.552(9) | Pb(4)–O(5)d | 2.30(1) |
| <Pb(3)–φ> | 2.89 | Pb(4)–OH(2) | 2.94(2) |
| | | <Pb(4)–φ> | 2.59 |
| S(1)–S(2) | 1.98(1) | | |
| S(1)–O(1) | 1.42(2) | | |
| S(1)–O(2) | 1.49(3) | OH(1)......OH(2) | 2.81(3) |
| S(1)–O(3) | 1.52(1) | | |
| <S(1)–φ> | 1.60 | OH(2)......S(2)g | 3.49(2) |
| | | | |
| S(2)–O(1) | 2.85(2) | S(2)–S(1)–O(1) | 113(1) |
| S(2)–O(2) | 2.78(3) | S(2)–S(1)–O(2) | 106(1) |
| S(2)–O(3) | 2.85(2) | S(2)–S(1)–O(3) | 108(1) |
| O(1)–O(2) | 2.41(4) | O(1)–S(1)–O(2) | 111(1) |
| O(2)–O(3) | 2.44(3) | O(2)–S(1)–O(3) | 108(1) |
| O(1)–O(3) | 2.42(2) | O(1)–S(1)–O(3) | 110(1) |
| <φ–φ> | 2.63 | <φ–S(1)–φ> | 109 |

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

TABLE 4. BOND-VALENCE ($vu$) TABLE FOR SIDPIETERSITE

| | Pb(1) | Pb(2) | Pb(3) | Pb(4) | S(1) | H(1) | H(2) | Σ |
|---|---|---|---|---|---|---|---|---|
| S(2) | | 0.18 | 0.13 0.09 0.07 | | 1.28 | | 0.20 | 1.95 |
| O(1) | | 0.08 0.08 | | | 1.74 | | | 1.90 |
| O(2) | | 0.14 | 0.15 | 0.15 | 1.44 | | | 1.88 |
| O(3) | 0.12 | 0.13 | 0.14 | 0.18 | 1.32 | | | 1.89 |
| O(4) | 0.55 0.46 | | 0.59 | 0.50 | | | | 2.10 |
| O(5) | 0.51 | 0.49 | | 0.55 0.52 | | | | 2.07 |
| OH(1) | 0.26 | 0.49 | 0.44 | | | 0.80 | | 1.99 |
| OH(2) | | 0.44 | 0.41 | 0.14 | | 0.20 | 0.80 | 1.99 |
| Σ | 1.90 | 2.03 | 2.02 | 2.04 | 5.78 | 1.00 | 1.00 | |

Bond-valence curves: Pb–O: Brown (1981); S–O, Pb–S, S–S: Brese & O'Keeffe (1991).

$S(2) = S^{2-}$. Full-matrix least-squares refinement with unit weights and anisotropic-displacement parameters converged to an $R$ index of 3.0%. Positional and displacement parameters are given in Table 2, selected interatomic distances and angles in Table 3, and a bond-valence analysis in Table 4. Observed and calculated structure-factors are available from The Depository of
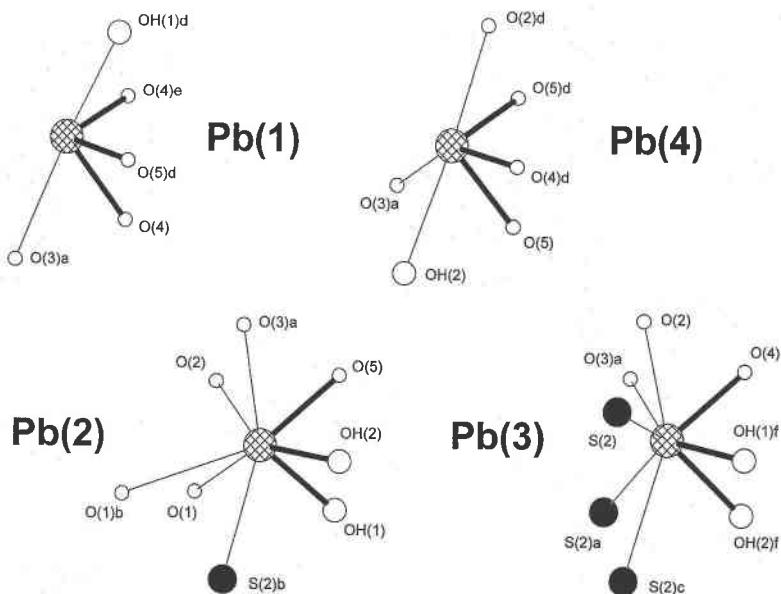


FIG. 1. The coordination of the $Pb$ sites in sidpietersite; large cross-hatched circles: $Pb$, large black circles: $S(2)$, medium unshaded circles: OH, small unshaded circles: O atoms, heavy lines: short bonds (≤ 2.4 Å) involving $Pb$, thin lines: long bonds (> 2.6 Å) involving $Pb$.

CATION COORDINATION

*The Pb sites*

There are four symmetrically distinct *Pb* sites; the local stereochemistry at each site, plus consideration of the overall electroneutrality, indicate that Pb is present at each site as $Pb^{2+}$. Each Pb atom bonds to three O atoms at distances between 2.25 and 2.40 Å, and these O atoms all lie to one side of the cation (Fig. 1). The other anions lie at much longer distances from the central cations ($<<Pb–\phi>> = 3.055$ Å; $\phi$: unspecified anion). This type of arrangement is characteristic of $Pb^{2+}$ with a stereoactive lone-pair of electrons. There is a considerable variation in $<Pb–\phi>$ distances, from 2.51 to 2.89 Å. This variation is partly a result of variation in coordination number, from [5] and 2.51 Å for *Pb*(1) to [8] and 2.89 Å for *Pb*(2), and partly the result of an unusually wide dispersion in anion size, from 1.34 Å for $OH^-$ to 1.84 Å for $S^{2-}$ (Shannon 1976).

*The thiosulfate group*

Details of the $S(1)$ coordination are shown in Figure 2. The central $S(1)$ is linked to three O atoms at a mean distance of 1.48 Å and the $S(2)$ anion at a distance of
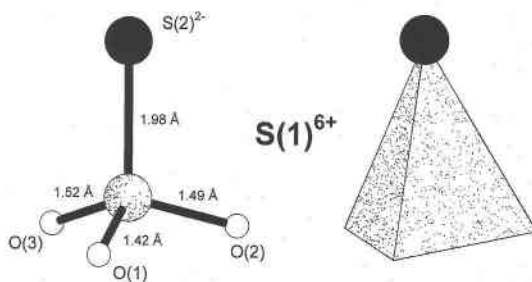


FIG. 2.    The coordination of the $S(1)$ site, shown as atoms (left) and as a tetrahedron (right) in which the $S(2)$ atom is identified as a large black circle; legend as in Figure 1, with a large random-dot-shaded circle as the $S(1)$ site.

1.98 Å, the four anions forming a very distorted tetrahedron. Despite the large dispersion in the $S(1)–\phi$ ($\phi$: $O^{2-}$, $S^{2-}$) distances, the angular distortion of the tetrahedron is not particularly large, and the mean tetrahedral angle, 109.3°, is close to the ideal value, 109.47° (Table 3).

As sidpietersite is the first thiosulfate mineral to be characterized structurally, the geometry of the thiosulfate group is of more than passing interest; this geometry is compared with the range in geometry from seventeen synthetic structures ($R$ in the range 2–9%)
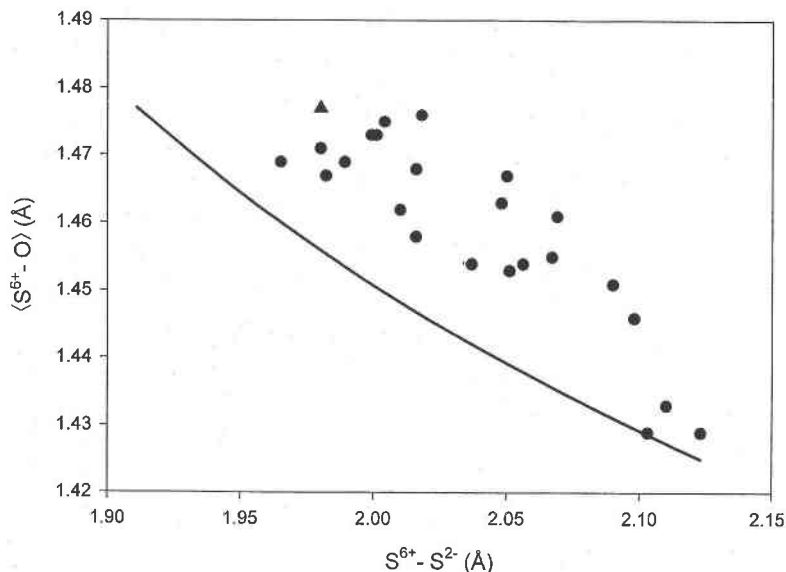


FIG. 3.    The $<S^{6+}–O>$ distance as a function of $S^{6+}–S^{2-}$ distance in thiosulfate groups from the synthetic compounds listed in Table 5 and ammonium thiosulfates (black circles), and sidpietersite (black triangle). The line shows the relation for ideal bond-valence satisfaction at the central $S^{6+}$ cation.

TABLE 5. THIOSULFATE COMPOUNDS[1]

| | | Formula | | Cation/S$_2$O$_3$ Ratio | Ref. |
|---|---|---|---|---|---|
| Na$_2$ | | S$_2$O$_3$ | | 2 | [1] |
| Na$_2$ | | S$_2$O$_3$ | (H$_2$O)$_{2/3}$ | 2 | [2] |
| Na$_2$ | | S$_2$O$_3$ | (H$_2$O)$_5$ | 2 | [3] |
| Na$_3$ | Au$^{1+}$ | (S$_2$O$_3$)$_2$ | (H$_2$O)$_2$ | 2 | [4] |
| [2]Na | Ag$^{1+}$ | S$_2$O$_3$ | H$_2$O | 2 | [5] |
| [3]K$_2$ | | S$_3$O$_6$ | | 1 | [6] |
| [2]K$_2$ | | S$_2$O$_3$ | (H$_2$O)$_{1/3}$ | 2 | [7] |
| K$_2$ | S$^{2+}$ | (S$_2$O$_3$)$_2$ | (H$_2$O)$_{3/2}$ | 1,5 | [8] |
| [2]Rb$_2$ | Te$^{2+}$ | (S$_2$O$_3$)$_2$ | (H$_2$O)$_{3/2}$ | 1,5 | [9] |
| [2]Tl$^{1+}$$_2$ | | S$_2$O$_3$ | | 2 | [10] |
| Mg | | S$_2$O$_3$ | (H$_2$O)$_6$ | 1 | [11] |
| Ni$^{2+}$ | | S$_2$O$_3$ | (H$_2$O)$_6$ | 1 | [12] |
| Cd | | S$_2$O$_3$ | (H$_2$O)$_2$ | 1 | [13] |
| Ba | | S$_2$O$_3$ | H$_2$O | 1 | [14] |
| Ba | Te$^{2+}$ | (S$_2$O$_3$)$_2$ | (H$_2$O)$_3$ | 1 | [15] |
| [2]Pb | | S$_2$O$_3$ | | 1 | [16] |

References: [1] Teng *et al.* (1984); [2] Hesse *et al.* (1993); [3] Uraz & Armağan (1977); [4] Ruben *et al.* (1974); [5] Cavalca *et al.* (1970); [6] Christidis & Rentzeperis (1985); [7] Csordas (1969); [8] Marøy (1971a); [9] Marøy (1971b); [10] Andersson & Bosson (1976); [11] Elerman *et al.* (1983); [12] Elerman *et al.* (1978); [13] Baggio *et al.* (1997); [14] Aka *et al.* (1980); [15] Gjerrestad & Marøy (1973); [16] Christensen *et al.* (1991)

[1] excluding ammonium-bearing compounds;
[2] structural data not included in Figure 3;
[3] contains O$_3$S$^{6+}$–S$^{2-}$–S$^{6+}$O$_3$ group.

containing twenty-three distinct thiosulfate groups (Table 5). The variation in $<S^{6+}–O>$ as a function of $S^{6+}–S^{2-}$ is shown in Figure 3; there is a negative correlation, as expected from the valence-sum rule (Brown 1981, Hawthorne 1994, 1997). The data for sidpietersite lie on the general trend, albeit near the lower end of the range of $S^{6+}–S^{2-}$ distances. The curve in Figure 3 shows ideal agreement with the valence-sum rule calculated using the observed $<S–O>$ distances. There is reasonable agreement between the slopes of the curve and of the data, but the curve is displaced approximately 0.02 Å below the trend of the data. The bond-valence curve for $S^{6+}–O$ can be considered as reliable. The value reported by Brese & O'Keeffe (1991) is the same as that reported by Brown (1981), and gives close-to-ideal bond-valence sums at $S^{6+}$ in (SO$_4$) groups. The problem must therefore be with the $S^{6+}–S^{2-}$ bond-valence curve of Brese & O'Keeffe (1991).

## STRUCTURE TOPOLOGY

The basic features of the sidpietersite structure are shown in Figure 4. A ladder of Pb [$Pb$(1) and $Pb$(4)] and O atoms extends along the *a* axis; note that this is a motif from the PbO structure (Cooper & Hawthorne 1994, Fig. 4). This ladder is decorated on either side by a staggered arrangement of Pb [$Pb$(2) and $Pb$(3)] and O atoms to form a ribbon that extends along the *a* axis. These ribbons are linked in the *c* direction by (S$^{6+}$O$_3$S$^{2-}$)

groups such that the $S^{2-}$ anions [$S$(2)] form an almost linear array in projection (Fig. 4).

This linkage forms thick slabs orthogonal to [001]. In Figure 5, the "*Pb*–O" ladders are seen "end-on"; they are linked into slabs orthogonal to [001] by thiosulfate groups and *Pb*–O bonds. These slabs are linked in the *c* direction by long weak *Pb*–$S$(2) bonds; note that in this orientation, the *Pb*(2), *Pb*(3) and $S$(2) atoms form a ladder resembling the *Pb*–O ladder in Figure 4.

### COMPARISON WITH OTHER STRUCTURES

Sidpietersite is a unique structure both with regard to minerals and to synthetic compounds. Inspection of Table 5 shows that all the structures have cation:S$_2$O$_3$ ratios between 1 and 2, and the structural arrangements all involve thiosulfate tetrahedra floating in a network of weak cation–oxygen bonds, usually involving H or alkali cations. Sidpietersite has a cation:S$_2$O$_3$ ratio of 4, and contains relatively strongly bonded and polymerized fragments of the PbO structure. However, there does not seem to be anything particularly exotic about the structure of sidpietersite, except for the occurrence of the thiosulfate group in a mineral, and there seems to be no intrinsic reason why structures with cation:S$_2$O$_3$ ratios higher than 2 should not be common. In this regard, Kucha *et al.* (1996) reported that viaeneite, (Fe,Pb)$_4$S$_8$O, contains both $S^{2-}$ and $S^{6+}$, and can be written as (Fe,Pb)$_{12}$ (S$_2$$^{2-}$)$_{11}$ (S$_2$O$_3$), although there are no structural data available for this mineral.

### THE FORMAL VALENCES OF S IN THE THIOSULFATE GROUP

On the basis of XANES spectroscopy, Vairavamurthy *et al.* (1993) proposed that the valences of S in thiosulfate are 5$^+$ and 1$^-$ instead of the conventionally assigned 6$^+$ and 2$^-$. This proposal may be tested in a very simple manner using structural data and bond-valence theory. The bond-valence incident at the O anions of the thiosulfate group from the rest of the structure is calculated independently of the formal charges of S in the structure. Hence the $S$(1)–O bond-valence can be calculated from the valence-sum rule, and the total bond-valence incident at $S$(1) from the O anions of the thiosulfate group can be derived; the value is 4.83 *vu* (valence units). If the formal charge on $S$(1) were 5$^+$, the bond-valence for $S$(1)–$S$(2) [$S^{6+}–S^{2-}$] bond would be 0.17 *vu*. This result seems unlikely from several perspectives. First, the four long *Pb*–$S$(2) bonds would be required to supply 0.83 *vu*, at a mean Pb$^{2+}$–$S^{2-}$ bond-valence of 0.21 *vu*. This requirement is not in accord with the incident bond-valence sums around the *Pb* sites, as it would require a bond-valence sum around *Pb*(3) of ~2.36 *vu*. Second, it is unlikely that the thiosulfate group would be a prominent complex in aqueous solutions at a range of pH (and Eh) values if it were defined by such a weak $S^{6+}–S^{2-}$ bond. Third, it seems intuitively unlikely
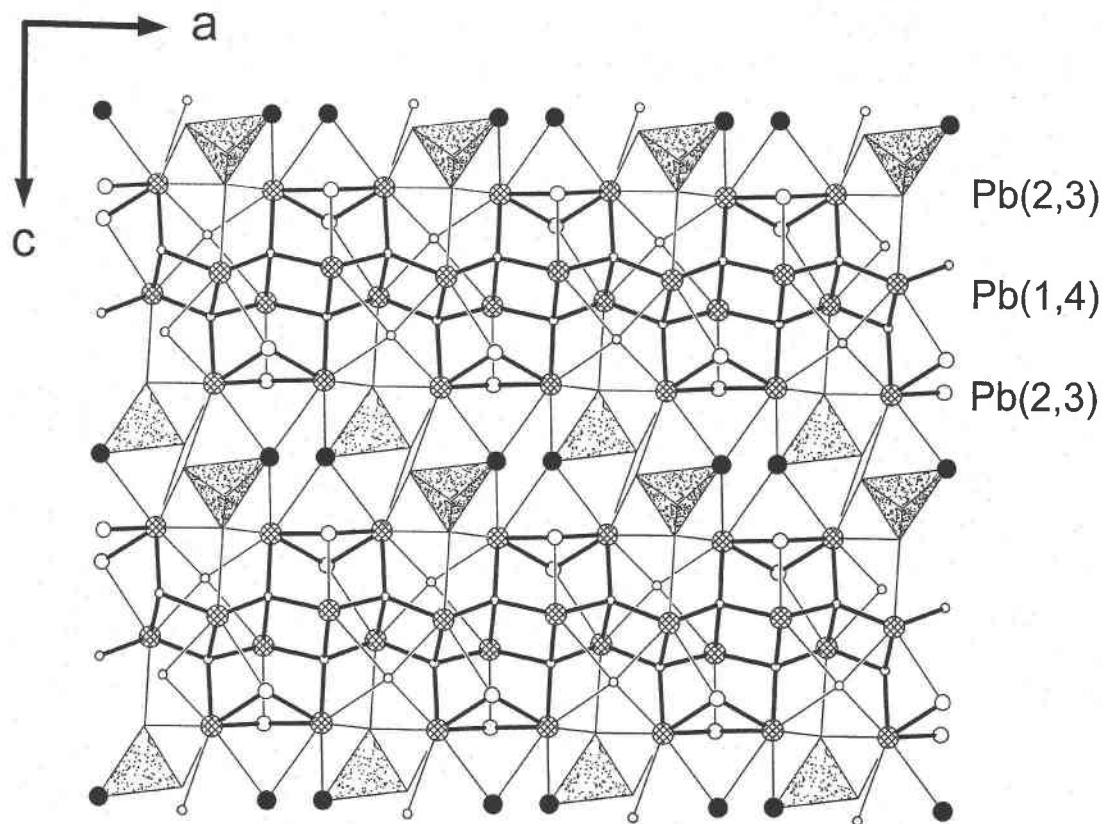
FIG. 4.    The crystal structure of sidpietersite viewed down an axis 5° from [010]; legend as in Figures 1 and 2.

that a group involving such a weak bond would occur with such reproducible stereochemistry in a range of structures. Thus it does not seem possible that the formal valences of S in the thiosulfate group are $5^+$ and $1^-$.

## REFERENCES

AKA, Y., ARMAĞAN, N. & URAZ, A.A. (1980): An X-ray diffraction study of barium thiosulphate monohydrate, $BaS_2O_3 \cdot H_2O$. Z. Kristallogr. **151**, 61-66.

ANDERSSON, J.-E. & BOSSON, B. (1976): Thallium(I) thiosulphate. Acta Crystallogr. **B32**, 2225-2227.

BAGGIO, S., PARDO, M.I., BAGGIO, R. & GONZÁLEZ, O. (1997): Cadmium thiosulfate dihydrate. Acta Crystallogr. **C53**, 1521-1523.

BRESE, N.E. & O'KEEFFE, M. (1991): Bond-valence parameters for solids. Acta Crystallogr. **B47**, 192-197.

BROWN, I.D. (1981): The bond-valence method: an empirical approach to chemical structure and bonding. In Structure and Bonding in Crystals II (M. O'Keeffe and A. Navrotsky, eds.). Academic Press, New York, N.Y. (1-30).

CAVALCA, L., MANGIA, A., PALMIERI, C. & PELIZZI, G. (1970): The crystal and molecular structure of $NaAgS_2O_3 \cdot H_2O$. Inorg. Chim. Acta **4**, 299-304.

CHRISTENSEN, N.A., HAZELL, R.G., HEWAT, A.W. & O'REILLY, K.P.J. (1991): The crystal structure of Pb $S_2O_3$. Acta Chem. Scand. **45**, 469-473.

CHRISTIDIS, P.C. & RENTZEPERIS, P.J. (1985): Experimental charge density in polythionate anions. I. X-ray study of electron density distribution in potassium trithionate, $K_2S_3O_6$. Z. Kristallogr. **173**, 59-74.
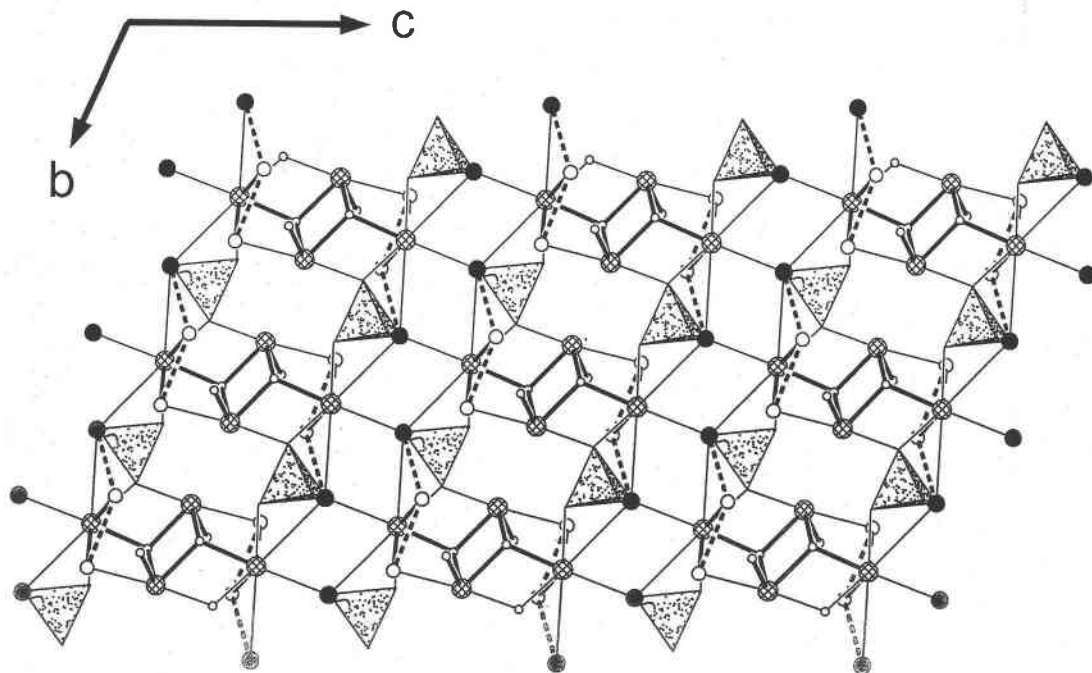
FIG. 5.   The crystal structure of sidpietersite viewed down an axis 3° from [100]; legend as in Figures 1 and 2; the broken lines indicate H bonds.

COOPER, M. & HAWTHORNE, F.C. (1994): The crystal structure of kombatite, $Pb_{14}(VO_4)_2O_9Cl_4$, a complex heteropolyhedral-sheet mineral. *Am. Mineral.* **79**, 550-554.

CSORDAS, L. (1969): The crystal structure of potassium thiosulphate 1/3 hydrate. *Acta Chim. Acad. Sci. Hungar.* **62**, 371-393.

ELERMAN, Y., BATS, J.W. & FUESS, H. (1983): Deformation density in complex anions. IV. Magnesium thiosulfate hexahydrate, $MgS_2O_3 \cdot 6H_2O$. *Acta Crystallogr.* **C39**, 515-518.

_____, URAZ, A.A. & ARMAĞAN, N. (1978): An X-ray diffraction study of nickel thiosulphate hexahydrate. *Acta Crystallogr.* **B34**, 3330-3332.

GJERRESTAD, K. & MARØY, K. (1973): The crystal structure of barium telluropentathionate trihydrate. *Acta Chem. Scand.* **27**, 1653-1666.

HAWTHORNE, F.C. (1994): Structural aspects of oxides and oxysalt crystals. *Acta Crystallogr.* **B50**, 481-510.

_____ (1997): Short-range order in amphiboles: a bond-valence approach. *Can. Mineral.* **35**, 201-216.

HESSE, W., LEUTNER, B., BOEHN, K.H. & WALKER, N.P.C. (1993): Structure of a new sodium thiosulfate hydrate. *Acta Crystallogr.* **C49**, 363-365.

INTERNATIONAL TABLES FOR X-RAY CRYSTALLOGRAPHY (1992): Vol. C., Kluwer Academic Publishers, Dordrecht, The Netherlands.

KUCHA, H., OSUCH, W. & ELSEN, J. (1996): Viaenite, $(Fe,Pb)_4S_8O$, a new mineral with mixed sulphur valencies from Engis, Belgium. *Eur. J. Mineral.* **8**, 93-102.

MARØY, K. (1971a): The crystal structure of potassium pentathionate hemitrihydrate. *Acta Chem. Scand.* **25**, 2580-2590.

_____ (1971b): The crystal structure of rubidium telluropentathionate hemitrihydrate. *Acta Chem. Scand.* **25**, 2557-2568.

ROBERTS, A.C., COOPER, M.A., HAWTHORNE, F.C., CRIDDLE, A.J., STANLEY, C.J., KEY, C.L. & JAMBOR, J.L. (1999): Sidpietersite, $Pb^{2+}_4(S^{6+}O_3S^{2-})O_2(OH)_2$, a new thiosulfate-bearing mineral species from Tsumeb, Namibia. *Can. Mineral.* **37**, 1269-1273.

RUBEN, H., ZALKIN, A., FALTENS, M.O. & TEMPLETON, D.H. (1974): Crystal structure of sodium gold(I) thiosulfate dihydrate, $Na_3Au(S_2O_3)_2 \cdot 2H_2O$. *Inorg. Chem.* **13**, 1836-1839.

SHANNON, R.D. (1976): Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Crystallogr.* **A32**, 751-767.

TENG, S.T., FUESS, H. & BATS, J.W. (1984): Refinement of sodium thiosulfate, $Na_2$ $S_2O_3$ at 120K. *Acta Crystallogr.* **C40**, 1785-1787.

URAZ, A.A. & ARMAĞAN, N. (1977): An X-ray diffraction study of sodium thiosulfate pentahydrate, $Na_2S_2O_3 \bullet 5H_2O$. *Acta Crystallogr.* **B33**, 1396-1399.

VAIRAVAMURTHY, A., MANOWITZ, B., LUTHER, G.W., III & JEON, Y. (1993): Oxidation state of sulfur in thiosulfate and implications for anaerobic energy metabolism. *Geochim. Cosmochim. Acta* **57**, 1619-1623.