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Calcium and strontium thiosulfate, $CaS_2O_3\cdot6H_2O$ and $SrS_2O_3\cdot5H_2O$

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In contrast to former morphological studies, the results presented here show that calcium(II) thiosulfate hexahydrate, $CaS_2O_3\cdot6H_2O$, crystallizes centrosymmetrically in the pinacoidal class (point group $\bar{1}$). The structure is characterized by chains, parallel to [100], of alternating S_2O_3 and $Ca(H_2O)_6O_2$ groups sharing common O atoms. The composition of each chain link is $[Ca(H_2O)_6(S_2O_3)]$. The geometry is analysed and compared in detail with the structural features of monoclinic strontium(II) thiosulfate pentahydrate, $SrS_2O_3\cdot5H_2O$, which forms layers, parallel to (100), of alternating S_2O_3 and $Sr(H_2O)_4O_5$ groups connected *via* common O atoms and O–O edges. Each layer contains $[Sr(H_2O)_3O(S_2O_3)]_\infty$ as the unique repeat unit.

Comment

Because of its distinct asymmetric morphology, many textbooks on crystallography use calcium thiosulfate hexahydrate as the classic example of a compound that crystallizes in the triclinic pedial class (point group $\bar{1}$; Fig. 1*a*). It is of historical interest that $CaS_2O_3\cdot6H_2O$ served Mitscherlich (1826) as an example and proof of the existence of the so-called 'diclinic' crystal system. Not until 1862 did von Zepharovich assign these crystals to the triclinic system; his description agrees well with the results of our morphological studies. Earlier morphological studies are summarized by Groth (1908).

Surprisingly, we found no structural information about $CaS_2O_3\cdot6H_2O$ in the literature. The crystal structures of hydrated thiosulfates of alkaline earth cations are known only for $MgS_2O_3\cdot6H_2O$ (Nardelli *et al.*, 1962; Baggio *et al.*, 1969; Elerman *et al.*, 1982, 1983) and $BaS_2O_3\cdot H_2O$ (Manojlović-Muir, 1975; Nardelli & Fava, 1962; Aka *et al.*, 1980). Both compounds have been investigated in detail by X-ray and neutron diffraction methods. Further structural analyses of thiosulfates with divalent cations have been performed for $CdS_2O_3\cdot2H_2O$ (Baggio *et al.*, 1997) and $NiS_2O_3\cdot6H_2O$ (Elerman *et al.*, 1978), which are isostructural with the magnesium compound. All structurally known thiosulfates of divalent cations are hydrated and crystallize in centrosymmetric space groups. The present paper, which presents the crystal structures of $CaS_2O_3\cdot6H_2O$ and $SrS_2O_3\cdot5H_2O$, extends our knowledge of the crystal chemistry of alkaline earth thiosulfates. Until now, for both compounds, only the unit-cell parameters have been reported (Keglevich, 1958). In contrast to the results of earlier morphological studies, our structure analysis, based on single-crystal X-ray diffraction data, shows that $CaS_2O_3\cdot6H_2O$ crystallizes in the triclinic pinacoidal point group.

In $CaS_2O_3\cdot6H_2O$, the geometry and the bonding properties of the $S_2O_3{}^{2-}$ anions are closely related to those in $MgS_2O_3\cdot6H_2O$ (*e.g.* Elerman *et al.*, 1983) and $NiS_2O_3\cdot6H_2O$ (Elerman *et al.*, 1975). The bond angles around atom S1 deviate from the ideal tetrahedral arrangement only slightly [mean 109.5 (9)°]; the angles and lengths correspond to the π-bonding character of the S—O [mean 1.468 (6) Å] and S—S bonds. Within the standard uncertainties, the S—S distance is equal to those in magnesium and nickel thiosulfate hexahydrates.

The Ca^{2+} cations are eightfold coordinated by O atoms of six symmetry-independent water molecules and of two S_2O_3 groups [mean Ca—O = 2.45 (5) Å; Table 1], thus forming a distorted square antiprism, *viz.* $[Ca(H_2O)_6O_2]$. All water molecules are included in the coordination sphere of the Ca^{2+} cation.

The main characteristics of the $CaS_2O_3\cdot6H_2O$ structure are chains, parallel to [100], of alternating S_2O_3 and $Ca(H_2O)_6O_2$

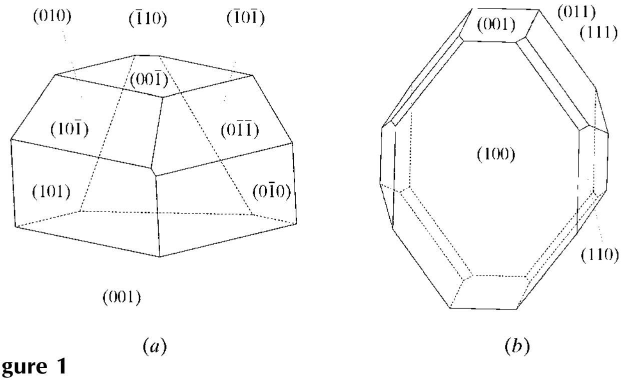

Figure 1
The crystal morphology of (*a*) $CaS_2O_3\cdot6H_2O$ and (*b*) $SrS_2O_3\cdot5H_2O$.

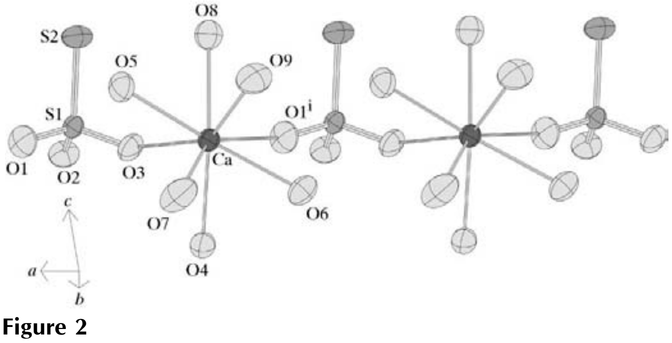

Figure 2
An *ORTEP*III (Burnett & Johnson, 1996) projection of the zigzag chain, *viz.* $[Ca(H_2O)_6(S_2O_3)]_\infty$ (which is parallel to [100]), of alternating S_2O_3 and $Ca(H_2O)_6O_2$ groups, with the atom-numbering scheme. Non-H atoms are shown as 50% probability displacement ellipsoids and H atoms have been omitted for clarity. [Symmetry code: (i) $x + 1, y, z$.]

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groups, which are connected *via* common O atoms (Fig. 2). Each chain link has the composition $[Ca(H_2O)_6(S_2O_3)]$. The arrangement of the atoms, $[\text{–Ca—O—S—O–}]_\infty$, leads to the formation of a zigzag chain in which the Ca atoms are turned towards atoms O1 to form the shortest Ca—O distance inside the Ca coordination polyhedron. Inside the chain, all S_2O_3 and all $Ca(H_2O)_6O_2$ polyhedra are aligned in the same manner.

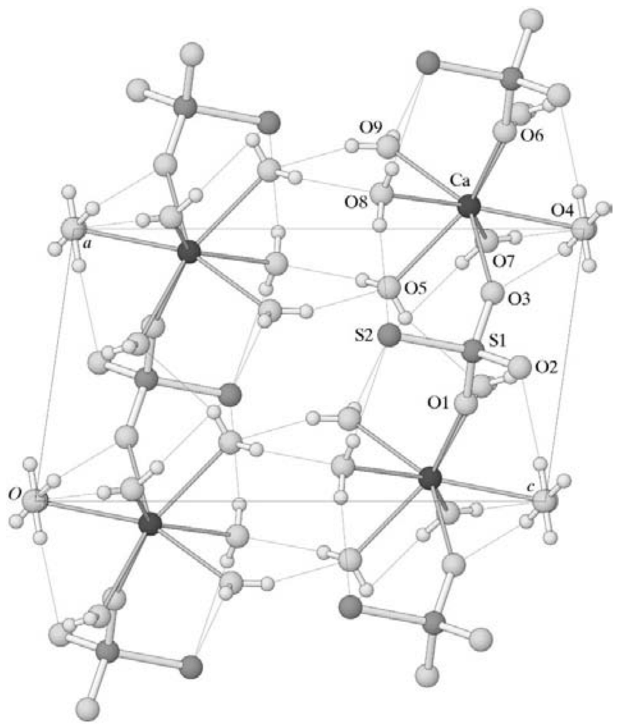

Figure 3
A projection of $CaS_2O_3{\cdot}6H_2O$ along $[0\bar{1}0]$. Hydrogen bonds are shown as thin lines.

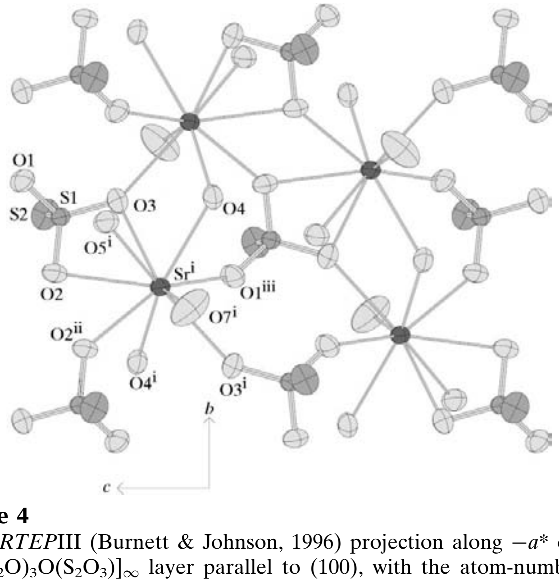

Figure 4
An *ORTEP*III (Burnett & Johnson, 1996) projection along $-a^*$ of the $[Sr(H_2O)_3O(S_2O_3)]_\infty$ layer parallel to (100), with the atom-numbering scheme. Non-H atoms are shown as 50% probability displacement ellipsoids and H atoms have been omitted for clarity. [Symmetry codes: (i) $-x+\frac{1}{2}, y-\frac{1}{2}, -z+\frac{1}{2}$; (ii) $-x+\frac{1}{2}, -y-\frac{1}{2}, -z+\frac{1}{2}$; (iii) $x, -y, z-\frac{1}{2}$.]

A system of hydrogen bonds (Table 2) plays an important role in the stability of the structure. Hydrogen bonds between water molecules and between water molecules and terminal S atoms exist among the chain links and inside the chains (Fig. 3).

As expected, in $SrS_2O_3{\cdot}5H_2O$, the bond distances and angles of the $S_2O_3^{2-}$ anions are similar to those in $BaS_2O_3{\cdot}H_2O$ (*e.g.* Manojlović-Muir, 1975) and $CaS_2O_3{\cdot}6H_2O$. The S—S distance is, however, significantly shorter than that in $CaS_2O_3{\cdot}6H_2O$ (difference 0.013 Å) and longer than that in $BaS_2O_3{\cdot}H_2O$ (difference 0.016 Å), while the S—O distances [mean 1.475 (7) Å] are almost equal. The mean bond angles are nearly the ideal tetrahedral values [mean O—S—O = 109 (2)° and mean S—S—O = 109.4 (6)°], but the O2—S1—O3 angle differs significantly from the average. The thiosulfate group serves as a bidentate ligand and, as a result, the O2$\cdots$O3 distance in the coordination sphere of the Sr^{2+} cation is shorter than the other O$\cdots$O separations.

The Sr^{2+} cation is ninefold coordinated by O atoms of four water molecules (2 × O4, O5 and O7) and four $S_2O_3^{2-}$ anions (one bidentate and three monodentate groups), with a mean distance of 2.67 (8) Å (Table 3). The coordination polyhedron, like that in $CaS_2O_3{\cdot}6H_2O$, can be described as a distorted square antiprism, although it is capped by an additional atom (O2) to form an $Sr(H_2O)_4O_5$ unit.

The main features of the $SrS_2O_3{\cdot}5H_2O$ structure are layers, parallel to (100), of alternating S_2O_3 and $Sr(H_2O)_4O_5$ groups sharing common O atoms and O–O edges, with $[Sr(H_2O)_3O(S_2O_3)]_\infty$ as the unique repeat unit (Fig. 4). The

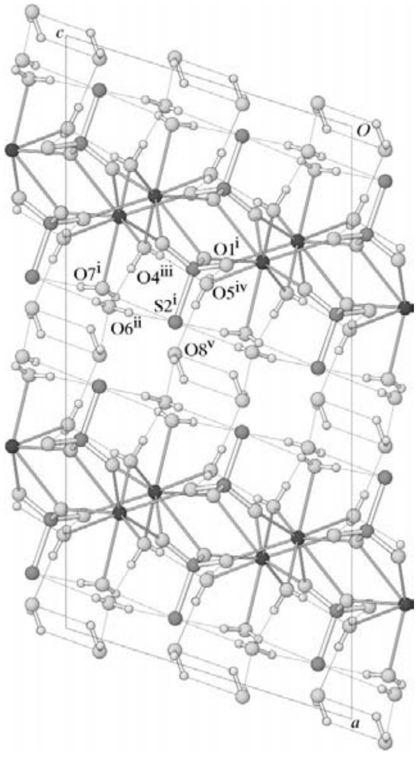

Figure 5
A projection of $SrS_2O_3{\cdot}5H_2O$ along $[0\bar{1}0]$. Hydrogen bonds are shown as thin lines. [Symmetry codes: (i) $x+\frac{1}{2}, y+\frac{1}{2}, z$; (ii) $-x+\frac{1}{2}, y, -z+\frac{1}{2}$; (iii) $-x+1, y, -z+\frac{1}{2}$; (iv) $x+\frac{1}{2}, -y+\frac{1}{2}, z+\frac{1}{2}$; (v) $x+\frac{1}{2}, y-\frac{1}{2}, z$.]

unit cell consists of two layers with a thickness of about 7 Å each and a separation of about 3.5 Å (Fig. 5). The core of the layer is built up from differently oriented symmetry-equivalent $\mathrm{Sr(H_2O)_4O_5}$ groups, while $\mathrm{S_2O_3}$ groups together with water molecules form the border of the layer. All terminal S atoms are directed towards the space between the layers. Both border atoms (S2 and O7) show high thermal motion parallel to the layer plane. Their large anisotropic vibration indicates weak interaction between the layers.

In contrast to that of the Ca compound, the structure of $\mathrm{SrS_2O_3{\cdot}5H_2O}$ contains water molecules outside the coordination sphere of the alkaline earth atom. Two of the five symmetrically independent water molecules (O6 and O8) are positioned between the layers. Both water molecules connect the polyhedron layer *via* hydrogen bonds to water molecules O4, O5 and O7, which belong to the Sr coordination sphere (Fig. 5 and Table 4). Inside the polyhedron layer, hydrogen bonds exist between water molecules O6 and O7 and terminal S2 atoms. As for the Ca compound, the angles between the S—S bond and the H atoms of the bridges are about 90°, whereas the bridge itself is almost linear.

Experimental

Both title alkaline earth thiosulfates were synthesized in two different ways, *viz.* (*a*) *via* reaction of $\mathrm{(NH)_2S_2O_3}$ with $\mathrm{Ca(OH)_2}$ [or $\mathrm{Sr(OH)_2{\cdot}8H_2O}$] in aqueous solution and crystallization of the compounds by evaporation of the solvent at room temperature, and (*b*) *via* reaction of concentrated aqueous solutions of $\mathrm{Na_2S_2O_3{\cdot}5H_2O}$ and $\mathrm{CaCl_2{\cdot}2H_2O}$ [or $\mathrm{Sr(NO_3)_2}$] and crystallization of the compounds by evaporation of the solvent at room temperature. To increase the chemical purity of the crystals, the crystallization was repeated. In both cases, crystals of up to several millimeters were obtained easily. Because the aqueous solutions tend to decompose, the growth of large single crystals suitable for measurements of physical properties is more difficult; to date, all growth experiments have failed. In contrast, crystals of $\mathrm{CaS_2O_3{\cdot}6H_2O}$ and $\mathrm{SrS_2O_3{\cdot}5H_2O}$ are stable for several weeks if they are kept in inert liquids (*e.g.* paraffin oil). The crystal morphologies of both kinds of crystals are shown in Fig. 1.

$\mathrm{CaS_2O_3{\cdot}6H_2O}$

Crystal data

$\mathrm{CaS_2O_3{\cdot}6H_2O}$
$M_r = 260.32$
Triclinic, $P\overline{1}$
$a = 5.8204\ (4)$ Å
$b = 7.4391\ (7)$ Å
$c = 11.2946\ (8)$ Å
$\alpha = 72.537\ (6)°$
$\beta = 81.447\ (6)°$
$\gamma = 87.282\ (6)°$
$V = 461.31\ (7)$ Å^3
$Z = 2$
$D_x = 1.874$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 14.6$–$17.5°$
$\mu = 1.15$ mm^{-1}
$T = 293\ (2)$ K
Parallelepiped, colourless
0.27 × 0.25 × 0.23 mm

Data collection

Enraf–Nonius MACH3 diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (*MolEN*; Fair, 1990)
$T_{\min} = 0.921$, $T_{\max} = 0.999$
5584 measured reflections
2794 independent reflections
2493 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.016$
$\theta_{\max} = 30.4°$
$h = -8 \rightarrow 8$
$k = -10 \rightarrow 10$
$l = -16 \rightarrow 16$
3 standard reflections
frequency: 60 min
intensity decay: 0.4%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.019$
$wR(F^2) = 0.053$
$S = 1.06$
2794 reflections
158 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0286P)^2 + 0.0904P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.42$ e Å^{-3}
$\Delta\rho_{\min} = -0.36$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.895 (13)

Table 1
Selected interatomic distances (Å) for $\mathrm{CaS_2O_3{\cdot}6H_2O}$.

Ca—O1$^{\rm i}$	2.3973 (9)	Ca—O6	2.4854 (9)
Ca—O7	2.3991 (11)	Ca—O8	2.5467 (10)
Ca—O9	2.4066 (10)	S2—S1	2.0080 (4)
Ca—O5	2.4584 (9)	S1—O1	1.4617 (9)
Ca—O4	2.4626 (9)	S1—O2	1.4707 (8)
Ca—O3	2.4834 (8)	S1—O3	1.4717 (8)

Symmetry code: (i) $1 + x, y, z$.

Table 2
Hydrogen-bonding geometry (Å, °) for $\mathrm{CaS_2O_3{\cdot}6H_2O}$.

D—H···A	D—H	H···A	D···A	D—H···A
O4—H41···O3$^{\rm i}$	0.77 (3)	2.13 (3)	2.8834 (13)	166 (2)
O4—H42···O2$^{\rm ii}$	0.79 (2)	2.15 (2)	2.9035 (13)	160 (2)
O5—H51···O8$^{\rm iii}$	0.81 (2)	2.09 (2)	2.8667 (13)	161.5 (18)
O5—H52···O6$^{\rm iv}$	0.74 (2)	2.28 (2)	2.9878 (14)	160 (2)
O6—H61···O2$^{\rm v}$	0.81 (2)	2.08 (2)	2.8861 (13)	173 (2)
O6—H62···O2$^{\rm i}$	0.74 (2)	2.20 (2)	2.9118 (12)	165 (2)
O7—H71···S2$^{\rm vi}$	0.81 (2)	2.68 (2)	3.4904 (11)	175 (2)
O7—H72···O4$^{\rm vii}$	0.75 (3)	2.12 (3)	2.8656 (14)	171 (2)
O8—H81···S2$^{\rm viii}$	0.74 (2)	2.68 (2)	3.4116 (10)	168.1 (19)
O8—H82···S2	0.82 (3)	2.52 (3)	3.3177 (10)	164 (2)
O9—H91···S2$^{\rm v}$	0.74 (3)	2.74 (3)	3.4437 (12)	159 (3)
O9—H92···O5$^{\rm iii}$	0.78 (2)	2.20 (2)	2.9034 (15)	151 (2)

Symmetry codes: (i) $1 - x, -y, 1 - z$; (ii) $-x, -y, 1 - z$; (iii) $1 - x, -y, -z$; (iv) $x - 1, y, z$; (v) $1 + x, y - 1, z$; (vi) $x, y - 1, z$; (vii) $1 - x, -1 - y, 1 - z$; (viii) $1 + x, y, z$.

$\mathrm{SrS_2O_3{\cdot}5H_2O}$

Crystal data

$\mathrm{SrS_2O_3{\cdot}5H_2O}$
$M_r = 289.84$
Monoclinic, $C2/c$
$a = 21.005\ (3)$ Å
$b = 8.1371\ (6)$ Å
$c = 10.587\ (1)$ Å
$\beta = 107.78\ (1)°$
$V = 1723.2\ (3)$ Å^3
$Z = 8$
$D_x = 2.234$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 13.3$–$16.3°$
$\mu = 6.75$ mm^{-1}
$T = 293\ (2)$ K
Parallelepiped, colourless
0.25 × 0.24 × 0.22 mm

Data collection

Enraf–Nonius MACH3 diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (*MolEN*; Fair, 1990)
$T_{\min} = 0.889$, $T_{\max} = 1.000$
6468 measured reflections
2614 independent reflections
1605 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.085$
$\theta_{\max} = 30.5°$
$h = -29 \rightarrow 29$
$k = -11 \rightarrow 11$
$l = -15 \rightarrow 15$
3 standard reflections
frequency: 60 min
intensity decay: −14.6%

Table 3
Selected interatomic distances (Å) for $SrS_2O_3\cdot 5H_2O$.

Sr—O2^{i}	2.568 (3)	Sr—O3^{ii}	2.730 (3)
Sr—O4^{ii}	2.624 (3)	Sr—O2^{ii}	2.840 (3)
Sr—O4	2.638 (3)	S1—O1	1.467 (3)
Sr—O3	2.637 (3)	S1—O2	1.477 (3)
Sr—O5	2.650 (3)	S1—O3	1.481 (3)
Sr—O7	2.651 (4)	S1—S2	1.9952 (14)
Sr—O1^{iii}	2.672 (3)		

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

Table 4
Hydrogen-bonding geometry (Å, °) for $SrS_2O_3\cdot 5H_2O$.

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O4—H41$\cdots$O5^{i}	0.75 (4)	1.98 (4)	2.725 (4)	171 (6)
O4—H42$\cdots$O6	0.94 (6)	1.83 (6)	2.767 (5)	174 (5)
O5—H51$\cdots$O1^{ii}	0.71 (5)	2.19 (5)	2.898 (4)	174 (6)
O5—H52$\cdots$O8^{ii}	0.85 (6)	1.87 (6)	2.720 (6)	175 (6)
O6—H61$\cdots$S2^{iii}	0.75 (4)	2.58 (4)	3.320 (4)	166 (6)
O6—H62$\cdots$S2^{iv}	0.86 (4)	2.46 (4)	3.321 (4)	173 (8)
O7—H71$\cdots$S2^{v}	0.82 (5)	2.72 (5)	3.518 (6)	168 (11)
O7—H72$\cdots$S2	0.77 (4)	2.58 (4)	3.346 (5)	172 (6)
O8—H81$\cdots$O6^{vi}	0.93 (5)	2.00 (8)	2.841 (7)	150 (11)
O8—H82$\cdots$O7^{vii}	0.89 (5)	2.20 (5)	2.994 (7)	148 (2)

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

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.031$
$wR(F^2) = 0.082$
$S = 1.04$
2614 reflections
141 parameters
All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0259P)^2$
$+ 3.0808P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.95$ e Å^{-3}
$\Delta\rho_{min} = -0.91$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0032 (2)

For $CaS_2O_3\cdot 6H_2O$, refinement calculations were carried out in space groups $P1$ and $P\overline{1}$. The results of the centrosymmetric setting showed significantly smaller residual factors ($\Delta R1 = -0.002$ and $\Delta wR2 = -0.011$), together with lower standard uncertainties of the atomic coordinates and distances (75–80% less). We tried to detect the piezoelectric effect in order to prove the absence of the centre of symmetry. However, measurements of several crystals were ambiguous because the method is sensitive to traces of surface decomposition products. The decomposition of the crystals in the laser beam prevented our attempts of SHG (second harmonic generation) power testing. For $SrS_2O_3\cdot 5H_2O$, distance restraints were placed on the O4—H41, O6—H61, O6—H62, O7—H71, O7—H72, O8—H81 and O8—H82 distances [with a target value of 0.82 (5) Å].

For both compounds, data collection: *MACH*3 *Server Software* (Enraf–Nonius, 1993); cell refinement: *MACH*3 *Server Software*; data reduction: *MolEN* (Fair, 1990); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ATOMS* (Dowty, 2002) and *ORTEP*III (Burnett & Johnson, 1996); software used to prepare material for publication: *SHELXL*97.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ1168). Services for accessing these data are described at the back of the journal.

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