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Structure Redetermination of $SrS_2O_6.4H_2O$

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Abstract

The present structure determination of $SrS_2O_6.4H_2O$ has been performed in a unit cell which is four times larger than assumed in previous structure determinations, *i.e.* relatively faint reflections with h or k odd have now been included in the calculation. The disordered structural model in the small (incorrect) unit cell is compatible with eight different ordered arrangements in the large unit cell; diffraction data clearly favour one of these arrangements. The structure is trigonal, being minutely deviated from hexagonal symmetry. There are weak hydrogen bonds between water molecules, as well as between water and dithionate molecules. Each Sr atom is coordinated by four water molecules and four dithionate oxygens.

Introduction

The aim of this work was to determine the correct space group and to derive the structural model of $SrS_2O_6.4H_2O$ in a large unit cell, using relatively weak reflections, $h = 2n + 1$ or $k = 2n + 1$, which have been overlooked in previous structure determinations (Hargreaves & Stanley, 1972; de Matos Gomes, 1991*b*).

There have been contradictory reports concerning the symmetry of the title compound. Ferrari, Cavalca & Nardelli (1946) determined in their pioneering work the lattice parameters of $SrS_2O_6.4H_2O$ ($a = 12.84$, $c = 19.28$ Å), suggesting $P6_1$ or $P6_122$ (or the respective enantiomorphic space groups). Hargreaves & Stanley (1972) and de Matos Gomes (1991*b*) reported the space group to be $P6_2$ and $P6_422$, respectively; however, the latter two structure determinations were performed in a small incorrect unit cell, the length of the lattice parameter a (and b) being only half that reported by Ferrari, Cavalca & Nardelli (1946).

Koval'chuk & Perekalina (1972) concluded from the observation of second harmonics along the optical axis (ruby laser) that $SrS_2O_6.4H_2O$ is trigonal and not hexagonal, and they proposed crystal class 32. The results of electrorestrictive and electrooptic studies (Haussuehl, 1994; Haussuehl & Chrosch, 1991) favoured trigonal symmetry (point group 32). Haussuehl (1994) studied the elastic properties of $SrS_2O_6.4H_2O$. The elastic constant c_{14} was found to be too small for an unambiguous assignment of trigonal symmetry.

Haussuehl (1994) also mentioned the frequent occurrence of twinning in $SrS_2O_6.4H_2O$, which can be deduced from the morphology of the crystals; the dominant twin operation is a twofold axis parallel with the c-axis.

Information on compounds similar to $CaS_2O_6.4H_2O$ and $PbS_2O_6.4H_2O$ is given at the end of the article.

Precession photographs (de Matos Gomes, 1992) revealed the existence of faint reflections, which indicated doubling of the length of the a and b crystal axes with respect to the previous structure determinations; the lattice parameters thus correspond to those found by Ferrari, Cavalca & Nardelli (1946). These reflections were observed on different samples (de Matos Gomes, 1992), including those used in the previous structure determination (de Matos Gomes, 1991*b*).

The existence of weak reflections implied that the structure model proposed by de Matos Gomes (1991*b*), which exhibited disordered dithionate molecules in $P6_422$, may be considered as a superposition of the contents of the four subcells of the large unit cell, whose dimensions are equal to the dimension of the small unit cell. The subcells are linked by the translations $(t_1,t_2,0)$, where t_1 and t_2 may equal 0 or $\frac{1}{2}$.

Structure determination

Crystal data and experimental conditions are given in Table 1, while refinement data of different structural models are given in Table 2. The raw data were processed by the program *ZPRAC* (Fábry, 1993) and the scattering factors were taken from Cromer & Mann (1968).

Idealized positions of Sr atoms and water oxygens in the large unit cell can be unequivocally derived by copying these atoms from the small into the large unit cell, *i.e.* the resulting positions of the respective atoms are related by the translations $(\frac{1}{2},0,0)$, $(0,\frac{1}{2},0)$ and $(\frac{1}{2},\frac{1}{2},0)$. However, the dithionate molecules in the previous structure determination are disordered (Fig. 1) and, therefore, several different structure models without disorder may be inferred.

In the first step, the disordered molecules A, B and C in Fig. 1 are considered to be unrelated by symmetry, *i.e.* no symmetry condition is imposed on a structural pattern generated in the large unit cell. The only condition which

Table 1. *Summary of crystal data and data collection*

Crystal data	
Chemical formula	$SrS_2O_6.4H_2O$
M_r	319.79
Crystal system	Trigonal
Space group	$P3_2$
a (Å)	12.692 (5)
b (Å)	19.186 (9)
V (Å^3)	2676
Z	12
$F(000)$	1896
D_x (Mg m^{-3})	2.380
No. of reflections for cell parameters	22
Radiation	Mo $K\alpha$
λ (Å)	0.71073
θ range for cell parameters (°)	10–19
μ (mm^{-1})	6.342
T (K)	290
Crystal source	Reaction of $Sr(OH)_2$ with an aqueous solution of MnS_2O_6; crystals were grown by slow evaporation at 290 K
Crystal form	Sphere (*International Tables for X-ray Crystallography*, 1959, Vol. II, Table 5.3.6B)
Crystal size (mm)	$r = 0.22$
Crystal colour	Clear, colourless; became reddish (*cf.* Hargreaves & Stanley, 1972)
Data collection	
Diffractometer	Enraf–Nonius CAD-4 (graphite monochromator)
Scan	$\omega/2\theta$
Absorption correction	Sphere
T_{min}	0.146
T_{max}	0.172
Observation criterion	$I > 3\sigma(I)$
No. of measured reflections	16 058 (8533 observed)
No. of independent reflections	10 330 (5789 observed)
θ_{max} (°)	30
Range of $h, k, l,$	$0 \rightarrow 17$ $-17 \rightarrow 15$ $-26 \rightarrow 26$
R_{int} (all/observed only)	0.0393/0.0265
R_{esd}* (all/observed only)	0.0810/0.0260
No. of standards	3
Monitoring interval (s)	7200
Variation of standards (%)	5

* R_{esd} is defined as $\sum_h$ e.s.d. $(F_h)/\sum_h F_h$.

a structural pattern in the large unit cell must fulfil is that each set of four molecules, which is derived from the respective A, B and C positions (Fig. 1), must consist of two pairs of parallel molecules. Fig. 2 depicts all the possible arrangements of A, B and C molecules. Any $A_xB_yC_z$ pattern resulting from the combination of any arrangement of A_x, B_y and C_z ($x,y,z \in \langle 1,6 \rangle$), given in Fig. 2, is compatible with the disordered structure in the small unit cell (Fig. 1). However, some of these $A_xB_yC_z$ patterns ($x,y,z \in \langle 1,6 \rangle$) are equivalent through the translations $t_1 = (0,\frac{1}{2},0)$, $t_2 = (\frac{1}{2},0,0)$ and $t_3 = (\frac{1}{2},\frac{1}{2},0)$; they only differ by the choice of the origin of the unit cell. The rotations of the point group 622 about the origin of the unit cell or the points translated by t_1, t_2 and t_3 may also bring some of the patterns into coincidence. The rotations permute the A,B,C patterns. All operations are

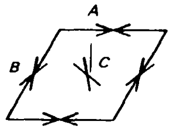

Fig. 1. Projection (along the c-axis) of the arrangement of disordered dithionate molecules in the small unit cell (see text). The dithionate molecules are represented by S—S connections. The disordered pairs of dithionate molecules labelled as A, B and C are related by the 6_2 (3_2) or 6_4 (3_1) axes. The orientation of the unit cell is the same as in Fig. 4.

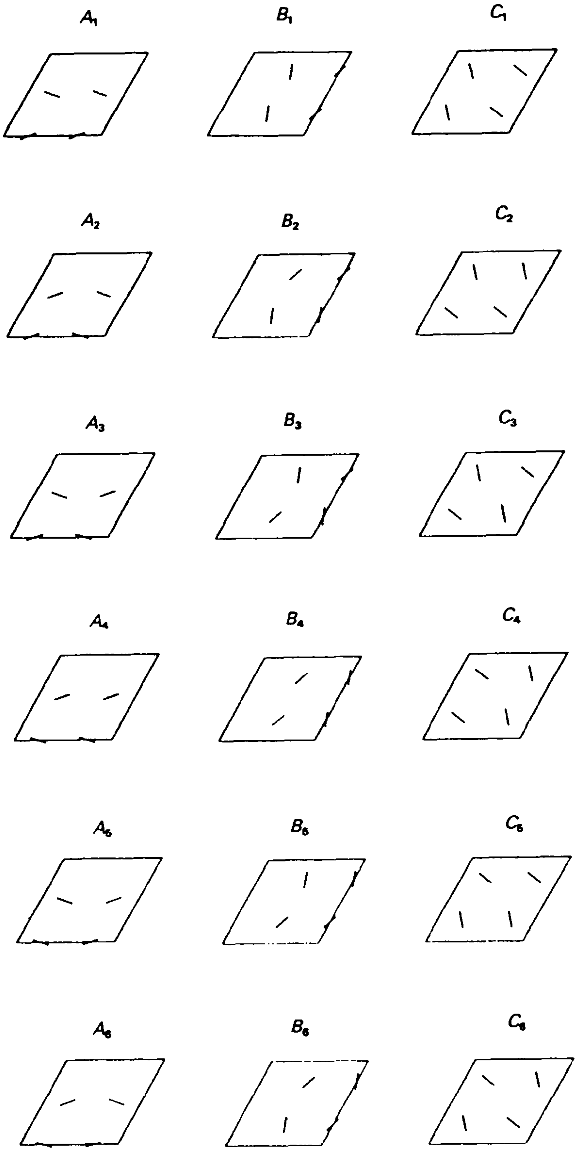

Fig. 2. All possible arrangements of the A, B and C dithionate molecules in the large unit cell (orientation as in Fig. 4). The labels and z-coordinates of the dithionate molecules correspond to those given in Fig. 1

Table 2. *Results of refinement of different models*

The weights in all cases were $w = [\sigma^2(F_o) + (0.01|F_o|)^2]^{-1}$.

Space group	$P3_2$*	$P3_1$	$P6_2$	$P6_4$	$P6_222$†	$P6_422$†
No. of refined parameters	468	468	236	236	49	49
No. of reflections used in refinement (all/observed)	10330/5789	10330/5789	5175/3333	5175/3333	651/603	651/603
$R_{\rm int}$ (all/observed)	0.0393/0.0265	0.0393/0.0265	0.0702/0.0573	0.0702/0.0573	0.0504/0.0484	0.0504/0.0484
$R_{\rm esd}$‡ (all/observed)	0.0810/0.0260	0.0810/0.0260	0.0522/0.0229	0.0522/0.0229	0.0106/0.0084	0.0106/0.0084
$R_{\rm all}$	0.1109	0.1208	0.1031	0.1119	0.0459	0.0525
$wR_{\rm all}$	0.0589	0.0685	0.0690	0.0761	0.0890	0.0920
$R_{\rm obs}$	0.0436	0.0557	0.0537	0.0637	0.0420	0.0488
$wR_{\rm obs}$	0.0506	0.0614	0.0613	0.0694	0.0861	0.0892
S	2.08	2.42	2.85	3.15	2.56	2.65
$\Delta/\sigma_{\rm max}$	0.03	0.03	0.01	0.01	0.01	0.01
$\Delta\rho_{\rm max}$ (e Å^{-3})	3.36	4.74	2.86	3.94	1.05	1.04
$\Delta\rho_{\rm min}$ (e Å^{-3})	−3.05	−5.04	−2.77	−4.89	−1.21	−1.11
Maximum correlation	0.721	0.747	0.770	0.780	0.898	0.902

* The coordinates, $U_{\rm eq}$, and relevant interatomic distances and angles pertinent to the refinement of this model are given in Tables 6, 7 and 8.

† Refinement of this model has been performed in a small unit cell using the reflections with *h* and *k* even only.

‡ $R_{\rm esd}$ is defined as $\sum_h$ e.s.d. $(F_h)/\sum_h F_h$.

equivalent to the selection of different unit cells within a pattern $A_xB_yC_z$.

In order to test which variants of $A_xB_yC_z$ are equivalent, two computer programs were written: the first performed the multiplications of the aforementioned symmetry operations acting on the A_x, B_y and C_z patterns and yielded the transformations of the A_x, B_y and C_z patterns by the powers of sixfold rotations, their products with twofold rotations and *vice versa*, and the products of all these operations with the translations t_1, t_2 and t_3. The second program tested the coincidence of the A_x,B_y,C_z patterns after performing these transformations, and selected the patterns which could not be brought into coincidence. These patterns are $A_1B_1C_1$, $A_1B_1C_3$, $A_1B_2C_1$, $A_1B_2C_2$, $A_1B_3C_1$, $A_2B_2C_1$, $A_2B_2C_2$ and $A_2B_3C_2$ and are shown in Figs. 3(*a*–*h*).

So far no assumption has been made about the symmetry of the deduced $A_xB_yC_z$ patterns. The imposed symmetry bears another restriction on the patterns. The six- and threefold symmetries impose constraints on the arrangements of *A*, *B* and *C* molecules. In fact, among the patterns given above there is only one with hexagonal and only one with trigonal symmetry. When the origin of the unit cell is chosen to lie on the corresponding six- and threefold axes, the arrangements $A_4B_1C_3$ [Fig. 3(*a*)] and $A_2B_6C_2$ [Fig. 3(*b*)] are obtained, respectively.

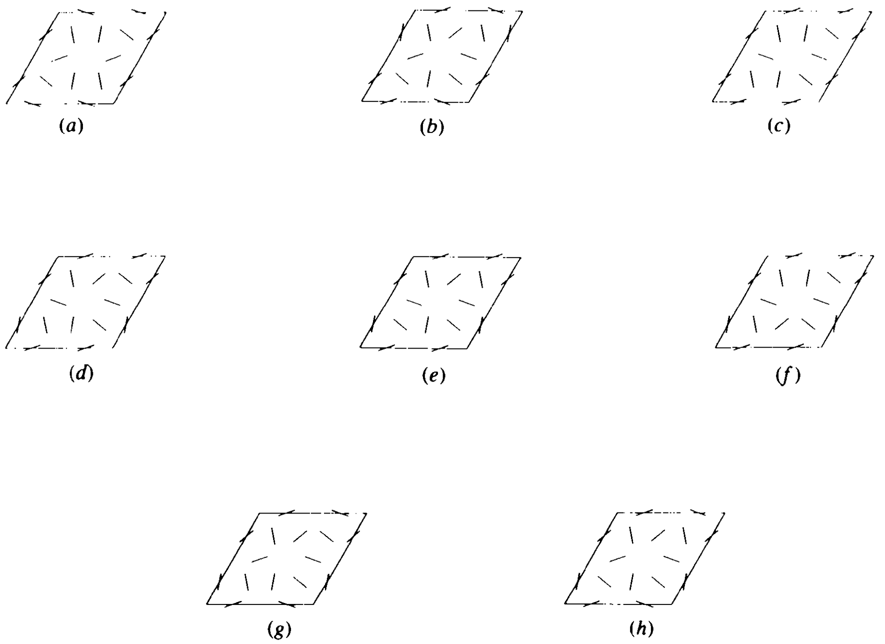
(*a*) (*b*) (*c*) (*d*) (*e*) (*f*) (*g*) (*h*)

Fig. 3. The different $A_xB_yC_z$ arrangements of the dithionate molecules in the large unit cell (orientation as in Fig. 4). (*a*) $A_4B_1C_3 = A_1B_1C_3$ (this arrangement is compatible with hexagonal symmetry); (*b*) $A_2B_6C_2 = A_2B_3C_2$ (this arrangement is incompatible with a hexagonal symmetry, but it is compatible with trigonal or triclinic); (*c*) $A_1B_1C_1$ ($P1$); (*d*) $A_1B_2C_1$ ($P1$); (*e*) $A_1B_2C_2$ ($P1$); (*f*) $A_1B_3C_1$ ($P1$); (*g*) $A_2B_2C_1$ ($P1$); (*h*) $A_2B_2C_2$ ($P1$).

Table 3. *Averaging of 60° reflection segments*

Segment 1 ($h \ge 0 \cap k > 0$) contains 5158 reflections; segment 2 ($h \ge 0 \cap k \le 0 \cap h > |k|$) contains 5154 reflections; segment 3 ($h > 0 \cap k \le 0 \cap h \le |k|$) contains 5156 reflections.

Averaging of all reflections	Segments 1 & 3	Segments 1 & 2	Segments 2 & 3
Reflections ($h = 2n \cup 2n + 1$; $k = 2n \cup 2n + 1$)			
Number of reflections after averaging unobserved/observed only	5161/3097	5160/3146	5159/3109
R_{int}: unobserved/observed only	0.0398/0.0269	0.0614/0.0552	0.0596/0.0545
*R_{esd}: unobserved/observed only	0.0653/0.0252	0.0661/0.0258	0.0675/0.0256
Reflections with h and k even			
Number of reflections after averaging unobserved/observed only	1277/1063	1277/1095	1277/1082
R_{int}: unobserved/observed only	0.0199/0.0117	0.0434/0.0420	0.0425/0.0412
*R_{esd}: unobserved/observed only	0.0187/0.0156	0.0195/0.0123	0.0200/0.0121
Reflections with at least one of the indices h, k odd			
Number of reflections after averaging unobserved/observed only	3884/2034	3883/2051	3882/2027
R_{int}: unobserved/observed only	0.0654/0.0472	0.0831/0.0789	0.0802/0.0786
*R_{esd}: unobserved/observed only	0.1210/0.0492	0.1230/0.0498	0.1252/0.0500
Averaging of reflections for which $I \ge 10\sigma(I)$ (segments 1, 2 & 3 contain 1533, 1472 and 1484 reflections, respectively)			
Reflections ($h = 2n \cup 2n + 1$; $k = 2n \cup 2n + 1$)			
number of reflections after averaging	1569	1653	1626
R_{int}	0.0140	0.0313	0.0308
*R_{esd}	0.0104	0.0112	0.0111
Reflections with h and k even			
number of reflections after averaging	812	854	840
R_{int}	0.0127	0.0272	0.0272
*R_{esd}	0.0078	0.0083	0.0082
Reflections with at least one of the indices h, k odd			
number of reflections after averaging	757	799	786
R_{int}: unobserved/observed only	0.0185	0.0461	0.0439
*R_{esd}: unobserved/observed only	0.0189	0.0203	0.0205
Averaging of reflections for which $I \ge 30\sigma(I)$ (segments 1, 2 & 3 contain 817, 807 and 806 reflections, respectively)			
Reflections ($h = 2n \cup 2n + 1$; $k = 2n \cup 2n + 1$)			
number of reflections after averaging	821	850	844
R_{int}	0.0129	0.0237	0.0235
*R_{esd}	0.0065	0.0066	0.0067
Reflections with h and k even			
number of reflections after averaging	608	621	622
R_{int}	0.0122	0.0218	0.0219
*R_{esd}	0.0062	0.0062	0.0063
Reflections with at least one of the indices h, k odd			
number of reflections after averaging	213	229	222
R_{int}: unobserved/observed only	0.0184	0.0406	0.0369
*R_{esd}: unobserved/observed only	0.0088	0.0093	0.0094

* R_{esd} is defined as $\sum_h$ e.s.d. $(F_h)/\sum_h F_h$.

$A_xB_yC_z$ arrangements compatible with twofold symmetry are combinations of the patterns A_1, B_1, C_3, A_4, B_4 and C_6, since each of these possesses twofold symmetry. However, such a combination is equivalent to the pattern possessing sixfold symmetry. Thus, an arrangement which exhibits twofold but not sixfold symmetry cannot be constructed unless the condition that the arrangement of the respective A, B and C molecules be in two parallel pairs is abandoned.

Therefore, other listed patterns are only compatible with the space group $P1$ [Figs. 3(*c*)–(*h*)]. The calculation of Patterson maps from these $P1$ variants revealed that no two structures are homometric.

The observed systematic absences 00l, $l \neq 3n$, indicate that the space groups $P6_4$ or $P3_1$ and their enantiomorphic counterparts agree best with the observed diffraction pattern. (The space groups $P6_422$, $P3_121$ and $P3_112$, as well as the respective enantiomorphic variants, are excluded from further consideration relating to a structural model in a large unit cell, since the twofold rotations perpendicular to the main axis would restore the pattern given in Fig. 1, which does not explain the observed reflections with h or k odd.) Averaging the reflections indicated that threefold symmetry should be preferred (Table 3). The measured reflections from one half of the reflection sphere may be divided into three 60° segments, each pair of segments being linked by either 60 or 120° rotations. Averaging the reflections from these pairs of segments, which are related by six- or threefold symmetry, favours the trigonal symmetry of the studied crystal. Table 3 provides evidence that all parity classes of indices are sensitive to distinguishing between trigonal and hexagonal symmetries. It may also be seen that the proportion of reflections with the indices

Table 4. *Results of refinement of different models in $P3_2$ with assumed twinning (twofold rotation about a trigonal axis)*

The weights in all cases were $w = [\sigma^2(F_o) + (0.01 \cdot |F_o|)^2]^{-1}$.

Model	Refinement on all reflections; anisotropic displacement factors	Refinement on all reflections; isotropic displacement factors	Refinement on observed reflections only; anisotropic displacement factors	Refinement on observed reflections only; isotropic displacement factors
No. of refined parameters	469	209	469	209
No. of reflections used in refinement, all/observed	10 330/5789	10 330/5789	5789/5789	5789/5789
R_{all}	0.1037	0.1162	—	—
wR_{all}	0.0575	0.0723	—	—
R_{obs}	0.0436	0.0584	0.0427	0.0581
wR_{obs}	0.0503	0.0663	0.0494	0.0661
S	2.03	2.52	2.37	3.10
$\Delta/\sigma_{\text{max}}$	0.03	0.03	0.03	0.03
Maximal correlation between refined parameters	0.764	0.720	0.760	0.741
Domain fraction parameter f	0.158 (3)	0.224 (2)	0.120 (4)	0.208 (3)

h and *k* even increases with the growing intensity of the reflections, while the deviation from hexagonality becomes less recognizable on these reflections.

Least-squares refinement (Table 2) with the *SDS* program system (Petříček & Malý, 1988) favours the arrangement of dithionate molecules given in Fig. 3(*a*). The ratio of *wR* (all reflections) of the refinements in $P6_2$ and $P3_2$ is 6.90/5.89 = 1.171. $R_{232,9862,0.005} = 1.014$ [*International Tables for X-ray Crystallography* (1974, IV); Hamilton, 1965; Winter, 1981]. This result also suggests that the structure is trigonal and not hexagonal.

At the beginning of the refinement in $P3_2$, the dithionate molecules were constrained to a fixed geometry and their molecular and positional parameters were refined. The molecular geometry was obtained from the refinement in space group $P6_2$ (the differences between the two dithionate molecules which resulted from the refinement in $P6_2$ were negligible). After this refinement converged, all the atoms were refined independently.

The absolute configuration (*i.e.* the choice between space groups $P3_2$ and $P3_1$) was determined using the formalism given by Flack (1983). The inversion twin parameter x was refined in $P3_2$ to the value 0.042 (16). As the crystals were grown from aqueous solution, this value is very close to the physically realistic value 0.0, which was adopted at the final stages of the refinement.

The results of the refinements in different space groups given in Table 2 indicate that the models of the same chirality are favoured in all cases. With regard to the connection between the optical chirality and the absolute configuration established by de Matos Gomes (1991*a*), we conclude that the present crystal ($P3_2$) is, therefore, laevorotatory.

Successful refinement in $P6_422$ in the small unit cell was possible due to additional pseudo-symmetry: R_{int} (calculated on observed reflections with $h = 2n$, $k = 2n$ only) equals 0.0484, 0.0422 and 0.0166, if the symmetry of the diffraction pattern is assumed to be 622, 6 and 3, respectively.

The maxima and minima in the difference electron-density map were found at 0.2–0.55 Å from the Sr atoms.

The results of refinements of different models with twinning included (twinning operation is a twofold rotation parallel to the *c*-axis) are given in Table 4.

Discussion

The results of this study together with the previous experiment of Koval'chuk & Perekalina (1972) suggest that the present structure is trigonal, even though it only slightly deviates from hexagonal symmetry.

In fact, the refinement of the model which included refinement of the domain fraction resulted in lower *R*-factors and goodness-of-fit (Table 4) and even the Hamilton *R*-ratio test favours the model with twinning ($R_{1,9861,0.005} = 1.0004$, while the ratio of the weighted *R*-factors of the models without and with twinning is 0.0589/0.0575 = 1.0243).

However, there are certain indications which make the presence of twinning in the present model rather dubious:

(1) The result is influenced by the unobserved reflections. The refinement on observed reflections yields a value significantly different to the domain fraction (Table 4).

(2) When performing a refinement with isotropic displacement factors, the values of the domain factor again differ (Table 4). This is not in accordance with the same type of twinning observed in $K_3Na(CrO_4)_2$, which crystallizes in space group $P\bar{3}m1$ (Fábry, Breczewski & Madariaga, 1994).

Table 3 suggests that the more intensive reflections $h = 2n$ and $k = 2n$ are less sensitive to deviations of the structure from hexagonality, and that this parity class prevails among the most intensive reflections (see also Table 5). On the other hand, Table 5, which lists the dependence of *R*-factors on the magnitudes of $|F_{\text{obs}}|$, shows that the most intensive reflections with h and k even are accounted for with a minute difference for either of the models. Table 5 also shows that only part

Table 5. *Partial R-factors of the models without and with twinning* [$f = 0.158\,(3)$, *cf.* *Table* 4] *for all reflections, reflections with h and k even and reflections with h or k odd*

Lower/upper limits of $\lvert F_{obs}\rvert$	0.0 ≤ 7.2	7.2 ≤ 8.5	8.5 ≤ 9.8	9.8 ≤ 11.4	11.4 ≤ 13.8	13.8 ≤ 20.1	20.1 ≤ 43.8	43.8 ≤ 195.2
All reflections								
number of reflections	690	735	725	733	725	731	725	725
average $I_{obs}/\sigma(I_{obs})$	4.83	6.00	7.86	11.31	16.63	30.40	53.58	81.15
R-factors								
model: $P3_2$ (no twinning)	0.1278	0.1067	0.0763	0.0551	0.0431	0.0406	0.0331	0.0279
model: $P3_2$ (twinned)	0.1287	0.1042	0.0752	0.0559	0.0444	0.0399	0.0325	0.0282
Reflections with $h = 2n \cap k = 2n$								
number of reflections	76	96	100	130	181	265	501	725
average $I_{obs}/\sigma(I_{obs})$	4.43	5.50	6.7	9.75	13.45	24.85	54.15	81.15
R-factors								
model: $P3_2$ (no twinning)	0.1540	0.1452	0.1224	0.0916	0.0695	0.0437	0.0360	0.0279
model: $P3_2$ (twinned)	0.1636	0.1283	0.1057	0.0884	0.0703	0.0438	0.0359	0.0282
Reflections with $h = 2n + 1 \cup k = 2n + 1$								
number of reflections	614	639	625	603	544	466	224	0
average $I_{obs}/\sigma(I_{obs})$	4.88	6.08	8.05	11.64	17.69	33.55	52.25	—
R-factors								
model: $P3_2$ (no twinning)	0.1241	0.1013	0.0689	0.0472	0.0336	0.0386	0.0237	—
model: $P3_2$ (twinned)	0.1238	0.1009	0.0703	0.0488	0.0351	0.0375	0.0216	—

of the reflections is better accounted for by the model with assumed twinning (especially the most intensive reflections with *h* or *k* odd). The properties of the refinements of the models described above share a common feature – that different structure parameters affect considerably the values of the refined domain parameter. Therefore, we conclude that the presence of twinning in the studied crystal cannot be confirmed unambiguously. It should be noted, however, that the differences in the coordinates of the twinned and single-domain models are quite small: the ratio of the absolute value of the difference of the pertinent coordinates to the mean of their e.s.d. values is *ca* six in the extreme.

It is also worthwhile noting that the refinement of the untwinned structural model (f = 0.0), used as a starting model with a twinning parameter fixed at f = 1.0, converges to a virtually identical minimum. Changing the value of f from 0.0 to 1.0 is equivalent to the transformation of indices $hkl \rightarrow \bar{h}\bar{k}l$, and consequently the atoms of both models with f = 0.0 and 1.0 are related by twofold rotation. Thus, the least-squares minimum seems to be quite flat compared with the twinning parameter f.

Atomic coordinates and equivalent isotropic displacement parameters are listed in Table 6 and relevant bond distances and angles are given in Table 7. The structure is depicted in Fig. 4.

The dithionate molecules reveal approximate symmetry 2 (the twofold axis is parallel to the crystallographic *c*-axis and passes through the centre of the S—S bond).

Each water molecule is coordinated to one Sr atom. Each Sr atom is surrounded by eight O atoms; four belong to water molecules and the other four are dithionate oxygens. The water oxygens are on average *ca* 0.05 Å further from the Sr atoms than the dithionate oxygens.

Only two oxygen species of the dithionate molecule are involved in the coordination of the Sr atom, *i.e.* O(x1) and O(x2), where x represents the S atom to which the pertinent oxygens are bonded. O(x3), which has a slightly longer bond (on average *ca* 0.2 Å) to the S atom than O(x1) and O(x2), most probably is involved in hydrogen bonding, while the other dithionate oxygens are not (see below).

Clearly, in the present structure the dithionate oxygens may only act as hydrogen-bond acceptors, while water oxygens may be both donors and acceptors.

According to Brown (1976), the shorter the O···O distance between the oxygens linked by a hydrogen bond, the smaller the deviation of the O—H···O angle from 180°. The majority of the structures with O···O between 2.7 and 2.9 Å exhibit moderately bent hydrogen bonds with the O—H···O angle lying in the range 160–180°. Since the distances between water oxygens as well as between water oxygens and dithionate oxygens O(x3) fall into this range (Table 8), it may be expected that the H atoms would not be situated too far from the connecting lines between the O atoms, which are thought to be involved in the hydrogen-bonding pattern.

It may also be supposed that water oxygens are coordinated to Sr atoms *via* their lone pairs and that water

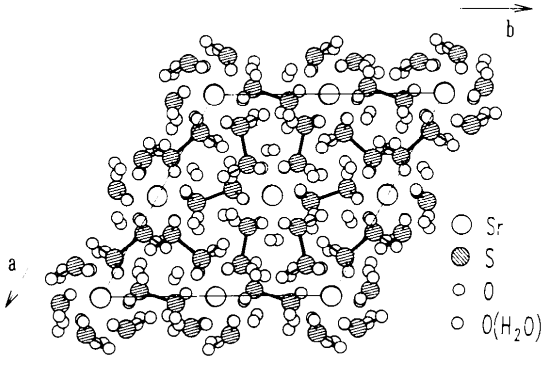

Fig. 4. Projection of the structure $SrS_2O_6.4H_2O$ along the *c*-axis.

Table 6. *Fractional atomic coordinates and equivalent isotropic thermal parameters* ($Å^2$) *with e.s.d.'s in parentheses*

Atoms containing '*A*' would be linked in the space group $P6_2$ with their respective counterparts without '*A*' by the operation $x - y$, x, $\frac{1}{3} + z$ (and lattice translations).

$$U_{\rm eq} = (1/3)\textstyle\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i . \mathbf{a}_j .$$

	x	y	z	$U_{\rm eq}$
Sr(1)	0.00239 (9)	0.00204 (7)	0*	0.0118 (3)
Sr(2)	0.49952 (9)	0.49957 (9)	0.00225 (5)	0.0133 (3)
Sr(3)	0.50039 (9)	0.50287 (9)	0.66894 (5)	0.0113 (3)
Sr(4)	0.49792 (7)	0.49899 (7)	0.33813 (6)	0.0116 (3)
S(1)	0.8439 (2)	0.5334 (2)	0.5052 (1)	0.0160 (8)
S(2)	0.6538 (2)	0.4688 (2)	0.5049 (1)	0.0170 (8)
O(11)	0.8656 (5)	0.4849 (5)	0.4422 (3)	0.0257 (26)
O(12)	0.8637 (5)	0.4865 (5)	0.5689 (3)	0.0289 (28)
O(13)	0.8995 (5)	0.6658 (5)	0.5048 (3)	0.0263 (25)
O(21)	0.6364 (5)	0.5245 (5)	0.5663 (3)	0.0305 (29)
O(22)	0.6338 (5)	0.5131 (5)	0.4401 (3)	0.0289 (27)
O(23)	0.5939 (5)	0.3362 (5)	0.5088 (3)	0.0300 (26)
S(3)	0.8098 (2)	0.9664 (2)	0.4988 (1)	0.0165 (8)
S(4)	0.6840 (2)	1.0308 (2)	0.4999 (1)	0.0160 (8)
O(31)	0.8795 (5)	1.0140 (5)	0.5615 (3)	0.0267 (27)
O(32)	0.8776 (5)	1.0145 (6)	0.4353 (3)	0.0311 (29)
O(33)	0.7341 (5)	0.8353 (5)	0.4982 (3)	0.0271 (27)
O(41)	0.6102 (5)	0.9746 (6)	0.4388 (3)	0.0334 (30)
O(42)	0.6206 (5)	0.9873 (5)	0.5656 (3)	0.0284 (28)
O(43)	0.7584 (5)	1.1638 (5)	0.4956 (3)	0.0303 (26)
S(1*A*)	0.3178 (2)	0.8473 (2)	0.8381 (1)	0.0161 (8)
S(2*A*)	0.1904 (2)	0.6580 (2)	0.8388 (1)	0.0167 (8)
O(11*A*)	0.3818 (5)	0.8666 (5)	0.7733 (3)	0.0287 (26)
O(12*A*)	0.3898 (5)	0.8643 (5)	0.8997 (3)	0.0297 (27)
O(13*A*)	0.2450 (5)	0.9086 (5)	0.8417 (3)	0.0275 (27)
O(21*A*)	0.1231 (5)	0.6399 (5)	0.9018 (3)	0.0297 (27)
O(22*A*)	0.1216 (5)	0.6361 (5)	0.7757 (3)	0.0294 (26)
O(23*A*)	0.2645 (5)	0.6002 (5)	0.8394 (3)	0.0278 (28)
S(3*A*)	0.8462 (2)	0.8170 (2)	0.8337 (1)	0.0170 (8)
S(4*A*)	0.6569 (2)	0.6902 (2)	0.8336 (1)	0.0162 (8)
O(31*A*)	0.8663 (5)	0.8809 (5)	0.8989 (3)	0.0257 (24)
O(32*A*)	0.8629 (5)	0.8901 (5)	0.7723 (3)	0.0312 (27)
O(33*A*)	0.9072 (5)	0.7443 (5)	0.8297 (3)	0.0306 (29)
O(41*A*)	0.6379 (5)	0.6211 (5)	0.7706 (3)	0.0290 (27)
O(42*A*)	0.6363 (5)	0.6213 (5)	0.8969 (3)	0.0251 (25)
O(43*A*)	0.5995 (5)	0.7640 (5)	0.8331 (3)	0.0276 (27)
O(W1)	0.5923 (5)	0.7280 (5)	0.3764 (3)	0.0245 (24)
O(W2)	0.5901 (5)	0.3671 (5)	0.9619 (3)	0.0210 (24)
O(W3)	0.0913 (5)	0.8673 (5)	0.9590 (3)	0.0237 (25)
O(W4)	0.7224 (5)	0.6332 (5)	0.0433 (3)	0.0235 (24)
O(W5)	0.2743 (5)	0.3967 (5)	0.2958 (3)	0.0245 (24)
O(W6)	0.1026 (5)	0.2229 (5)	0.3805 (3)	0.0326 (26)
O(W7)	0.3767 (5)	0.6035 (5)	0.7112 (3)	0.0240 (24)
O(W8)	0.3776 (6)	0.2730 (5)	0.6258 (3)	0.0330 (28)
O(W1*A*)	0.8669 (5)	0.5909 (5)	0.7123 (3)	0.0239 (26)
O(W2*A*)	0.2249 (5)	0.5917 (5)	0.2940 (3)	0.0231 (23)
O(W3*A*)	0.2282 (5)	0.0926 (5)	0.2946 (3)	0.0237 (24)
O(W4*A*)	0.0918 (5)	0.7245 (5)	0.3779 (3)	0.0245 (24)
O(W5*A*)	0.8802 (6)	0.2766 (5)	0.6244 (3)	0.0292 (26)
O(W6*A*)	0.8762 (5)	0.1016 (5)	0.7088 (3)	0.0244 (25)
O(W7*A*)	0.7737 (5)	0.3771 (6)	0.0460 (3)	0.0312 (27)
O(W8*A*)	0.1039 (5)	0.3768 (5)	0.9603 (3)	0.0231 (24)

* The fixed coordinate.

Table 7. *Relevant interatomic distances* (Å) *and angles* (°) *in* $SrS_2O_6.4H_2O$

S(1)—S(2)	2.125 (3)	S(3)—S(4)	2.126 (4)
S(1)—O(11)	1.445 (7)	S(3)—O(31)	1.436 (6)
S(1)—O(12)	1.435 (7)	S(3)—O(32)	1.440 (6)
S(1)—O(13)	1.462 (6)	S(3)—O(33)	1.446 (6)
S(2)—O(21)	1.446 (7)	S(4)—O(41)	1.446 (6)
S(2)—O(22)	1.440 (7)	S(4)—O(42)	1.448 (6)
S(2)—O(23)	1.462 (6)	S(4)—O(43)	1.468 (5)
S(1*A*)—S(2*A*)	2.122 (3)	S(3*A*)—S(4*A*)	2.120 (3)
S(1*A*)—O(11*A*)	1.438 (6)	S(3*A*)—O(31*A*)	1.443 (6)
S(1*A*)—O(12*A*)	1.443 (7)	S(3*A*)—O(32*A*)	1.447 (7)
S(1*A*)—O(13*A*)	1.477 (8)	S(3*A*)—O(33*A*)	1.474 (9)
S(2*A*)—O(21*A*)	1.429 (7)	S(4*A*)—O(41*A*)	1.442 (7)
S(2*A*)—O(22*A*)	1.436 (6)	S(4*A*)—O(42*A*)	1.442 (6)
S(2*A*)—O(23*A*)	1.454 (9)	S(4*A*)—O(43*A*)	1.446 (8)
Sr(1)—O(31$^{\rm i}$)	2.574 (6)	Sr(2)—O(11$^{\rm ii}$)	2.607 (8)
Sr(1)—O(32$^{\rm ii}$)	2.569 (8)	Sr(2)—O(11*A*$^{\rm i}$)	2.568 (7)
Sr(1)—O(31*A*$^{\rm iii}$)	2.540 (5)	Sr(2)—O(42$^{\rm i}$)	2.555 (6)
Sr(1)—O(32*A*$^{\rm i}$)	2.570 (7)	Sr(2)—O(42*A*$^{\rm iv}$)	2.608 (5)
Sr(1)—O(W3$^{\rm v}$)	2.597 (7)	Sr(2)—O(W2$^{\rm iv}$)	2.586 (7)
Sr(1)—O(W6$^{\rm vi}$)	2.639 (5)	Sr(2)—O(W4)	2.589 (5)
Sr(1)—O(W3*A*$^{\rm vi}$)	2.631 (9)	Sr(2)—O(W2*A*$^{\rm vii}$)	2.611 (9)
Sr(1)—O(W6*A*$^{\rm viii}$)	2.585 (7)	Sr(2)—O(W4*A*$^{\rm vii}$)	2.606 (5)
Sr(3)—O(21)	2.542 (7)	Sr(4)—O(12$^{\rm ii}$)	2.570 (8)
Sr(3)—O(21*A*$^{\rm vii}$)	2.551 (7)	Sr(4)—O(12*A*$^{\rm i}$)	2.562 (7)
Sr(3)—O(41$^{\rm ix}$)	2.545 (6)	Sr(4)—O(22)	2.553 (6)
Sr(3)—O(41*A*)	2.546 (5)	Sr(4)—O(22*A*$^{\rm vii}$)	2.576 (7)
Sr(3)—O(W7)	2.600 (8)	Sr(4)—O(W1)	2.635 (6)
Sr(3)—O(W7*A*$^{\rm x}$)	2.653 (10)	Sr(4)—O(W1*A*$^{\rm ii}$)	2.590 (8)
Sr(3)—O(W8*A*$^{\rm vii}$)	2.596 (7)	Sr(4)—O(W5*A*$^{\rm ii}$)	2.640 (6)
Sr(3)—O(W8)	2.660 (6)	Sr(4)—O(W5)	2.592 (6)
S(2)—S(1)—O(11)	104.8 (3)	S(2*A*)—S(1*A*)—O(11*A*)	104.2 (3)
S(2)—S(1)—O(12)	104.1 (3)	S(2*A*)—S(1*A*)—O(12*A*)	103.3 (3)
S(2)—S(1)—O(13)	104.3 (3)	S(2*A*)—S(1*A*)—O(13*A*)	105.8 (2)
O(11)—S(1)—O(12)	115.2 (5)	O(11*A*)—S(1*A*)—O(12*A*)	114.9 (4)
O(11)—S(1)—O(13)	113.6 (3)	O(11*A*)—S(1*A*)—O(13*A*)	113.6 (3)
O(12)—S(1)—O(13)	113.4 (4)	O(12*A*)—S(1*A*)—O(13*A*)	113.5 (4)
S(1)—S(2)—O(21)	103.3 (3)	S(1*A*)—S(2*A*)—O(21*A*)	104.1 (3)
S(1)—S(2)—O(22)	103.9 (3)	S(1*A*)—S(2*A*)—O(22*A*)	105.0 (3)
S(1)—S(2)—O(23)	106.3 (3)	S(1*A*)—S(2*A*)—O(23*A*)	104.6 (2)
O(21)—S(2)—O(22)	114.4 (5)	O(21*A*)—S(2*A*)—O(22*A*)	115.1 (4)
O(21)—S(2)—O(23)	113.8 (4)	O(21*A*)—S(2*A*)—O(23*A*)	113.5 (4)
O(22)—S(2)—O(23)	113.7 (4)	O(22*A*)—S(2*A*)—O(23*A*)	113.1 (4)
S(4)—S(3)—O(31)	104.6 (4)	S(4*A*)—S(3*A*)—O(31*A*)	104.0 (3)
S(4)—S(3)—O(32)	104.5 (4)	S(4*A*)—S(3*A*)—O(32*A*)	103.5 (3)
S(4)—S(3)—O(33)	104.4 (3)	S(4*A*)—S(3*A*)—O(33*A*)	106.0 (2)
O(31)—S(3)—O(32)	114.8 (3)	O(31*A*)—S(3*A*)—O(32*A*)	114.6 (4)
O(31)—S(3)—O(33)	114.0 (4)	O(31*A*)—S(3*A*)—O(33*A*)	113.3 (4)
O(32)—S(3)—O(33)	113.2 (4)	O(32*A*)—S(3*A*)—O(33*A*)	113.9 (4)
S(3)—S(4)—O(41)	103.2 (4)	S(3*A*)—S(4*A*)—O(41*A*)	104.1 (3)
S(3)—S(4)—O(42)	104.1 (4)	S(3*A*)—S(4*A*)—O(42*A*)	104.7 (3)
S(3)—S(4)—O(43)	105.5 (3)	S(3*A*)—S(4*A*)—O(43*A*)	104.8 (3)
O(41)—S(4)—O(42)	114.7 (3)	O(41*A*)—S(4*A*)—O(42*A*)	114.4 (4)
O(41)—S(4)—O(43)	113.7 (4)	O(41*A*)—S(4*A*)—O(43*A*)	113.7 (4)
O(42)—S(4)—O(43)	114.0 (4)	O(42*A*)—S(4*A*)—O(43*A*)	113.7 (4)

Symmetry codes: (i) $-x+y$, $-x+1$, $-\frac{2}{3}+z$; (ii) $-y+1$, $x-y$, $-\frac{1}{3}+z$; (iii) $x-1$, $y-1$, $z-1$; (iv) x, y, $z-1$; (v) x, $y-1$, $z-1$; (vi) $-y$, $x-y$, $-\frac{1}{3}+z$; (vii) $-y+1$, $x-y+1$, $-\frac{1}{3}+z$; (viii) $-x+y+1$, $-x+1$, $-\frac{2}{3}+z$; (ix) $-x+y$, $-x+1$, $\frac{1}{3}+z$; (x) $-y+1$, $x-y$, $\frac{2}{3}+z$.

hydrogens should be directed towards O(x3) dithionate atoms, which in general are closer to the pertinent water oxygens than O(x1) or O(x2).

Taking into account the sp^3 state of the water oxygens, the prevailing sp^3 state of the dithionate oxygens and the tetrahedral coordination of the S atoms, these assumptions thus imply that the angles between pertinent oxygens involved in hydrogen bonding should not deviate much (about 10–20°, 25° in the extreme) from the ideal value of the tetrahedral angle (109.47°).

Since the pertinent angles are in accordance with this hypothesis,* we may draw the following conclusions:

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* Lists of structure factors, anisotropic displacement parameters and relevant bond angles for hydrogen bonding have been deposited with the IUCr (Reference: SH1083). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 8. *Relevant distances* (Å) *for discussion of the hydrogen-bonding pattern in* $SrS_2O_6.4H_2O$

(a) Distances between water oxygens

O(W1)—O(W3^{i})	2.820 (7)	O(W5)—O(W2*A*)	2.841 (10)
O(W1)—O(W7^{vii})	2.816 (11)	O(W7)—O(W2*A*^{ix})	2.760 (10)
O(W2)—O(W5*A*^{xi})	2.861 (7)	O(W1*A*)—O(W3*A*^{xi})	2.821 (9)
O(W2)—O(W7*A*^{xii})	2.783 (9)	O(W1*A*)—O(W7*A*^{x})	2.835 (7)
O(W3)—O(W8^{ix})	2.848 (7)	O(W3*A*)—O(W8*A*^{xiii})	2.821 (11)
O(W4)—O(W6^{vii})	2.847 (11)	O(W4*A*)—O(W6*A*^{vi})	2.828 (11)
O(W4)—O(W8^{viii})	2.784 (11)	O(W4*A*)—O(W8*A*^{i})	2.764 (7)
O(W5)—O(W6)	2.729 (7)	O(W5*A*)—O(W6*A*)	2.729 (9)

(b) Distances between water oxygens and dithionate oxygens O(x3)

O(W1)—O(33)	2.846 (7)	O(W1*A*)—O(33*A*)	2.851 (8)
O(W2)—O(23^{xi})	2.881 (9)	O(W2*A*)—O(23*A*^{i})	2.857 (7)
O(W3)—O(13*A*)	2.850 (8)	O(W3*A*)—O(13^{ii})	2.862 (8)
O(W4)—O(43^{xiv})	2.870 (9)	O(W4*A*)—O(43*A*^{vii})	2.867 (7)
O(W5)—O(43*A*^{i})	2.859 (9)	O(W5*A*)—O(43^{xv})	2.886 (8)
O(W6)—O(13*A*^{vii})	2.885 (9)	O(W6*A*)—O(13^{xi})	2.843 (9)
O(W7)—O(23*A*)	2.832 (8)	O(W7*A*)—O(23^{ii})	2.881 (8)
O(W8)—O(33*A*^{ii})	2.890 (8)	O(W8*A*)—O(33^{ix})	2.835 (8)

Symmetry codes (as in Table 7 including): (xi) $-x+y+1, -x+1, \frac{1}{3}+z$; (xii) $x, y, z+1$; (xiii) $-x+y, -x, -\frac{2}{3}+z$; (xiv) $-y+2, x-y+1, z-\frac{1}{3}$; (xv) $x, y-1, z$.

(1) Presumably water oxygens are coordinated to Sr atoms *via* their lone pairs.

(2) Each water molecule takes part in hydrogen-bonding with two other water molecules, which are coordinated to different Sr atoms. One of these water molecules acts as a hydrogen-bond donor, the other as an acceptor. Disorder regarding the positions of the hydrogens involved in the hydrogen-bond contacts between water oxygens may exist.

(3) Each O(x3) atom acts most probably as a hydrogen-bond acceptor for two different water molecules. These hydrogen-bond contacts are slightly longer than those between water oxygens. Taking into account the pertinent angles, it is likely that the H atoms should also be situated along water–oxygen···O(x3) connecting lines.

(4) This hypothesis concerning the hydrogen-bonding pattern allows the conclusion that neither O(x1) nor O(x2) are involved in hydrogen-bonding interactions, although some of the distances between these oxygens and water oxygens are as short as 2.88 (8) Å. However, the average distance between water oxygens and the closest O(x1) or O(x2) atom is 2.989 Å, which is significantly longer than the average distance between water oxygens and O(x3) atoms (2.862 Å). The pertinent angles regarding O(x1) and O(x2) exceed 140°.

We now consider the crystallographic data of the related compounds $CaS_2O_6.4H_2O$ and $PbS_2O_6.4H_2O$.

There seem to be contradictory pieces of information about the crystal data of these compounds. Ferrari, Cavalca & Nardelli (1946) determined the lattice parameters of $CaS_2O_6.4H_2O$ (a = 12.41, c = 18.72 Å) and suggested $P6_122$ or $P6_1$ or the respective enantiomorphic space groups for this compound. In Haussuehl's (1994) article, the lattice parameters of this compound are reported, a = 6.211 and c = 18.763 Å. de Matos Gomes (1991*a*) claimed that '$CaS_2O_6.4H_2O$ is a superstructure of $SrS_2O_6.4H_2O$ with doubling of all three axes'. This would mean that the c-axis may also be doubled with respect to the lattice parameters given by Ferrari, Cavalca & Nardelli (1946), which correspond to the present determination of $SrS_2O_6.4H_2O$. de Matos Gomes (1991*a*) also described the average structure of $CaS_2O_6.4H_2O$, which has been determined with disordered dithionate molecules, similarly as $SrS_2O_6.4H_2O$. Koval'chuk & Perekalina (1972) concluded from the observation of a second harmonic generation along the optical axis (ruby laser) that $CaS_2O_6.4H_2O$ is trigonal and not hexagonal, and they reported the crystal class to be 32. Haussuehl (1994) could not confirm the trigonal symmetry of $CaS_2O_6.4H_2O$ since the elastic constant c_{14} is too small.

de Matos Gomes (1991*b*) found that $PbS_2O_6.4H_2O$ is hexagonal, $P622$, a = 6.3413 (9), c = 6.4622 (9) Å, Z = 1. The structure analysis also resulted in a disordered structure.

Kizel', Klimova, Koval'chuk & Perekalina (1973) observed the second harmonic generation (ruby and Nd lasers were used) along the optical axis of $PbS_2O_6.4H_2O$, and concluded from the absence of the second harmonic in the [100] direction that the crystal class of this structure ought to be 32 and not 3.

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