Crystal Structures of Strontium and Lead Dithionate Tetrahydrate

By E. de Matos Gomes*

Clarendon Laboratory, Parks Road, Oxford OX1 3PU, England

Abstract

$SrS_2O_6.4H_2O$, $M_r = 319.8$, hexagonal, $P6_422$, $a = 6.3529$ (9), $c = 19.218$ (3) Å, $V = 671.71$ Å^3, $D_x = 2.373$ g cm^{-3}, $Z = 3$, Mo $K\alpha$ radiation, $\lambda = 0.71069$ Å, $\mu = 59.93$ cm^{-1}, $F(000) = 474$, room temperature, $R = 0.040$ for 336 unique observed reflections. $PbS_2O_6.4H_2O$, $M_r = 439.4$, hexagonal, $P622$, $a = 6.3413$ (9), $c = 6.4622$ Å, $V = 225.04$ Å^3, $D_x = 3.22$ g cm^{-3}, $Z = 1$, Mo $K\alpha$ radiation, $\lambda = 0.71069$ Å, $\mu = 193.56$ cm^{-1}, $F(000) = 202$, room temperature, $R = 0.015$ for 144 unique observed reflections. The crystal structure and absolute optical chirality of strontium dithionate tetrahydrate, $SrS_2O_6.4H_2O$, and lead dithionate tetrahydrate, $PbS_2O_6.4H_2O$, have been determined at room temperature by a combination of single-crystal X-ray diffraction, taking account of anomalous scattering, and optical measurements. The structure of $SrS_2O_6.4H_2O$ is disordered about the twofold axis along [110]. Disorder arises from the fact that the $S_2O_6^{2-}$ ion occupies two sites on either side of this axis. The space group $P6_422$ has been assigned to a dextrorotatory crystal. $PbS_2O_6.4H_2O$ is a substructure of $SrS_2O_6.4H_2O$ with a c axis three times smaller. The $S_2O_6^{2-}$ ion is disordered at two sites on either side of [110] plus three sites around [001]. The water O atoms occupy three sites around [001]. The space group $P622$ has been assigned to a laevorotatory crystal.

1. Introduction

The first crystallographic investigation of strontium and lead dithionate tetrahydrate (hereafter referred to as SrDH and PbDH, respectively) was made by Ferrari, Cavalca & Nardelli (1946), who suggested for SrDH the space groups $P6_122$ or the enantiomorphous $P6_522$ based on the reflection condition $00l = 6n$ and the optical activity displayed by the crystals. For lead dithionate tetrahydrate they were not able to assign any symmetry since their crystals were twinned.

Second harmonic generation measurements were carried out by Koval'chek & Perekalina (1972) on SrDH and by Kizvel', Klimova, Koval'chuk & Perekalina (1973) on PbDH, and showed that the point group had to be 32 and not 6 or 622. Silker (1964) on the other hand, observed no electro-optic effect for light travelling in the direction of the optic axis when an electric field was applied to the Y face of a crystal. In point group 32 the linear electro-optic coefficient r_{11} is allowed by symmetry.

The first complete determination of the structure of $SrS_2O_6.4H_2O$ was carried out by Hargreaves & Stanley (1972). They initially assigned the space groups $P6_{2,4}22$ on the basis of the overall reflection condition $00l = 3n$ for observed intensities and on the displayed diffraction symmetry of $6/mmm$. The unit-cell parameters were found to be $a = 6.32$ (2), $c = 19.29$ (3) Å with $Z = 3$. They subsequently ruled out this space group arguing that the threefold positions required for the three dithionate ions $S_2O_6^{2-}$ had, in that space group, symmetry 222 which was not a possible symmetry for the ion. They therefore assumed that the space group was $P6_2$ (Laue symmetry $6/m$) and the extra symmetry was considered to arise from twinning. The structure was solved with a 50% contribution from each twin component. The agreement factor obtained was $R = 0.119$ after refinement of atomic coordinates and isotropic temperature factors for all the atoms. No attempt was made to assign absolute chirality, that is to differentiate between the space groups $P6_2$ or $P6_4$.

Here we report a redetermination of the structure of $SrS_2O_6.4H_2O$ and a determination, for the first time, of the structure of $PbS_2O_6.4H_2O$, which has not been previously reported.

2. Preparation of the samples

SrDH was prepared by addition of strontium hydroxide to an aqueous solution of MnS_2O_6 (Mellor, 1957). Optically active crystals in the form of (001) plates were obtained by slow evaporation at room temperature.

PbDH was prepared by addition of lead carbonate to a solution of dithionic acid, $H_2S_2O_6$ (Mellor, 1957). Slow evaporation at room temperature

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* On leave from the Department of Physics, University of Coimbra, 3000 Coimbra, Portugal.

yielded prismatic crystals. The crystals were of good optical quality and displayed natural optical activity.

3. Structure of $SrS_2O_6.4H_2O$

3.1. Experimental

A small, good quality, dextrorotatory single crystal was mounted on a CAD-4 diffractometer. Details of the data collection are presented in Table 1.

The parameters of the hexagonal cell were found to be $a = 6.3529$ (9), $c = 19.218$ (3) Å, and $V = 671.71$ Å^3. As the density (D_x) is 2.373 g cm^{-1} (Handbook of Chemistry and Physics, 1973) and the molecular weight is 319.81, the number of $SrS_2O_6.4H_2O$ molecules per unit cell is three. The overall reflection condition observed was $00l = 3n$ and the Laue diffraction symmetry $6/mmm$. This then suggests as possible space groups $P6_222$ or $P6_422$.

3.2. Structure determination

Twinning in $SrS_2O_6.4H_2O$. As was pointed out by Hargreaves & Stanley (1972), in the space group $P6_222$ (or $P6_422$) the three 222 point-symmetry positions available for the three dithionate ions are not possible. We also initially considered the extra symmetry as arising from twinning. According to Donnay & Donnay (1974), one can distinguish two main types of twinning: twinning by twin lattice symmetry (TLS) with a single orientation of the reciprocal lattice and twinning by twin lattice quasi-symmetry (TQLS) where two or more reciprocal lattices with a common origin but different orientation give rise to double or multiple spots in an X-ray diffraction experiment. In a Laue X-ray photograph only single diffraction spots were observed. We therefore conclude that if twinning were present it should be of the TLS type. For a crystal of class 6 where TLS twinning occurs, the possible twin operations (Curien & Le Corre, 1958) and their influence on the sense of optical activity (Klapper, Hahn & Chung, 1987), for equal twin components, are as shown below.

Twin law	Sense of optical rotation	Apparent symmetry of twinned crystal	Apparent Laue class of twinned crystal
$m \perp [001]$	Reversed	$6/m$	$6/m$
$m \parallel [001]$ in $\{100\}$ or in $[110]$	Reversed	$6mm$	$6/mmm$
$2 \parallel \langle 100 \rangle$ or (210)	Unchanged	622	$6/mmm$

As no changes in the sense of optical activity were observed in SrDH throughout the crystal, we concluded that the twin operation would be a twofold rotation about [100]. In this type of twinning every hkl reflection has a contribution from the two twin components, that is

$$I_{total}(hkl) = s_1 I_1(hkl) + s_2 I_2(hkl)$$

Table 1. *Summary of experimental conditions for* $SrS_2O_6.4H_2O$ *and* $PbS_2O_6.4H_2O$

All measurements were made at room temperature on an Enraf–Nonius CAD-4 diffractometer, using graphite-monochromated Mo $K\alpha$ radiation, $\lambda = 0.71069$ Å.

	$SrS_2O_6.4H_2O$	$PbS_2O_6.4H_2O$
Crystal colour, shape and size (mm)	Colourless parallelepiped, dimensions < 0.3	Colourless parallelepiped, dimensions < 0.1
μ (cm^{-1})	59.93	193.56
Scan mode	ω–2θ	ω–2θ
No. of reflections, angular range for lattice parameters (°)	25, 4 < θ < 17	25, 4 < θ < 15
Range of h, k, l	−1 to 7, −1 to 7, −22 to 22	−1 to 7, −1 to 7, −7 to 7
Range of 2θ (°)	0 < 2θ < 50	0 < 2θ < 50
Intensity control	Monitored every 3600 s, no significant variation	Monitored every 3600 s, no significant variation
Orientation control	Every 250 reflections	Every 250 reflections
No. of reflections measured	3253	1100
No. of unique observed reflections	336 $[I_{obs} > 3.0\sigma(I_{obs})]$	144 $[I_{obs} > 3.0\sigma(I_{obs})]$
No. of unobserved reflections	1294	151
R_{int} on F_{obs}	0.0344	0.0358
$F(000)$	474	202
Corrections applied	Polarization, Lorentz and absorption (Watkin et al., 1985)	Polarization, Lorentz and absorption (Watkin et al., 1985)
Max./min. absorption correction, ψ scans	1.30/1.00	1.39/1.01

where $I_1(hkl)$ and $I_2(hkl)$ are the intensities diffracted by the twin components 1 and 2, respectively, s_1 and s_2 are the twin components related by $s_1 + s_2 = 1$, and I_{total} is the measured intensity for that reflection. Using the atomic coordinates of Hargreaves & Stanley (1972), a refinement of the structure using the program CRYSTALS (Watkin, Carruthers & Betteridge, 1985) was carried out assuming the existence of twinning. Atomic positions, isotropic temperature factors and twin components were refined (27 parameters) to R and wR values of 0.10 and 0.13 respectively, with $s_1 = 0.50$ (2) and $s_2 = 0.50$ (2). Here and elsewhere in this paper full-matrix least-squares refinement on F_{obs} with $w = 1/\sigma^2(F_{obs})$ [$\sigma(F_{obs})$ defined from counting statistics] was employed and neutral-atom scattering factors, f and f', were taken from International Tables for X-ray Crystallography (1974, Vol. IV). Attempts to refine atomic coordinates and anisotropic temperature factors together, resulted in the mean-square displacement matrix becoming nonpositive definite for some of the O atoms. As no further improvements could be made in the structure determination, the twinning model was abandoned.

Disorder in $SrS_2O_6.4H_2O$. The Laue symmetry displayed can in fact be accounted for if the structure is disordered. If the $S_2O_6^{2-}$ ion is disordered about [110], $P6_222$ or $P6_422$ are possible space groups for this crystal. A close inspection of the atomic coordinates of the water O atoms in the structure determination by Hargreaves & Stanley (1972), shows that their atomic coordinates are almost related by a twofold rotation about [110].

These coordinates were taken as a starting model for the refinements in space group $P6_222$ with the following modifications:

(i) In this space group the twofold axis in the [110] direction is situated at $z = \frac{1}{3}$, and so the z atomic coordinates of all the atoms have to be raised by $\frac{1}{3}$ on going from space group $P6_2$ to $P6_222$ in order to be consistent with *International Tables for Crystallography* (1983, Vol. *A*).

(ii) As there are 12 symmetry operations in this space group and as the water O atoms are in general positions, the two independent water oxygens [O(4) and O(5)] in space group $P6_2$, are replaced by one [O(4)] in $P6_222$.

Using the program *XTAL2.6* (Hall & Stewart, 1989), atomic coordinates and isotropic temperature factors together with scale factor, extinction and absolute structure parameter (Flack, 1983) were refined for all non-H atoms to give R and wR values of 0·044 and 0·040, respectively, for 24 refined parameters. When anisotropic thermal parameters for all non-H atoms were introduced the U_{ij} matrix for one of the O atoms of the dithionate ion became nonpositive definite and the correlation between some parameters was very high, probably because the disordered atoms O(1) and O(2) of the two ions related by the twofold rotation are very close together [distance 0·42 (5) Å]. Accordingly, in the final refinements, isotropic thermal vibrations for O(1) and O(2) and anisotropic thermal vibrations for all the other atoms were adjusted. The absolute structure parameter (Flack, 1983) indicated that the real space group of our dextrorotatory crystal was $P6_422$. This space group was used in the final refinement of 41 parameters to give $R = 0·040$, $wR = 0·036$, $S = 3·1$ for 336 reflections; maximum (average) shift/e.s.d. $= 0·6 \times 10^{-3}$ $(0·1 \times 10^{-3})$; maximum/minimum in the difference Fourier synthesis $= 0·7/-0·6$ e Å^{-3}; extinction, correction mosaic distribution 0·10 (3); absolute structure parameter 0·0 (1).

In Table 2* the refined atomic coordinates and anisotropic temperature factors for all the atoms are reported. In Table 3 the main interatomic distances and bond angles are listed. In Table 4 the bond lengths are compared with those obtained for other structure determinations of similar compounds.

3.3. *Discussion of the structure*

A projection of the structure on (001) is shown in Fig. 1. The interatomic distances and angles in the

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* Lists of structure factors, anisotropic thermal parameters, and bond distances and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53508 (30 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Atomic coordinates and anisotropic thermal parameters (Å^2) for* $SrS_2O_6.4H_2O$ *in space group* $P6_422$, *and isotropic thermal parameters (Å^2) for* $PbS_2O_6.4H_2O$ *in space group* $P622$, *with e.s.d.'s in parentheses*

$$T = \exp[-2\pi^2(U_{11}h^2a^{*2} + ... + 2U_{12}hka^*b^* + ...)].$$

$SrS_2O_6.4H_2O$

	x	y	z
Sr	0	0	$\frac{1}{3}$
S	0·3095 (5)	0·9346 (6)	0·4976 (4)
O(1)	0·267 (3)	0·035 (2)	0·5608 (7)
O(2)	0·273 (3)	0·041 (2)	0·4354 (5)
O(3)	0·196 (2)	0·672 (2)	0·4939 (5)
O(4)	0·806 (1)	0·5501 (9)	0·6242 (2)

	U_{11}/U_{iso}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Sr	0·0161 (6)	0·0161 (6)	0·0135 (5)	0·0096 (7)	0	0
S	0·013 (2)	0·020 (3)	0·014 (1)	0·007 (2)	0·001 (2)	0·003 (4)
O(1)	0·037 (4)					
O(2)	0·022 (3)					
O(3)	0·028 (6)	0·020 (5)	0·022 (4)	0·002 (5)	0·002 (6)	0·005 (4)
O(4)	0·024 (4)	0·018 (3)	0·031 (2)	0·007 (2)	0·003 (2)	−0·003 (2)

$PbS_2O_6.4H_2O$

	x	y	z	U_{iso}
Pb	0	0	0	0·0184 (4)
S	0·689 (1)	0·634 (1)	0·49 (1)	0·023 (2)
O(1)	0·733 (5)	0·795 (6)	0·666 (4)	0·021 (7)
O(2)	0·698 (7)	0·741 (6)	0·281 (4)	0·034 (9)
O(3)	0·824 (5)	0·503 (6)	0·49 (2)	0·050 (8)
O(4)	0·199 (3)	0·744 (3)	0·874 (2)	0·036 (4)

Table 3. *Interatomic distances (Å) and angles (°) within the dithionate ion and coordination of the* Sr^{2+} *and* Pb^{2+} *ions in* $SrS_2O_6.4H_2O$ ($P6_422$) *and* $PbS_2O_6.4H_2O$ ($P622$), *respectively, with e.s.d.'s in parentheses*

Dithionate ion

$SrS_2O_6.4H_2O$		$PbS_2O_6.4H_2O$	
S^{ii}—S^{ix}	2·131 (4)	S—S^i	2·138 (7)
S^{ii}—O(1)^{ii}	1·46 (2)	S—O(1)	1·45 (4)
S^{ii}—O(2)^{ii}	1·45 (2)	S—O(2)	1·51 (4)
S^{ii}—O(3)^{ii}	1·45 (2)	S—O(3)	1·46 (4)
S^{ii}—S^{ix}—O(1)^{ii}	104·6 (7)	S—S—O(1)	108 (2)
S^{ii}—S^{ix}—O(2)^{ii}	103·5 (7)	S—S—O(2)	98 (2)
S^{ii}—S^{ix}—O(3)^{ii}	105·3 (6)	S—S—O(3)	107 (1)
O(1)^{ii}—S^{ii}—O(2)^{ii}	112 (2)	O(1)—S—O(2)	116 (5)
O(2)^{ii}—S^{ii}—O(3)^{ii}	113 (1)	O(1)—S—O(3)	116 (2)
O(1)^{ii}—S^{ii}—O(3)^{ii}	117 (1)	O(2)—S—O(3)	111 (5)

Sr^{2+} coordination		Pb^{2+} coordination	
Sr^{ii}—O(1)^{ii}	2·54 (1)	Pb—O(1)	2·65 (2)
Sr^{ii}—O(2)^x	2·59 (1)	Pb—O(2)	2·55 (3)
Sr^{ii}—O(4)^{ii}	2·61 (1)	Pb—O(4)	2·64 (2)

For $P6_422$ the symmetry codes are (i) $-x$, $-y$, z; (ii) $-x+y$, $-x$, $\frac{1}{3}+z$; (iii) $x-y$, x, $\frac{2}{3}+z$; (iv) $-y$, $x-y$, $\frac{1}{3}+z$; (v) y, $-x+y$, $\frac{1}{3}+z$; (vi) $x-y$, $-y$, $-z$; (vii) $-x+y$, y, $-z$; (viii) y, x, $\frac{1}{3}-z$; (ix) $-x$, $-x+y$, $\frac{2}{3}-z$; (x) $-y$, $-x$, $\frac{1}{3}-z$; (xi) x, $x-y$, $\frac{2}{3}-z$; and for $P622$ the symmetry codes are (i) $-x$, $-y$, z; (ii) y, x, $-z$; (iii) $-y$, $-x$, $-z$; (iv) $-y$, $x-y$, z; (v) y, $-x+y$, z; (vi) $-x$, $-x+y$, $-z$; (vii) $x-y$, $-y$, $-z$; (viii) x, $x-y$, $-z$; (ix) $-x+y$, y, $-z$; (x) $-x+y$, $-x$, z; (xi) $x-y$, x, z.

$S_2O_6^{2-}$ ion are in agreement with the values reported for other dithionates (see Table 4) with an S—S distance of 2·131 (4) Å, a mean S—O distance of 1·45 (2) Å, and mean angles S—S—O of 104·5 (7)° and O—S—O of 114 (1)°.

Table 4. *Comparison of mean bond lengths (Å) and angles (°) within the dithionate ion with other structure determinations*

	S—S	S—O	S—S—O	O—S—O
(1) $(NH_4)_3ClS_2O_6$	2·15	1·43		
(2) $NaS_2O_6.2H_2O$	2·16	1·46	103	
(3) $MgS_2O_6.H_2O$	2·123 (1)	1·448 (2)	104·5 (1)	114·0 (1)
(4) $NiS_2O_6.H_2O$	2·123 (1)	1·449 (3)	104·5 (3)	113·9 (2)
(5) $ZnS_2O_6.H_2O$	2·127 (1)	1·451 (2)	104·5 (1)	114·0 (1)
(6) $BaS_2O_6.H_2O$	2·150 (4)	1·462 (9)	104·4 (4)	114·1 (5)
(7) $Cs_2S_2O_6$	2·112 (3)	1·454 (3)	104·4 (3)	114·1 (3)
(8) $K_2S_2O_6$	2·15 (2)	1·43 (5)	105 (1)	
(9) $Rb_2S_2O_6$	2·08	1·50		
(10) $SrS_2O_6.4H_2O$	2·131 (4)	1·45 (2)	104·5 (7)	114 (1)
(11) $PbS_2O_6.4H_2O$	2·138 (7)	1·47 (2)	104 (2)	114 (4)

References: (1) Guttormson & Stanley (1969); (2) Kirfel & Will (1980); (3), (4), (5) Black, Griffith & Robertson (1975); (6) Rausell-Collone & Garcia-Blanco (1966); (7) Liminga, Abrahams & Bernstein (1980); (8) Stanley (1956); (9) Barnes & Wendling (1938); (10), (11) present work.

The Sr^{2+} ion is in contact with eight dithionate ions through O(1) and O(2) with distances 2·54 (1) and 2·59 (2) Å respectively, and with four water O atoms at 2·61 (1) Å (Fig. 2).

The atomic positions of the H atoms could not be found in the final difference Fourier map. Neutron
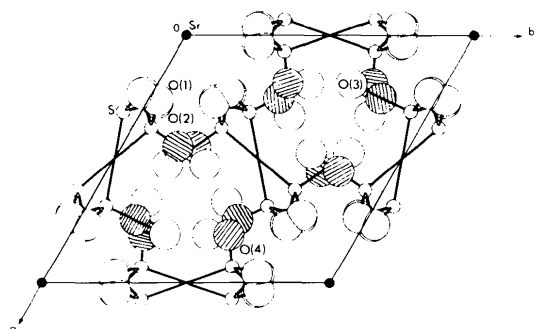

Fig. 1. (001) projection of the structure of $SrS_2O_6.4H_2O$. Sr atoms are shown as solid circles, the S and O(S) atoms as open and O(W) atoms as crossed circles. Only S—S and S—O bonds are shown. The atom numbering corresponds to that in Table 2.
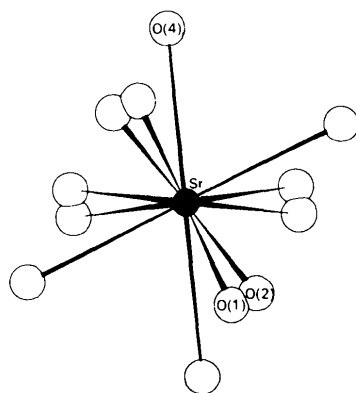

Fig. 2. Coordination of the Sr^{2+} ion [(001) projection].

diffraction experiments are in progress to determine the H-atom positions in the structure as well as their role in the disorder process.

4. Structure of $PbS_2O_6.4H_2O$

4.1. Experimental

A small laevorotatory crystal was mounted on a CAD-4 diffractometer. Details of the data collection are given in Table 1. The parameters of the hexagonal cell were found to be $a = 6.3413$ (9), $c = 6.4622$ (9) Å and $V = 225.04$ Å^3. The density (D_x) is 3.22 g cm^{-1} (*Handbook of Chemistry and Physics*, 1973) and the molecular weight is 439.38. There is one molecule per unit cell. The Laue diffraction symmetry observed is 6/*mmm* and, as no restrictions on the reflections of type 00*l* exist, the space group is $P622$.

4.2. Structure determination

Comparing the lattice parameters with those of SrDH, we find that they have almost identical values for a (6·3413 in PbDH and 6·3522 Å in SrDH) while the c axis of the PbDH compound is about one third that in SrDH, 6·4622 and 19·218 Å, respectively. As the space group $P622$ is a possible supergroup of $P6_422$ with a c axis of $\frac{1}{3}$, we could assume that PbDH is a substructure of SrDH. In fact, the observed reflections for SrDH can be divided into two groups: (i) strong reflections of the type $h,k,l = 3n$, and (ii) weaker superstructure reflections of type $h,k,l = 3n \pm 1$. The number of observed reflections (i) and (ii) are, in $P6_422$, 140 and 196, respectively, and $R_{int} = 0.0217$ for (i) and 0·0631 for (ii). This is in accord with our assumption of a substructure–superstructure relationship between the PbDH and SrDH structures. In PbDH the reflections measured were all very strong, *i.e.* no superstructure reflections. This means that one atom in the PbDH unit cell is the projection of three atoms with coordinates $(x,y,z/3) + [(0,0,0); (0,0,\frac{1}{3}); (0,0,\frac{2}{3})]$ in the SrDH unit cell. The atomic coordinates of all the atoms can be deduced from those in the SrDH unit cell if there is disorder not only of the dithionate ion but also of the water O atoms. The structure of SrDH was therefore taken as a starting model for the refinements with the modifications: (i) the z coordinates of all the atoms were multiplied by three; (ii) because all the atoms, apart from Pb, are in general positions, the population parameter of all the atoms in the dithionate ion is $\frac{1}{6}$ whereas for the water O atoms it is $\frac{1}{3}$.

With the program *XTAL*2.6 (Hall & Stewart, 1989), the scale factor, extinction, absolute structure parameter (Flack, 1983), atomic coordinates and isotropic temperature factors for all the atoms were refined. As the number of reflections to be used in

the refinements was only 144 no attempt was made to allow for vibrational anisotropy. In the final calculation $R = 0.015$, $wR = 0.017$, $S = 1.7$ for 24 parameters and 144 reflections; maximum (average) shift/e.s.d. $= 0.003$ (0.001); maximum/minimum in the difference Fourier synthesis $= 0.9/-0.8$ e Å^{-3}; extinction correction, mosaic distribution 0.12 (1); absolute structure parameter 0.0 (2).

In Table 2 atomic coordinates (corresponding to the absolute chirality of the structure) and isotropic thermal parameters for all the atoms are listed. In Table 3 the main bond lengths and angles are summarized and the coordination of the Pb^{2+} ion is listed.

4.3. Discussion

If we compare the bond lengths and angles found here for the dithionate ion with those for SrDH and other structures containing this ion (Table 4), we find that in this structure the ion is more asymmetrical, the main differences occurring in the S—O(2) bond and S—S—O(2) angle. The mean value of the S—O
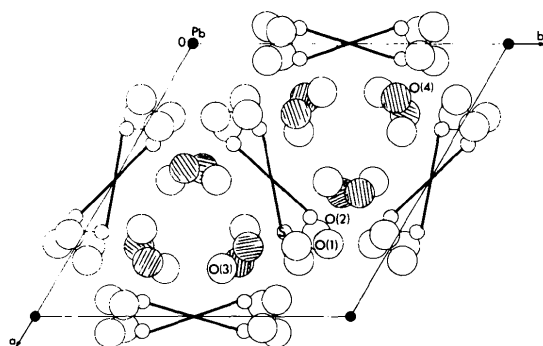

Fig. 3. (001) projection of the structure of PbS$_2$O$_6$.4H$_2$O. Pb atoms are shown as solid circles, the S and O(S) atoms as open and O(W) atoms as crossed circles. Only S—S bonds are shown. The numbering corresponds to that in Table 2.
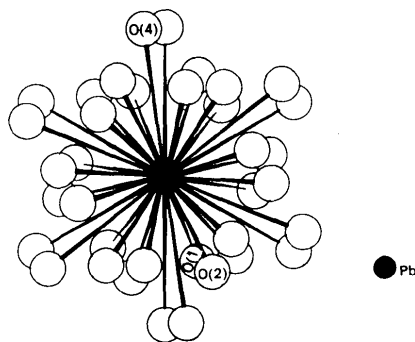

Fig. 4. Coordination of the Pb^{2+} ion [(001) projection].

distance is now 1.47 (2) Å and the mean values of the S—S—O and O—S—O angles are, respectively, 104 (2) and 114 (4)°, which are within the range of values obtained for other similar structures. In SrDH the S—S—O (2) angle was only a little smaller than the others but in PbDH is considerably smaller. Probably, these observed differences in bond lengths and angles in PbDH result from the statistical disorder of the dithionate ion over six positions plus the disorder of the water O atoms over three positions.

A projection of the structure on the (001) plane is shown in Fig. 3. The Pb^{2+} ion is coordinated by 24 dithionate ions through O(1) and O(2), and by 12 oxygens from the water molecules (Fig. 4).

We conclude that the SrDH structure is a more ordered form of the PbDH structure at room temperature and that the superstructure reflections in SrDH result from the full ordering of the water oxygens and partial ordering of the dithionate ion in the unit cell.

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A New Approach to Describing Non-Molecular Crystal Structures

BY A. VEGAS, A. ROMERO AND M. MARTÍNEZ-RIPOLL

Instituto Rocasolano-CSIC, UEI de Cristalografía, Serrano 119, E-28006 Madrid, Spain

Abstract

A new model which relates the structure of a given compound to that of the parent metal is reported. The structures of oxides are regarded as the metal structure, sometimes deformed, sometimes opened up by the inclusion of other atoms, but maintaining the topology and interatomic distances of the parent metal structure. The model describes all the Mg-containing borates and silicates of the humite and leucophoenicite series as derived from their common parent h.c.p. Mg structure. The cation array of apatite and the alloy Ca_2Si are also analyzed in terms of the structures of elemental calcium.

Introduction

It is well known that the traditional ionic model assumes the existence of close-packed anion arrays (normally h.c.p. or f.c.c.), with small cations inserted into the octahedral and/or tetrahedral interstices. Location of cations in one of these holes, and hence the coordination number of the cation, is determined by the radius ratio (r^+/r^-). Consequently, inorganic crystal structures have been described as being formed by such interconnected polyhedra. This approach, although widely used to describe and understand inorganic crystal structures, cannot be generally applied and many 'complicated' structures do not find any satisfactory explanation in terms of this model. Obvious failures have been pointed out by Hyde (1986).

An alternative model, with the emphasis placed on the cation arrays, has been proposed by O'Keeffe & Hyde (1981, 1985), in which cation–cation repulsions and the coordination number of anions by cations are considered to be responsible for determining a given structure, the size of a cation being quantified by the so-called 'non-bonding radius' (O'Keeffe & Hyde, 1981). An additional feature observed by these authors is that, in many oxides and fluorides, the cation arrays are more regular than those of anions and that they have the structure of either elements or simple alloys. Thus, in TiO_2 (rutile), the Ti atom arrangement is that of the tetragonal body-centered β-Hg. In forsterite (Mg_2SiO_4), the Mg_2Si array is that of the Ni_2In alloy. Further, the structure of Si is maintained in cristobalite (SiO_2). In view of this, the structures could be better described as 'anion-stuffed alloys', which are the inverse of the traditional ionic model (cation-stuffed anion arrays). These principles were applied successfully to minerals, like the humite and the leucophoenicite families (White & Hyde, 1982*a,b*, 1983), leading to a simpler description of both structural families, and to a new structural relation between them that was not possible in terms of connected MO_6 octahedra (Belokoneva, Simonov & Belov, 1973). Application to other structure types was the subject of a further report (O'Keeffe & Hyde, 1985).

We think that this catonic approach represents an advance in both description and explanation of crystal structures, but unfortunately the crucial question, *i.e.* why a crystal structure has its actual structure and not another one, is far from being answered as yet. Even though the alternative model succeeds in many aspects not accounted for by the ionic model, we believe that some other considerations could be added. This is the aim of the present contribution.

Probably the most significant observation of O'Keeffe & Hyde (1985) is that in some oxides the cation arrangements are identical to those of the constituent elements, *i.e.* Si in high cristobalite SiO_2, Ca_2Si in β-Ca_2SiO_4, Y_5Si_3 in $Y_5(SiO_4)_3N$, Cu in