The Crystal Structure of PbS$_2$O$_3$

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The crystal structure of lead thiosulfate, PbS$_2$O$_3$, was solved from X-ray and neutron diffraction data. The unit cell was obtained by indexing Guinier film data. The positions of the lead atoms were found by direct methods from single crystal X-ray diffraction data, while the positions of the atoms of the thiosulfate ion were derived from neutron powder diffraction data. The structure was refined by profile analysis of neutron powder diffraction data, and the validity of the structure was tested by profile analysis of synchrotron X-ray powder diffraction data.

The structure was solved and refined in the orthorhombic space group $Pbca$ (No. 61) with the lattice parameters $a = 7.1802(3)$, $b = 6.9199(3)$, $c = 16.1156(8)$ Å and $Z = 8$. The lead atom in the structure is coordinated by six oxygen atoms and three sulfur atoms.

Structure determinations from powder patterns are possible. In combining information from X-ray and neutron powder diffraction data, structure models with acceptable precisions may be found. However, the difficult task in such structure determinations is the indexing of the powder patterns, the determination of the space group of the structure, and the solution of the structure from the powder diffraction data. In some cases, the level of ambiguity in one or more of these steps may be such that even modest data from a single crystal diffraction measurement may supply the additional information that can overcome the ambiguity, so that the structure can be solved. However, for compounds that are normally produced as powders it is often difficult or impossible to obtain single crystals large enough for single crystal X-ray diffractometry.

The crystal structures of PbC$_2$O$_4$[1] and PbSO$_3$[2] were recently solved from powder diffraction data. In attempts to investigate the structure of PbS$_2$O$_3$, single crystals of Pb$_3$(S$_2$O$_3$)$_2$(CH$_3$COO)$_2$ were formed in an experiment involving diffusion crystal growth.[3] Extremely thin single crystals of PbS$_2$O$_3$ have now been obtained in a new series of diffusion growth experiments. The crystal structure of PbS$_2$O$_3$ is reported below. The structure was solved by combining information from X-ray single crystal and powder diffraction data, and from neutron powder diffraction data, and the structure was refined with the latter set of data. Finally, the model of the structure was tested with data from a synchrotron X-ray powder pattern.
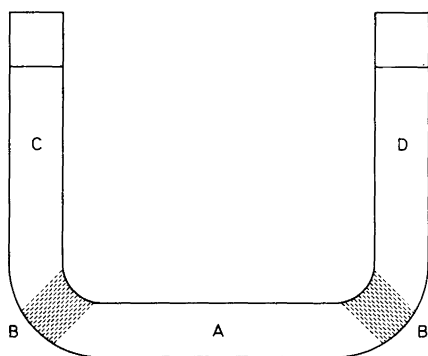
Experimental

Sample preparation. A white crystalline precipitate of PbS$_2$O$_3$ is formed when a solution of lead nitrate is mixed with a solution of sodium thiosulfate. A solution of 22.7 g Pb(NO$_3$)$_2$ (Merck p.a.) in 500 ml water was added dropwise to a solution of 19.0 g Na$_2$S$_2$O$_3 \cdot$5H$_2$O (Ferak p.a.) in 500 ml water. The solution was stirred, and the addition of the lead nitrate solution resulted in a precipitate that was redissolved immediately until approximately 30 % of the lead nitrate solution had been added. When all the Pb(NO$_3$)$_2$ solution had been added, the precipitate formed was washed by decanting, filtered, washed on the filter and dried in air at room temperature. A Guinier photograph of the compound showed that the phase was pure PbS$_2$O$_3$ according to the JCPDS card No. 1-390.[4] (The pattern on this card is unindexed and no reference is given to the

Fig. 1. U-shaped Pyrex glass tube used for diffusion growth: (A) pure water, (B) plug of paper towel, (C) solution of Pb(NO$_3$)$_2$, (D) solution of Na$_2$S$_2$O$_3 \cdot$5H$_2$O. The inside diameter of tube was 22 mm, and the length of the horizontal section was 200 mm.

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origin of the pattern.) In a similar way, a sample of PbS$_2$O$_3$ was precipitated from a solution of 26.0 g Pb(CH$_3$COO)$_2$·3H$_2$O (Merck p.a.) in 500 ml water and 19.0 g Na$_2$S$_2$O$_3$·5H$_2$O (Ferak p.a.) in 500 ml water. In this preparation a permanent precipitate was formed when approximately 20% of the lead acetate solution had been added. A Guinier photograph showed that the compound formed was also pure PbS$_2$O$_3$.

Slow mixing by diffusion of a solution of lead acetate with a solution of sodium thiosulfate results in the formation of white crystalline needles of Pb$_3$(S$_2$O$_3$)$_2$(CH$_3$COO)$_2$.[3] Crystals of PbS$_2$O$_3$ were formed by diffusion mixing of a 0.01 M Pb(NO$_3$)$_2$ (Merck p.a.) solution with a 0.01 M Na$_2$S$_2$O$_3$·5H$_2$O (Ferak p.a.) solution in a U-shaped Pyrex glass tube (Fig. 1). Pure water was first placed in the horizontal part of the U-tube, and a loosely packed plug made of paper towel was placed in each of the bends. The two solutions were then simultaneously poured slowly into the two sides of the U-tube and left at room temperature for six weeks. Extremely thin blades of PbS$_2$O$_3$ were formed during the crystal growth experiment. The crystals formed were washed with water and dried in air. In appearance the white crystals resembled mother-of-pearl. Under a polarizing microscope the thin crystals showed a rectangular habit with parallel extinction of the polarized light, indicating orthorhombic symmetry.

X-Ray powder diffraction. Guinier photographs were taken of the samples of PbS$_2$O$_3$ with a Guinier–Nonius camera using Cu $K\alpha_1$ radiation ($\lambda = 1.540\,598$ Å) and silicon as internal standard ($a_{Si} = 5.430\,50$ Å). The positions and intensities of the Bragg reflections of a pattern were measured on a photometer. The pattern was then indexed by the program FZON,[5] with an orthorhombic cell, $a = 7.178$, $b = 6.918$, $c = 16.108$ Å, and a figure of merit $M_{20} = 49.8$.

The powder pattern of PbS$_2$O$_3$ was also measured on a Stoe diffractometer with a position-sensitive detector and Cu $K\alpha_1$ radiation. The diffractometer was calibrated with standards of Si ($a_{Si} = 5.430\,50$ Å) and Ag$_8$Ge$_{10}$P$_{12}$ ($a = 10.312$ Å).

The synchrotron X-ray powder pattern of PbS$_2$O$_3$ was measured on the powder diffractometer at Station 8.3 at Daresbury,[6] at a wavelength of 1.232 34 Å. The pattern was measured in the 2θ range 5.0–90.0° in steps of 0.01°. The sample was a flat plate of PbS$_2$O$_3$, rotated to reduce the effect of preferred orientation. However, the pattern showed strong preferred orientation for the 00*l* reflections. This pattern was also indexed with the program FZON,[5] yielding practically the same orthorhombic unit cell as above, with $M_{20} = 20.0$. The reflections observed were in agreement with the space group $P2_12_12_1$ (No. 19). However, the reflection at $d = 4.222$ Å has contributions from 112 and 013 that showed an almost perfect overlap. If 013 could be regarded as absent, the first 20 reflections of the two powder patterns were in agreement with the orthorhombic space group *Pbca* (No. 61). A MAS NMR

spectrum of PbS$_2$O$_3$ indicates that the asymmetric unit cell of the structure has only one lead atom position.[7] For this reason, the space group *Pbca* was chosen for the structure determination.

X-Ray single crystal diffraction. A crystal of PbS$_2$O$_3$ with dimensions 0.003×0.20×0.55 mm^3 was used. The extremely thin dimension of the crystal proved to be in the [001] direction. Precession photographs taken with Ag $K\alpha$ radiation ($\lambda = 0.5608$ Å) of the planes *h0l*, *h1l*, *h2l*, and *hk0* gave cell dimensions comparable with the results obtained from the indexing of the powder patterns. Exposure times of 8–12 h were needed for the precession photographs.

A Huber four-circle diffractometer with Ag $K\alpha$ radiation was used to measure all reflections in an octant with $0 \le h \le 6$, $0 \le k \le 6$ and $0 \le l \le 14$. The ω-2θ scan technique was used with a scan width in 2θ of $1.6 + 0.7 \tan \theta$. A total of 452 reflections were measured, including two standard reflections for every 50 reflections. Corrections for absorption by Gaussian integration with $\mu_{Ag} = 240$ cm^{-1} were made, and 77 reflections with $I > 4\sigma(I)$ were obtained.

Neutron powder diffraction. A neutron diffraction powder pattern of PbS$_2$O$_3$ was measured at room temperature on the multi-detector diffractometer D2B at the Institut Laue–Langevin, Grenoble,[8] using 1.5946 Å neutrons. The pattern was measured in the 2θ range 10.0–165.0° in steps of 0.05°. The sample was housed in an 18 mm diameter vanadium container.

Structure determination

Lead thiosulfate is a heavy-atom compound with respect to X-ray diffraction. The average scattering contribution per atom is Pb, 92.3%; S, 2.8%; O, 0.7%. In the case of neutron diffraction, the scattering contributions are more evenly distributed between the three types of atoms, where the average scattering contribution per atom is Pb, 43.0%;

Table 1. Refined parameters for the structure of PbS$_2$O$_3$ (neutron powder diffraction data, space group *Pbca*).[a]

Atom	x/a	y/b	z/c	B/Å^2
Pb	0.9792(6)	0.3377(7)	0.3798(3)	1.47(6)
S1	0.5115(20)	0.3342(20)	0.4000(7)	0.96(22)
S2	0.6075(24)	0.1949(25)	0.2920(10)	2.61(35)
O1	0.4539(12)	0.1778(11)	0.4540(5)	1.91(12)
O2	0.6482(13)	0.4627(13)	0.4262(5)	1.79(13)
O3	0.3413(11)	0.4465(13)	0.3720(5)	1.82(14)

[a]Refined parameters: zero = $-1.023(2)°$, $U = 0.171(6)$, $V = -0.280(6)$, $W = 0.273(4)$, $a = 7.1801(5)$, $b = 6.9197(5)$, $c = 16.1154(13)$ Å. $R_p = 5.9\%$, $R_{wp} = 8.2\%$, $R_F = 8.4\%$, $R_I = 13.5\%$, $R_E = 4.8\%$. For definitions of the *R*-values see Refs. 1 and 18. The FWHM is calculated from the profile parameters as FWHM = $(U\tan^2\theta + V\tan\theta + W)^{1/2}$.
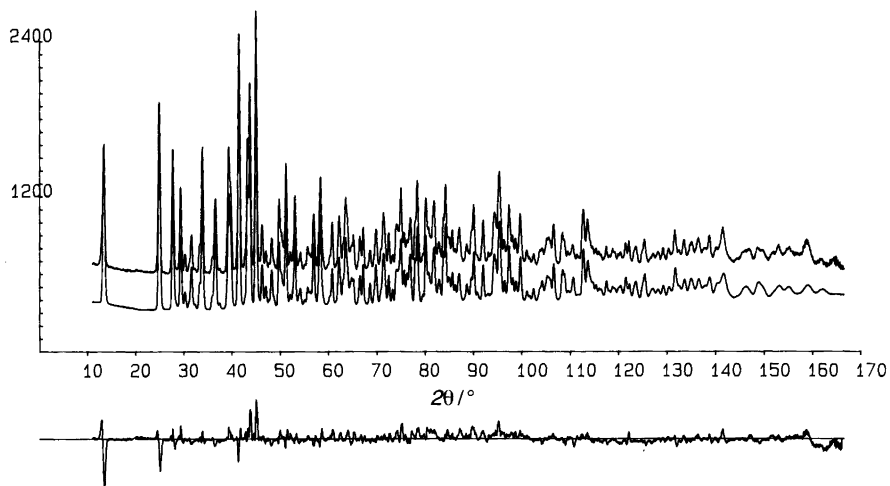
Fig. 2. Neutron difraction powder pattern of PbS_2O_3. The upper and lower curves represent the observed and calculated profiles, respectively, with the difference shown in the lower part of the figure.

S, 3.9%; O, 16.4%. For the structure determination and refinement it is thus an advantage to use a combination of diffraction data from X-ray and from neutron scattering.

With the samples of PbS_2O_3 available it was not possible to measure the density with an acceptable precision by the method of Archimedes. Assuming eight formula units in an orthorhombic cell with dimensions from the indexing of the Guinier film data, the calculated density was 5.30 g cm⁻³, in acceptable agreement with the published density[9] of 5.18 g cm⁻³.

The Stoe X-ray powder pattern and the neutron diffraction powder pattern were decomposed with the program ALLHKL.[10] The observed reflections with $F > \sigma(F)$

obtained from those patterns, from the Guinier photographs and from the single crystal diffractometer data with $I > 4\sigma(I)$ all indicated the same orthorhombic space group.

The intensities of some of the low-angle reflections on the Guinier film were as follows: weak for 002, 102 and 020; medium strong for 004 and 200. A lead atom in the position $(1.000 \pm \delta, 0.375 \pm \delta, 0.375 \pm \delta)$ will qualitatively give the intensity distribution for the abovementioned five reflections for δ-values from 0 to 0.02. This position was also derived from packing considerations: the volume of the unit cell of PbS_2O_3 is approximately twice that of $PbSO_3$.[2] A calculation of the intensities of the powder pattern made by assuming this model and using the

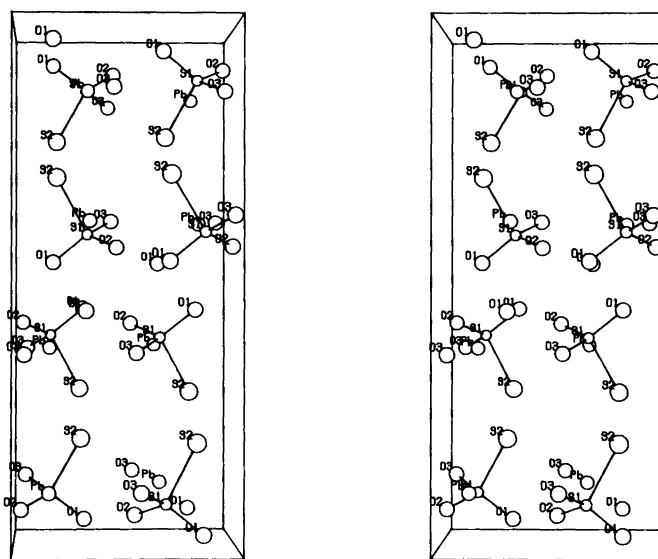Fig. 3. Projection of the structure of PbS_2O_3 along [100]. The b-axis is along the page.

program LAZY PULVERIX[11] confirmed this qualitative agreement between the intensities of the calculated and observed powder patterns for PbS_2O_3.

The single crystal X-ray diffractometer data set was of very low quality. However, the 77 reflections with $I > 4\sigma(I)$ were used in a direct-method determination of the position of the lead atom. The program MULTAN was applied,[12] and one solution was found. The position of the strongest peak corresponding to the position of a lead atom was (0.980, 0.338, 0.378). A structure factor calculation with the X-ray single crystal data using 96 reflections with $I > 3\sigma(I)$, the least-squares program LINUS[13] and scattering contributions from neutral atoms[14] gave a traditional R-value of 31.0 % after a least-squares refinement of the lead atom position. It was thus impossible to determine the positions of the remaining atoms within the structure using this set of data.

The neutron powder diffraction data set was used in the remaining structure determination and structure refinement. The model arrived at by direct methods for the lead atom position was used in a structure-factor calculation with the profile refinement[15] program EDINP[16] and nuclear scattering contributions from Ref. 17. The program gave a list of Miller indices and structure factors for the reflections of the powder pattern. These pseudo-single-crystal data were used in a structure factor calculation with LINUS[13] and in a series of Fourier map calculations until the positions of all atoms in the $S_2O_3^{2-}$ ion were located. The model was then refined in a least-squares profile-refinement analysis[15] using EDINP.[16] Table 1 shows a list of the refined parameters. Fig. 2 displays the observed and calculated neutron diffraction powder pattern with a difference plot, and Fig. 3 shows a projection of the structure along [100].

The structure found was tested by aid of the synchrotron X-ray powder pattern in a least-squares profile-refinement analysis by applying the program DBW3.2S, with neutral

Table 2. Refined parameters for the structure of PbS_2O_3 (synchrotron X-ray powder diffraction data, space group *Pbca*).[a]

Atom	x/a	y/b	z/c	B/Å²
Pb	0.9789(2)	0.3384(2)	0.3803(1)	2.13(3)
S1	0.5010(13)	0.3318(13)	0.3916(3)	0.20(12)
S2	0.6166(13)	0.1752(18)	0.2917(3)	1.13(16)
O1	0.4662(33)	0.1827(34)	0.4463(6)	1.65(38)
O2	0.6423(29)	0.4703(37)	0.4240(7)	0.83(45)
O3	0.3341(24)	0.4406(30)	0.3754(7)	0.00(38)

[a] Refined parameters: zero = 0.0569(3)°, U = 0.0279(32), V = 0.0003(18), W = 0.0039(2). Mixing parameters: NA = 0.684(16), NB = 0.256(1). The pseudo-Voigt function is given by $\eta L + (1-\eta)G$, L and G are the Lorentzian and Gaussian contributions to the reflection, and the mixing parameter η = NA + NB × 2θ. a = 7.1800(1), b = 6.9195(1), c = 16.1096(2) Å. Preferred orientation parameters G_1 = $-6.16(6)$ and G_2 = 0.105(1) are used in the formula I_{corr} = $I_{obs}[G_2+(1-G_2)\exp(-G_1\alpha^2)]$; α is the acute angle between the scattering vector and the orientation direction of preferred orientation [001]. R_p = 7.7 %, R_{wp} = 10.8 %, R_I = 8.1 %, R_E = 4.2 %.

atom scattering contributions.[19] The refined parameters are listed in Table 2, and Fig. 4 shows the observed and calculated synchrotron X-ray diffraction powder pattern with a difference plot.

Description of the structure

The crystal structure of PbS_2O_3 has one independent lead atom and one independent $S_2O_3^{2-}$ ion. The lead atom is coordinated by six oxygen atoms and three sulfur atoms. The packing of the Pb^{2+} and $S_2O_3^{2-}$ ions on top of each other (Fig. 3) resembles the packing of Ba^{2+} and $S_2O_3^{2-}$ ions in $BaS_2O_3 \cdot H_2O$.[20] Table 3 summarises the most important interatomic distances in the structure of PbS_2O_3,
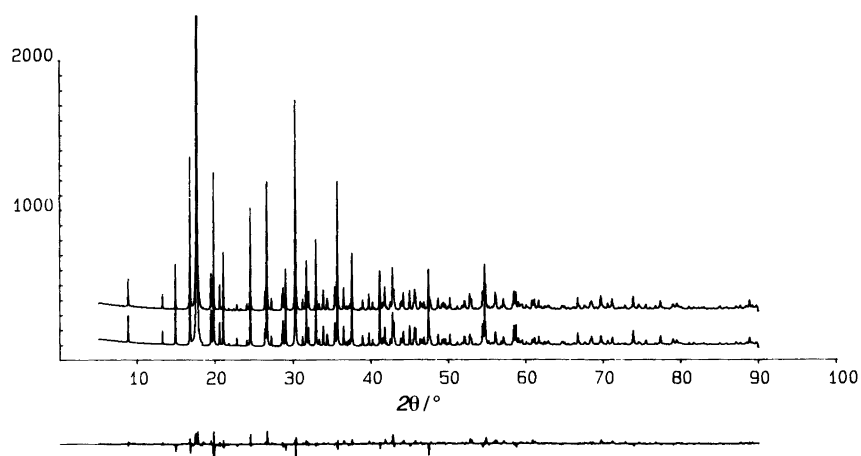

Fig. 4. Synchrotron X-ray powder pattern of PbS_2O_3. The upper and lower curves represent the observed and calculated profiles, respectively, with the difference shown in the lower part of the figure.

Table 3. Interatomic distances (in Å) of PbS_2O_3 and related compounds.

Atoms	Distances	Literature values
Pb−O1	2.68(1)	$Pb_3(S_2O_3)_2(CH_3COO)_2$[a]
Pb−O1	2.69(1)	Pb−O 2.44(2) to 2.96(2)
Pb−O2	2.64(1)	Pb−S 3.012(7) to 3.022(6)
Pb−O2	2.85(1)	S−O 1.46(2) to 1.48(2)
Pb−O3	2.71(1)	S−S 2.045(9)
Pb−O3	3.00(1)	
Pb−S2	2.92(2)	$BaS_2O_3 \cdot H_2O$[b]
Pb−S2	3.08(2)	S−O 1.47(2) to 1.48(2)
Pb−S2	3.18(2)	S−S 1.964(8)
S1−O1	1.45(2)	$Na_2S_2O_3 \cdot 5H_2O$[c]
S1−O2	1.39(2)	S−O 1.459(3) to 1.481(3)
S1−O3	1.52(2)	S−S 2.024(4)
S1−S2	2.11(2)	

[a]Ref. 3. [b]Ref. 20. [c]Ref. 21.

showing acceptable agreement with corresponding distances in $Pb_3(S_2O_3)_2(CH_3COO)_2$,[3] $BaS_2O_3 \cdot H_2O$,[20] and $Na_2S_2O_3 \cdot 5H_2O$.[21]

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