

A Single-Crystal X-Ray Structure Determination of $\text{Pb}_3(\text{S}_2\text{O}_3)_2(\text{CH}_3\text{COO})_2$

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Christensen, A. N. and Hazell, R. G., 1991. A Single-Crystal X-Ray Structure Determination of $\text{Pb}_3(\text{S}_2\text{O}_3)_2(\text{CH}_3\text{COO})_2$. – Acta Chem. Scand. 44: 1077–1079.

Lead forms a number of compounds with low solubility. These compounds are often obtained as microcrystalline powders when precipitated from aqueous solutions. This is the case for the compound PbS_2O_3 , the structure of which is not known in great detail, as well as for the compounds PbC_2O_4 and PbSO_3 , where the crystal structures were recently investigated from X-ray and neutron powder diffraction data.^{1,2} Structure determinations from powder patterns are thus possible,^{1,2} but another approach is to test different crystal growth methods, that may eventually result in crystals large enough for single-crystal X-ray diffractometry. Such efforts resulted in single crystals of lead thiosulfate acetate, $\text{Pb}_3(\text{S}_2\text{O}_3)_2(\text{CH}_3\text{COO})_2$, by slow mixing (diffusion) of a solution of lead acetate with a solution of sodium thiosulfate. The crystal structure of $\text{Pb}_3(\text{S}_2\text{O}_3)_2(\text{CH}_3\text{COO})_2$ is reported below from single-crystal X-ray diffractometry.

Experimental

Sample preparation. White crystal needles of $\text{Pb}_3(\text{S}_2\text{O}_3)_2(\text{CH}_3\text{COO})_2$ were formed in slow mixing by diffusion of a solution of lead acetate with a solution of sodium thiosulfate. The two solutions were made from 9.48 g $\text{Pb}(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$ (Merck p.a.) in 25 ml of water and from 6.20 g $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ (Ferak p.a.) in 25 ml of water. The crystal growth experiment was made in a U-shaped Pyrex glass tube. A plug of Pyrex glass wool was placed in the lower part of the U-tube to reduce the mixing of the two solutions by convection. The two solutions were simultaneously slowly poured into the two sides of the U-tube and left at room temperature for two weeks. The crystals formed were washed with water and dried in air.

X-Ray diffraction. A Guinier photograph of $\text{Pb}_3(\text{S}_2\text{O}_3)_2(\text{CH}_3\text{COO})_2$ was taken with a Guinier camera using $\text{Cu K}\alpha_1$ radiation ($\lambda = 1.540598 \text{ \AA}$) and an internal standard of silicon ($a_{\text{Si}} = 5.43050 \text{ \AA}$). The positions and intensities of the diffraction lines were measured on a double-beam

photometer. The pattern was indexed with the orthorhombic cell $a = 17.530(4)$, $b = 9.226(3)$, $c = 8.800(2) \text{ \AA}$, found in the single-crystal measurements (see below). The X-ray powder pattern was also measured with a Stoe diffractometer with a position-sensitive detector and $\text{Cu K}\alpha_1$ radiation. The detector is curved and covers 40° in 2θ , and with two positions of the detector a 2θ range of 80° is measured. Before the measurement the diffractometer was calibrated with a standard of $\text{Ag}_6\text{Ge}_{10}\text{P}_{12}$ ($a = 10.312 \text{ \AA}$).

A needle-shaped crystal of $\text{Pb}_3(\text{S}_2\text{O}_3)_2(\text{CH}_3\text{COO})_2$ with dimensions $0.038 \times 0.013 \times 0.625 \text{ mm}^3$ was mounted on a goniometer. The needle axis proved to be along the $[001]$ direction. Precession photographs of the planes $h0l$, $h1l$, $0kl$ and $1kl$ gave the preliminary values of the unit cell parameters. The conditions for the observed reflections on the precession photographs indicated the space group $Pccn$ (No. 56).

A four-circle diffractometer (Huber) using $\text{Mo K}\alpha$ radiation ($\lambda = 0.7107 \text{ \AA}$) and the ω - 2θ step-scan technique was used in the data collection. The total scan width in 2θ was $1.6 + 0.692 \tan \theta$. The extent of the reflection was determined with the $\sigma(I)/I$ method.³ Two standard reflections were measured for every 50 reflections. A total of 3584 reflections were measured, corrected for absorption ($\mu = 355 \text{ cm}^{-1}$) by Gaussian integration, and averaged to 1495 independent reflections with $I > \sigma(I)$.

The unit cell parameters determined on the four-circle diffractometer in a least-squares fit with 25 reflections measured at high and low χ and at positive and negative θ were: $a = 17.530(4)$, $b = 9.226(3)$, $c = 8.800(2) \text{ \AA}$.

Structure determination

The structure was solved by direct methods using the measured structure factors and the program MULTAN.⁴ The four highest peaks found by the program were interpreted as positions for two lead atoms and two sulfur atoms. Phased on this model the remaining atoms in the structure were found by structure-factor and Fourier-map calculations. The structure was refined (LINUS)⁵ by a least-

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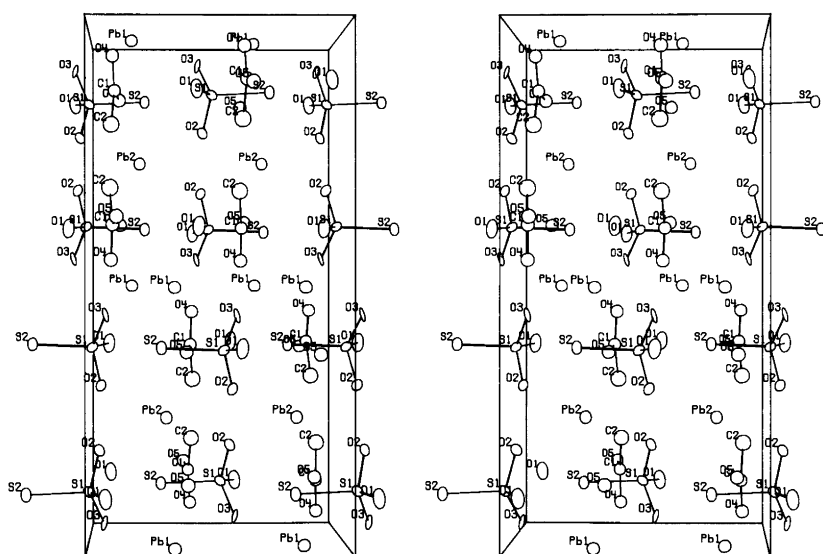


Fig. 1. Stereoscopic projection of the structure of $\text{Pb}_3(\text{S}_2\text{O}_3)_2(\text{CH}_3\text{COO})_2$ along [010]. The c -axis is along the page.

squares procedure using neutral atoms for the scattering factors.⁶ The scattering contribution from the lead atoms was corrected for anomalous dispersion.⁷ No attempts were made to locate the hydrogen atoms in the acetate ions. The final $R(F)$ -value was 6.0% [$R(F) = 100 \times \sum |F_{\text{obs}}| - |F_{\text{calc}}| / \sum |F_{\text{obs}}|$]. A list of observed and calculated structure factors is available on request from the authors. The positional and thermal parameters of the structure are listed in Table 1, and Fig. 1 is a stereoscopic drawing of the structure viewed along the [010] direction.

The model of the structure arrived at was used to calculate the profile of the X-ray powder pattern of the compound and to compare the calculated profile with the observed profile in a least-squares procedure using the program EDINP.⁸ This calculation showed that the crystal investigated was representative for the bulk sample.

Discussion

The diffusion crystal growth experiment with solutions of lead acetate and sodium thiosulfate resulted in crystals of $\text{Pb}_3(\text{S}_2\text{O}_3)_2(\text{CH}_3\text{COO})_2$. The intention with this growth experiment was to produce single crystals of PbS_2O_3 , but at the experimental conditions used crystals of $\text{Pb}_3(\text{S}_2\text{O}_3)_2(\text{CH}_3\text{COO})_2$ were formed in preference to crystals of PbS_2O_3 .

The single-crystal structure investigation of $\text{Pb}_3(\text{S}_2\text{O}_3)_2(\text{CH}_3\text{COO})_2$ shows a layer character of the structure with layers of lead atoms parallel to the bc -plane. The layers are held together by the $\text{S}_2\text{O}_3^{2-}$ and the CH_3COO^- ions. The lead atom Pb1 is eight-coordinated with seven oxygen atoms and one sulfur atom, and the lead atom Pb2 is eight-coordinated with six oxygen atoms and two sulfur atoms. The interatomic distances are listed in Table 2 and are compared with the lead–oxygen distances found in the crystal structures of PbC_2O_4 ,¹ PbSO_3 ,² PbSO_4 ⁹ and $\text{Pb}(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$.¹⁰ However, the standard deviations

on the interatomic distances are twice as large as found for the structures of PbC_2O_4 ,¹ PbSO_3 ,² $\text{Pb}(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$ ¹⁰ and $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$.¹¹ This is due to the heavy-atom nature of the structure, where a considerable scattering contribution comes from the lead atom in the X-ray case, and to the rather small size of the crystal investigated. Only 1495 independent reflections were used in the structure refinement. The structures of Refs. 1, 2 and 11 were refined with neutron diffraction data, where the heavy-atom nature of the compounds less pronounced than in the X-ray scattering case. The structure of Ref. 10 was derived from single-crystal X-ray diffraction data. The compound $\text{Pb}(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$ readily crystallizes from aqueous solutions, so it is easy to select crystals with optimum size for an X-ray diffraction experiment for this compound, and this was not the case for $\text{Pb}_3(\text{S}_2\text{O}_3)_2(\text{CH}_3\text{COO})_2$.

Table 1. Atomic coordinates and equivalent isotropic temperature factor parameters, $U_{\text{eq}} \times 10^4$,^a for $\text{Pb}_3(\text{S}_2\text{O}_3)_2(\text{CH}_3\text{COO})_2$. For the last four atoms isotropic U -values are given.

Atom	x/a	y/b	z/c	$U_{\text{eq}}/U_{\text{iso}}$
Pb1	0.4986(1)	0.2075(1)	0.1658(1)	193(4)
Pb2	0.2500	0.2500	0.1979(2)	176(5)
S1	0.3812(3)	0.0542(7)	0.4860(7)	137(26)
S2	0.3863(4)	0.0504(7)	0.7182(7)	178(29)
O1	0.3867(12)	0.9077(18)	0.4232(21)	220(93)
O2	0.3075(10)	0.1222(21)	0.4508(21)	196(85)
O3	0.4447(10)	0.1468(20)	0.4326(18)	170(80)
O4	0.9499(11)	0.0917(21)	0.4064(22)	210(38)
O5	0.8723(11)	0.8932(21)	0.3830(22)	215(38)
C1	0.8850(15)	0.0311(28)	0.3998(32)	194(49)
C2	0.8146(18)	0.1268(36)	0.4108(38)	318(67)

$$^a U_{\text{eq}} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$$

Table 2. Interatomic distances (in Å) of $\text{Pb}_3(\text{S}_2\text{O}_3)_2(\text{CH}_3\text{COO})_2$ and a comparison with related literature values.

Distances	Literature data
Pb1–O5 2.44(2)	PbC ₂ O ₄ , Ref. 1
Pb1–O3 2.59(2)	
Pb1–O3 2.63(2)	Pb–O 2.432(7) to 2.903(8)
Pb1–O4 2.68(2)	
Pb1–O1 2.84(2)	PbSO ₃ , Ref. 2
Pb1–O4 2.96(2)	
Pb1–O4 2.96(2)	Pb–O 2.726(3) to 3.020(3)
Pb1–S2 3.012(7)	
Pb2–O5 2.62(2)	PbSO ₄ , Ref. 9
Pb2–O5 2.62(2)	
Pb2–O2 2.67(2)	Pb–O 2.63 to 3.25
Pb2–O2 2.67(2)	
Pb2–O2 2.71(2)	Pb(CH ₃ COO) ₂ ·3H ₂ O, Ref. 10
Pb2–O2 2.71(2)	
Pb2–S2 3.022(6)	Pb–O 2.45(1) to 2.74(1)
Pb2–S2 3.022(6)	
C1–C2 1.52(4)	C–C 1.53(1)
C1–O4 1.27(3)	C–O 1.22(1) to 1.26(1)
C1–O5 1.30(3)	
S1–S2 2.045(9)	Na ₂ S ₂ O ₃ ·5H ₂ O, Ref. 11
S1–O1 1.46(2)	
S1–O2 1.47(2)	S–S 2.024(4)
S1–O3 1.48(2)	S–O 1.459(3), 1.461(3) and 1.481(3)

The interatomic distances of the $\text{S}_2\text{O}_3^{2-}$ and the CH_3COO^- ions are also listed in Table 2 and are compared with distances in the structures of $\text{Pb}(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$ ¹⁰ and $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$.¹¹

Acknowledgements. Teknologistyrelsen is acknowledged for making the Stoe X-ray diffractometer available, and the four-circle diffractometer was obtained by grants from *Carlsbergfondet* and *Statens naturvidenskabelige Forskningsråd*. Mrs. M. A. Chevallier is acknowledged for valuable assistance.

References

- Christensen, A. N., Cox, D. E. and Lehmann, M. S. *Acta Chem. Scand.* 43 (1989) 19.
- Christensen, A. N. and Hewat, A. W. *Acta Chem. Scand.* 44 (1990) 688.
- Lehmann, M. S. and Larsen, F. K. *Acta Crystallogr., Sect. A* 30 (1974) 580.
- Main, P., Lessinger, L., Woolfson, M. M., Germain, G. and Declercq, J.-P. *MULTAN*, Universities of York, England and Louvain, Belgium 1977.
- Busing, W. R., Martin, K. O. and Levy, H. A. *ORFLS: A Fortran Crystallographic Least Squares Program*, ORNL-TM-305 Oak Ridge National Laboratory, Oak Ridge, TN 1962. LINUS is a 1971 version of ORFLS.
- Cromer, D. T. and Mann, J. B. *Acta Crystallogr., Sect. A* 24 (1968) 321.
- Lonsdale, K. *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham 1962, Vol. III, p. 216.
- Pawley, G. S. *J. Appl. Crystallogr.* 13 (1980) 630.
- Sahl, K. *Beitr. Mineral Petrogr.* 9 (1963) 111.
- Bryant, R. G., Chacko, V. P. and Etter, M. C. *Inorg. Chem.* 23 (1984) 3580.
- Lisensky, G. C. and Levy, H. A. *Acta Crystallogr., Sect. B* 34 (1978) 1975.

Received April 26, 1990.