Preparation, Infrared Spectra and Crystal Structure of Aquabis(hydroxymethanesulfonato)lead(II)

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A reaction product formed by degradation of lead in a water-saturated atmosphere containing formaldehyde and sulfur dioxide has been characterized by IR spectroscopy and X-ray diffraction. The IR spectra indicated that the compound is a salt of hydroxymethanesulfonic acid containing water, and the crystal structure determination shows the compound to be aquabis(hydroxymethanesulfonato)lead(II), which crystallizes in $P2_1/c$ with $Z = 4$. At 122 K the cell dimensions are $a = 5.471(1)$, $b = 17.679(3)$, $c = 9.481(1)$ Å and $\beta = 91.93°(2)$. The structure was refined to $R = 0.024$ using 4095 observed reflections. The lead atom is surrounded by nine coordinating oxygen atoms, coming from the water molecule and five different anions, which form five- and four-membered chelate rings. A comparison is made with other lead(II) complexes having organic oxygen ligands. The crystal packing is determined by the lead–oxygen interactions and hydrogen bonds forming a three-dimensional network.

The degradation of lead in contaminated air has recently been investigated.[1] During these studies it was discovered that a plate of lead degrades very fast in water-saturated atmospheric air containing significant amounts of formaldehyde and sulfur dioxide. One of the degradation products was isolated, and its infrared spectrum indicated that it was a salt of hydroxymethanesulfonic acid. In order to establish its identity, the degradation product was subjected to X-ray diffraction studies which showed the compound to be aquabis(hydroxymethanesulfonato)lead(II). Previously, only sodium and potassium have been reported to form salts of hydroxymethanesulfonic acid, and the structure of the potassium salt has been published.[2] Recently, the crystal structures of the aluminium and magnesium salts have also been described.[3]

Below, details of preparation, IR spectra and crystal structure of the degradation product are reported, along with a discussion of the relation of this salt to other known structures of lead complexes with organic oxygen ligands.

Experimental

Preparation. Details of the degradation reaction of lead are given elsewhere.[1] The aquabis(hydroxymethanesulfonato)-lead(II) crystals used for the IR spectra and the X-ray crystallographic studies were prepared by the simple method described below.

In a closed 2 l glass container two beakers (25 ml), with aqueous formaldehyde (37 %) and sulphur dioxide

(saturated), respectively, were placed. A plate of lead (0.1 × 1 × 7 cm) was placed on a watch glass in the container. It was preferable to bend the lead plate a little, and place it so that only its ends were in contact with the watch glass. Within a few hours the lead was obviously affected,[1] and after about 24 h a colourless liquid was formed on the watch glass. If the watch glass was removed and placed for evaporation, rod- and plate-like white crystals were formed within a week.

Potassium hydroxymethanesulfonate needed for the comparative IR spectroscopic studies was prepared by a method similar to the one used for the sodium salt.[4] Equivalent molar amounts of an aqueous solution of $K_2S_2O_5$ (2.75 g in 6 ml water) and 1.9 ml of 37 % formaldehyde were mixed and stirred for 15 min at room temperature. 14 ml of ethanol were added to the solution, which was stirred for an additional 10 min followed by cooling at 5 °C for 24 h. The white crystalline aggregates formed were washed with cooled ethanol and dried at room temperature.

IR spectra. The IR spectra were recorded on a Perkin Elmer 580 grating spectrometer (double beam) in the region 4000–300 cm^{-1}. The specimens for examination were prepared by the KBr technique and the mull technique[5] using nujol and poly(chlorotrifluoroethylene) oil.

Crystal structure determination. A crystal suitable for the diffraction study was selected from the crystalline material formed on the watch glass. Weissenberg photographs recorded at room temperature showed that they belong to the monoclinic system; the space group is uniquely determined to be $P2_1/c$.

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Table 1. Crystal data and a summary of data collection and refinement results.

Formula	[(HOCH$_2$SO$_3$)$_2$H$_2$O)]Pb(II)	
Formula weight/g mol^{-1}	447.40	
Space group	P2$_1$/c	
Crystal size/mm	0.19×0.26×0.04	
Temperature/K	122	
Radiation, λ/Å	MoKα 0.710 73	
linear absorption coefficient, μ/cm^{-1}	190.10	
Cell parameters	*at 122 K*	*at 298 K*
a/Å	5.471(1)	5.48
b/Å	17.679(3)	18.84
c/Å	9.481(1)	9.63
β/°	91.934(15)	91.8
V/Å^3	916.5(5)	980
Z	4	
d$_{calc}$/g cm^{-3} (at 298 K)	3.18	
θ-Range/°	1–47	
Scan type	ω/2θ	
Scan range, Δω/°	0.8 + 0.35 tan θ	
Max. scan time/s	60	
Octants measured	h k ±l	
No. of measured reflections	8995	
No. of contributing reflections ($|F|^2 \geq 3.0$ σ($|F|^2$))	4095	
Weights, [a]w^{-1} = σ^2(f)	σ^2$_{cs}$(F) + 0.0009$|F|^2$	
No. of variables, m	127	
R	0.024	
R$_w$	0.034	
Max. shift/error	0.01	
S = {ΣwΔF^2/(n−m)}$^{1/2}$	0.89	

[a]σ$_{cs}$ (F) is the standard deviation calculated from counting statistics.

Table 2. Fractional coordinates and equivalent isotropic displacement parameters, B$_{iso}$.

Atom	x	y	z	B$_{iso}$/Å^2
Pb	0.37254(2)	0.39282(1)	0.13455(1)	0.782(1)
S1	−0.1291(1)	0.35681(4)	0.38963(7)	0.75(1)
O11	0.1221(5)	0.3802(2)	0.3690(3)	1.23(4)
O12	0.0619(5)	0.3719(2)	−0.0670(3)	1.28(4)
O31	−0.1477(5)	0.3030(2)	0.5059(3)	1.07(4)
C1	−0.2984(6)	0.4392(2)	0.4378(3)	0.94(4)
O41	−0.3507(5)	0.4841(1)	0.3198(3)	1.08(4)
S2	−0.1458(1)	0.41647(5)	−0.11944(8)	0.78(1)
O21	−0.2530(5)	0.3293(1)	0.2597(3)	1.13(4)
O22	−0.2660(5)	0.4585(2)	−0.0072(3)	1.34(4)
O32	−0.0903(5)	0.4650(2)	−0.2371(3)	1.46(4)
C2	−0.3705(6)	0.3499(2)	−0.1825(3)	0.95(4)
O42	−0.4629(5)	0.3103(1)	−0.0673(3)	0.98(3)
O3	0.2596(5)	0.2541(2)	0.1648(3)	1.29(4)

$$^aB_{iso} = \frac{8\pi^2}{3} \sum_i \sum_j U_{ij}\, \mathbf{a}_i \cdot \mathbf{a}_j\, a_i^*\, a_j^*.$$

anisotropic displacement parameters had been introduced, the subsequent difference density showed clearly the posi-
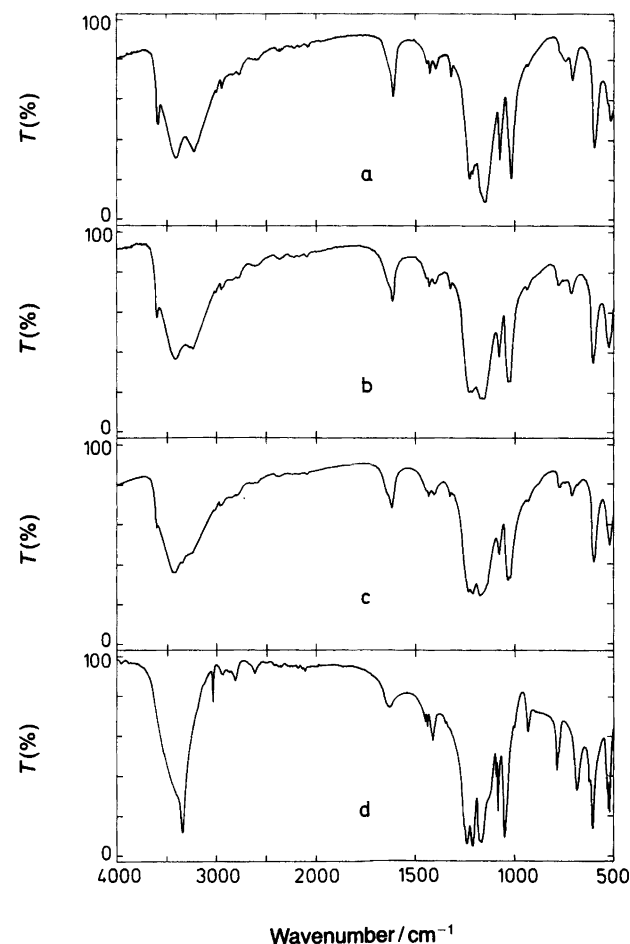
Fig. 1. IR spectra in the region 4000–500 cm^{-1} using the KBr technique: [(a), (b) and (c)] different samples of aquabis(hydroxymethanesulfonato)lead(II), (d) potassium hydroxymethanesulfonate.

A CAD4 diffractometer with monochromatized MoKα radiation was used for the data collection. The crystal was cooled to 122 K by an Enraf–Nonius gas-flow low-temperature device; the temperature was monitored with a thermocouple in the exhaust pipe placed a few centimetres above the crystal and remained constant within 1 K during the experiment. The unit cell dimensions were determined from 22 reflections (18.9 < θ < 22.2°).

The crystal data and a summary of the data reduction and the structure refinement results are presented in Table 1. The intensities of three standard reflections were measured at 10^4 s intervals, and the orientation of the crystal was checked every 300 reflections. These measurements showed that no deterioration or mis-setting had occurred during the data collection. The data reduction included corrections for background, Lorentz, polarization and absorption effects. The Gaussian integration procedure with grid size 8×8×8 was used for the latter correction; the transmission factors were in the range 0.046–0.441. Symmetry-related reflections were averaged, R$_{int}$ = 0.020, resulting 8348 independent reflections.
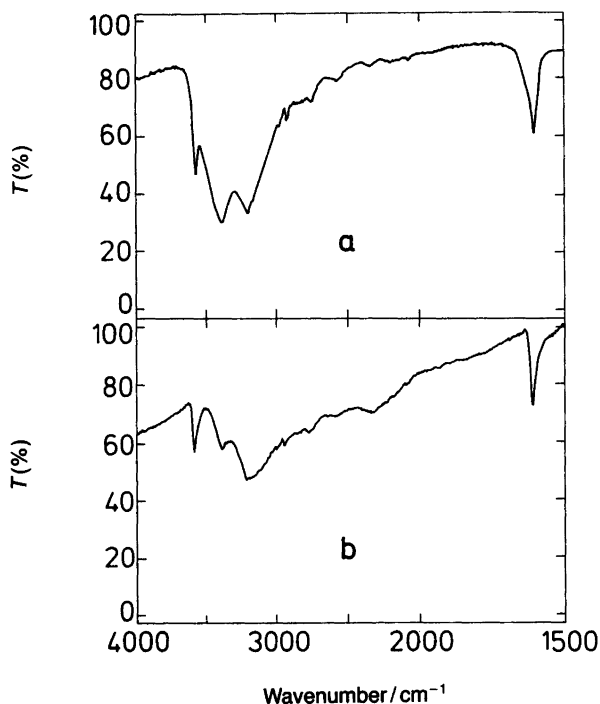
The position of the lead atom was determined from the Patterson function; the remaining non-hydrogen atoms were found through successive difference Fourier calculations. The full-matrix least-squares method, minimizing Σw ($|F_o|-|F_c|)^2$, was used for the structure refinement. After

Fig. 2. IR spectrum in the region 4000–1500 cm^{-1} of catena-aquabis(hydroxymethanesulfonato)lead(II) (a) using the KBr technique and (b) using the mull technique.

tions of all the hydrogen atoms. However, for the final refinement, hydrogen atoms bonded to carbon atoms were introduced in idealized positions. A fixed isotropic displacement parameter of 2.5 Å^2 was used for the hydrogen atoms, and their contribution was included in the structure factor calculation. The SDP system[6] was employed for the crystallographic computations. The atomic scattering factors, including the contribution from anomalous dispersion, were taken from Ref. 7. The final difference density map had peaks in the range −2.5 to 2.5 e Å^{-3}; virtually all the peaks with a numerical value above 1 e Å^{-3} were found close to the lead atom. The final positional parameters for the non-hydrogen atoms are listed in Table 2. The anisotropic displacement parameters for the non-hydrogen atoms, the positional parameters for the hydrogen atoms and lists of observed and calculated structure amplitudes are available from the authors.

Results and discussion

IR spectra. Figs. 1a–c show the spectra of different samples of aquabis(hydroxymethanesulfonato)lead(II) (PbHMS) obtained by the KBr technique. These spectra are not completely identical. The spectrum recorded of PbHMS using a given KBr pellet will change with time, until it looks like the spectrum of potassium hydroxymethanesulfonate (KHMS, Fig. 1d), indicating that an exchange of Pb^{2+} with K$^+$ occurs. The time needed for a full exchange varies from hours to days, presumably depending on small variations in the preparation of the samples and the quality of the crystals.
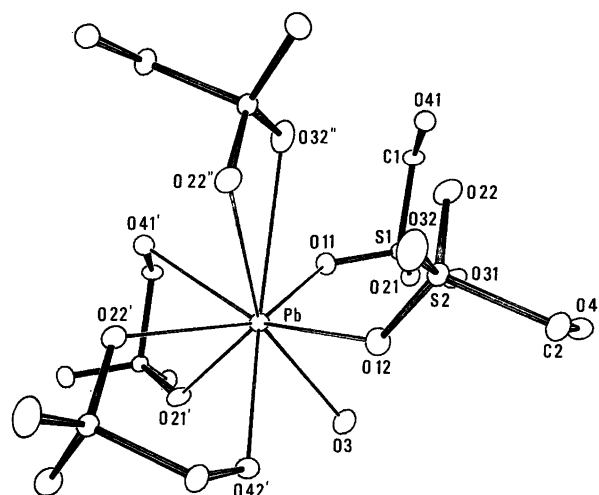

Fig. 3. Coordination of lead illustrated using an ORTEP[17] drawing. The thermal ellipsoids are scaled to enclose 50 % probability. The labelling refers to Tables 3 and 5.

The spectrum shown in Fig. 1a corresponds to PbHMS, where only a small exchange has taken place. This is confirmed from IR spectra using the mull technique. Fig. 2 shows part of the IR spectrum of PbHMS using the mull technique, compared with its KBr spectrum. The difference between the spectra is mainly caused by water in the KBr used for the preparation of the KBr pellet. In the region below 1500 cm^{-1} the mull spectra and the KBr spectra are identical.

The IR spectrum of PbHMS (Fig. 2) shows relatively sharp lines at 3589 and 1613 cm^{-1}, positions characteristic of OH streching vibrations in free OH groups and HOH bending in crystal water, respectively.[5] The lines disappear as the exchange between Pb^{2+} and K$^+$ takes place, corresponding to the fact that KHMS does not contain crystal water.[2] As a consequence the lines are assigned to the water in PbHMS, where at least one of the hydrogen atoms is free in the sense that it does not participate in hydrogen bonding.

The spectra of PbHMS and KHMS (Figs. 1a and d) are very similar below 1600 cm^{-1}, with the exception of minor differences in the region 850–650 cm^{-1}, where the C–OH torsion mode is expected.[5] In the 3600–2500 cm^{-1} region the spectra differ significantly. The IR spectrum of PbHMS (Fig. 1a) shows a broad structural band in the region 3500–

Table 3. Coordination of Pb, distances (in Å) and angles (in °).

Pb–O11	2.660(3)	O11–Pb–O12	105.4(1)
Pb–O21'	2.589(3)	O12–Pb–O22'	99.9(1)
Pb–O41'	2.794(3)	O22'–Pb–O41'	70.9(1)
Pb–O12	2.542(3)	O41'–Pb–O11	78.8(1)
Pb–O22'	2.691(3)	O22'–Pb–O42'	66.1(1)
Pb–O42'	2.592(3)	O41'–Pb–O21'	63.8(1)
Pb–O3	2.547(3)	O11–Pb–O3	72.1(1)
Pb–O22"	2.944(3)	O22'–Pb–O22"	63.2(1)
Pb–O32"	3.122(4)	O22"–Pb–O32"	46.8(1)

$'(1+x, y, z); "(2-x, 1-y, -z).$

Table 4. Lead complexes with oxygen ligands from organic molecules.

Compound	Coordination no.	Range of Pb–O distances	Oxo-bridge	4-Ring	5-Ring	Ref.
Aquabis(hydroxymethanesulfonato)lead(II)	9	2.54–3.12	–S–O	O–S–O	2×O–S–C–O	
Aquabis(p-hydroxybenzoato)lead(II) monohydrate	8	2.50–2.89	–C–O	O–C–O	–	8
Lead(II) formate	8	2.47–2.87	–C–O	–	–	15
Lead(II) malonate	8	2.41–2.99	–C–O	–	–	16
Catena-μ-(aquabis(phenoxyacetato-O)lead(II)bis(oxyacetato)lead(II))	8	2.51–2.96	–C–O	O–C–O	O–C–C–O	9
Lead(II) crotonate	6	2.35–2.64	2×–C–O	O–C–O	–	10
Lead(II) monoglycerate	6	2.24–3.09	3×–C–O	–	2×O–C–C–O	13
Aquabis(salicylato-O,O')lead(II)	6	2.40–2.99	–	2×O–C–O	–	11
Diaquadiacetatolead monohydrate	9	2.45–3.11	2×–C–O	2×O–C–O	–	12
Lead(II) D-gluconate	6	2.43–2.71	–	–	O–C–C–O	14

2500 cm^{-1} in contrast to the spectrum of KHMS (Fig. 1d), where a relatively sharp and strong line at 3320 cm^{-1} dominates the region. The simple spectrum of KHMS is in accordance with the fact that no crystal water is present and that the hydroxymethanesulfonate anion forms cyclic dimers,[2] with an inversion symmetry, giving rise to only one IR-active OH stretching mode (asymmetric stretch). In contrast (*vide infra*), three different hydrogen bonds are formed in the crystals of PbHMS, two involving the hydroxy group in the two independent anions and the third involving one of the water hydrogen atoms. Assignment of the OH stretching region is not possible without further experiments including Raman spectra. However, the observed spectra are in accordance with the relatively complicated hydrogen bond pattern in aquabis(hydroxymethanesulfonato)lead(II).

Crystal structure

Coordination of lead(II). The structure determination

Table 5. Bond distances (in Å) and angles (in °) for the hydroxymethanesulfonate anions.

	j = 1	j = 2
Sj–O1j	1.455(3)	1.467(3)
Sj–O2j	1.468(3)	1.471(3)
Sj–O3j	1.462(3)	1.447(3)
Sj–Cj	1.793(4)	1.790(4)
Cj–O4j	1.394(4)	1.406(4)
O1j–Sj–O2j	113.1(2)	112.9(2)
O2j–Sj–O3j	112.1(2)	111.7(2)
O3j–Sj–O1j	112.1(2)	113.7(2)
Cj–Sj–O1j	107.6(2)	106.1(2)
Cj–Sj–O2j	104.7(2)	104.8(2)
Cj–Sj–O3j	106.7(2)	107.0(2)
Sj–Cj–O4j	110.6(2)	109.2(2)

Torsion angles:

O4j–Cj–Sj–O1j	−76.7	−68.7
O4j–Cj–Sj–O2j	44.1	50.9

proved that the degradation product is aquabis(hydroxymethanesulfonato)lead(II). Fig. 3 illustrates the environment of lead in the crystal. The lead atom is coordinated by nine oxygen atoms, one oxygen from the water molecule and the remaining eight from five different HMS anions. Two five-membered chelate rings (Pb–O4i–Ci–Si–O2i, i = 1,2) are formed by the two independent anions, and one symmetry-related anion (Table 3) contributes with a four-membered chelate ring (Pb–O22–S2–O23). The two remaining symmetry-related anions each contribute with one sulfonate oxygen (O1i). The nine coordinating oxygen atoms have Pb–O distances in the range 2.542–3.122 Å. The coordination geometry of lead is illustrated in Table 3, which demonstrates that the nine coordinating oxygen atoms constitute an irregular polyhedron around the lead. Four of them, O11, O12, O22' and O41', almost form a square. O22" and O32", with the longest Pb–O distances, are on one side of this square, and O3, O42' and O21', are on the opposite side in a triangular arrangement. O22" forms an oxo bridge to another lead atom.

The coordination polyhedra in lead(II) salts reported in the literature are in most cases very irregular, with coordination numbers in the range 6–9. A survey is presented in Table 4 of structures of lead(II) oxygen complexes of ligands containing water and organic oxygen. Four-membered chelate rings have been observed in several carboxylate salts: hydroxybenzoate,[8] phenoxyacetate,[9] crotonate,[10] salicylate[11] and acetate.[12] A five-membered ring is found in the structure of phenoxyacetate,[9] monoglycerate[13] and gluconate.[14] Oxo bridges occur in the formate[15] and malonate[16] and the abovementioned carboxylates except salicylate. All these structural elements are found in the coor-

Table 6. Hydrogen-bond distances (in Å) and angles (in °).

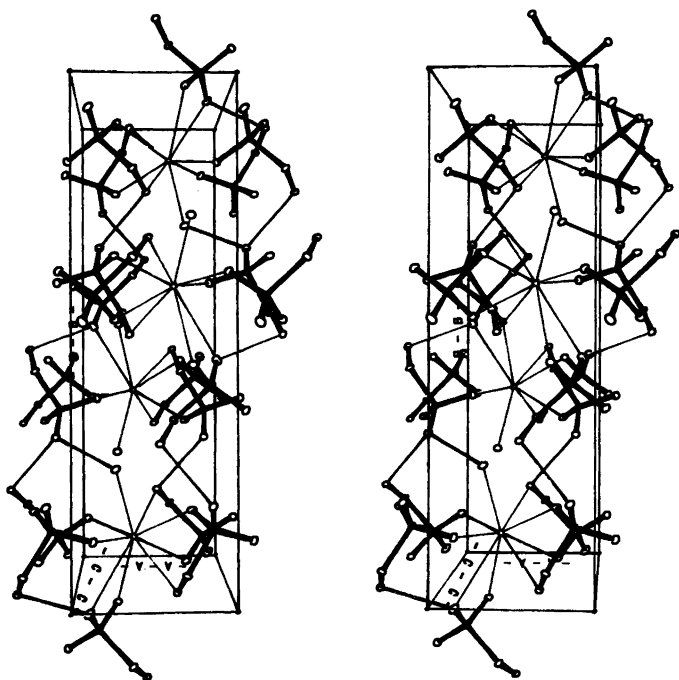| Donor–H···acceptor	D–A/Å	∠D–H···A/°
O42–H42···O31'''	2.714(4)	166
O41–H41···O32''	2.715(4)	169
O3–H23···O31'''	2.833(4)	163

'' (2−x, 1−y, −z); ''' (x, ½−y, z+½).

Fig. 4. Stereo view of the crystal packing seen in the direction of the c-axis. The hydrogen bonds are indicated as thin lines.

dination of lead in the present structure, which makes it unique.

It is remarkable that there are no systematic variations in the Pb–O distances with respect to the type of oxygen involved. The distance to the water oxygen varies from 2.45 to 3.11 Å, to the hydroxy oxygen from 2.48 to 2.99 Å, and to charged oxygens from 2.24 to 3.12 Å. The distance between lead and the ether oxygen in the phenoxyacetate complex[9] is 2.96 Å.

The hydroxymethanesulfonate anions. The bond lengths and angles observed for the hydroxymethanesulfonate anion in the present structure are listed in Table 5. The values are quite similar for the two independent anions and agree well with those observed in the HMS salts of K^+,[2] Mg^{+2} and Al^{3+}.[3] The similarity between the torsion angles $O4j–Cj–Sj–O1j$ in the two independent anions is probably due to the limited flexibility of the five-membered chelate rings.

Crystal packing. Hydrogen bonding plays a very important role in the crystal packing, and in Table 6 the geometries of the hydrogen bonds are listed. An extended three-dimensional network of hydrogen bonds and lead–oxygen interactions is observed in the crystal as illustrated in the stereo-packing diagram in Fig. 4.

In the direction of the b-axis hydrogen bonds are formed between the hydroxy group from one anion and the sulfur oxygen O3i from a symmetry-related anion, linking the anions in a head-and-tail arrangement forming bent anion

chains. The oxo bridge formed by the sulfur oxygen O22 connects the lead atoms.

Two lead atoms related by translation symmetry along the a-axis are connected by the two independent anions with O2i and O4i (i = 1,2) ligating to one lead atom and with O1i ligating to the other lead atom.

In the direction of the c-axis there are weaker interactions between different anion chains through coordination to the lead atoms forming a zig-zag type of arrangement.

The water molecule plays a minor role in the three-dimensional network. Both protons in the water molecule were located with O–H distances of 0.8 Å and an H–O–H angle of 120°. One of the protons forms a hydrogen bond to the sulfur oxygen O31. The observation that only one of the protons of the water molecule takes part in hydrogen bonding is in agreement with the IR spectroscopic results. In the direction of the b-axis the water molecule connects a lead atom to an anion related by a glide plane.

The intermolecular interactions described above explain the morphology of the crystals: they are elongated in the direction of the b-axis or form plates with the face (001).

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