2.

THE STRUCTURE OF LEAD(II) HYDROXY-BROMIDE

BY

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Synopsis

Pb(OH)Br can be prepared from aqueous solutions of lead bromide with an excess of bromide at elevated temperatures, or by mixing aqueous solutions of sodium hydroxide and lead bromide. By the former method the compound is obtained as white needles, birefringent with γ' parallel with the needle axis. The X-ray analysis shows that they are orthorhombic belonging to space group no. 62 Pmnb with $a = 4.089$ Å, $b = 7.384$ Å and $c = 10.010$ Å. It appears that the lead atoms and the hydroxyl groups form chainlike poly-ions, $(Pb(OH)^+)_n$ running parallel with the a-axis. The halogen atoms are distributed between the poly-ions. The compound is isostructural with SbSBr.

Introduction

In order to find the conditions under which the white $CsPbBr_3$ mentioned in the previous paper could be prepared, aqueous solutions with varying concentrations of CsBr were saturated with $PbBr_2$. A few drops of the solutions were placed in a hollow microscope slide on a hot stage and watched through a microscope. After heating to 70–80°C for some time it was often observed that thin white crystals began to grow from the edge of the solution. In the hope that they were the wanted white crystals of $CsPbBr_3$, some of them were isolated and examined optically and by X-rays. It turned out that the crystals did not undergo a phase transition to the yellow $CsPbBr_3$ at 140°C as described by WELLS[1] so that it seemed doubtful from the very beginning what they were. However, from the X-ray diagrams it was possible to identify them as Pb(OH)Br, a compound which may be formed under just those conditions[2].

An X-ray investigation of Pb(OH)Cl (laurionite) has been made by BRASSEUR[3] and of Pb(OH)I by NÄSÄNEN, MERILÄINEN, UGGLA and HYLE[4], so that it might seem rather useless to enter into a detailed investigation of Pb(OH)Br also. However, in Brasseur's work the OH-groups, and partly also the Cl-atoms, were located from space-filling considerations and no comparison is given of observed and calculated structure factors. In the other work the positions of all the atoms were obtained by the method of steepest descents, but it appears that one of the OH-I distances is unlikely short: 3.15Å compared with the sum of the ionic (or van der Waals) radii of I and OH: $2.2 + 1.4 = 3.6$Å. Hence it was considered worth while to look more closely at the structure of Pb(OH)Br, although one could scarcely hope to localize the OH-groups. Unfortunately, no Mo X-ray tube was available at the time of the investigation and so the X-ray diagrams were taken with CuK_α-radiation, which may influence the intensities through absorption and dispersion effects.

[1] H. L. WELLS, Z. anorg. Chem. **3**, 195 (1893).

[2] "X-ray diffraction patterns of lead compounds" from The Shell Petroleum Company Ltd., Thornton Research Centre 1954.

[3] H. Brasseur, Bull. Soc. Roy. des Sciences de Liege No. 11, 1940.

[4] R. NÄSÄNEN, P. MERILÄINEN, R. UGGLA and M. HYLE, Suomen Kemistilehti **37** no. 4 B p. 45–46 (1964).

Preparation and properties of Pb(OH)Br

While single crystals suitable for X-ray work could be prepared as mentioned above, larger quantities of the compound were more easily prepared by precipitation: To a saturated solution of $PbBr_2$ in water a 0.1 molar solution of NaOH was added. A pure white precipitate was immediately formed (pH $\sim$ 4–6). On further addition of NaOH to pH about 8 or more the precipitate turned pale yellow. The precipitates were separated from the supernatant liquid on a glass filter by suction, washed several times with water and finally with ethyl alcohol and dried at 50°C.

Both the yellowish and the white precipitate gave the same X-ray powder pattern in a Guinier type focusing camera. The sharpness of the powder lines indicated that the substances consisted of rather well-defined crystals.

From preliminary values of the axes in the orthorhombic unit cell as determined from oscillation and Weissenberg diagrams all the powder lines except two weak ones could be indexed, and refined values for the axes could thus be obtained:

$$a = 4.089 \pm 0.005\,\text{Å}; \quad b = 7.384 \pm 0.01\,\text{Å}; \quad c = 10.010 \pm 0.01\,\text{Å}.$$

The volume of 6.023×10^{23} unit cells is $0.6023 \times a \times b \times c \times 10^{24} = 183$ cc. The molar volumes of $PbCl_2$ and $PbBr_2$ are 47.6 cc and 55.0 cc, respectively, and if it is assumed that the molar volume of Pb(OH)Br is not too different from that of $PbCl_2$, this suggests that there are 4 molecules in the unit cell of Pb(OH)Br.

The single crystals prepared as described above were white, usually very thin and needle-shaped. Under the polarizing microscope they showed parallel extinction with γ' parallel with the needle axis, which is also the a-axis.

Determination of the structure

A single crystal 0.24 mm long and 0.015×0.020 mm^2 in cross section was selected for the X-ray work. Oscillation and Weissenberg diagrams with CuK_{α}-radiation were taken with the a-axis as rotational axis, and the intensities were visually estimated and corrected in the usual way. (For details see reference[5]). The absorption was treated as a "reversed temperature factor" which seemed legitimate considering the smallness of the crystals.

Reflections of the following types were absent: $h0l$ for $h+l$ odd and $hk0$ for k odd. Hence the space group could be either no. 62, Pmnb or no. 33, Pbn2$_1$.

[5] C. K. Møller, The structure of cæsium plumbo iodide. Mat. Fys. Medd. Dan. Vid. Selsk. **32**, No. 1 (1959).

TABLE 1. Observed and calculated $\sin^2\theta$-values for Pb(OH)Br. CuK_α-radiation.

Indices	Estimated intensity	$10^4 \times \sin^2\theta_{obs}$	$10^4 \times \sin^2\theta_{calc}$	Indices	Estimated intensity	$10^4 \times \sin^2\theta_{obs}$	$10^4 \times \sin^2\theta_{calc}$
011	w-m	0169	0168	113	vw?	0999	0998
002	w-m	0239	0239	122	vw	1029	1029
012	vs	0347	0348	031	m	1040	1038
101	vw?	0414	0414	014	m	1058	1058
020	w-m	0435	0435	032	m-w	1218	1218
?	vw	0458		123	m	1325	1324
021	m	0494	0494	131	vw?	1397	1393
111	vs	0523	0523	200	m	1423	1422
?	vw?	0553		132	vw	1572	1573
013	w	0642	0643	211	vw?	1590	1590
022	w-m	0672	0674	212	w-m, diff.	1768	1770
112	m	0703	0703	105	vw	1838	1838
120	vw	0789	0790	221	(v)w	1916	1916
121	m	0850	0849	115	w-m	1948	1947
103	m	0889	0889	213	vw	2061	2065
004	vw	0949	0949	222	(w)-m	2098	2096
023	vw	0968	0968	134	w	2283	2283

TABLE 2. Atomic parameters in Pb(OH)Br.

All the atoms are in the special positions:

$$\frac{1}{4}\,yz; \quad \frac{3}{4}\,\bar{y}\bar{z}; \quad \frac{3}{4}\,\frac{1}{2}-y\,\frac{1}{2}+z; \quad \frac{1}{4}\,\frac{1}{2}+y\,\frac{1}{2}-z;$$

and for

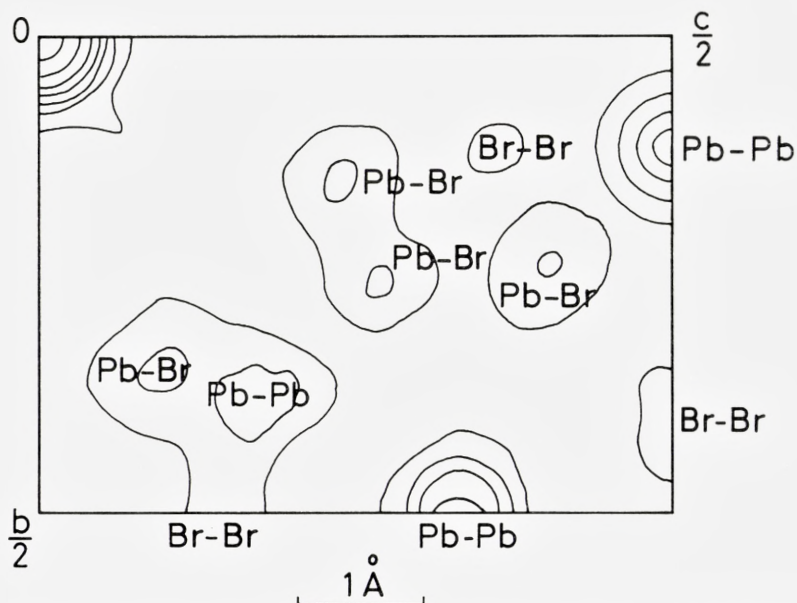|			
Pb	$x = \dfrac{1}{4}$	$y = 0.197$	$z = 0.084$
Br	$x = \dfrac{1}{4}$	$y = 0.452$	$z = 0.820$
O	$x = \dfrac{1}{4}$	$y = 0.394$	$z = 0.456$

Fig. 1. Patterson projection of Pb(OH)Br on (100). Contours are drawn at the relative densities 0, 50, 100, 150, 200, 300 and 400.

Furthermore it was observed that the $I(0kl)$ were equal to the $I(2kl)$ for all k and l, thus suggesting $|F(hkl)| = |F(h+2n, k, l)|$ where n is an integer. This is the kind of relation one would expect for space group no. 62 if there are four molecules in the unit cell so that all the atoms are in the special positions:

$$\frac{1}{4}yz; \quad \frac{3}{4}\bar{y}\bar{z}; \quad \frac{3}{4}\frac{1}{2}-y \; \frac{1}{2}+z; \quad \frac{1}{4}\frac{1}{2}+y \; \frac{1}{2}-z.$$

The arguments for obtaining the atomic positions from now on are nearly the same as in reference[5]. First a Patterson projection on (100) was calculated (fig. 1), and the three strongest maxima were localized which were interrelated in the following way:

$$(2y, 2z) \quad \left(\frac{1}{2}, \frac{1}{2}-2z\right) \quad \left(\frac{1}{2}-2y, \frac{1}{2}\right).$$

They were identified as lead-lead vector maxima and the parameters (y, z) could immediately be obtained. Next an electron projection was evaluated with only those $F(0kl)$ whose signs could be determined from the lead
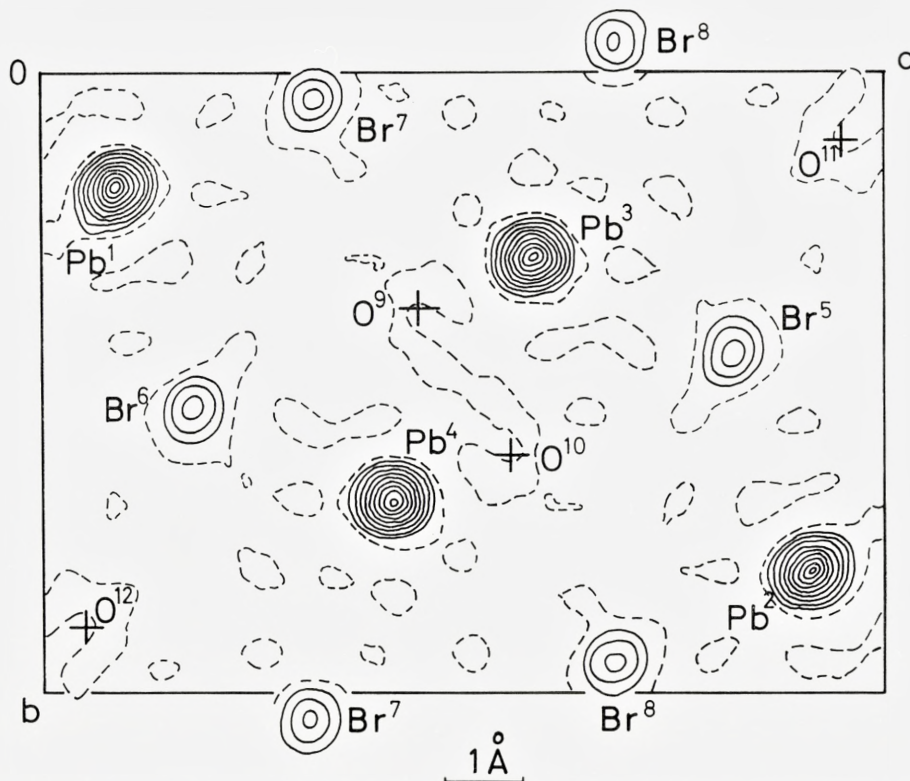
Fig. 2. Electron projection of Pb(OH)Br on (100). Contours are drawn at an interval of 50 of the relative electron density. The zero contour is dashed. The oxygen atoms (from the difference synthesis) are indicated by crosses.

contributions alone with a fair degree of certainty. The electron projection gave two possibilities for the Br-positions but comparison with the Patterson map allowed a decision to be made and in fact all the observed maxima on the Patterson projection could now be assigned to interatomic vectors. Structure factors were now calculated on a GIER-electronic computer using Danielsen's "master program" and atomic scattering factors from FORSYTH and WELLS[6, 7]. Having brought the observed and calculated structure factors on common basis, difference maps were calculated and final parameters for Pb and Br obtained in this way. The difference maps also indicated the positions of the O-atoms, although they could not be located with the same

[6] J. DANIELSEN, Acta Cryst. **16** Suppl. A 171 (1963).
[7] J. B. FORSYTH and M. WELLS, Acta Cryst. **12**, 412 (1959).

certainty as the other atoms. They are marked with crosses in the electron projection (fig. 2).

Structure factors calculated from the finally accepted atomic positions in Table 2 are compared with the observed values in Table 3.

It was also tried to find the oxygen positions from minimization of the reliability index R by systematic variation of the oxygen parameters, again using one of Danielsen's programs[6]. But these attempts were not successful because the minima were not well defined. Hence the determination from the difference map is considered the more reliable.

Atomic arrangement and discussion

Interatomic distances calculated on the basis of the parameters in Table 2 are given in Table 4 where a comparison is made with the distances in Pb(OH)I obtained from reference[4], and also with some of the distances in orthorhombic SbSBr. While the arrangement of the lead and the halogen atoms is very similar in the two former compounds, this cannot be said about the oxygen atoms. Although the location of the O-atoms should be taken with some reservation, their positions in Pb(OH)Br do seem more satisfactory than in Pb(OH)I where some of the OH-I-distances apparently are shorter than the sum of the ionic radii for I^- and OH^-: 3.15 Å against 3.6 Å.

Although one of the Pb-O-distances in Pb(OH)Br appears to be unusually short: 2.3 Å, this is not unlikely short. If we compare the shortest lead-halogen distances which have been found in this series of investigation: 3.01 Å in $CsPbI_3$[8], 2.82 Å in $CsPbBr_3$[9], 2.80 Å in $PbCl_2$[10] with the ionic radii of the halogens, an "ionic radius" of 0.9–1.0 Å is estimated for lead in these cases and would presumably also be expected in Pb(OH)Br. (Still shorter Pb(II)-O-distances have been found in orthorhombic PbO and in Pb_3O_4: 2.21 Å, respectively 2.15 and 2.23 Å[11]). The short bonds between the lead atoms and the hydroxyl groups produce chain-like polynuclear ions $(Pb(OH)^+)_n$ running parallel with the a-axis of the crystal. That the same kind of catena-ions occurs also in Pb(OH)I is very likely because Pb-Pb-distances of 3.90_5 Å are found in this crystal which is the same as the analogous distances of 3.93 Å in Pb(OH)Br within the uncertainty of the measurements.

[8] C. K. Møller, The structure of $CsPbI_3$, Mat. Fys. Medd. Dan. Vid. Selsk. 32 No. 1 (1959).
[9] A. Marstrander and C. K. Moller, The structure of white $CsPbBr_3$. See preceding paper.
[10] R. L. Sass, E. B. Brackett and T. E. Brackett, J. Phys. Chem. 67, 2863 (1963).
[11] See e. g. A. F. Wells, Structural Inorganic Chemistry, 3rd ed. Oxford University Press 1962.

Table 3. Comparison of calculated and observed structure factors
for Pb(OH)Br (brought on the same relative scale).

Indices $h\,k\,l$	F_{calc} without O	F_{calc} with O	$|F_{obs}|$	Indices $h\,k\,l$	F_{calc} without O	F_{calc} with O	$|F_{obs}|$
0 0 2	22.0	31.4	36	0 3 9	6.6	7.5	—
0 0 4	− 52.1	− 48.6	48	0 3 10	− 32.0	− 31.2	23
0 0 6	− 47.9	− 48.3	50	0 3 11	− 38.6	− 37.8	33
0 0 8	− 47.7	− 49.9	44	0 4 0	29.0	23.6	18
0 0 10	30.7	28.2	26	0 4 1	12.3	13.0	12
0 0 12	46.1	44.2	36	0 4 2	1.9	− 2.3	—
0 1 1	10.8	19.5	21	0 4 3	75.5	77.2	73
0 1 2	− 71.2	− 67.8	67	0 4 4	− 10.0	− 11.8	—
0 1 3	35.5	40.3	43	0 4 5	42.5	44.4	42
0 1 4	− 79.4	− 75.2	70	0 4 6	− 6.7	− 6.4	—
0 1 5	− 46.3	− 45.4	52	0 4 7	− 46.3	− 44.9	49
0 1 6	5.9	8.9	7	0 4 8	− 11.6	− 10.1	7
0 1 7	− 16.9	− 18.1	16	0 4 9	− 32.9	− 32.2	28
0 1 8	51.1	52.9	49	0 4 10	6.8	8.6	—
0 1 9	14.6	12.7	16	0 4 11	− 14.3	− 14.2	11
0 1 10	32.1	32.7	27	0 5 1	56.6	52.3	52
0 1 11	− 2.9	− 4.7	—	0 5 2	24.4	24.0	32
0 1 12	1.5	1.3	—	0 5 3	0.7	− 2.0	—
0 2 0	− 41.8	− 39.4	36	0 5 4	− 16.8	− 17.5	20
0 2 1	− 50.3	− 47.7	49	0 5 5	− 50.5	− 51.1	46
0 2 2	− 55.6	− 53.8	52	0 5 6	9.0	8.4	—
0 2 3	− 48.9	− 43.2	43	0 5 7	− 41.1	− 40.1	36
0 2 4	27.6	28.4	29	0 5 8	2.7	2.3	—
0 2 5	− 12.4	− 6.9	—	0 5 9	2.6	4.3	—
0 2 6	72.7	72.6	69	0 5 10	− 16.9	− 17.0	17
0 2 7	7.2	10.9	—	0 6 0	19.4	17.1	26
0 2 8	4.6	4.1	—	0 6 1	− 45.5	− 46.2	41
0 2 9	38.3	40.0	39	0 6 2	14.7	12.7	17
0 2 10	− 15.2	− 15.8	—	0 6 3	− 45.1	− 46.9	42
0 2 11	12.8	13.0	—	0 6 4	− 10.5	− 11.4	19
0 2 12	− 22.3	− 22.8	20	0 6 5	− 10.8	− 12.9	14
0 3 1	− 71.9	− 74.9	72	0 6 6	− 23.1	− 22.9	27
0 3 2	59.6	63.1	55	0 6 7	4.8	3.1	—
0 3 3	20.0	18.2	21	0 6 8	− 4.7	− 3.9	—
0 3 4	12.3	16.9	15	0 6 9	43.5	42.6	43
0 3 5	38.2	37.8	39	0 7 1	− 27.1	− 27.2	22
0 3 6	7.8	11.6	18	0 7 2	− 17.2	− 18.7	23
0 3 7	42.3	42.8	42	0 7 3	− 8.3	− 8.4	7
0 3 8	− 19.3	− 17.0	—	0 7 4	− 42.0	− 44.2	40

TABLE 3 (continued).

Indices h k l	F_{calc} without O	F_{calc} with O	$\lvert F_{obs} \rvert$	Indices h k l	F_{calc} without O	F_{calc} with O	$\lvert F_{obs} \rvert$
0 7 5	34.5	34.4	24	1 2 11	− 14.2	− 14.3	18
0 7 6	7.2	5.0	—	1 3 1	27.2	33.2	32
0 7 7	23.5	23.6	22	1 3 2	43.1	44.5	48
0 7 8	27.0	25.5	34	1 3 3	21.8	25.3	29
0 8 0	− 50.7	− 49.4	64	1 3 4	67.5	69.4	64
0 8 1	− 0.1	− 0.7	—	1 3 5	− 46.3	− 45.6	47
0 8 2	− 11.0	− 9.9	—	1 3 6	− 7.9	− 6.3	—
0 8 3	21.4	20.1	13	1 3 7	− 23.8	− 24.9	24
0 8 4	20.6	21.2	26	1 3 8	− 40.1	− 39.2	33
0 8 5	14.3	12.6	12	1 3 9	10.4	8.7	—
0 8 6	23.5	23.4	24	1 3 10	− 18.2	− 17.9	12
0 9 2	36.4	36.1	37	1 3 11	6.2	4.6	—
1 0 1	− 11.8	− 14.6	20	1 4 0	97.1	99.6	94
1 0 3	− 98.9	− 105.1	90	1 4 1	0.6	1.9	—
1 0 5	− 54.0	− 59.8	60	1 4 2	17.9	19.7	20
1 0 7	55.2	51.4	52	1 4 3	− 18.0	− 14.9	12
1 0 9	35.8	34.1	28	1 4 4	− 36.0	− 35.2	39
1 0 11	14.5	14.3	8	1 4 5	− 11.3	− 8.1	—
1 1 1	− 84.5	− 78.7	56	1 4 6	− 35.8	− 35.9	35
1 1 2	− 55.6	− 59.3	53	1 4 7	12.7	15.0	—
1 1 3	11.6	14.8	20	1 4 8	− 34.2	− 34.9	29
1 1 4	7.6	2.9	—	1 4 9	5.6	6.7	—
1 1 5	55.0	55.6	60	1 4 10	22.0	21.3	18
1 1 6	− 10.8	− 14.4	17	1 4 11	2.6	2.8	—
1 1 7	48.6	47.7	51	1 5 1	− 4.7	− 5.5	—
1 1 8	8.1	6.1	—	1 5 2	− 54.0	− 52.0	51
1 1 9	2.0	0.6	—	1 5 3	21.0	20.5	19
1 1 10	25.9	25.2	18	1 5 4	− 45.6	− 42.6	42
1 1 11	− 34.8	− 35.9	28	1 5 5	− 19.8	− 20.0	28
1 1 12	− 10.3	− 10.0	6	1 5 6	0.8	3.4	—
1 2 0	− 35.3	− 26.9	24	1 5 7	− 2.8	2.7	—
1 2 1	64.0	63.4	55	1 5 8	34.4	36.1	28
1 2 2	− 39.5	− 33.0	34	1 5 9	10.3	10.6	14
1 2 3	58.5	57.3	52	1 6 0	− 29.2	− 31.7	32
1 2 4	21.3	24.0	27	1 6 1	− 15.2	− 14.7	27
1 2 5	13.3	12.1	18	1 6 2	− 35.2	− 37.2	42
1 2 6	51.7	51.3	55	1 6 3	− 20.0	− 18.5	24
1 2 7	− 6.2	− 7.0	—	1 6 4	18.9	18.0	17
1 2 8	4.8	3.1	—	1 6 5	− 6.7	− 5.1	—
1 2 9	− 45.1	− 45.4	35	1 6 6	51.4	51.5	41
1 2 10	− 11.0	− 12.9	12	1 6 7	5.2	6.4	—

TABLE 3 (continued).

Indices h k l	F_{calc} without O	F_{calc} with O	$|F_{obs}|$	Indices h k l	F_{calc} without O	F_{calc} with O	$|F_{obs}|$
1 6 8	2.8	3.6	—	1 7 7	20.1	20.7	16
1 7 1	− 33.1	− 35.5	31	1 8 0	27.0	25.4	18
1 7 2	34.1	34.1	27	1 8 1	7.3	7.0	—
1 7 3	14.0	12.3	14	1 8 2	2.2	0.8	—
1 7 4	17.5	17.6	12	1 8 3	34.4	33.6	30
1 7 5	13.2	12.8	16	1 8 4	− 9.9	− 10.5	—
1 7 6	2.5	2.6	—	1 8 5	19.5	18.5	14

TABLE 4. Interatomic distances in Pb(OH)Br and in related compounds.

Distance	From this investigation $X = Br$	From reference[4] $X = I$	Corresponding distance in SbSBr
Pb^3-X^5	3.32 Å	3.41 Å	
Pb^3-X^6	4.43 -	4.54 -	
Pb^3-X^7	3.24 -	3.49 -	
Pb^3-X^8	3.44 -	3.70 -	2.94 Å
Pb^3-O^9	2.50 -	2.71 -	2.67 -
Pb^3-O^{10}	2.27 -	2.84 -	2.49 -
Pb^3-Pb^4	3.93 -	3.90 -	3.83 -
X^6-O^9	3.62 -	3.70 -	
X^7-O^9	3.54 -	3.15 -	
X^6-O^{12}	3.54 -	3.15 -	
X^6-X^7	4.00 -	4.15 -	
X^7-X^8	4.20 -	4.40 -	
O^9-O^{10}	2.72 -		

In this connection it is interesting that PEDERSEN[12] from pH-measurements on lead(II)nitrate solutions has obtained evidence for the formation of polynuclear ions of the type $Pb_2(OH)$ as well as $(PbOH)_4$, both of which may be regarded as fragments of the poly-ion in the crystals of Pb(OH)Br.

It seems to be a characteristic feature of many crystals containing lead (II) that the lead atoms are incorporated in some kind of polynuclear catena-ions, thus in $CsPbI_3$, $CsPbBr_3$, Pb(OH)Br and presumably also in

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[12] K. J. PEDERSEN, The acid dissociation of the hydrated lead ion and the formation of polynuclear ions. Mat. Fys. Medd. Dan. Vid. Selsk. XXII No. 10 (1945).

PbCl₂ (though less obvious here). The existence of these chainlike poly-ions in the crystals may explain why these compounds are slightly soluble in water. It also explains why the crystals are needle-shaped and that the refractive index is highest for light vibrating parallel with the needle axis i. e. parallel with the catena-ion.

Within the mentioned poly-ions one of the lead-anion distances is usually much shorter than the others, i. e. the bonding between the lead atom and this particular anion is especially strong and may persist even after dissolution of the crystal. It is in accordance with this that aqueous solutions of the lead halogenides with an excess of halogenide ions contain a fair proportion of the lead as undissociated PbX^+-ions.

The shortest OH-OH-distance is 2.7_2 Å, and—if reliable—might indicate hydrogen bonding between the hydroxyl groups within the $(PbOH)_n$-framework.

In both Pb(OH)Br and Pb(OH)I the lead-halogen distances are longer than the sum of the ionic radii for the halide ion and lead(II), which is 3.15 Å for Pb-Br and 3.4 Å for Pb-I. The halogen atoms in these crystals may be considered to exist as anions held in positions between the positively charged poly-ions by mere electrostatic forces. Pictorially, one could say that the halogen ions form a system of parallel "tubes", one around each poly-ion.

Finally, it should be pointed out that the structure deduced for Pb(OH)Br is very similar to that found for SbSBr by CHRISTOFFERSON and McCULL-OUGH[13]. In fact, the two compounds are isostructural; to the chain-like $(PbOH^+)_n$-ion in the former corresponds the poly-ion $(SbS^+)_n$ in the latter, and the Sb-S distances, 2.49 Å and 2.67 Å, are analogous to the Pb-OH distances which have been discussed above (see Table 4).

An unambiguous determination of the oxygen positions in Pb(OH)Br could presumably be made only by neutron diffraction, which might also reveal the hydrogen atoms. This would require bigger crystals than used for the X-ray work, and it could perhaps be done more easily on Pb(OH)Cl which occurs as the mineral laurionite.

¹³ G. D. CHRISTOFFERSON and J. D. McCULLOUGH, Acta Cryst. **12**, 14 (1959).

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