ACTA CHEMICA SCANDINAVICA 26 (1972) 3505–3514

The Crystal Structure of β-$[Pb_6O(OH)_6](ClO_4)_4.H_2O$

ÅKE OLIN[a] and RUNE SÖDERQUIST (†)[b]

[a] *Institute of Chemistry, University of Uppsala, S-751 21 Uppsala, Sweden.* [b] *Research Institute of National Defence (FOA), S-172 04 Sundbyberg 4, Sweden*

The compound $[Pb_6O(OH)_6](ClO_4)_4.H_2O$ crystallizes in two modifications. The structure of the β-form has been determined from three-dimensional X-ray data. The crystals are orthorhombic, space group No. 61: *Pbca*. The unit cell has the dimensions: $a = 19.953 \pm 0.007$ Å, $b = 17.624 \pm 0.006$ Å, $c = 13.383 \pm 0.005$ Å and contains 8 formula units. Discrete groups, $[Pb_6O(OH)_6^{4+}]$, are present in the structure. The six lead atoms occupy the corners of three distorted tetrahedra connected by common faces. The central tetrahedron contains an oxygen atom at its centre. The outer tetrahedra have one hydroxide oxygen outside each of their six unshared faces. The same group has been found earlier in α-$[Pb_6O(OH)_6](ClO_4)_4.H_2O$.

In 1969 Spiro, Templeton and Zalkin [1] reported the crystal structure of a compound of composition $Pb_3(OH)_4(ClO_4)_2$, which had been obtained from a hydrolysed lead(II) perchlorate solution. They found that the lead atoms form discrete groups with six atoms in each group. The metal atoms in the unit are bound together by oxygen atoms and the formula of the entire group is $[Pb_6O(OH)_6^{4+}]$. The boat-shaped metal atom cluster is shown in Fig. 1.

X-Ray and Raman scattering measurements on hydrolysed metal salt solutions have, often in conjunction with results from crystal structure determinations, been used to find the structures of the ionic species present in such solutions. Such data [2] indicate that the unit $[Pb_6O(OH)_6^{4+}]$ is also present in solution. A hexanuclear species had earlier been suggested by Olin [3] from emf measurements on hydrolysed lead(II) perchlorate solutions. The complex was then written as $Pb_6(OH)_8^{4+}$. Since this type of measurement cannot differentiate between one O^{2-} and two OH^-, the equilibrium and structural data are consistent. In connection with the potentiometric study, several solid lead(II) hydroxide perchlorates were prepared and preliminary X-ray diffraction studies performed on them. Two solids with a ratio OH/Pb = 4/3 were obtained. They had the same analytical composition, $Pb_3(OH)_4(ClO_4)_2$, could be assigned the same space group, and their asymmetric units contained six lead atoms. They were named α-$Pb_3(OH)_4(ClO_4)_2$, which later turned out to be identical with the compound studied by Spiro *et al.*, and β-$Pb_3(OH)_4(ClO_4)_2$, whose crystal structure is now reported.

EXPERIMENTAL

Preparation of crystals. The crystals were prepared from solutions obtained by dissolving PbO in perchloric acid solution under gentle heating. 1.4 mol PbO was dissolved per mol $HClO_4$. The resulting solution was cooled to *ca.* 290 K and filtered. (Any crystals separating during this cooling invariably belonged to the α-phase.) On further cooling (in a refrigerator) rectangular, prismatic crystals of the β-phase are formed. The crystallization should take place quite slowly, since it has been observed that rapid crystallization often results in the formation of the α-phase.

Analysis. The crystals were dissolved in water and the solution analysed in the same way as described earlier [3] for hydrolysed lead(II) perchlorate solutions. This established the composition as $Pb_3(OH)_4(ClO_4)_2$.

X-Ray diffraction measurements. The space group was determined from equi-inclination Weissenberg photographs and the unit cell parameters from powder photographs taken with a Guinier-Hägg focussing camera using Cr$K\alpha_1$ ($\lambda = 2.28962$ Å)[4] radiation with silicon ($a = 5.4305$ Å)[5] as internal standard.

The intensity data were collected with a Stoe Weissenberg diffractometer using Ni-filtered Cu$K\alpha$ radiation and equi-inclination geometry. 3254 independent reflections were measured from eleven layers. Reflections, which according to the space group should be systematically absent, were not measured. The scan rate varied from 0.25°/min for the weakest to 4°/min for the strongest reflections. The angle scanned was 1° for the lowest l and then gradually increased to 1.4° for the highest value of l (= 10). The background was measured for 60 sec both at the beginning and at the end of the scan interval. The data were corrected for background and converted to the standard scan rate 1°/min using the formula:

$$I = [C - t_c(B_1 + B_2)/(t_1 + t_2)] \times \omega/t_c$$

where I is the corrected intensity, B_1 is the number of counts collected before, C during, and B_2 after the scan; t_1, t_c, and t_2 are the corresponding measuring times and ω the angle through which the crystal was rotated during the scan. The standard deviation of I, $\sigma(I)$, was calculated from

$$\sigma(I) = \{C + [t_c/(t_1 + t_2)]^2(B_1 + B_2)\}^{1/2} \times \omega/t_c$$

The size of the crystals was *ca.* $0.03 \times 0.035 \times 0.15$ mm^3 and the calculated linear absorption coefficient 865 cm^{-1}. The crystals decomposed in the X-ray beam so each crystal could be used to collect only two layers of data. Inter-layer scale factors, which should take account of the different crystal sizes and the decomposition of the crystals, were obtained from measurements made at regular intervals of three "standard reflections" chosen from the zero layer. The values of the intensities of these reflections half-way through the collection of a given layer were determined by interpolation. The ratios between these values were used as the scale factors. The correction for the effect of decomposition of the crystals is approximate. By successive measurements of the zero layer it was found that the rate of decline in the intensity varied somewhat for different reflections. It is estimated from these measurements that the systematic error introduced by neglecting the time-dependence of the decomposition is *ca.* 5% in the $|F|$-values of the worst affected reflections.

$|F|$- and $\sigma(F)$-values were calculated from I- and $\sigma(I)$-values by applying absorption, Lorentz and polarization corrections.

Computation. The main programs used in this investigation were CELSIUS, DRF, LALS, DISTAN and ORTEP, presented briefly in Refs. 6, 7, and EFACT, XDATA and Long's sign-determining program presented in Ref. 8. The calculations have been carried out on the CDC 3600 computer in Uppsala and the IBM 7090 of FOA, Stockholm.

UNIT CELL AND SYMMETRY

Formula unit:	$Pb_3(OH)_4(ClO_4)_2$
Diffraction symmetry:	*m m m*
Crystal system:	orthorhombic

Lattice parameters (3σ):	$a = 19.953 \pm 7$ Å; $b = 17.624 \pm 6$ Å; $c = 13.383 \pm 5$ Å; $V = 4706 \pm 5$ Å^3.

(Axes chosen to agree with the standard setting of the assumed space group as given in Int. Tables for X-Ray Cryst., 1952.)

Density (measured):	4.98 g cm^{-3}
Number of formula units per unit cell:	16
Density (calculated):	5.016 g cm^{-3}
Linear absorption coefficient:	865 cm^{-1} (Cu$K\alpha$)
Systematic absences:	$0kl$ for $k = 2n+1$, $h0l$ for $l = 2n+1$ and $hk0$ for $h = 2n+1$
Space group:	*Pbca*
Coordinates of equivalent positions:	$\pm(x,y,z;\ 1/2+x,\ 1/2-y,-z;-x,\ 1/2+y,\ 1/2-z;\ 1/2-x,-y,\ 1/2+z)$

STRUCTURE SOLUTION

Long's sign-determining program [9] was used to solve the structure. The data were converted to normalized structure factor amplitudes, E, using a scale factor and an overall temperature factor obtained by Wilson's method.[10] 223 values of $|E| > 1.75$ were used as input in Long's program, which uses Sayre's relation $s(E_{hkl} \approx s(E_{h'k'l'}) \cdot s(E_{h-h',k-k',l-l'})$, to predict the signs. Three reflections (h,k,l,E; 13,7,3,3.83; 8,9,2,3.27; 1,10,8,3.19) were given plus phases in order to fix the origin of the unit cell. The phases of four others (h,k,l,E; 11,11,1,3.66; 1,14,3,3.22; 7,7,3,3.16; 11,9,6,2.97) were varied systematically giving 16 sign combinations in all. The most consistent combination converged in 4 cycles and the consistency index [9] was 0.72. The E-map calculated from this set showed six large peaks of almost equal heights. These were assigned to the six lead atoms in the asymmetric unit. No further atomic positions could be determined with certainty from this map. Of the 223 predicted signs all agreed with those in the final list of calculated structure factors. In these and subsequent calculations the atomic scattering factors given by Hanson *et al.*[11] were used. The real part of the dispersion correction [12] was introduced. When the lead positions were refined by least squares treatment using the 1042 reflections with $\sin\theta/\lambda < 0.40$ the R-value became 0.16 after three cycles.

The chlorine atoms, the oxygen atoms bound to lead and in the perchlorate groups and finally the water oxygen were located from consecutive Fourier syntheses of ΔF alternating with least squares refinements. For each step in these calculations the range in $\sin\theta/\lambda$ was increased.

The final refinement of the structure was carried out with anisotropic temperature factors for the lead atoms. Reflections with $|F| < 3\sigma(F)$ were excluded from the refinement. No correction for extinction was applied. $\sum w(|F_o| - |F_c|)^2$ was minimized and the weight, w, calculated from $w^{-1} = \sigma^2(F) + (k\,F)^2$. No other weighting function was tried and k was varied until $w(|F_o| - |F_c|)^2$

Table 1. Final positional and thermal parameters. Estimated standard deviations here and elsewhere in the paper refer to the least significant digits.

Atom	x	y	z	B (Å^2)
Pb(1)	0.08860(6)	0.14211(8)	−0.06125(13)	
Pb(2)	0.22845(6)	0.26237(7)	0.01507(11)	See below
Pb(3)	0.26851(6)	0.05564(7)	0.02460(10)	
Pb(4)	0.26234(7)	0.14153(8)	−0.20792(11)	
Pb(5)	0.40539(5)	0.19853(7)	−0.03111(10)	
Pb(6)	0.41953(6)	0.01261(7)	−0.15358(11)	
O(1)	0.2923(9)	0.1699(10)	−0.0497(14)	2.3(3)
O(2)	0.1656(10)	0.2281(12)	−0.1273(16)	3.1(4)
O(3)	0.1671(10)	0.1587(11)	0.0653(15)	2.8(4)
O(4)	0.3964(11)	0.0712(12)	0.0034(17)	3.5(4)
O(5)	0.4023(12)	0.1413(14)	−0.1811(19)	4.2(5)
O(6)	0.3046(8)	0.0252(10)	−0.1369(14)	2.2(3)
O(7)	0.1795(10)	0.0741(11)	−0.1174(16)	2.8(4)
Cl(1)	0.0183(4)	0.3172(4)	−0.2435(6)	2.9(1)
Cl(2)	0.3062(3)	0.3558(4)	−0.2362(6)	2.4(1)
Cl(3)	0.3794(4)	0.4304(5)	0.0668(7)	3.1(1)
Cl(4)	0.0947(4)	0.3799(5)	0.0762(7)	3.4(2)
O(11)	0.087(1)	0.338(1)	−0.238(2)	5.0(5)
O(12)	0.012(2)	0.238(2)	−0.204(2)	6.1(6)
O(13)	−0.016(1)	0.362(1)	−0.177(2)	4.6(5)
O(14)	−0.003(1)	0.329(2)	−0.345(2)	5.8(6)
O(21)	0.340(2)	0.429(2)	−0.237(2)	5.5(6)
O(22)	0.239(2)	0.376(2)	−0.212(3)	7.2(8)
O(23)	0.328(2)	0.301(2)	−0.161(2)	6.9(7)
O(24)	0.310(1)	0.323(1)	−0.329(2)	4.7(5)
O(31)	0.425(2)	0.485(2)	0.009(2)	6.9(7)
O(32)	0.321(2)	0.422(2)	−0.004(2)	6.1(7)
O(33)	0.358(2)	0.469(2)	0.157(2)	6.1(7)
O(34)	0.409(2)	0.362(2)	0.082(3)	6.7(8)
O(41)	0.137(1)	0.402(1)	−0.004(2)	4.8(6)
O(42)	0.066(2)	0.304(2)	0.047(3)	9.7(10)
O(43)	0.037(2)	0.431(2)	0.071(3)	8.9(9)
O(44)	0.127(3)	0.393(3)	0.160(4)	13.4(15)
O(8)	0.030(2)	0.019(2)	−0.188(2)	6.3(7)

Coefficients ($\times 10^5$) in the expression $\exp[-(B_{11}hh+\ldots+2B_{12}hk+\ldots)]$ for the anisotropic temperature factors for lead.

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Pb(1)	93(13)	358(3)	762(6)	17(12)	−32(3)	40(4)
Pb(2)	151(3)	224(5)	598(11)	42(3)	2(4)	64(5)
Pb(3)	163(3)	209(4)	467(11)	−19(3)	10(4)	58(4)
Pb(4)	220(3)	276(5)	401(12)	−2(3)	−48(4)	42(5)
Pb(5)	124(3)	221(4)	526(11)	−29(3)	−9(4)	−54(5)
Pb(6)	122(3)	240(4)	580(11)	13(3)	26(4)	−54(5)

did not show a systematic trend with $|F_o|$. The value of k used in the final cycles was 0.07. The refinement was carried out in blocks since the core memory of the computer would have been exceeded by varying all the parameters simultaneously. The parameters of a different pair of perchlorate oxygens were kept constant in each successive cycle. This was repeated until the shifts in the parameters of the lead and chlorine atoms were less than one fifth of their estimated standard deviations. The shifts – expressed as fractions of the estimated standard deviations – for the other atoms were somewhat larger. The mean value for the oxygens bound to lead was 0.2 with a maximum value 0.5; for the perchlorate oxygens the corresponding values are 0.35 and 1.2, respectively. Since the aim of this investigation was mainly to establish whether or not the lead atoms occurred as discrete groups in the structure, this level of refinement was considered satisfactory. The conventional R-value for the last cycle was 0.071 for the 2713 reflections ($|F| > 3\sigma(F)$) included. The atomic parameters from this cycle are listed in Table 1.

The ΔF synthesis calculated with the final parameters showed areas with electron densities of $3-5$ e$^-$/Å^3 close to the Pb positions and $2-4$ e$^-$/Å^3 close to the Cl positions. No attempt was made to remove the latter areas by introducing anisotropic temperature factors for chlorine. There were also a number of areas with densities $2-3$ e$^-$/Å^3, which may be compared with densities $5-7$ e$^-$/Å^3 for the oxygen atoms in the ΔF synthesis used to locate these atoms and based on 1934 reflections.

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

The lead atoms form six-membered groups of the same boat-shaped type as found for the α-phase. This group can be regarded as built from three Pb_4-tetrahedra sharing faces as indicated in Fig. 1. Of the seven oxygen atoms

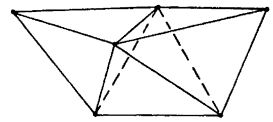

Fig. 1. Arrangement of the lead atoms in the Pb_6-unit at the corners of three face-sharing tetrahedra.

associated with this group, one is found inside the central tetrahedron. The other six atoms are situated outside the unshared faces of the outer tetrahedra. The basicity of the compound requires 8 OH^- or 6 $OH^- + 1$ O^{2-} or 4 $OH^- +$ 2 O^{2-} *etc.* per 6 lead atoms. The central oxygen is therefore most likely an oxide oxygen and the others hydroxide oxygens. The formula of the cluster would then be $[Pb_6O(OH)_6^{4+}]$ (see also Fig. 2). This is the same conclusion as that arrived at by Spiro *et al.* for the α-phase. The two clusters are, in fact, quite similar, as can be seen from Table 2 in which the interatomic distances in the two groups are compared. The largest difference in a Pb – Pb distance occurs for the pair Pb(4) – Pb(6) and amounts to 0.15 Å. For the other pairs the mean difference is only 0.04 Å. The deviations from C_2 symmetry in the Pb_6-group are larger for the β- than for the α-phase. The deviations are in fact

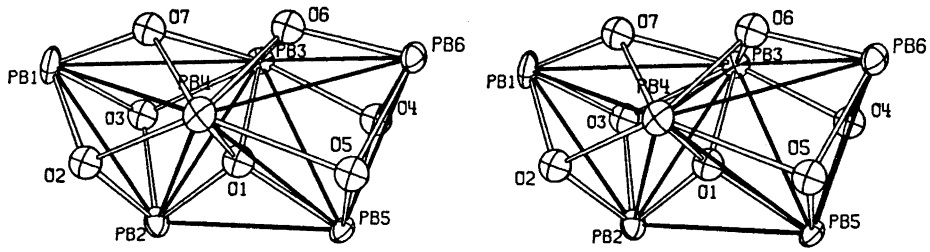

Fig. 2. Stereoscopic pair showing the arrangement of the atoms in β-$[Pb_6O(OH)_6^{4+}]$.

Table 2. Interatomic distances (Å) in α- and β-$Pb_6O(OH)_6^{4+}$.

Atoms	α-cluster	β-cluster	Atoms	α-cluster	β-cluster
Pb(1)–Pb(2)	3.674(6)	3.650(1)	Pb(3)–Pb(4)	3.440(5)	3.462(2)
Pb(1)–Pb(3)	4.086(6)	4.067(2)	Pb(3)–Pb(5)	3.779(6)	3.789(1)
Pb(1)–Pb(4)	3.949(6)	3.983(2)	Pb(3)–Pb(6)	3.846(5)	3.917(2)
Pb(2)–Pb(3)	3.795(5)	3.732(2)	Pb(4)–Pb(5)	3.778(5)	3.841(2)
Pb(2)–Pb(4)	3.786(5)	3.725(2)	Pb(4)–Pb(6)	4.086(6)	3.940(2)
Pb(2)–Pb(5)	3.790(5)	3.756(1)	Pb(5)–Pb(6)	3.667(6)	3.674(2)
O(1)–Pb(2)	2.29(6)	2.24(2)	O(4)–Pb(5)	2.23(4)	2.30(2)
O(1)–Pb(3)	2.22(6)	2.30(2)	O(4)–Pb(6)	2.37(4)	2.39(2)
O(1)–Pb(4)	2.35(6)	2.26(2)			
O(1)–Pb(5)	2.29(6)	2.33(2)	O(5)–Pb(4)	2.67(5)	2.82(2)
			O(5)–Pb(5)	2.21(5)	2.25(2)
O(2)–Pb(1)	2.32(5)	2.33(2)	O(5)–Pb(6)	2.34(5)	2.32(2)
O(2)–Pb(2)	2.30(5)	2.36(2)			
O(2)–Pb(4)	2.55(5)	2.69(2)	O(6)–Pb(3)	2.24(5)	2.34(2)
			O(6)–Pb(4)	2.53(5)	2.41(2)
O(3)–Pb(1)	2.36(6)	2.33(2)	O(6)–Pb(6)	2.33(5)	2.31(2)
O(3)–Pb(2)	2.18(6)	2.30(2)			
O(3)–Pb(3)	3.02(6)	2.77(2)	O(7)–Pb(1)	2.27(5)	2.30(2)
			O(7)–Pb(3)	2.49(5)	2.62(2)
O(4)–Pb(3)	2.53(4)	2.58(2)	O(7)–Pb(4)	2.47(5)	2.37(2)

quite small for the α-phase. The distances between the non-adjacent lead atoms Pb(1)–Pb(5), Pb(2)–Pb(6), and Pb(1)–Pb(6) are also somewhat different in the two clusters. In the more symmetric α-cluster the first two distances are almost equal (6.36 Å), whereas they are certainly unequal (6.25 and 6.41 Å) in the β-cluster. The Pb(1)–Pb(6) distance is 7.10 Å in this cluster, which is 0.04 Å less than that found for the α-cluster. In the X-ray scattering study on hydrolysed lead(II) perchlorate solutions by Johansson and Olin,[2] next nearest neighbours were found at 6.37 and 7.14 Å. Due to the broadness of the peaks in the radial distribution function at large interatomic distances, these measurements cannot be used to decide which of the two clusters is most closely related to the species occurring in solution. The $[Pb_6O(OH)_6^{4+}]$-group might, however, be expected to be more symmetric in solution than in the solid phase and therefore more closely related to the α-cluster.

The Pb – O distances show a wide variation, 2.24 – 2.82 Å. Inspection of Table 2 again indicates similarities between the α- and β-$[Pb_6O(OH)_6^{4+}]$-groups. The variations in the atomic distances follow the same pattern for the α- and β-form, although the individual pairs show rather large differences. The tendency for the outer oxygens, O(2) – O(7), to coordinate lead with two short and one long bond is more pronounced in the present structure.

The three oxygen atoms on the surfaces of an outer Pb_4-tetrahedron form together with the central oxygen atom a distorted tetrahedron. The oxygens O(1) – O(7) thus form two tetrahedra with a common apex, O(1). The mean value of the lengths of the edges in these tetrahedra, which correspond to O – O distances, is 2.85 Å. This value is somewhat longer than the shortest O – O distance in PbO(tetr.), 2.80 Å, but shorter than the corresponding distances in PbO(orthorh.). The expected distance for two O(–II) in van der Waals or ionic contact is 2.8 Å.

The central oxygen, O(1), is four-coordinated and the other oxygens three-coordinated with respect to lead. The total number of oxygen-lead links is thus 22. Two lead atoms, Pb(3) and Pb(4), are five-coordinated and the others three-coordinated with respect to oxygen atoms belonging to the cluster.

Three types of Pb – O – Pb bridges may be discerned. There are six oxide bridges involving O(1), Pb(2), Pb(3), Pb(4), and Pb(5). They are fairly symmetric (see Table 2) with a mean Pb – O distance of 2.28 Å. The hydroxide bridges may somewhat arbitrarily be divided into "symmetric" and "asymmetric". In a symmetric bridge the difference between the two O – Pb distances does not exceed 0.1 Å. The lengths of the bonds are in the range 2.24 – 2.41 Å. In an asymmetric bridge, there is one short bond in this range, whereas the other bond length is in the range 2.58 – 2.82 Å. There is no bridge having two long Pb – O vectors. The division into symmetric bridges with two short and asymmetric bridges with one short and one long Pb – O bond gets some support from the fact that, in the former, the Pb – O distances are in the range of closest Pb – O contacts in the two common polymorphs of lead(II) oxide.[13,14] The shortest Pb – Pb distance, 3.46 Å, is found between Pb(3) and Pb(4). This is the only Pb pair connected by three bridges, one of each type. The next shortest distances are between Pb(1) and Pb(2), 3.65 Å, and between Pb(5) and Pb(6), 3.67 Å. These are the only pairs connected by two symmetric hydroxide bridges. The remaining nine short Pb – Pb distances in the Pb_6-group lie between 3.73 and 4.09 Å. Of these the Pb(2) – Pb(5) pair, 3.76 Å, is joined by an oxide bridge. This is the only pair coupled by one bridge alone. Seven are connected by one asymmetric hydroxide bridge and one oxide or symmetric hydroxide bridge. The pairs having an oxide bridge are shorter, 3.73 – 3.84 Å, than those having only hydroxide bridges, 3.92 – 3.98 Å. Finally there is one pair, Pb(1) – Pb(3), with two asymmetric hydroxide bridges. Here we find the longest Pb – Pb separation, 4.07 Å. There is therefore some degree of correlation between the Pb – Pb distances in the cluster and the types of oxygen bridges which join them.

The chlorine-oxygen distances in the perchlorate groups are presented in Table 3. The mean distance is 1.44 Å. A recent value reported for this distance is 1.45 Å.[15] The perchlorate groups appear to be distorted but the uncertainties in the bond lengths are so large that none of the sixteen distances differs by

Table 3. Chlorine-oxygen distances (Å) in the perchlorate groups.

Atoms	Dist.	Atoms	Dist.
Cl(1) – O(11)	1.42(3)	Cl(3) – O(31)	1.53(3)
– O(12)	1.48(3)	– O(32)	1.50(3)
– O(13)	1.39(3)	– O(33)	1.46(3)
– O(14)	1.46(3)	– O(34)	1.35(4)
Cl(2) – O(21)	1.47(3)	Cl(4) – O(41)	1.44(5)
– O(22)	1.42(4)	– O(42)	1.49(4)
– O(23)	1.45(3)	– O(43)	1.46(4)
– O(24)	1.38(3)	– O(44)	1.33(5)

more than three standard deviations from the mean value. There is nothing in the list of interatomic distances which suggests that the most distorted perchlorate oxygens are involved in any special type of bonding. The "distortions" are therefore most probably artifacts of errors in the experimental data. The high values of B for most of the perchlorate oxygens suggest that the perchlorate groups exhibit some degree of orientational disorder. This is not unexpected in a structure comprising large cations of fairly low charge. Most of the closest distances between a lead atom and a perchlorate oxygen exceed 3 Å, which tends to indicate weak interatomic interactions. The shortest distances between the hydroxide oxygens and the perchlorate oxygens fall in the range 2.91 – 3.07 Å. Hence, interactions between the cluster and the perchlorate groups are probably weak. The water oxygen, O(8), has one perchlorate oxygen, O(31), at 2.86 Å. This distance indicates hydrogen bonding. There are two lead atoms, a Pb(1) and a Pb(6), from different clusters, at 2.99 and 3.06 Å and another perchlorate oxygen at 3.09 Å. Other atoms are at least 3.2 Å distant from the water oxygen. The four nearest neighbours do, however, deviate considerably from tetrahedral positions around the water molecule.

If oxygen atoms at distances less than 3.1 Å are included in the coordination sphere of a lead atom, the lead-oxygen coordination numbers are found to vary between 4 and 7. With the coordinated lead atoms also included, the coordination numbers range between 8 and 12.

Fig. 3 shows the arrangement of the $[Pb_6O(OH)_6^{4+}]$-groups, which form layers running parallel to the b-axis. The perchlorate groups, which for clarity are omitted from the figure, are situated in the layers as well as between them. The Cl(1) perchlorate groups are found in the space between the layers and form bonds with both layers. The other perchlorate groups interact chiefly with atoms belonging to the same layer. A Pb_6-group has two neighbouring groups at a distance of 4.13 Å. The close contacts are between the Pb(2) and Pb(4) atoms. The structure may therefore also be described as consisting of strings of such groups running in the c-direction. The Pb(2) – Pb(4) pairs may be considered to be linked by a perchlorate group; but the oxygen-lead distances, 3.05 and 3.17 Å, indicate that the interactions are weak. The van der Waals radius of lead(II) has been estimated [16] to be 2.0 – 2.25 Å. Hence the

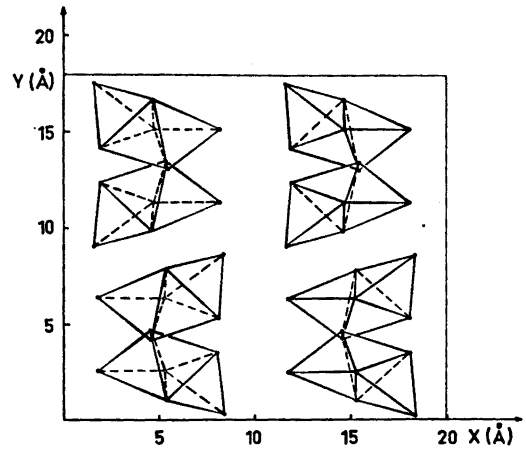

Fig. 3. Projection of the structure of β-[Pb$_6$O(OH)$_6$](ClO$_4$)$_4$.H$_2$O along the *c*-axis showing the arrangement of the Pb$_6$-groups in the unit cell. The size of the unit cell is indicated by thin lines.

units are probably in van der Waals contact and, since there are no strong perchlorate bridges between the lead atoms, the description of the structure in terms of isolated [Pb$_6$O(OH)$_6^{4+}$]-groups seems appropriate. In the α-phase there is a corresponding Pb – Pb contact at 4.29 Å.

Since the bonding schemes between the [Pb$_6$O(OH)$_6^{4+}$]-groups and the perchlorate groups in both the α- and the β-phase are somewhat unclear, the comparison between the two structures will be restricted to a description of the stacking of the Pb$_6$-units. The two structures appear very similar in a projection onto the *xy*-plane. In the β-phase the plane $x = 1/4$ and in the α-phase the plane $x = 1/2$ passes approximately midway through the Pb$_6$-group in the asymmetric unit. The symmetry operations of the space group will therefore centre the eight Pb$_6$-groups in the unit cell on the planes at $x = 1/4$ and $x = 3/4$ in the β-phase (see Fig. 3) and at $x = 0$ and $x = 1/2$ in the α-phase. Because of the shorter *a*-axis (10.81 Å) in the α-phase, the units are much closer together in the *xy*-projection of the structure of this phase than in the projection of the present structure. Since the arrangement and distances in the *y*-direction are much the same in both structures, the groups must be much further apart along the *c*-axis in the α-phase than in the β-phase in order to provide the necessary space for the atoms. In fact, the *c*-axis is almost twice as long in the α-phase as it is in the β-phase, 26.27 and 13.38 Å, respectively. Since the unit cell volumes of the two structure are very close, 4746 and 4706 Å^3 for α- and β-[Pb$_6$O(OH)$_6$](ClO$_4$)$_4$.H$_2$O, respectively, these constitute two almost equally efficient ways of arranging the structural units. This is also reflected in the ease with which one phase is transformed into the other *via* an aqueous phase.

Acknowledgements. We thank Professor Ivar Olovsson for the facilities placed at our disposal. Thanks are also due to Drs. Rolf Hesse, Per-Gunnar Jönsson, Åke Kvick and Jan-Olof Lundgren and Mr. Hilding Karlsson for their generous help during various stages of this work. The manuscript has been much improved through helpful discussions with Dr. Georg Johansson. The English text was corrected by Dr. John O. Thomas.

REFERENCES

1. Spiro, T. G., Templeton, D. H. and Zalkin, A. *Inorg. Chem.* **8** (1969) 856.
2. Johansson, G. and Olin, Å. *Acta Chem. Scand.* **22** (1968) 3197.
3. Olin, Å. *Acta Chem. Scand.* **14** (1960) 126.
4. Lonsdale, K. *Acta Cryst.* **3** (1950) 400.
5. Parrish, W. *Acta Cryst.* **13** (1960) 838.
6. Jönsson, P.-G. and Liminga, R. *Acta Chem. Scand.* **25** (1971) 1729.
7. Åberg, M. *Acta Chem. Scand.* **23** (1969) 791.
8. Jönsson, P.-G. *To be published.*
9. Long, R. E. *Thesis*, University of California, Los Angeles 1965.
10. Wilson, A. J. C. *Nature* **150** (1942) 151.
11. Hanson, H. P., Herman, F., Lea, J. D. and Skillman, S. *Acta Cryst.* **17** (1964) 1040.
12. Saravia, L. R. and Caticha-Ellis, S. *Acta Cryst.* **20** (1966) 927.
13. Moore, W. J. and Pauling, L. *J. Am. Chem. Soc.* **63** (1941) 1392.
14. Kay, M. I. *Acta Cryst.* **14** (1961) 80.
15. Olovsson, I. *J. Chem. Phys.* **49** (1968) 1063.
16. Dickens, B. *J. Inorg. Nucl. Chem.* **27** (1965) 1495.

Received March 8, 1972.