The Crystal Structure of $[Pb_4(OH)_4](ClO_4)_4.2H_2O$

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The crystal structure of $[Pb_4(OH)_4](ClO_4)_4.2H_2O$ has been determined from three-dimensional X-ray data. The crystals are monoclinic and the space group is $P2_1/c$. The dimensions of the unit cell are $a = 16.665 \pm 0.009$ Å, $b = 9.168 \pm 0.006$ Å, $c = 14.227 \pm 0.006$ Å, $\beta = 112.09 \pm 0.03°$ and it holds 4 formula units. The uncertainties given are three times the estimated standard deviations.

The structure contains discrete $[Pb_4(OH)_4{}^{4+}]$-units in which the lead atoms occupy the corners of a slightly distorted tetrahedron and the hydroxide groups are located outside the faces of this tetrahedron. The same unit has previously been found in $[Pb_4(OH)_4]_3(CO_3)$-$(ClO_4)_{10}.6H_2O$ as well as in the solution from which the title compound crystallizes.

From solutions containing more than one mol but less than two mol of $HClO_4$ per mol of PbO crystalline lead(II) hydroxide perchlorates can be prepared. According to Ref. 1 Marignac apparently was the first to report on these compounds. He obtained two solids to which he ascribed the same formula, $Pb_2O(ClO_4)_2.2H_2O$. Only one of them was stable in contact with air. These findings were later confirmed by Weinland and Stroh,[2] but the formula was changed to $Pb_2(OH)_2(ClO_4)_2 . 1.5H_2O$ which agreed better with their analysis. The solutions from which these solids crystallize contain $[Pb_4(OH)_4{}^{4+}]$ as a main species. X-Ray scattering studies [3,4] on solutions containing the complex have been interpreted in terms of a Pb_4-tetrahedron with one hydroxide group outside each of the four faces of the tetrahedron. This interpretation is corroborated by the crystal structure determination of $[Pb_4(OH)_4]_3(CO_3)(ClO_4)_{10}.6H_2O.$[5] This compound was, however, obtained from solutions which has been exposed to the carbon dioxide of the air. Since the compound written above

as $Pb_2(OH)_2(ClO_4)_2 . 1.5H_2O$ is normally formed a crystal structure determination of this solid was considered appropriate.

EXPERIMENTAL

Preparation and analysis of the crystals. The crystals were obtained from a hydrolysed lead(II) perchlorate solution prepared by dissolving lead(II) oxide in perchloric acid to give a ratio OH:Pb = 0.8 (mol-mol) in the resulting solution. This ratio should be well below 1 since otherwise α-$[Pb_6O(OH)_6] (ClO_4)_4.H_2O$ may be formed together with the desired compound. This observation may explain why Willard and Kassner,[6] who worked with solutions with OH:Pb = 1, could not confirm the earlier works by Marignac, and Weinland and Stroh.

After dissolution in water the crystals were analysed as follows. The lead content was determined gravimetrically as $PbSO_4$ and the number of basic groups was found from a titration with standard perchloric acid using a Gran plot to obtain the equivalence point. No analysis of the water content was made. The ratio OH:Pb was found to be 0.98 and the lead content 62.18 %. Calculated lead content for $Pb_2(OH)_2$-$ClO_4)_2.H_2O = 62.28$ % and for $Pb_2(OH)_2$-$(ClO_4)_2 . 1.5H_2O = 61.45$ %.

X-Ray diffraction measurements. The space group was determined from oscillation and equi-inclination Weissenberg photographs. The unit cell dimensions were calculated from 42 indexed lines on a powder photograph taken with a Guinier-Hägg focussing camera using $CrK\alpha_1$ ($\lambda = 2.28962$ Å) with silicon ($a = 5.4305$ Å) as internal standard. The intensity data were collected with a Stoe Weissenberg diffractometer using Ni-filtered $CuK\alpha$ radiation under essentially the same experimental conditions as described previously.[7] The data were corrected for background and converted to the standard scan rate 1°/min. The expressions in Ref. 7 were used in the calculations of the corrected intensities, I, and their standard deviations, $\sigma(I)$. The crystal was rotated about the b-axis and 2047 independent reflections

were measured from 8 layers. The crystals decompose in the X-ray beam. Therefore a new crystal was mounted for each layer. The scale factors between the different crystals were obtained from three standard reflections in the zero layer, which were measured before the crystal was used to collect the data for a layer. An approximate correction for the decomposition was obtained as follows. Three reflections were remeasured at regular intervals during the recording of a layer. The mean of the relative values of the intensities of these reflections at the beginning and at the end of an interval were used by linear interpolation to correct the data collected during the interval. The correction so introduced was 30 % or more in I for the last reflections measured in a layer.

$|F|$- and $\sigma(F)$-values were calculated from I- and $\sigma(I)$-values by applying absorption, Lorentz and polarization corrections. The atomic scattering factors were taken from Hanson et al.[8] and the real part of the dispersion correction was introduced.

CRYSTAL DATA

Formula unit:	$[Pb_4(OH)_4](ClO_4)_4.2H_2O$
Lattice parameters	
(σ):*	$a = 16.665(3)$ Å;
	$b = 9.168(2)$ Å;
	$c = 14.227(2)$ Å;
	$\beta = 112.09(1)°$;
	$V = 2014$ Å³
Density (measured):	4.39 g cm⁻³
Number of formula units per unit cell:	4
Density calculated:	4.389 g cm⁻³
Linear absorption coefficient:	698 cm⁻¹ (CuKα)
Systematic absences:	$0k0$ for $k = 2n+1$
	$h0l$ for $l = 2n+1$
Space group:	$P2_1/c$

STRUCTURE SOLUTION

The $|F|$-values were converted to $|E|$-values and 216 of these with $|E| > 1.70$ were used to solve the structure by means of the sign-determining program written by Long.[5] This program uses Sayre's relation $s(E_{hkl}) \approx s(E_{h'k'l'})s(E_{h-h',k-k',l-l'})$ to predict the signs.

The starting set consisted of seven $|E|$-values. Three of these (h,k,l,E $-7,3,5,3.72$; $-11,4,3,3.35$; $-6,2,7,2.77$) were given plus signs in order to fix the origin of the unit cell. The signs of the remaining four (h,k,l,E; $-9,4,9,3.38$; $4,3,5,3.11$; $8,0,2,2.57$; $4,1,2,2.50$) were varied systematically. Of the 16 starting sets of signs so obtained, two had a consistency index[9] greater than 0.99 and converged in 7 cycles. E maps were calculated for these sets. Only the set with the highest consistency index (0.999) showed the required four large peaks from the four lead atoms in the asymmetric unit. The positions of these atoms were checked against a three-dimensional Patterson synthesis. All the expected maxima corresponding to Pb−Pb vectors were found. The predicted signs were later found to all agree with those in the final list of calculated structure factors.

The chlorine atoms, the oxygen atoms bound to the lead atoms, and the water oxygens were found without difficulty from consecutive Fourier synthesis of ΔF alternating with least squares refinements. Most of the perchlorate oxygens were found in the same way but a few of them were quite poorly resolved. These were allocated to maxima consistent with the known geometry of the perchlorate ion.

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 and no correction for extinction was applied. $\Sigma w(|F_o| - |F_c|)^2$ was minimized and the weighting function $w^{-1} = \sigma^2(F) + (kF)^2$ was used. The value of k in the final cycles was 0.05. The refinement was continued until the shifts were less than 0.2σ except for some of the perchlorate oxygen coordinates. It was found necessary to fix the coordinates from the ΔF map of one of the perchlorate oxygens, O(44), since the refinement shifted this atom to a position with an improbable Cl−O distance. The conventional R-value for the last cycle was 0.074 for 1840 reflections. The atomic parameters from this cycle are listed in Table 1.

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

The lead atoms and the hydroxide groups form units of composition $Pb_4(OH)_4^{4+}$. The

Table 1. Final positional and thermal parameters with standard deviations (σ) within parentheses. $O(1) - O(4)$ are hydroxide and $O(5) - O(6)$ water oxygens.

Atom	x	y	z	$B(\text{Å}^2)$
Pb(A)	0.2296(1)	0.3346(2)	0.0963(1)	
Pb(B)	0.3252(1)	0.6829(2)	0.2463(1)	see below
Pb(C)	0.1623(1)	0.4597(2)	0.3044(1)	
Pb(D)	0.3985(1)	0.3105(2)	0.3652(1)	
O(1)	0.315(2)	0.529(3)	0.373(2)	4.3(5)
O(2)	0.365(1)	0.436(2)	0.210(2)	3.4(4)
O(3)	0.251(2)	0.257(3)	0.269(2)	4.7(5)
O(4)	0.195(1)	0.549(2)	0.168(2)	3.0(4)
O(5)	0.073(2)	0.302(4)	0.114(3)	5.1(7)
O(6)	0.187(2)	0.757(4)	0.325(3)	5.3(8)
Cl(1)	0.3704(6)	0.569(1)	−0.0145(7)	2.1(2)
O(11)	0.401(3)	0.708(4)	−0.038(3)	6.0(9)
O(12)	0.444(3)	0.497(4)	0.064(3)	6.5(9)
O(13)	0.347(3)	0.470(4)	−0.103(3)	8(1)
O(14)	0.298(3)	0.596(4)	0.012(3)	6.2(8)
Cl(2)	0.4282(7)	0.091(1)	0.1393(8)	3.0(2)
O(21)	0.358(3)	0.161(4)	0.059(3)	5.9(8)
O(22)	0.491(4)	0.058(6)	0.092(5)	12(2)
O(23)	0.479(4)	0.190(6)	0.223(5)	11(2)
O(24)	0.420(7)	−0.060(9)	0.143(8)	18(3)
Cl(3)	0.0604(6)	0.071(1)	0.3518(7)	2.3(2)
O(31)	0.087(2)	−0.013(3)	0.440(2)	4.9(7)
O(32)	0.053(2)	−0.005(5)	0.268(4)	9(1)
O(33)	−0.018(3)	0.144(4)	0.328(3)	7(1)
O(34)	0.128(2)	0.177(4)	0.364(3)	5.3(7)
Cl(4)	0.1512(8)	−0.069(1)	0.0522(8)	3.5(2)
O(41)	0.198(6)	−0.028(8)	0.158(7)	17(3)
O(42)	0.103(4)	−0.179(7)	0.066(5)	12(2)
O(43)	0.219(6)	−0.113(9)	0.027(7)	18(3)
O(44)	0.117(−)	0.018(−)	−0.024(−)	15(−)

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

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Pb(A)	295(8)	922(30)	328(10)	102(12)	44(7)	−230(13)
Pb(B)	298(8)	439(28)	554(12)	−72(11)	132(8)	95(13)
Pb(C)	265(8)	1040(30)	477(11)	77(12)	217(7)	147(14)
Pb(D)	210(7)	619(26)	315(10)	65(11)	65(6)	113(12)

arrangement of these units, the perchlorate ions, and the water molecules is shown in Fig. 1. The metal atoms, Pb(A) − Pb(D), are at the corners of a slightly distorted tetrahedron and the hydroxide oxygens, O(1) − O(4), are situated outside the faces of this tetrahedron. The metal atoms are thus joined by double hydroxide bridges. The oxygen atoms form another, slightly distorted, tetrahedron. The two tetrahedra are positioned with respect to each other so, that the lead and oxygen atoms

are at the alternate corners of a distorted cube; See Fig. 1.

The Pb − Pb and Pb − O distances in the [Pb₄(OH)₄⁴⁺]-group are presented in Table 2. The metal-metal distances range between 3.72 and 3.95 Å with a mean value of 3.81 Å. The mean deviation of an Pb − Pb − Pb angle from 60° is 1.5° and the largest difference 3.1°. An hydroxide oxygen coordinates three lead atoms and the Pb − O distances range between 2.34 and 2.54 Å with a mean value of 2.41 Å.
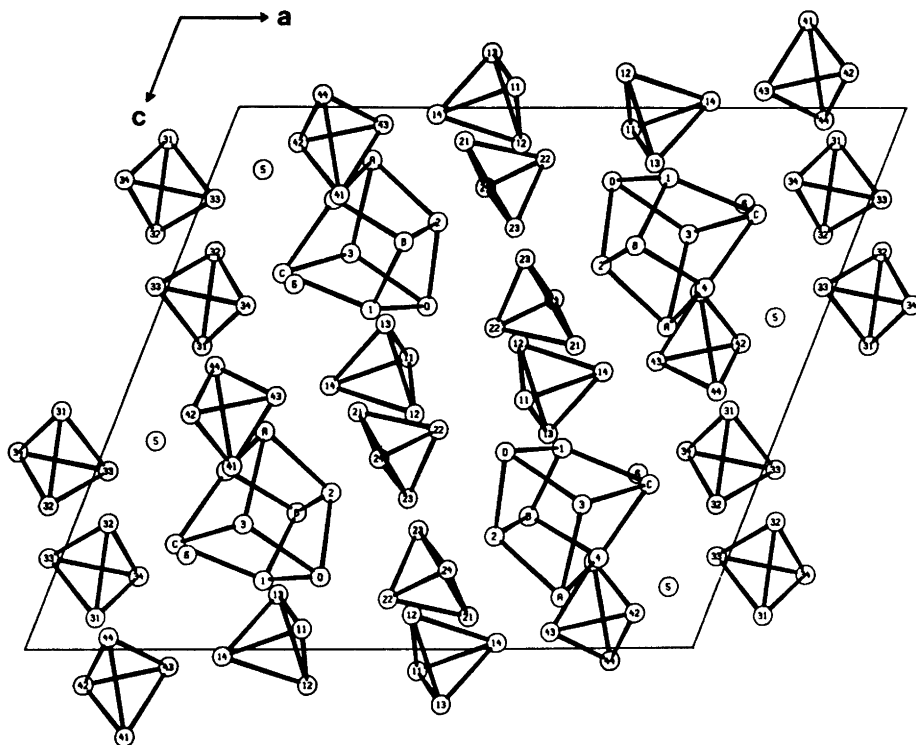
Fig. 1. Projection of the structure of $[Pb_4(OH)_4](ClO_4)_4 \cdot 2H_2O$ along the *b*-axis. A−D lead atoms, 1−4 hydroxide, 5−6 water, and 11−44 perchlorate oxygen atoms.

The hydroxide oxygens are apparently in van der Waals contact since the O−O distances range between 2.84 and 3.00 Å with a mean value of 2.89 Å. The mean deviation of an O−O−O angle from 60° is 1.4° and the largest difference 3.6°.

Of the four perchlorate groups, $ClO_4(1)$− $ClO_4(4)$, two, $ClO_4(1)$ and $ClO_4(3)$, are better resolved than the others as can be seen from the *B*-values. The chlorine-oxygen distances [excluding $Cl(4)-O(44)$] are within $2\sigma (\lesssim 0.1$ Å) equal to the expected value of 1.45 Å[10] and range between 1.35 and 1.48 Å with a mean value of 1.42 Å.

The electron density map showed only two molecules of water per $[Pb_4(OH)_4^{4+}]$-group. This is in agreement with Marignac's analytical data and our lead analysis of the compound. Since, however, the presence of three molecules of water has also been suggested [2] the structure was searched for cavities. The largest spherical hole found had a radius of 2.3 Å. The shortest

distance between a water oxygen and another atom in the lead hydroxide perchlorates so far investigated exceeds 2.7 Å.[5,7,11] We may therefore conclude that there is not room for another water molecule.

The $[Pb_4(OH)_4^{4+}]$-units definitely occur as discrete groups since the shortest distance between a metal atom and an hydroxide oxygen in an adjacent unit is 4.88 Å. The shortest inter-unit metal-metal vector is 4.72 Å. The closest perchlorate oxygen is situated 2.80 Å ($\sigma \approx 0.05$ Å) from a lead atom. From this value on there is a "continuous" range of distances and no definite statements can be made about the coordination of the metal atoms by the perchlorate groups. If, for instance, perchlorate oxygens less distant than approximately 3.1 Å are considered coordinated the $[Pb_4(OH)_4^{4+}]$-units may be considered linked through O(34). The link is between a Pb(A) and a Pb(C) atom. The distances are Pb(A)−O(34) 3.10 Å and Pb(C)−O(34) 2.85 Å. The angle Pb(A)−

Table 2. Some distances (Å) in the [Pb$_4$(OH)$_4$$^{4+}$]-unit. Standard deviations (σ) within parentheses.

Atoms		Distance	Atoms		Distance
Pb(A)	−Pb(B)	3.838(2)	Pb(B)	−Pb(C)	3.732(2)
	−Pb(C)	3.721(2)		−Pb(D)	3.802(2)
	−Pb(D)	3.810(2)		−O(1)	2.34(3)
	−O(2)	2.41(2)		−O(2)	2.47(2)
	−O(3)	2.45(3)		−O(4)	2.37(2)
	−O(4)	2.38(2)			
Pb(C)	−Pb(D)	3.945(2)	Pb(D)	−O(1)	2.47(2)
	−O(1)	2.44(3)		−O(2)	2.37(2)
	−O(3)	2.54(3)		−O(3)	2.37(3)
	−O(4)	2.35(2)			

O(34)−Pb(C) is 105°. The metal−metal distance is the smallest inter-unit distance, 4.72 Å, mentioned above.

Each hydroxide oxygen has one or two perchlorate or water oxygens at distances between 2.83 and 2.95 Å ($\sigma \approx 0.05$ Å) to which hydrogen bonds may be formed. One might expect the O−H vector to be essentially perpendicular to and directed away from the plane formed by the three lead atoms bound to the hydroxide group (with one exception the Pb−OH−Pb angles are quite close to the tetrahedral value). In no case, however, is the presumed acceptor oxygen close to this direction. This circumstance and the uncertainty in the bond lengths do not allow any assignment of hydrogen bonds to be made.

The water molecules, O(5) and O(6), are coordinated to one lead atom each at 2.74 and 2.75 Å, respectively. The next lead atom is 2.93, and 3.00 Å away, respectively. The closest oxygen atom is approximately 2.9 Å from a water molecule. This fairly long O−O distance and the Pb−O(H$_2$O)−O angle (50°) suggests the absence of hydrogen bonds.

The [Pb$_4$(OH)$_4$$^{4+}$]-unit present in [Pb$_4(OH)_4$](ClO$_4$)$_4$.2H$_2$O, I, is the same as previously found in [Pb$_4$(OH)$_4$]$_3$(CO$_3$)(ClO$_4$)$_{10}$.6H$_2$O, II.[5] The interatomic distances are, however, more varied in I than in II. In I the Pb−Pb distances range between 3.72 and 3.95 Å, and in II between 3.76 and 3.85 Å. The mean values are almost the same 3.81 and 3.78 Å, respectively. The value for I is thus closer to the mean Pb−Pb distance, 3.85 Å, observed for this group in solution.

In II the [Pb$_4$(OH)$_4$$^{4+}$]-group possesses a plane of symmetry. This plane is very nearly retained by the Pb$_4$-tetrahedron in I but is lost when the hydroxide oxygens are added. The Pb−O distances vary between 2.34 and 2.54 Å in I, and 2.29 and 2.49 Å in II. The mean values are 2.41 and 2.38 Å. If the two groups are compared so as to minimize the differences between the Pb−Pb distances (mean difference 0.05 Å, max. difference 0.10 Å), the greatest difference in a Pb−O link becomes 0.18 Å and the mean difference 0.07 Å. Differences of this magnitude were also observed between the [Pb$_6$O(OH)$_6$$^{4+}$]-units in α- and β-[Pb$_6$O(OH)$_6$](ClO$_4$)$_4$.H$_2$O.[7] The cause of these differences and the reason why these clusters do not possess the higher symmetry permitted by their topology is not understood.

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