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On the Crystal Structure of $[Pb_4(OH)_4]_3(CO_3)(ClO_4)_{10}.6H_2O$

SAM-HYO HONG and ÅKE OLIN

Institute of Chemistry, University of Uppsala, S-751 21 Uppsala, Sweden

The crystal structure of $[Pb_4(OH)_4]_3(CO_3)(ClO_4)_{10}.6H_2O$ has been determined from three-dimensional X-ray data. The crystals are hexagonal and the space group is $P6_3/m$. The unit cell contains two formula units (24 lead atoms) and has the dimensions: $a=b=14.121\pm0.003$ Å and $c=16.316\pm0.006$ Å.

The crystals contain discrete $[Pb_4(OH)_4{}^{4+}]$-units. The four lead atoms occupy the corners of a slightly distorted tetrahedron and the hydroxide groups are located outside the faces of this tetrahedron. The unit is probably closely related to one of the main species formed in hydrolyzed lead(II)perchlorate solutions.

Complex formation between Pb^{2+} and OH^- in the acid and neutral pH-range yields two main species. The composition and structure of one of these species, $[Pb_6O(OH)_6]^{4+}$, is well established by the combined results from the crystal structure determinations [1,2] of the two known polymorphs of $[Pb_6O(OH)_6](ClO_4)_4.H_2O$ and an X-ray scattering study [3] on hydrolyzed lead(II)perchlorate solutions. The six lead atoms in the complex occupy the corners of three distorted tetrahedra connected by common faces. There is an oxygen atom at the center of the central tetrahedron and an hydroxide oxygen outside each of the six unshared faces of the outer tetrahedra.

The other complex formed has been shown from emf measurements [4] to contain four lead atoms and its composition is usually written $Pb_4(OH)_4{}^{4+}$. X-Ray scattering measurements [3,5] on solutions containing this complex indicate that the lead atoms are at the corners of a tetrahedron. The hydroxide groups have been assumed to be situated outside the faces of the Pb_4-tetrahedron. Since emf measurements at constant water activity cannot differentiate between two OH^- and one O^{2-} some uncertainty exists as to the exact formula and structure of the complex.

There have been no crystal structure determinations made on solids formed from solutions containing $Pb_4(OH)_4{}^{4+}$. Several such solids have been described [6,7] but the compound $[Pb_4(OH)_4]_3(CO_3)(ClO_4)_{10}.6H_2O$ whose crystal structure is reported in this paper has apparently not been prepared before.

EXPERIMENTAL

Preparation, description and analysis of the crystals

Crystals of the compound $[Pb_4(OH)_4]_3(CO_3)(ClO_4)_{10}.6H_2O$, henceforth for convenience called *A*, were incidently obtained in experiments which aimed at the preparation of $PbOHClO_4$ from hydrolyzed lead(II) perchlorate solutions. In some of these solutions, which were not sufficiently concentrated for $PbOHClO_4$ to crystallize, *A* was formed in small amounts on long standing. No method of preparation, which gave good yields, was found even when it later became obvious that the crystals contained carbonate. The following recipe may, however, be given. 0.2 mol of PbO is dissolved in 0.28 mol of $HClO_4$ and the resulting solution diluted to 50 cm³ and filtered. No precaution should be taken to exclude the carbon dioxide of the air during these operations. On standing in a closed vessel, crystals of *A* are formed after a couple of weeks. They consist of transparent, hexagonal prisms terminated by pyramidal faces, $\{10\bar{1}1\}$, and are not changed in contact with the atmosphere.

The lead content of the compound was determined by evaporation with H_2SO_4 and weighing the residue as $PbSO_4$. The number of basic groups was found by a potentiometric titration with standard $HClO_4$ in the following way. A known amount of the solid was added to a known volume of water. The acid was then gradually added, allowing sufficient time for it to react with the solid. The emf's beyond the equivalence point, where all the solid had disappeared, were used to determine this point by a Gran extrapolation. The analytical results obtained were: Pb 64.58 %; mol H^+ consumed/mol Pb 1.17. Calculated values for $[Pb_4(OH)_4]_3(CO_3)(ClO_4)_{10}.6H_2O$:Pb 64.54 %; mol H^+ consumed/mol Pb 1.17.

When *A* was dissolved in acid, whilst observing the process under the microscope, gas bubbles (CO_2) were seen. It was left as a matter for the structure analysis to determine how many of the basic groups that were carbonate groups.

X-Ray diffraction measurements

The space group was determined from oscillation and equi-inclination Weissenberg photographs. The unit cell dimensions were calculated from 59 indexed lines on a powder photograph talen with a Guinier-Hägg focussing camera using $CrK\alpha_1$ ($\lambda = 2.28962$ Å)[8] with silicon ($a = 5.4305$ Å)[9] as internal standard.

The intensity data were collected with a Stoe Weissenberg diffractometer using Ni-filtered $CuK\alpha$ radiation and equi-inclination geometry. The crystals were rotated about the *c*-axis. The diffractometer, which is paper-tape controlled, was programmed to collect the data as if the crystal was monoclinic ($\beta = 120°$). Thus each independent reflection was recorded three times. 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 values of *l* and then gradually increased to 1.4°. The background was measured for 30 sec 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. In the calculations of the corrected intensities, *I*, and their standard deviations, $\sigma(I)$, the expressions presented in Ref. 2 were used. 1414 independent reflections were measured from 14 layers. A new crystal was used for each layer in order to avoid the introduction of a correction for the decomposition of the crystals in the X-ray beam. Inter-layer scale factors, which should take account of the different crystal sizes, were obtained from measurements of three "standard reflections" chosen from the zero-layer. These measurements were done twice, once before and once after the data had been collected for a layer. When these experimental scale factors were refined at the end of the least squares treatment of the data, it was found that they changed by less than 5 %.

An *I*-value is generally based on the mean of the three measurements of a reflection as described above. $|F|$- and $\sigma(F)$-values were calculated from *I*- and $\sigma(I)$-values by applying absorption, Lorentz and polarization corrections. The linear absorption coefficient is estimated to be 738 cm⁻¹. It was therefore necessary to use small crystals. Very small crystals, besides being difficult to handle, had less welldeveloped faces and were unsuitable for that reason. The crystals used were ca 0.1 mm long and had a very regular hexagonal cross-section. The distance between the $\{10\bar{1}0\}$ faces was 0.04 mm.

Computation

The main programs used in this work were CELSIUS, DRF, LALS (UPALS), DISTAN, and ORTEP: The calculations have been performed on the CDC 3600, IBM 370/155 and 1800 computers in Uppsala. The atomic scattering factors were taken from Hanson *et al.*[10] and the real part of the dispersion correction [11] was introduced.

CRYSTAL DATA

Formula unit:	$[Pb_4(OH)_4]_3(CO_3)(ClO_4)_{10}.6H_2O$
Diffraction symmetry:	$6/m$
Crystal system:	hexagonal
Lattice parameters (σ):*	$a=b=14.121(1)$ Å $c=16.316(2)$ Å $V=2818$ Å^3
Density (measured):	4.54(2) g cm^{-3}
Number of formula units per unit cell:	2
Density (calculated):	4.541 g cm^{-3}
Linear absorption coefficient:	738 cm^{-1}
Systematic absences:	$00l$ for $l=2n+1$
Space group:	$P6_3/m$ or $P6_3$
Coordinates of equivalent positions:	$P6_3$: x,y,z; $-y, x-y, z$; $y-x, -x,z$; $-x, -y, 1/2+z$; $y, y-x, 1/2+z$; $x-y, x, 1/2+z$ $P6_3/m$: Above plus centrosymmetric positions

DETERMINATION OF THE STRUCTURE

A rather detailed description of the structure determination will be given since some uncertainty as to the correct space group arose during this part of the work. Furthermore the exact composition of the compound had to be established from the structure determination as this was not possible from the chemical analysis alone.

From a three-dimensional Patterson synthesis one set of lead atoms was found to occupy a general twelve-fold position and two other sets to occupy two special six-fold positions in the mirror plane of the assumed space group, $P6_3/m$. After refinement of these positions the chlorine atoms were next located from a ΔF synthesis. The positions found have the following notations in $P6_3/m$: 12(*i*) x,y,z; 4(*f*) 1/3, 2/3, z; 2(*d*) 1/3, 2/3, 3/4, and 2(*b*) 0, 0, 0. Thus all of the twenty chlorine atoms have been located. The last two positions are, however, not consistent with the geometry of the perchlorate group. For

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* Estimated standard deviations here and elsewhere in the paper refer to the least significant digits.

instance the latter position is at a center of symmetry. This symmetry element is not present in the perchlorate ion.

The symmetry was therefore lowered and the space group was assumed to be $P6_3$, *i.e.* the center of symmetry was removed. After the lead atom positions had been refined in this space group, they were used to calculate difference syntheses from which all the lighter atoms were located. These atoms were found to take up nearly centrosymmetric positions. The light atom parameters did, however, not refine properly. The B-values of several pairs of nearly centrosymmetric atoms moved in different directions ending in one low and one high value. A few B-values even became negative. This behaviour is probably not caused by poor data, since each $|F|$-value is based on the mean of three I-values, which very seldom differed by more than $3\sigma(I)$ or $0.05I$ from the mean. The space group $P6_3$ was abandoned and an approximate structure solution with two disordered perchlorate groups was sought in the higher space group.

From the difference syntheses calculated in $P6_3/m$ the following assignments beside the perchlorate oxygens were made. Four well-defined maxima were assigned to oxygens bound to lead. A peak in the special position 0, 0, $-1/4$ was assigned to the carbon atom and an adjacent peak also on the mirror plane to an oxygen atom in a carbonate group. The two other oxygen atoms in the carbonate group are generated from this atom by the symmetry operations. There would then be two carbonate groups in the unit cell. Since the chemical analysis had shown that the number of equivalents of acid consumed per mol of Pb was $1.17 = 7/6$, the number of base equivalents per unit cell is 28. The CO_3^{2-}-groups take care of 4 of these leaving 24, which fit in if the 24 oxygens bound to lead are hydroxide oxygens.

Only one peak now remained to be assigned. It was assumed to be due to a water molecule. No chemical analysis for water has been made, but the assumption is supported by the lead analysis. The calculated lead content of the material is 66.39 % without any water included. With the amount of water of crystallization indicated by the structure analysis it is 64.58 %. The experimental value is 64.54 %, which thus is in very close agreement with the expected value for the hypothesis advanced.

The later ΔF syntheses also showed that the chlorine atom, which had originally been placed at 1/3, 2/3, 3/4, was better approximated by two half chlorine atoms slightly off the mirror plane. The structure would then be disordered with respect to this chlorine atom and to the oxygen atoms of the perchlorate group at the origin.

In the final refinements data with $|F| < 3\sigma(F)$ were excluded and the weight, w, was calculated as $w^{-1} = \sigma^2(F) + (kF)^2$ and $w(|F_o| - |F_c|)^2$ minimized. k was varied until $w(|F_o| - |F_c|)^2$ did not show a systematic trend with $|F_o|$. The value of k used in the final cycles was 0.05 and the estimated standard deviation of an observation of unit weight was 1.10. No correction for extinction was introduced. The refinement was continued until the shifts, with few exceptions, were less than 0.2σ. The R-value ($R = \sum||F_o| - |F_c||/\sum|F_o|$) became 0.060 for the 1095 reflections with $|F_o| > 3\sigma(F)$. The final parameters are listed in Table 1 with the following exceptions. O(42) was found to oscillate and its z-coordinate was therefore so fixed that the Cl(4) – O(42) distance became

Table 1. Final positional and thermal parameters with standard deviations (σ) within parenthesis.

Atom	*x*	*y*	*z*	*B* (Å^2)
Pb(1)	0.22033(14)	0.22285(14)	−0.13474(10)	
Pb(2)	0.44783(12)	0.21413(13)	−1/4	See below
Pb(3)	0.42327(13)	0.47349(13)	−1/4	
O(1)	0.2611(18)	0.1460(19)	−1/4	2.8(4)
O(2)	0.2427(17)	0.3329(17)	−1/4	2.0(4)
O(3)	0.4191(14)	0.3282(14)	−0.1668(11)	3.3(3)
O(4)	0.1309(22)	0.6696(22)	−0.0978(16)	7.0(6)
C(1)	0	0	−1/4	2.1(9)
O(5)	0.0422(25)	0.1099(24)	−1/4	4.5(6)
Cl(1)	0.3335(5)	0.3272(5)	0.0928(5)	2.8(1)
O(11)	0.3233(40)	0.2559(40)	0.1530(28)	13.8(13)
O(12)	0.2358(25)	0.3288(25)	0.0803(18)	8.3(7)
O(13)	0.4098(50)	0.4277(47)	0.1168(34)	16.3(17)
O(14)	0.3713(38)	0.3093(38)	0.0195(27)	13.3(13)
Cl(2)	1/3	2/3	0.0632(7)	2.7(2)
O(21)	0.4242(19)	0.6631(20)	0.0346(13)	5.9(5)
O(22)	1/3	2/3	0.1519(22)	5.2(8)
Cl(3)	0	0	0	3.7(3)
O(31)	0.0946(42)	0.0017(41)	−0.0376(29)	6.6(11)
O(32)	0	0	0.090(−)	10.5(32)
Cl(4)	1/3	2/3	−0.2296(12)	2.9(4)
O(41)	0.4462(25)	0.7119(24)	−1/4	4.7(6)
O(42)	1/3	2/3	−0.141(−)	8.9(23)

Coefficients ($\times 10^4$) in the expression $\exp -(B_{11}hh + ... + 2B_{12}hk + ...)$ for the anisotropic temperature factors for lead.

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Pb(1)	118(1)	123(2)	43(3)	92(1)	45(1)	42(1)
Pb(2)	44(1)	52(1)	44(3)	31(1)	0	0
Pb(3)	48(1)	34(1)	61(3)	13(1)	0	0

1.45 Å. One of the perchlorate oxygens, O(32), with a bond length differing by more than 0.1 Å from the expected value was moved to the positions indicated by the ΔF map. The C−O bond length in the carbonate group was 1.36 Å ($3\sigma = 0.08$ Å) with the oxygen position obtained from the least squares treatment. With the oxygen atom coordinates from the ΔF synthesis it was 1.31 Å. Since this value is closer to the value (1.294 Å)[13] expected for a free carbonate ion, the latter set of coordinates was accepted. The R-value was unaffected by these changes. The observed and with the parameters in Table 1 calculated structure factors are given in Table 2. The final ΔF synthesis showed 25 peaks with heights greater than 1 e$^-$/Å^3. The largest values, slightly less than 2 e$^-$/Å^3, were found close to the lead and one of the oxygen atoms. The last atom, O(13), was originally located from a rather broad peak with a peak height of *ca.* 4 e$^-$/Å^3.

Table 2. Observed and calculated structure factors. Columns are in order h, k, $10F_o$, $10F_c$. Reflexions with $|F_o| < 3\sigma(F)$ are not included. Reflexions with $0.5 < F_o/F_c > 1.5$ are marked with an asterisk.

H,K,0			
1	0	1842	1734
1	1	2404	2402
1	2	2902	2761
1	3	404	575
1	4	2757	2491
1	5	1824	1846
1	6	1595	1543
1	7	549	408
1	8	1624	1647
1	9	1295	1275
1	10	1053	925
1	11	701	799
1	12	869	845
2	0	763	851
2	1	499	374
2	2	925	837
2	3	1230	1365
2	4	3525	3449
2	5	1016	972
2	6	1455	1499
2	7	1865	1858
2	8	2396	2383
2	9	1609	1679
2	11	975	1041
2	12	1707	1710
3	0	2285	2282
3	1	2046	2052
3	2	2776	2911
3	3	456	879
3	4	2999	2957
3	5	853	967
3	6	437	175*
3	10	1114	1077
3	11	723	794
4	0	7460	8417
4	1	5554	5711
4	2	821	785
4	3	493	579
4	4	2003	1945
4	5	6036	6117
4	6	506	499
4	7	1283	1290
4	8	664	604
4	9	1978	1928
5	0	5680	5717
5	1	2679	2694
5	2	2575	2728
5	3	1748	1751
5	4	3777	3734
5	5	1691	1512
5	7	2176	2219
5	8	2325	2325
5	9	1072	1185
5	10	571	467
6	0	684	462
6	1	2993	3215
6	2	1893	1853
6	3	1836	1811
6	4	1249	1283
6	5	1150	1137
6	6	1448	1336
6	7	1420	1468
7	0	1836	1700
7	1	762	505
7	2	2924	3071
7	3	985	1008
7	4	1431	1481
7	5	694	704
7	6	698	618
7	7	1230	1170
7	8	434	155*
8	1	2000	1962
8	3	1168	1213
8	5	1442	1392
8	6	417	283
8	7	442	498
9	0	6173	6194
9	1	591	399
9	2	2108	2241
9	4	1733	1705
9	5	639	682
10	1	962	942
10	2	445	310
10	3	398	328
10	4	2000	1932
10	5	356	3*
11	0	1020	1024
11	1	1480	1394
11	2	1932	1854
11	3	924	851
11	4	1138	1095
12	0	875	747
12	1	772	691
13	0	1255	1335
13	1	614	655
H,K,1			
1	0	1368	1333
1	1	3786	3953
1	2	1804	1774
1	3	1315	1383
1	4	3738	3667
1	5	2514	2468
1	7	1876	1808
1	8	1018	1002
1	9	731	791
1	11	1459	1482
1	13	880	842
2	0	1622	1574
2	1	3668	3624
2	2	3843	3747
2	3	3313	3340
2	4	1800	1794
2	5	2054	2088
2	6	4246	4179
2	7	2045	2106
2	8	1494	1531
2	10	1511	1491
2	12	1013	1027
2	13	738	597
3	0	4792	5056
3	1	5691	6099
3	2	2254	2162
3	3	3435	3290
3	4	5624	5871
3	6	882	915
3	7	2188	2246
3	8	1819	1779
3	9	2361	2414
3	10	792	887
3	12	486	524
4	0	997	1059
4	1	1422	1335
4	2	2694	2773
4	4	726	733
4	7	648	598
5	0	1759	1676
5	1	444	359
5	2	2394	2432
5	3	1698	1832
5	5	714	816
5	7	709	706
5	8	483	541
5	9	767	758
5	10	588	595
5	11	495	549
6	0	614	664
6	1	2203	2174
6	2	1108	1030
6	3	2199	2189
6	4	1526	1581
6	5	1384	1293
6	6	2061	2007
6	9	1819	1672
7	0	1273	1202
7	1	2763	2740
7	2	1345	1348
7	3	2539	2443
7	4	539	418
7	5	1489	1494
7	6	1630	1736
7	7	2265	2274
7	9	1091	1023
8	0	3363	3436
8	1	2003	1968
8	2	1566	1453
8	3	1321	1322
8	4	2192	2161
8	5	1128	1225
8	6	643	611
8	7	379	184*
8	8	980	898
9	0	1306	1207
9	1	995	1016
9	2	1675	1687
9	4	833	824
9	5	780	842
10	2	711	757
10	3	1048	994
10	6	393	384
11	0	1331	1375
11	1	893	894
11	2	1213	1282
11	3	764	868
11	4	1141	1068
11	5	316	220
12	0	1648	1651
12	1	760	818
12	3	874	941
13	0	791	741
13	2	457	372
H,K,2			
0	1	1428	1430
0	2	1114	1132
0	3	3777	3982
0	4	3437	3546
0	5	1877	1972
0	6	2501	2687
0	7	1018	1055
0	8	1397	1386
0	9	1269	1376
0	10	939	921
0	11	972	848
0	12	913	916
1	1	1341	1297
1	2	474	489
1	3	1692	1612
1	4	529	477
1	5	520	154*
1	8	457	444
1	9	478	466
1	10	976	835
1	12	654	591
2	1	2073	2093
2	2	1285	1314
2	3	435	331
2	4	1181	1306
2	5	1778	1902
2	6	577	454
2	7	559	548
2	8	1795	1880
2	9	918	779
2	10	1002	869
2	12	987	975
2	13	615	583
3	1	2974	3178
3	2	1474	1546
3	3	1951	1699
3	4	2820	2841
3	5	1288	1192
3	6	1517	1477
3	7	993	980
3	8	1278	1274
3	9	1609	1558
3	10	1010	958
3	12	1501	1516
4	1	1936	1835
4	2	1212	1151
4	3	1772	1789
4	4	501	525
4	5	2818	2719
4	6	1052	1082
4	7	1413	1470
4	8	1197	1371
4	9	598	492
4	10	705	777
5	1	2209	2154
5	2	1301	1130
5	3	2332	2411
5	4	1884	1776
5	5	512	364
5	7	1791	1791
5	8	1493	1481
5	9	654	542
5	11	386	398
6	1	4515	4490
6	3	674	757
6	4	1180	1278
6	5	1562	1505
6	6	1183	1246
6	7	537	505
	9	811	837
6	10	870	884
7	1	568	578
7	2	2188	2116
7	4	1202	1228
7	5	691	704
7	6	507	450
7	7	652	442
7	9	460	489
8	1	745	792
8	3	1936	1818
8	4	538	615
8	6	549	420
8	7	896	874
8	8	337	231
9	1	521	489
9	2	1397	1423
9	3	1395	1315
9	4	691	707
9	6	840	886
9	7	496	630
10	1	654	672
10	4	1343	1278
10	6	1273	1277
11	1	1664	1685
11	2	1314	1293
11	4	984	974
11	5	423	390
12	1	953	910
12	2	502	598
12	3	342	234
H,K,3			
1	0	417	286
1	1	1150	1110
1	2	3645	3740
1	3	1547	1467
1	4	1817	1745
1	5	479	460
1	6	4460	4486
1	7	471	445
1	8	769	750
1	10	1122	1158
1	12	442	582
1	13	649	776
2	0	2729	2591
2	1	3878	4024
2	2	3731	3662
2	3	746	818
2	4	4509	4560
2	5	2195	2232
2	6	1482	1581
2	7	1846	1758
2	8	2339	2288
2	9	539	555
2	11	1194	1306
2	12	512	453
3	0	4444	4663
3	1	4530	4593
3	3	4963	4768
3	4	2243	2248
3	5	1702	1721
3	6	1513	1478
3	7	688	624
3	9	1731	1635
3	10	1038	1034
4	0	1261	1157
4	3	2237	2259
4	4	843	935
4	5	706	680
4	6	840	756
4	7	1433	1374
4	8	1326	1321
4	10	773	772
4	11	720	717
5	0	1372	1322
5	1	1645	1854
5	2	2407	2406
5	3	1473	1522
5	5	2730	2777
5	6	1440	1440
5	7	723	487
5	9	913	912
5	10	1346	1290
6	0	931	843
6	1	1851	1808
6	2	3119	3024
6	3	1469	1496
6	4	2541	2479
6	5	597	507
6	6	673	474
6	9	1238	1290
7	0	915	874
7	2	1562	1540
7	3	487	294
7	4	2212	2147
7	5	1674	1796
7	6	937	813
7	7	818	847
7	8	1087	1203
8	0	2236	2187
8	1	894	852
8	2	1054	1082
8	3	1399	1334
8	4	1345	1319
8	5	679	535
8	6	763	882
8	7	799	842
9	0	1260	1200
9	1	1598	1598
9	2	554	702
9	3	489	641
9	4	1239	1171
9	5	1274	1360
9	6	937	831
10	1	779	846
10	2	507	554
10	3	1076	1089
10	4	662	751
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11	1	856	858
11	4	1454	1568
12	0	1432	1417
13	0	642	681
H,K,4			
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1	1	2316	2334
1	2	3414	3531
1	3	1995	2020
1	4	4150	3825
1	6	1768	1684
1	7	1523	1434
1	10	1654	1502
1	12	426	587
2	0	3686	3454
2	1	5228	5410
2	2	4847	4639
2	3	2697	2646
2	5	3661	3629
2	6	2548	2571
2	7	987	946
2	10	1725	1799
2	11	793	793
3	0	3084	3099
3	1	3006	3019
3	3	4737	4566
3	4	939	998
3	5	1711	1743
3	6	1265	1248
3	7	2530	2509
3	8	2330	2224
3	9	1540	1435
3	10	844	858
3	12	1738	1835
4	0	1960	2011
4	1	2463	2196
4	2	969	912
4	3	2591	2478
4	4	3009	2982
4	5	449	179*
4	6	1770	1773
4	7	2328	2231
4	8	1551	1621
4	9	782	811
4	10	1261	1389
5	0	2995	2929
5	1	3076	3000
5	2	1042	860
5	3	1945	1886
5	4	1150	1031
5	5	2344	2327
5	7	990	929
5	8	833	840
5	9	474	560
6	0	2861	3024
6	1	5870	5885
6	2	1851	1840
6	3	1277	1275
6	4	1319	1405
6	5	1652	1709
6	6	2088	2180
6	7	516	477
6	9	832	798
6	10	825	1074
7	1	597	567
7	3	1537	1506
7	7	747	698
7	8	682	666
8	0	2558	2570
8	1	566	616
8	2	1504	1429
8	3	2807	2898
8	4	597	684
8	5	580	672
8	7	1431	1441
9	0	1587	1516
9	1	1749	1789
9	2	432	338
9	3	872	824
9	5	1249	1323
9	6	972	961
9	7	482	347
10	0	2119	2233
10	1	1251	1177
10	2	1332	1280
10	4	856	755
10	5	854	884
10	6	1150	1437
11	0	761	720
11	1	2076	2029
11	3	544	511
11	4	764	823
12	0	1191	1146
12	1	921	991
12	2	1022	1019
12	3	680	789
13	0	505	508
14	0	407	517
H,K,5			
1	0	1362	1476
1	1	2708	2514
1	2	6359	6660
1	3	2000	1693
1	4	2009	2126
1	6	4509	4349
1	7	2011	1986
1	8	1526	1586
1	9	563	512
1	10	1415	1852
1	11	816	742
1	12	544	650
2	0	1236	1396
2	1	3820	3786
2	2	2658	2665
2	4	4995	5088
2	5	1387	1183
2	6	695	783
2	7	2177	2216
2	8	3003	3064
2	9	791	578
2	11	1007	1123
2	12	811	754
3	0	3728	3841
3	1	2331	2382
3	2	579	386
3	3	5203	5434
3	4	1065	1116
3	5	1466	1479
3	6	1011	1083
3	7	573	503
3	8	1339	1293
3	9	1058	1093
3	10	752	693
4	0	1625	1560
4	3	2809	2810
4	4	1002	833
4	6	994	969
4	7	958	1007
4	8	1402	1387
4	10	510	401
5	0	730	729
5	1	1304	1191
5	2	1641	1619
5	5	1894	1894
5	6	1794	1785
5	7	522	548
5	8	444	173*
5	9	790	877
5	10	1182	1078
6	0	1201	1172
6	1	2783	2877
6	2	3373	3525
6	3	1650	1609
6	4	2203	2163
6	6	868	1026
6	7	1054	1079
6	9	1244	1223
7	0	741	788
7	1	1048	970
7	3	817	720
7	4	1966	1907
7	5	1707	1738
7	6	525	456
7	7	1263	1259
8	0	2282	2304
8	1	862	808
8	3	1450	1513
8	4	490	496
8	5	926	885
8	6	575	475
8	7	1023	1047
9	0	1104	1154
9	1	1672	1608
9	2	1481	1405
9	3	876	797
9	4	1326	1245
9	5	883	833
9	6	878	863
10	0	457	161*
10	1	1593	1543
10	2	968	1169
10	3	890	983
10	5	662	450
11	0	1420	1448
11	1	866	933
11	3	429	333
12	0	1170	1165
13	0	657	731
H,K,6			
0	1	2630	2813
0	2	1304	1296
0	3	1022	600
0	4	1558	1258
0	5	1346	1184
0	6	1524	1613
0	8	772	860
0	9	1428	1103
0	10	1991	2051
0	11	1142	1028
1	1	901	833
1	2	473	50*
1	3	1235	1342
1	4	2165	2246
1	5	1134	1102
1	6	534	534
1	7	503	485
1	8	594	564
1	10	453	429
1	12	788	808
2	1	3941	4066
2	2	2098	2000
2	3	978	1001
2	4	1090	1060
2	5	1934	1993
2	6	650	648
2	8	1016	1084
2	9	811	768
2	10	799	869
2	12	645	656
3	1	1858	1847
3	2	1188	1181
3	3	3627	3868
3	4	746	758
3	5	859	905
3	7	1240	1327
3	8	1426	1501
3	10	766	692
3	11	645	537
4	1	1020	822
4	2	662	726
4	3	1984	2110
4	4	1338	1325
4	5	1220	980
4	6	1646	1672
4	7	1317	1320
4	8	429	500
4	9	394	231
4	10	1174	1256
5	1	3161	3385
5	2	377	528
5	3	1433	1429
5	4	433	26*
5	5	1907	1851
5	6	811	804
5	7	1204	1236
5	8	1094	1008
5	9	406	419
6	1	3391	3349
6	2	848	886
6	3	1921	1877
6	4	1834	1826
6	5	672	703
6	6	1912	1973
7	2	901	925
7	3	461	419
7	4	836	743
8	3	2158	2226
8	7	725	870
9	1	1749	1776
9	2	1031	1020
9	4	405	333
9	5	839	945
9	6	559	565
10	2	532	564
10	4	650	624
11	1	1533	1504
11	2	780	766
12	1	660	708
12	2	643	618
H,K,7			
0	2	1681	1745
0	3	3355	3333
0	4	1307	1439
0	5	682	417
0	6	700	715
0	7	985	990
0	8	1768	1761
0	9	880	867
0	10	533	386
0	11	1196	1223
0	12	1028	1106
1	1	1697	1558
1	2	291	322
1	3	454	442
1	4	2542	2603
1	5	1935	2074
1	8	1026	970
1	11	727	774
1	12	479	323
2	1	1263	1268
2	2	788	744
2	3	2219	2313
2	4	2521	2646
2	5	1496	1440
2	6	2140	2059
2	7	2553	2550
2	8	1431	1457
2	9	1057	1010
2	10	989	885
2	11	506	510
3	1	3495	3556
3	2	1663	1632
3	3	491	598
3	4	2497	2462
3	6	474	435
3	7	1586	1559
3	8	832	760
3	9	1086	1246
3	10	677	732
3	11	403	327
4	1	1209	1247
4	2	1099	1080
4	3	1444	1294
4	4	372	376
4	5	656	762
4	8	700	656
5	1	478	510
5	2	1412	1362
5	3	1628	1594
5	4	538	389
5	8	395	457
6	1	1060	1083
6	3	1937	2055
6	4	1304	1337
6	5	1209	1149
6	6	1002	842
6	7	668	575
7	1	770	736
7	3	1882	1844
7	5	801	884
7	7	1999	1974
8	1	554	626
8	2	866	857
8	4	1315	1314
8	5	997	1151
9	1	631	436
9	2	1706	1581
9	3	717	590
9	4	921	1018
9	5	598	474
10	2	518	455
10	3	1023	1073
11	2	538	507
11	3	963	961
12	1	510	534
H,K,8			
1	0	1072	1736
1	1	1679	1638
1	2	1702	1592
1	4	1358	1201
1	5	460	303
1	6	971	918
1	8	1508	1475

Table 2. Continued.

1	9	819	917
1	12	706	658
2	0	275	221
2	1	411	395
2	2	752	653
2	3	383	263
2	4	1794	1731
2	7	1094	1103
2	8	1722	1643
2	9	1004	985
2	10	395	265
2	11	636	749
3	0	1476	1297
3	1	831	786
3	2	1698	1625
3	4	1520	1432
3	6	979	961
3	8	734	636
3	9	613	649
3	10	730	867
4	0	5591	5995
4	1	2910	2764
4	2	921	914
4	3	926	971
4	4	1415	1348
4	5	4007	4045
4	6	557	543
4	7	617	542
4	9	1485	1603
5	0	3947	4058
5	1	1177	1205
5	2	1938	1973
5	3	891	783
5	4	3079	3125
5	5	507	438
5	6	488	504
5	7	1186	1225
5	8	1567	1583
5	9	853	1020
6	0	1688	1774
6	1	1863	1785
6	2	1022	995
6	4	697	719
6	5	625	677
6	6	452	253
6	7	618	691
7	0	840	800
7	2	1581	1626
7	3	690	651
7	4	1172	1175
7	6	448	454
7	7	938	763
8	0	1057	943
8	1	1755	1758
8	3	1043	986
8	4	572	467
8	5	892	910
8	6	369	339
9	0	2921	2949
9	1	458	185*
9	2	1209	1317
9	3	614	700
9	4	1656	1660
9	5	474	613
10	4	1055	1181
11	0	704	662
11	1	1077	1087
11	2	1253	1288
H,K,9			
1	0	709	836
1	1	3575	3814
1	2	2617	2582
1	3	722	678
1	4	1300	1300
1	5	1750	1625
1	6	972	855
1	7	2249	2152
1	9	594	484
1	10	779	690
1	11	1390	1448
2	0	607	660
2	1	3088	3057
2	2	1285	1285
2	3	2498	2411
2	5	596	618
2	6	3299	3346
2	7	1149	1031
2	10	1222	1311
3	0	2804	2791
3	1	4093	3940
3	2	1875	1772
3	3	2131	2038
3	4	3870	3793
3	5	564	488
3	6	884	952
3	7	1850	1837
3	8	1922	1950
3	9	1657	1560
3	10	645	660
4	0	634	703
4	2	1877	1984
4	3	747	725
4	5	435	339
5	0	797	862
5	1	469	166*
5	2	1007	951
5	3	1655	1601
5	5	1022	1065
5	6	547	413
5	7	892	832
5	9	362	386
6	0	515	471
6	1	2179	2004
6	2	1139	1175
6	3	1115	994
6	4	612	638
6	5	717	777
6	6	1498	1616
6	7	418	400
6	8	390	257
7	0	722	799
7	1	2695	2630
7	2	995	984
7	3	1889	1905
7	5	589	529
7	6	1250	1324
7	7	1071	1076
8	0	1510	1571
8	1	1296	1100
8	2	1681	1724
8	3	970	1127
8	4	1703	1700
8	5	421	410
8	6	534	533
9	0	761	680
9	1	656	806
9	2	793	799
9	4	401	401
9	5	622	580
10	1	683	729
10	2	721	952
10	3	568	439
11	0	840	829
11	1	796	840
11	2	573	650
12	0	1094	1057
H,K,10			
0	1	209	286
0	2	407	356
0	3	2017	2059
0	4	2736	2643
0	5	2709	2643
0	6	1121	1046
0	7	1216	1320
0	8	899	834
0	9	1633	1756
0	12	697	698
1	1	292	167
1	2	1096	973
1	3	1079	1223
1	4	1018	1015
1	5	759	751
1	6	500	640
1	8	409	240
1	9	522	633
1	10	918	895
1	11	451	540
2	1	383	109*
2	2	416	342
2	3	557	410
2	4	1193	1159
2	5	958	877
2	7	986	962
2	8	783	851
2	9	662	680
2	10	446	330
3	1	1508	1474
3	2	1327	1253
3	4	2074	2174
3	5	945	938
3	6	876	799
3	9	1005	1042
3	10	566	515
4	1	2350	2220
4	2	602	587
4	3	393	317
4	5	2190	2360
4	7	829	763
4	8	1243	1209
4	9	411	517
5	1	523	496
5	2	762	655
5	3	1455	1408
5	4	1707	1740
5	5	1055	1152
5	7	1284	1292
5	8	872	1010
6	1	2083	1981
6	2	1032	982
6	3	453	9*
6	5	957	877
6	6	561	386
6	7	793	712
7	2	1548	1556
7	4	610	749
7	5	623	726
7	6	628	498
8	1	448	523
8	2	575	495
8	4	580	674
9	1	465	384
9	2	812	891
9	3	1009	1059
10	1	1021	957
10	3	525	311
11	1	660	682
H,K,11			
1	0	706	887
1	1	273	290
1	2	1185	1185
1	3	563	602
1	4	840	908
1	6	1355	1287
1	7	608	517
1	10	877	752
2	0	612	741
2	1	378	397
2	2	371	274
2	4	1692	1618
2	5	774	783
2	6	986	1007
2	8	1118	1092
3	0	2058	2114
3	1	2061	2072
3	2	1007	941
3	3	741	699
3	4	2402	2370
3	6	1288	1200
3	9	1327	1304
4	2	891	1018
4	3	649	612
4	6	572	442
5	0	744	818
5	1	777	794
5	2	652	615
5	3	512	469
5	5	1118	1173
5	6	1110	1015
6	0	632	492
6	1	757	772
6	4	1008	942
6	7	375	228
7	1	839	816
7	2	1335	1289
7	3	576	425
7	5	1227	1148
7	6	1004	1088
8	0	1509	1576
8	1	1384	1201
8	4	1033	936
8	5	443	377
9	0	544	507
9	1	1049	1103
10	1	649	596
10	2	405	266
11	0	597	607
H,K,12			
1	0	1005	1470
1	2	1328	1381
1	3	975	971
1	4	1331	1354
1	5	586	456
1	6	1169	1152
1	10	623	609
2	0	1097	1189
2	1	2124	2171
2	2	1152	1129
2	3	596	655
2	5	1458	1396
2	6	1077	1018
2	10	982	888
3	0	528	592
3	1	1552	1469
3	3	2775	2522
3	4	887	809
3	5	1094	1017
3	7	1290	1226
3	8	720	746
3	9	502	512
4	0	1078	982
4	1	800	769
4	2	630	563
4	3	853	799
4	4	1811	1686
4	5	476	218*
4	7	869	922
4	8	1144	976
5	0	863	884
5	1	942	839
5	3	1300	1176
5	5	595	584
5	6	646	676
5	7	694	542
6	1	2839	2765
6	2	962	948
6	3	945	831
6	4	472	452
6	5	1106	1013
6	6	1456	1558
7	2	486	278
7	3	1036	997
8	0	1788	1631
8	1	788	697
8	2	485	380
8	3	1281	1176
8	4	973	842
9	1	595	572
9	2	441	22*
9	3	416	225
10	1	733	602
10	2	692	788
11	0	399	56*
H,K,13			
1	0	339	370
1	1	1389	1499
1	2	2528	2525
1	3	975	995
1	4	1021	875
1	6	2607	2445
1	7	1177	1204
1	10	1138	1129
2	0	604	769
2	1	2203	2293
2	2	583	716
2	3	597	562
2	4	2028	2014
2	6	591	653
2	7	943	881
2	8	1707	1766
2	9	496	406
3	0	1434	1437
3	1	857	847
3	2	867	764
3	3	2304	2265
3	5	577	771
3	6	827	451
3	7	1119	976
3	8	832	841
3	9	476	574
4	0	525	450
4	1	536	434
4	2	610	454
4	3	1320	1261
4	7	440	364
4	8	521	524
5	1	1196	1098
5	2	589	449
5	3	1099	18*
5	5	513	403
5	6	1016	923
6	0	719	582
6	1	1364	1340
6	2	1760	1908
6	3	853	758
6	4	1412	1430
6	5	463	331
6	6	736	816
7	1	718	860
7	3	793	689
7	4	710	714
7	5	793	893
8	0	1031	958
8	1	468	394
8	3	905	987
9	1	647	427
10	1	971	920

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

The lead atoms, Pb(1) – Pb(3), occur in groups of four, which form the corners of a nearly regular tetrahedron. By virtue of the assumed space group this arrangement has a plane of symmetry. Five of the six lead-lead distances are almost equal (*ca.* 3.76 Å) as can be seen from Table 3, whereas the sixth

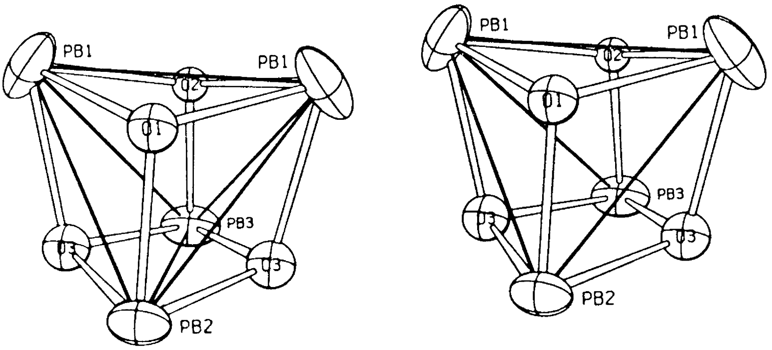

Fig. 1. Stereoscopic pair showing the arrangement of the atoms in the $[Pb_4(OH)_4{}^{4+}]$-unit.

Table 3. Some distances and angles in the [$Pb_4(OH)_4{}^{+4}$]-unit.[a]

A. Distances (Å). Standard deviations (σ) within parenthesis.

Atoms	Distance	Atoms	Distance
Pb(1)–Pb(1)′	3.761(3)	Pb(2)–Pb(3)	3.848(2)
–Pb(2)	3.777(2)	–O(1)	2.311(22)
–Pb(3)	3.759(2)	–O(3)	2.293(17)
–O(1)	2.381(14)	Pb(3)–O(2)	2.319(20)
–O(2)	2.358(16)	–O(3)	2.436(17)
–O(3)	2.488(16)		

B. Angles (°). The estimated standard deviation of a Pb–Pb–Pb angle is ± 0.1° and ± 2° of a Pb–O–Pb or O–Pb–O angle.

Atoms	Angle	Atoms	Angle
Pb(1)′–Pb(1)–Pb(2)	60.1	Pb(1)–O(1)–Pb(1)′	104
Pb(1)′– –Pb(3)	60.0	Pb(1)– –Pb(2)	107
Pb(2) – –Pb(3)	61.4		
O(1) – –O(2)	72		
O(1) – –O(3)	69		
O(2) – –O(3)	73		
Pb(1) –Pb(2)–Pb(1)′	59.7	Pb(1)–O(2)–Pb(1)′	106
Pb(1) – –Pb(3)	59.1	Pb(1)– –Pb(3)	107
O(1) – –O(3)	74		
O(3) – –O(3)′	73		
Pb(1) –Pb(3)–Pb(1)′	60.0	Pb(1)–O(3)–Pb(2)	104
Pb(1) – –Pb(2)	59.5	Pb(1)– –Pb(3)	100
O(2) – –O(3)	74	Pb(2)– –Pb(3)	109
O(3) – –O(3)′	68		

[a] Atoms with primed and unprimed symbols are related by the mirror plane at $z = -1/4$.

distance is *ca.* 0.1 Å longer. These values fall within the rather broad range of Pb–Pb distances found in the lead(II) oxides[14,15] and in α- and β-[$Pb_6O(OH)_6$]-$(ClO_4)_4.H_2O$.[1,2] There are four hydroxide oxygens, O(1)–O(3), associated with the Pb_4-unit. They are situated outside the four faces of the lead tetrahedron and the whole unit can be written [$Pb_4(OH)_4$]$^{4+}$, Fig. 1. The lead-oxygen distances are less regular than the Pb–Pb distances and vary between 2.29 and 2.49 Å; see Table 3. Each oxygen atom coordinates three lead atoms and neighbouring lead atoms in the Pb_4-cluster can be considered held together by two hydroxide bridges. It should, however, be noted that each hydroxide group is involved in three bridges. The cluster may be further stabilised by metal-metal bonds as discussed by Maroni and Spiro.[16] The hydroxide oxygens form a somewhat distorted tetrahedron. The six oxygen-oxygen distances lie between 2.72 and 2.87 Å (mean 2.80 Å) indicating van der Waals contacts between these atoms.

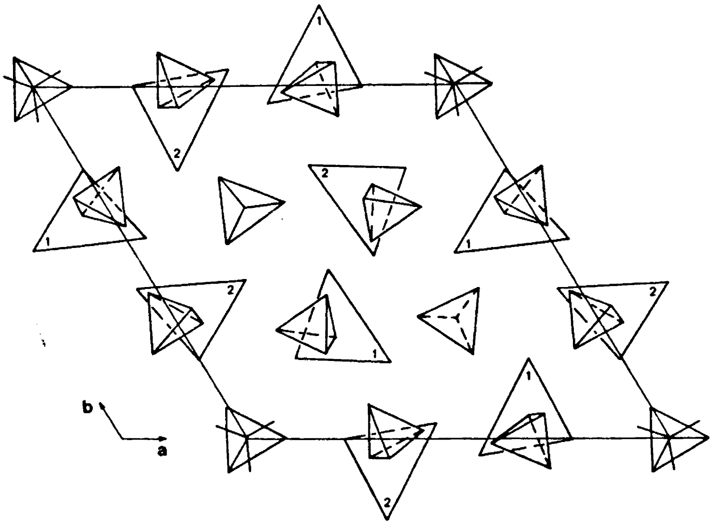

Fig. 2. Projection of the structure of $[Pb_4(OH)_4]_3(CO_3)(ClO_4)_{10}.6H_2O$ along the c-axis. For clarity some of the CO_3^{2-} and ClO_4^--groups along the symmetry axes as well as the OH^--groups in the $[Pb_4(OH)_4^{4+}]$-units have been excluded. The Pb_4-units appear as triangles and the units on and around the mirror planes at $z = -1/4$ and $1/4$ are marked with 1 and 2, respectively.

The $[Pb_4(OH)_4^{4+}]$-units are arranged in a pattern resembling hexagonal close-packing, Fig. 2. The shortest Pb–Pb and Pb–OH distances between atoms belonging to different units but in the same layer are 4.40 and 4.51 Å, respectively. The corresponding distances between atoms belonging to different layers exceed 5 Å. Thus, since there is no extended Pb–OH–Pb network in the structure the group $[Pb_4(OH)_4^{4+}]$ definitely occurs as a discrete unit.

The arrangement of the above units leads to "channels" in the structure centered around the axes of symmetry. The unit cell contains two carbonate and twenty perchlorate groups. Of these anions, eight of the perchlorates, $ClO_4(2)$–$ClO_4(4)$, and the two carbonates are found in these channels with the chlorine and carbon atoms situated on the axes. The arrangement of the various groups is indicated in Fig. 2 which is supplemented by Fig. 3, which gives the heights of the atoms along the c-axis.

The Cl–O bond lengths in the perchlorate groups are within $2\sigma(\sigma_{\max} = 0.05$ Å) equal to the expected value 1.45 Å.[17] The closest distance between a lead atom and a perchlorate oxygen is 2.96 Å. If oxygens closer than 3.25 Å are considered coordinated, the coordination numbers towards the perchlorate oxygens are five, four, and four for Pb(1), Pb(2), and Pb(3), respectively. The perchlorate group in general position, $ClO_4(1)$, is situated in a "tetrahedral hole" in the arrangement of the Pb_4-groups and is coordinated to the four surrounding Pb_4-groups. $ClO_4(3)$, which is in an "octahedral hole", is coordinated to six such groups. $ClO_4(2)$ and (4) are coordinated to only three

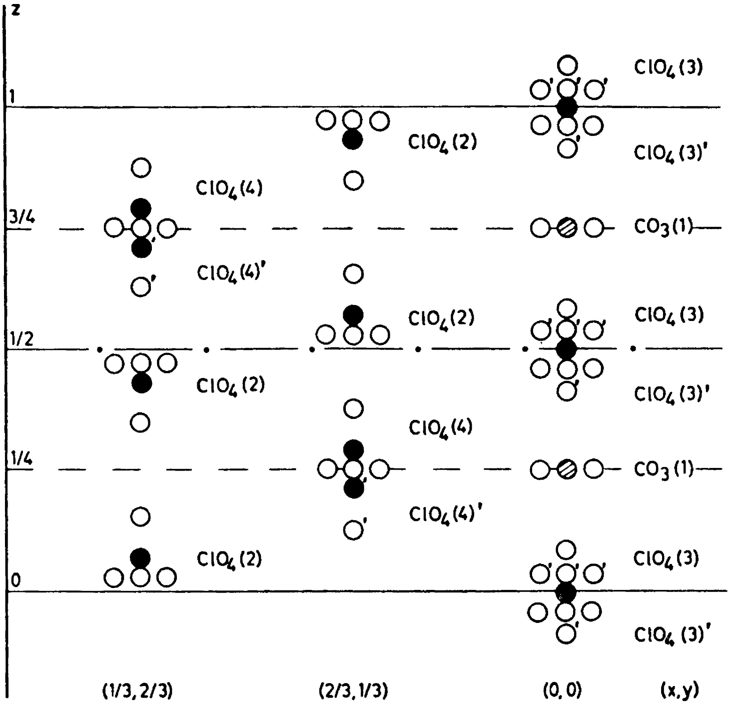

Fig. 3. Arrangement of the anions along the symmetry axes. Alternative positions are primed. ○ oxygen, ● chlorine, ◈ carbon.

groups and here O(21) and O(42) are uncoordinated. The closest distances between the hydroxide and perchlorate oxygens range between 2.88 and 3.14 Å. Although the shortest distance may indicate some hydrogen bonding from one of the hydroxide oxygens no definite conclusion can be drawn, partly because of the uncertainties in the bond lengths (σ *ca.* 0.05 Å). The observed atomic distances between the perchlorate groups and the $[Pb_4(OH)_4{}^{4+}]$-groups fall in the same ranges as was found for α- and β-$[Pb_6O(OH)_6](ClO_4)_4.H_2O$. These distances indicate that the interactions between these groups are weak.

In the carbonate group both the bond lengths (1.31 Å) and the bond angles (120°) are equal by symmetry. The carbonate oxygen, O(5), coordinates two Pb(1) atoms at 2.91 Å. This distance is appreciably longer than the values found in $2PbCO_3.Pb(OH)_2$ (2.75 Å) [18] and in $PbCO_3.PbO.2H_2O$ (2.65 Å) [19] from electron diffraction studies. Probably, the interaction is weak between the $[Pb_4(OH)_4{}^{4+}]$-unit and the carbonate ion.

The water molecule, O(4), may be considered attached to the Pb_4-cluster through interactions with Pb(3) and Pb(1), which are 2.78 and 2.98 Å distant, respectively. Its nearest oxygen neighbours are O(2), O(3), and O(42), which all are at a distance of *ca.* 2.96 Å from O(4).

The positional disorder of $ClO_4(3)$ and $ClO_4(4)$ may be explained by the fact that the interatomic distances are the same for the two alternative ways to place each of them; see Fig. 3. The suggested arrangement of anions along the symmetry axes results in a rather loose packing. The largest distance between two levels of oxygen atoms is *ca.* 3.6 Å along the screw axis and *ca.* 4.6 Å along the three-fold axes. If the disorder is static rather than dynamic, the holes on the latter axes are just big enough to have room for a water molecule. The presence of this water molecule cannot be decided upon from the F map, since its location can be expected to be close to an O(42) position in the centrosymmetric approach. Its presence should add extra electron density to this position and be reflected in the B-value of O(42). The temperature factor of O(42) is, however, not low compared to those of O(22) and O(32). When the electron densities are compared one finds for the not disordered O(22) 4.0 $e^-/Å^3$ and for O(32) 1.9 $e^-/Å^3$ and for O(42) 2.1 $e^-/Å^3$. There is thus no extra electron density at the O(42) position. The lead analysis, which should be quite accurate, does not either suggest that two additional water molecules should be included in the unit cell.

The general features of the arrangement of the atoms in the $[Pb_4(OH)_4{}^{4+}]$-unit are the same as those suggested for this unit in aqueous solution. The Pb–Pb distances are, however, significantly different in the two cases. In solution, where the diffraction data have been interpreted on the assumption of a regular Pb_4-tetrahedron, the Pb–Pb distance is 3.85 Å. This is 0.07 Å longer than the mean distance found in the solid. The Pb–O distance can be determined with much less accuracy and in Ref. 3 only a mean value of *ca.* 2.6 Å was reported for this distance in solution. The radial distribution curve, in fact, shows two peaks at 2.4 and 2.9 Å, respectively. These peaks can now be interpreted as arising from Pb–O interactions within the tetramer and between the tetramer and water and perchlorate oxygens. The mean Pb–O distance in the solid for the $[Pb_4(OH)_4{}^{4+}]$-unit is 2.38 Å. The $[Pb_6O(OH)_6{}^{4+}]$-unit in the structure of α- and β-$[Pb_6O(OH)_6](ClO_4)_4.H_2O$ may be considered as built from two $[Pb_4(OH)_4{}^{4+}]$-units with two lead and one oxygen atom in common. In it the Pb–Pb and Pb–O distances are quite varied and somewhat different in the two structures. The observed differences in bond lengths for $[Pb_4(OH)_4{}^{4+}]$ in the solid and in solution may thus be due to the difference in environment and the less regular Pb_4-unit in the solid caused by the unequal sets of nearest neighbours of the lead atoms.

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