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THE CRYSTAL STRUCTURE OF A HEXANUCLEAR BASIC LEAD(II) PERCHLORATE HYDRATE: $Pb_6O(OH)_6(ClO_4)_4 \cdot H_2O$

Thomas G. Spiro, David H. Templeton, and Allan Zalkin

October 1968

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CONTRIBUTION FROM THE LAWRENCE RADIATION LABORATORY AND DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, BERKELEY, CALIFORNIA 94720, AND DEPARTMENT OF CHEMISTRY, PRINCETON UNIVERSITY, PRINCETON, NEW JERSEY 08540

The Crystal Structure of a Hexanuclear Basic Lead(II) Perchlorate Hydrate; $Pb_6O(OH)_6(ClO_4)_4 \cdot H_2O$[1a]

BY THOMAS G. SPIRO[1b], DAVID H. TEMPLETON[1c], AND ALLAN ZALKIN[1c]

The structure of $Pb_6O(OH)_6(ClO_4)_4 \cdot H_2O$ has been determined by single-crystal X-ray diffraction. The crystals are orthorhombic, space group Pbca, Z = 8, a = 10.814±0.005, b = 16.706±0.006 and c = 26.273±0.008 Å, d_x = 4.973 g/cm^3, d_m = 5.07±0.03 g/cm^3. The structure was refined to a conventional R factor of 5.5%, using 791 intensities which were collected by counter methods. The crystal contains discrete $Pb_6O(OH)_6^{4+}$ units. Four of the lead atoms are found in a central tetrahedron (distorted) while the remaining two cover two of the tetrahedral faces, thereby forming two exterior tetrahedra. The adjacent Pb-Pb distances average 3.81 Å and range from 3.44 to 4.09 Å. A unique oxygen atom (oxide) is found at the center of the central lead tetrahedron. The remaining six oxygen atoms, presumably hydroxide, are located over the six external faces of the two exterior lead tetrahedra. These results contradict an earlier conclusion from Raman evidence that the lead atoms are at the corners of an octahedron.

Introduction

Recently Maroni and Spiro[2a,b,c] investigated the vibrational spectra of a series of hydroxy- and alkoxy-bridged polyhedra of Bi(III), Pb(II), and Tl(I). The most significant result was the finding of a set of low frequency Raman bands attributable almost entirely to the motions of the metal atoms. The high intensity of these bands was taken as evidence for some degree of metal-metal bonding and the simplicity of their pattern suggested that they might be useful in structural characterization of polynuclear species.

Of particular interest in the latter connection were the species present in perchlorate solutions of lead(II) containing 1.33 moles of hydroxide per mole of lead. Potentiometric[3] and ultracentrifuge[4] data were consistent with an equilibrium between $Pb_3(OH)_4^{2+}$ and $Pb_6(OH)_8^{4+}$. Crystals of composition $Pb_3(OH)_4(ClO_4)_2$ were described in 1930 by Willard and Kassner.[5] The Raman spectrum[2b] of these crystals showed three strong low frequency bands similar to those exhibited[2a] by octahedral $Bi_6(OH)_{12}^{6+}$. Since in the concentrated solutions from which the crystals were obtained $Pb_6(OH)_8^{4+}$ was presumably predominant, it was inferred that these crystals also contained this complex, and its structure was predicted to be octahedral.[2b] The eight hydroxide ions were presumed to lie above the eight trigonal faces of the lead octahedron, giving a structure analogous to that of $Mo_6Cl_8^{4+}$.[6] A normal coordinate analysis[2b] showed that this structure was capable of predicting all of the observed Raman and infrared bands of the crystals.

We report here a determination of the structure of these crystals by X-ray diffraction. The results are consistent with the chemical analysis by Willard and Kassner,[5] but indicate that the crystals should be formulated as

$Pb_6O(OH)_6(ClO_4)_4 \cdot H_2O$ and that the Raman prediction of structure is incorrect. Discrete hexanuclear complexes are indeed found, but the lead atoms are arranged at the corners of three face-sharing tetrahedra rather than at the corners of an octahedron. As indicated in the formula, this complex contains six rather than eight hydroxide ions and also one oxide ion, the latter being located at the center of the central tetrahedron of lead atoms.

Experimental Section

Crystals of composition $Pb_3(OH)_4(ClO_4)_2$ were prepared by the method of Willard and Kassner.[5] Various crystals were examined in preliminary experiments by the Weissenberg (with CuKα radiation) and counter techniques (MoKα radiation, λ = 0.71069 A). Two sets of intensity data were used in the analysis. The first was obtained with a crystal of irregular shape. For the final measurements, a crystal was ground and etched with water to a sphere of diameter 0.13 mm and glued to a glass fiber. The c axis was aligned coincident with the ϕ axis of our instrument. The cell dimensions and diffraction intensities were measured at a temperature of ca. 23° using a manually-operated General Electric XRD-5 goniostat equipped with a scintillation counter and pulse-height discriminator. The Mo X-ray tube was operated at 45 kvp and 20 ma. Each reflection was measured for 10 sec with the stationary-crystal stationary-counter technique. The background was measured near each reflection. The maximum intensity was 8785 counts in 10 sec for the 002 reflection. The minimum background was 55 counts in 10 sec at 2θ = 35°. Some difficulty was encountered with overlapping reflections, and we made some adjustments as best

we could to correct for this effect. Defects in this adjustment may be one of the limiting sources of error in the data. Measurements were made for 1111 independent reflections, including all but a few within the limit $2\theta < 35°$. Of these, 320 were recorded as less than 30 counts above background and were discarded. The remaining 791 reflections were used in the final analysis.

The linear absorption coefficient of the material is estimated as 419 cm^{-1} (MoKα), and $\mu R = 2.83$. The intensities were corrected for absorption on the basis of the tabulation for spherical crystals in the "International Tables."[7] The variance of each intensity was estimated to be:

$$\sigma^2(I) = I + 2B + (pI)^2 + q$$

where I = net counts, B = background, p = fraction of I which is included to represent non-statistical errors (0.10 in this case), and q = a constant (30 in this case) which represents additional error in the background. Structure factors were derived from the intensities with the usual corrections for Lorentz and polarization effects. Standard deviations of structure factors were taken as:

$$\sigma(F_o) = F_o - (kI - k\sigma(I))^{1/2}, \quad kI = F_o^2 \quad .$$

No intensity was used which was less than its standard deviation, and therefore the term under the square root is always positive. In the final least-squares refinement, observations were weighted as $w = [\sigma(F)]^{-2}$.

Calculations were made with a CDC-6600 computer. The data were adjusted to an absolute scale and expressed as normalized structure magnitudes $|E|$ using an unpublished program written by H. S. Maddox and M. L. Maddox. We used our own unpublished programs for data processing, Fourier series, full-matrix least squares, and interatomic distances. The function minimized in the method of least squares is $\Sigma w(\Delta F)^2/\Sigma w|F_o|^2$, where ΔF is the difference between the magnitudes of the observed and calculated structure factors F_o and F_c.

Atomic scattering factors and anomalous dispersion corrections for Pb^{+2} and neutral Cl and O were taken from the compilations of Cromer and Waber.[8] The real and imaginary dispersion corrections are respectively -3.79 and 10.18 for Pb and 0.15 and 0.19 for Cl.

The isotropic temperature factor is defined as $\exp(-B\lambda^{-2}\sin^2\theta)$, where B is the thermal parameter. The anisotropic temperature factor is $\exp(-\frac{1}{4}\Sigma\Sigma B_{ij}b_ib_jh_ih_j)$, for all values of i and j from 1 to 3; b_i is the ith reciprocal axis length, h_i is a Miller index, and B_{ij} is a thermal parameter.

In this paper we designate the conventional R-factor as $R = \Sigma|\Delta F|/\Sigma|F_o|$ and the weighted R-factor as $R_2 = (\Sigma w(\Delta F)^2/\Sigma w(F_o)^2)^{1/2}$.

Results

Unit Cell and Space Group. The crystals are orthorhombic, and the systematic absences ($0k\ell$, $k = 2n + 1$; $h0\ell$, $\ell = 2n + 1$; and $hk0$, $h = 2n + 1$) indicate space group Pbca, with eight-fold general positions: $\pm(x, y, z; 1/2 + x, 1/2 - y, -z; -x, 1/2 + y, 1/2 - z; 1/2 - x, -y, 1/2 + z)$. The cell dimensions are $a = 10.814\pm0.005$, $b = 16.706\pm0.006$, and $c = 26.273\pm0.008$ Å ($t = 23°$).

For eight formula units $Pb_6O(OH)_6(ClO_4)_4 \cdot H_2O$ per cell the calculated density is 4.973 g/cm^3. The density measured with pycnometer and carbon tetrachloride at 24° is 5.07±0.03 g/cm^3. Part of the discrepancy may be the result of contamination of the pycnometer sample, for example with lead carbonate (d = 6.6 g/cm^3).

Phase Determination. The structure was solved with 286 reflections from the first data set by use of the symbolic addition procedure[9] to determine the phases. We used only the Σ_2 relation, $sE_h \sim s\sum_k E_k E_{h-k}$, where s means "sign of." Long's program[10] was used to apply this relation to the 286 reflections of highest $|E|$. Three reflections were given plus phases in order to fix the origin and four others were assigned symbols a, b, c, or d. These are listed in Table I. Of the 16 combinations of initial signs for these symbols, three converged in 9 or 11 cycles to indications that a = +, b = +, c = -, and d = -. One of these gave a consistency index[10] of 0.49, while the next highest index was 0.39. No other starting set required less than 8 cycles to converge.

An E map (Fourier synthesis) was computed using the signs from the most consistent set. It showed six pronounced peaks, which could readily be identified with the six lead atoms in the hexanuclear unit. The positions of the six lead atoms were refined with isotropic temperature factors by least squares using the original data set. Four cycles reduced R to 0.17. A Fourier synthesis of ΔF then revealed four prominent peaks, assignable to the chlorine atoms in the four perchlorate groups, and many lesser peaks, some of which were assigned to oxygen in the perchlorate ions or bound to the lead atoms. Subsequent least-squares refinement, with anisotropic temperature factors for the lead atoms,

TABLE I

STARTING REFLECTIONS FOR Σ_2 PROCEDURE

Sign	h, k, l
+	2, 8, 9
+	1, 5, 14
+	5,10, 8
a	4, 7, 3
b	1, 5, 4
c	1, 2, 7
d	1, 9, 11

eventually reduced R to 0.10. However, several oxygen atoms refused to refine properly, giving unreasonable interatomic distances or excessive thermal parameters.

At this point it was judged that the intensities had been taken without proper attention to background, overlap, and absorption corrections, and it seemed evident that this inadequacy would prevent further clarification of the oxygen positions. Accordingly the final set of intensities were measured. The new data were used to refine the previously determined lead and chlorine positions, with anisotropic thermal parameters for lead. Two cycles of least squares led to R = 0.11. A difference Fourier synthesis was calculated, and 23 of the highest peaks could be assigned to oxygen bound to chlorine or lead. All of these oxygen atoms now refined properly, and R was reduced to 0.062 and R_2 to 0.073.

According to the chemical analysis[5] a water molecule remained to be included in the structure, and the experimental density corresponded to three additional molecules. A search for cavities in the structure revealed only one hole large enough for a water molecule. In a Fourier synthesis of ΔF, the largest peak (of height 2.6 $e^-/\mathring{A}^3$) coincided with that hole. Introduction of an oxygen atom (designated O(8)) at this location decreased R to 0.060 and R_2 to 0.070. This atom had been recognized in earlier Fourier maps, but had been rejected because a computational blunder caused it to have an unreasonably large thermal parameter.

Up to this time the 791 reflections had been assigned equal weight. After a few errors in the data were corrected, refinement was continued with various weighting schemes until one was found which corresponded reasonably well to the distribution of magnitudes of discrepancies as a function of

observed intensity. After the final refinement, R was 0.055, R_2 was 0.069, and the estimated standard deviation of an observation of unit weight was 1.09. In the last cycle, no coordinate or thermal parameter shifted more than 9 percent of its estimated standard deviation. A final synthesis of ΔF showed a maximum value of 1.6 $e^-/Å^3$ and 28 other peaks higher than 1.0 $e^-/Å^3$. Under these circumstances, a search for hydrogen atoms seemed unjustified.

The final values of the parameters are given in Table II for lead atom and in Table III for chlorine and oxygen atoms. Table IV contains the observed and calculated structure factors. Interatomic distances are listed in Tables V, VI, and VII. Some angles in the $Pb_6O(OH)_6^{4+}$ cluster are listed in Table VIII.

Discussion

Apart from the perchlorate ions, the asymmetric unit contains 8 oxygen atoms of three distinct types. These atoms possess 8 hydrogen atoms according to the chemical stoichiometry. On the basis of the structure we assign these as an oxide ion, O(1), a water molecule, O(8), and six hydroxide ions.

The lead atoms occur in discrete clusters of six, with 7 oxygen atoms intimately bound to each cluster as shown in Fig. 1. We formulate this cluster as $Pb_6O(OH)_6^{4+}$. These lead atoms are arranged at the corners of three face-sharing tetrahedra, as seen in Fig. 2. The structure of this cluster is related to that[11] of $Pb_4(OH)_4^{4+}$, in which the lead atoms form a single tetrahedron, and to that[12] of Sn_2OSO_4, in which an isolated Sn_8 unit has four tin atoms at the corners of a central tetrahedron all four faces of which are covered by the remaining tin atoms.

TABLE II

POSITIONAL COORDINATES AND THERMAL PARAMETERS FOR LEAD ATOMS IN $Pb_6O(OH)_6(ClO_4)_4 \cdot H_2O$[a]

Atom	x	y	z	B_{11}[b]	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Pb(1)	.3391(4)	-.0421(3)	.2050(2)	5.2(3)	3.2(2)	4.4(2)	.3(2)	.2(2)	.8(2)
Pb(2)	.2347(4)	.1505(3)	.1530(2)	2.9(2)	3.4(2)	5.0(2)	0.0(2)	.1(2)	.3(2)
Pb(3)	.5672(4)	.1527(3)	.1990(2)	3.9(2)	5.4(3)	3.2(2)	.7(2)	-.2(2)	-.9(2)
Pb(4)	.5078(4)	.0543(3)	.0866(2)	3.3(2)	4.1(2)	4.0(2)	.4(2)	0.0(2)	-1.2(2)
Pb(5)	.4734(4)	.2794(3)	.0863(2)	3.4(2)	3.8(2)	4.3(2)	-.1(2)	-.2(2)	1.1(2)
Pb(6)	.7958(4)	.2123(3)	.0935(2)	3.6(2)	5.8(3)	4.2(2)	-.7(2)	.4(2)	-.5(2)

[a]Standard deviations are given in parentheses and refer to the least signigicant digit.

[b]Thermal parameter units are A^2.

TABLE III

FINAL COORDINATES AND THERMAL PARAMETERS FOR CHLORINE AND OXYGEN ATOMS IN $Pb_6O(OH)_6(Cl\!O_4)_4 \cdot H_2O$[a]

Atom	x	y	z	B
O(1)	.440(6)	.166(4)	.133(2)	6(2)
O(2)	.301(5)	.025(3)	.129(2)	3(1)
O(3)	.309(6)	.096(4)	.222(2)	6(2)
O(4)	.630(4)	.267(3)	.141(2)	2(1)
O(5)	.605(5)	.192(3)	.054(2)	4(1)
O(6)	.689(5)	.111(3)	.136(2)	4(1)
O(7)	.519(5)	.012(3)	.176(2)	4(1)
O(8)	.388(7)	.116(5)	.482(3)	9(2)
Cl(1)	.890(2)	.296(2)	.233(1)	5.0(7)
Cl(2)	.978(3)	-.002(2)	.162(1)	4.9(6)
Cl(3)	.241(3)	.099(2)	-.002(1)	5.5(6)
Cl(4)	.107(2)	.335(2)	.084(1)	4.5(6)
O(11)[b]	.820(6)	.359(4)	.208(2)	7(2)
O(12)	.884(5)	.222(3)	.207(2)	5(2)
O(13)	.833(7)	.275(4)	.276(3)	8(2)
O(14)	.028(7)	.315(4)	.235(3)	7(2)
O(21)	.853(7)	-.033(4)	.174(3)	7(2)
O(22)	.056(8)	-.065(5)	.136(3)	10(3)
O(23)	-.022(6)	.067(4)	.134(3)	7(2)
O(24)	.044(6)	.016(4)	.207(2)	6(2)
O(31)	.315(6)	.028(4)	-.013(2)	6(2)
O(32)	.135(7)	.074(4)	.026(3)	8(2)
O(33)	.197(6)	.138(4)	-.044(3)	7(2)
O(34)	.317(8)	.152(5)	.024(3)	9(2)

TABLE III(cont.)

Atom	x	y	z	B
O(41)	.141(7)	.398(5)	.045(3)	9(2)
O(42)	.090(6)	.258(4)	.064(2)	5(1)
O(43)	.000(5)	.365(3)	.109(2)	3(1)
O(44)	.194(7)	.335(4)	.120(3)	7(2)

[a]Standard deviations, estimated by least squares, are given in parentheses and refer to the least significant digits.

[b]O(ij) refers to the jth oxygen bound to the ith chlorine in the perchlorate groups.

TABLE IV

OBSERVED AND CALCULATED STRUCTURE FACTORS

FOR $Pb_6O(OH)_6(ClO_4)_4 \cdot H_2O$

OBSERVED AND CALCULATED STRUCTURE FACTORS OF PB(6)O(OH)6(CLO(4))4.H2O.
FCA(0,0,0) = 2645

```
  L FOR FCA
H,K=  0,  0
  2 236-203
  4 456-502
  6 373-355
  8 413-404
 10 635 732
 12 280 259
 14 404 383
 16 509-495
 18 491-478
 20 347 352
H,K=  0,  2
  0 241-231
  1 391-387
  2 209-192
  3 229-199
  4 256 271
  5 290 304
  6 403 436
  7 140-141
  8  54 -43
 11  74  66
 12 255-271
 15 183-198
 16 165 136
 18  98  95
 19 211 224
 22 142-135
H,K=  0,  4
  0  99 107
  1 278 275
  2 109 113
  3 395-401
  4 134-134
  5 300-320
  6 504-541
  7 439 465
  8 112-118
 10 287 272
 11 295 316
 12 227 244
 13 271-275
 15  86 -83
 16 150-156
 18  77 -55
 19 114-115
H,K=  0,  6
  0 197 224
  1 382 373
  2 385-400
  3 463-483
  5 114-123
  6 423 426
  7 303 328
 10  92-108
 11  76  99
 12 170-180
 13 327-318
 15  82 107
 20 166 168
H,K=  0,  8
  0 191-184
  1 205-214
  3 149-140
  5 167 166
  6 302 309
  7  75 -77
  8  69  68
 10 236-231
 11 219 224
 12 162 167
 18 125 121
H,K=  0, 10
  0 431-441
  2 232 252
  4 104  83
  5  80  88
  6 144-151
  8 240 235
  9 144-144
 10 117-101
 12 114 129
 14 206-214
 15 105 107
H,K=  0, 12
  0 252-268
  1 168 181
  6 275 292
  8 273-287
  9 140-147
 10  92-103
 11 270-283
 12  92-100
 14 308 300
 15  72 116
 16  82 -82
H,K=  1,  5
  1 200 202
  2 192 195
  4 587 596
  5 281-288
  6 401-402
  7 157-150
H,K=  1,  1
  8 122-123
 10 262-282
 11 220 219
 13 112 134
 14 478 480
 15  95 -88
 17 160-159
H,K=  1,  6
  1 336 331
  2 187-189
  3 254-251
  6 266 258
  7 217-213
  8 156-173
H,K=  1, 13
  1 109 101
  2 133-126
  8 136 150
H,K=  1,  8
  1 230-219
  3  65  72
  4 119-109
  5 357 357
  6 134 125
  7 224-227
  9 175 162
 10  72  56
 13 230-220
 14 117-114
 15 223 239
H,K=  1,  9
  1 421 421
  3 176-181
  4  69 -51
  5 170-175
  7 413-417
  9 117 120
 11 365 353
 17 316-315
H,K=  1, 10
  0 447-467
  1 351 358
  2 160 153
  3 384-374
  6 158 149
  7 224 230
  8 189 172
  9 197-188
 10 106-294
 11 178 163
 13 235-233
 16 142 129
 18 106 107
 21 147 145
H,K=  2,  4
  0 267 267
  1 403-431
  2 131 125
  3 560-579
  4 210-204
  5 114-106
  6  96 100
  7 299 310
  9 375 359
 10 271-275
 11 182 177
 12 298 303
 13 320-330
 14  71 105
 15 409-410
 16 156-152
  9 222 234
 11 203 212
 12 168-173
 13 280-278
 14  82  88
 15 118 109
 16  93-102
 18 162 167
H,K=  1,  3
  1 131-130
  2  57  26
  3 186-178
  5 395 399
  7  83  76
  8  78 -69
 11 209-201
 13 224-214
 15 167 164
 17 143 130
H,K=  1,  4
  1 142-140
  2 227 220
  3 247-230
  4  83 109
  5 323 315
  6 309-312
  9 140-147
 10  92-103
 11 270-283
 12  92-100
 14 308 300
 15  72 116
 16  82 -82
H,K=  1,  5
  1 200 202
  2 192 195
  4 587 596
  5 281-288
  6 401-402
  7 157-150
H,K=  1,  1
  8 122-123
 10 262-282
 11 220 219
 13 112 134
 14 478 480
 15  95 -88
 17 160-159
H,K=  1,  6
  1 336 331
  2 187-189
  3 254-251
  6 266 258
  7 217-213
  8 156-173
H,K=  1, 13
  1 109 101
  2 133-126
  8 136 150
H,K=  2,  0
  0 140 131
  2  93  74
  8 312-341
 10 317 320
 12 164 167
 16  73  64
 18 280-261
 20 138-142
H,K=  2,  1
  0  88 -70
  1 129 128
  2 142 138
  4  72 -58
  5  49  44
 12  96 109
H,K=  2,  3
  0 145-143
  2 162-162
  3 129 137
  4 288 279
  5 170 167
  6  92  96
  7 174-165
  9 189-170
 10 188 187
 11  70  71
 12 210-207
 13 136 131
 14 108-106
 16 152 166
H,K=  2,  7
  9  99  96
 10 261-269
 11 244-245
 12 171 172
 13 166-153
 14 264 260
 15 196 190
 16 227 212
 18 178-200
 19 121 117
 20 140-157
H,K=  3,  2
  1 306 333
  2 153 150
  3 295-324
  4 367 395
  5 286 294
  6 172-172
  8 243-235
  9  86 -86
 10 187-193
 11  73  84
 13  76  61
 15 114-107
 16 127 134
H,K=  3,  8
 19 130-124
H,K=  4,  4
  1 142-155
  2 192 202
  3 141-143
  5 207-210
  6 319-316
  7 115  96
  8 117-112
  9 398 386
 10 194 159
 11 126 125
 13 156 144
 19 130-124
H,K=  4,  4
  1 142-155
  2 192 202
  3 141-143
  5 207-210
  6 319-316
  7 115  96
  8 117-112
  9 398 386
 10 194 159
 11 126 125
 13 156 144
 19 130-124
H,K=  4,  9
  0 493 529
  2 273 286
  4 540-588
  6 224-217
  8 138 143
  9 348 354
 10 291-285
 11 279-274
 13 105  96
 14  73  77
 19 135 145
H,K=  4,  2
  0  69 -92
  1 302-311
  3 134-133
  5 165 149
  8  72  50
 10  99 -98
 11 172 169
 15 224-214
 19 111 111
H,K=  4,  3
  0 122 124
  3 124 140
  5 152 132
  9 231-243
 11 126 125
 13 156 144
 19 130-124
H,K=  4,  4
  4  82 -73
  7 198 201
 11 169 164
 13 189-179
H,K=  4, 10
  0  98 -96
  3 171 158
 12 119-134
H,K=  4, 11
  8 123-113
  9 226-218
H,K=  4, 12
  2 145-157
  4 105 116
  6 202 197
 10 143-148
 11 218 196
 13 100 116
 15 133-124
 16 118 109
H,K=  5,  6
  1 174 173
  3  78  78
  5 371-354
  6 143 137
  7 181 182
  8 180-166
  9 125-114
 11 105  91
 12 124 125
 13 254 252
 14 122-122
 15 160-186
H,K=  5,  7
  1  80 -54
  3 131-112
  4 152 140
  5 213 214
  6  89-108
  7  75  64
  8  75 -49
 9 146-130
 11 111 107
 14 118 108
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  2  89 -90
  3 167 158
  5 149 134
 13 182-185
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  4 241 235
  5 154 148
  6 122-117
  7 268 259
  8 117-109
 11 218 234
H,K=  5, 10
  5 147-151
 13 104-100
 14 156 145
 17 237 240
H,K=  5, 11
  4 173-193
H,K=  6,  0
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  2 115 128
  6 120-120
  7 336 329
  8 100 -78
  1 235 239
  5 150-144
  7 193 197
 10 118-115
H,K=  7,  0
  2  88  88
  6 190-165
  8 224 204
H,K=  7,  1
  1 161-165
  2 222 210
  9  88  78
 11 105  91
 12 124 125
 13 254 252
 14 122-122
 15 160-186
H,K=  5,  7
  1  80 -54
  3 131-112
  4 152 140
  5 213 214
  6  89-108
  7  75  64
  8  75 -49
 9 146-130
 11 111 107
 14 118 108
H,K=  5,  8
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  3 167 158
  5 149 134
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H,K=  5,  9
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  4 241 235
  5 154 148
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H,K=  5, 10
  5 147-151
 13 104-100
 14 156 145
 17 237 240
H,K=  5, 11
  4 173-193
H,K=  6,  0
  0 201 197
  2 115 128
  6 120-120
  7 336 329
  8 100 -78
  1 235 239
  5 150-144
  7 193 197
 10 118-115
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  6 190-165
  8 224 204
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  2 222 210
 12 222 202
H,K=  6,  2
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  1 283 283
  2 175-165
  3 185-179
  5 185-170
H,K=  7,  2
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  7 218 227
  8 160-148
 10  97  93
 11  98  89
 13 159-158
H,K=  6,  3
  0 320-318
  1  96  98
  2 154-150
  4 239 229
  6 233 220
  7 144 130
  8  74  66
 10 173-166
 12 174-210
 16 142 146
H,K=  6,  4
  0 414 422
  1 152-153
  2 114-125
  3 241-254
  6  81  86
  7 245-251
  9  75  84
 10 117 118
 11 134 141
 13 102-108
 14 110 117
 15 112-125
H,K=  6,  5
  0 328 326
  2  87 -75
  4 117-103
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  0 291-292
  2  74  84
  3 163-160
  4 134 119
  5  83  69
 7 109 133
 10 156-163
H,K=  6,  7
  1 149-129
  6 391-402
  8 100 -78
  1 235 239
  5 150-144
  7 193 197
 10 118-115
H,K=  7,  0
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  6 190-165
  8 224 204
H,K=  7,  1
  1 161-165
  2 222 210
  4 286 265
  6 250-229
  7 110  94
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 13 117-128
 14 263 297
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  3 209-195
  4 175 164
 13  97 104
H,K=  7,  3
  2  96 -91
  5 166-169
  6  92 -70
  7 282 268
  9  78-104
 13 130 139
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  2 191-192
  3  76  54
  5 147 125
H,K=  7,  5
  2 160 159
  4 173 180
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 10 145-143
 12 162 156
H,K=  7,  6
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  2 140 142
  7 245-251
  9 140 133
H,K=  7,  7
  1  79 103
  7 221-225
  9 125 119
H,K=  7,  8
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  4 118-134
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H,K=  8,  0
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H,K=  8,  1
  7 109 133
H,K=  8,  2
  1 113 141
  2 140 142
  7 245-251
  9 140 133
H,K=  7,  7
  1  79 103
  7 221-225
  9 125 119
H,K=  7,  8
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  4 118-134
  5 178 198
H,K=  8,  0
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H,K=  8,  1
  7 109 133
H,K=  8,  2
  1 113 141
  2 140 142
  7 245-251
  9 140 133
H,K=  8,  3
  5  88 115
  8 104 112
  9 156-172
H,K=  8,  4
  5  80-121
  7  97 111
H,K=  8,  5
  0 225-240
  3 168-188
  7 136 125
```

TABLE V

INTERATOMIC DISTANCES(Å) IN $Pb_6O(OH)_6^{4+}$

Pb(3)-Pb(4)	3.440(5)[a]	O(2)-Pb(2)	2.30(5)
Pb(5)-Pb(6)	3.667(6)	O(2)-Pb(1)	2.32(5)
Pb(1)-Pb(2)	3.674(6)	O(2)-Pb(4)	2.55(5)
Pb(4)-Pb(5)	3.778(5)	O(3)-Pb(2)	2.18(6)
Pb(3)-Pb(5)	3.779(6)	O(3)-Pb(1)	2.36(6)
Pb(2)-Pb(4)	3.786(5)	O(3)-Pb(3)	3.02(6)
Pb(2)-Pb(5)	3.790(5)	O(4)-Pb(5)	2.23(4)
Pb(2)-Pb(3)	3.795(5)	O(4)-Pb(6)	2.37(4)
Pb(3)-Pb(6)	3.846(5)	O(4)-Pb(3)	2.53(4)
Pb(1)-Pb(4)	3.949(6)	O(5)-Pb(5)	2.21(5)
Pb(1)-Pb(3)	4.086(6)	O(5)-Pb(6)	2.34(5)
Pb(4)-Pb(6)	4.086(6)	O(5)-Pb(4)	2.67(5)
		O(6)-Pb(3)	2.24(5)
O(1)-Pb(3)	2.22(6)	O(6)-Pb(6)	2.33(5)
O(1)-Pb(2)	2.29(6)	O(6)-Pb(4)	2.53(6)
O(1)-Pb(5)	2.29(6)	O(7)-Pb(1)	2.27(5)
O(1)-Pb(4)	2.35(6)	O(7)-Pb(4)	2.47(5)
		O(7)-Pb(3)	2.49(5)

[a]Standard deviations in parentheses refer to the least significant digit.

TABLE VI

CHLORINE OXYGEN DISTANCES(Å) IN PRECHLORATE GROUPS

Cℓ(1)-O(11)	1.45(6)[a]	Cℓ(3)-O(31)	1.46(6)
Cℓ(1)-O(12)	1.42(6)	Cℓ(3)-O(32)	1.43(7)
Cℓ(1)-O(13)	1.33(7)	Cℓ(3)-O(33)	1.36(6)
Cℓ(1)-O(14)	1.53(7)	Cℓ(3)-O(34)	1.40(8)
Cℓ(2)-O(21)	1.48(7)	Cℓ(4)-O(41)	1.51(8)
Cℓ(2)-O(22)	1.52(8)	Cℓ(4)-O(42)	1.41(5)
Cℓ(2)-O(23)	1.37(6)	Cℓ(4)-O(43)	1.41(5)
Cℓ(2)-O(24)	1.43(6)	Cℓ(4)-O(44)	1.33(7)

[a]Standard deviations in parentheses refer to the least significant digits.

TABLE VII

DISTANCES(Å) INVOLVING THE WATER MOLECULE

Atoms	Distance
O(8)-Pb(6)	2.74(7)
O(8)-O(32)	2.77(9)
O(8)-O(41)	3.15(10)
O(8)-O(31)	3.25(9)
O(8)-O(23)	3.29(10)

TABLE VIII

SOME ANGLES (IN DEGREES) IN THE $Pb_6O(OH)_6^{4+}$ CLUSTER[a]

Pb(2)-Pb(1)-Pb(3)	58.3	Pb(1)-Pb(4)-Pb(5)	111.3	Pb(3)- O(1)-Pb(5)	114
Pb(2)-Pb(1)-Pb(4)	59.4	Pb(1)-Pb(4)-Pb(6)	125.5	Pb(4)- O(1)-Pb(5)	109
Pb(3)-Pb(1)-Pb(4)	50.7	Pb(2)-Pb(4)-Pb(3)	63.1	Pb(1)- O(2)-Pb(2)	105
Pb(1)-Pb(2)-Pb(3)	66.3	Pb(2)-Pb(4)-Pb(5)	60.2	Pb(1)- O(2)-Pb(4)	108
Pb(1)-Pb(2)-Pb(4)	63.9	Pb(2)-Pb(4)-Pb(6)	107.5	Pb(2)- O(2)-Pb(4)	103
Pb(1)-Pb(2)-Pb(5)	117.4	Pb(3)-Pb(4)-Pb(5)	62.9	Pb(1)- O(3)-Pb(2)	108
Pb(3)-Pb(2)-Pb(4)	54.0	Pb(3)-Pb(4)-Pb(6)	60.7	Pb(1)- O(3)-Pb(3)	98
Pb(3)-Pb(2)-Pb(5)	59.8	Pb(5)-Pb(4)-Pb(6)	55.4	Pb(2)- O(3)-Pb(3)	92
Pb(4)-Pb(2)-Pb(5)	59.8	Pb(2)-Pb(5)-Pb(3)	60.2	Pb(3)- O(4)-Pb(5)	105
Pb(1)-Pb(3)-Pb(2)	55.4	Pb(2)-Pb(5)-Pb(4)	60.0	Pb(3)- O(4)-Pb(6)	103
Pb(1)-Pb(3)-Pb(4)	62.6	Pb(2)-Pb(5)-Pb(6)	116.8	Pb(5)- O(4)-Pb(6)	106
Pb(1)-Pb(3)-Pb(5)	108.3	Pb(3)-Pb(5)-Pb(4)	54.2	Pb(4)- O(5)-Pb(5)	101
Pb(1)-Pb(3)-Pb(6)	128.5	Pb(3)-Pb(5)-Pb(6)	62.2	Pb(4)- O(5)-Pb(6)	109
Pb(2)-Pb(3)-Pb(4)	62.9	Pb(4)-Pb(5)-Pb(6)	66.6	Pb(5)- O(5)-Pb(6)	107
Pb(2)-Pb(3)-Pb(5)	60.1	Pb(3)-Pb(6)-Pb(4)	51.3	Pb(3)- O(6)-Pb(4)	92
Pb(2)-Pb(3)-Pb(6)	112.4	Pb(3)-Pb(6)-Pb(5)	60.3	Pb(3)- O(6)-Pb(6)	115
Pb(4)-Pb(3)-Pb(5)	62.9	Pb(4)-Pb(6)-Pb(5)	58.0	Pb(4)- O(6)-Pb(6)	115
Pb(4)-Pb(3)-Pb(6)	68.0	Pb(2)- O(1)-Pb(3)	115	Pb(1)- O(7)-Pb(3)	118
Pb(5)-Pb(3)-Pb(6)	57.5	Pb(2)- O(1)-Pb(4)	109	Pb(1)- O(7)-Pb(4)	113
Pb(1)-Pb(4)-Pb(2)	56.7	Pb(2)- O(1)-Pb(5)	112	Pb(3)- O(7)-Pb(4)	88
Pb(1)-Pb(4)-Pb(3)	66.7	Pb(3)- O(1)-Pb(4)	98		

[a]The estimated standard deviations of the Pb-Pb-Pb and the Pb-O-Pb angles are ±0.1 and ±2 degrees respectivelly.

The oxide ion is near the center of the central tetrahedron, at an average distance 2.29 Å from its lead neighbors. The oxygen atoms in tetragonal PbO have similar tetrahedral coordination, with lead neighbors at 2.30 Å.[13] Thus the central tetrahedron of the cluster can be considered as a fragment of the PbO structure. Oxygen with four metal neighbors in isolated complexes is relatively rare, but some examples are $Be_4O(CH_3COO)_6$ and $Zn_4O(CH_3COO)_6$,[14] $Mg_4OBr_6 \cdot 4C_4H_{10}O$,[15] and $Cu_4OCl_6((C_6H_5)_3PO)_4$.[16]

Each of the six hydroxide ions is adjacent to three lead atoms on an external face of a non-central tetrahedron, and all such faces are covered in this way. This topology gives the three lead atoms in each face of every tetrahedron one, and only one, oxygen neighbor in common. The oxide ion fills this role for four faces, while each hydroxide ion is involved with only one face.

The water molecule is only loosely bonded to this complex, at a distance 2.74 Å from Pb(6) on one corner. It is remote from any other lead atoms. Its nearest oxygen neighbor is O(32) at 2.77±0.09 Å and in a direction 116° from Pb(6); this distance and direction suggest hydrogen bonding. Other oxygen neighbors are at distances of 3.15 Å or more.

There is considerable variation in the Pb-Pb distances. The shortest one, 3.44 Å, is unique in that it is the only edge shared by all three tetrahedra. It may be compared with the distance 3.50 Å found in metallic lead. The other Pb-Pb neighbor distances in the cluster range from 3.67 to 4.09 Å, compared with 3.83 Å found in the $Pb_4(OH)_4^{4+}$ complex.[11] The cluster conforms only approximately to the symmetry mm2 (C_{2v}) which is permitted by its topology, but the lead positions are very close to symmetry 2 (C_2). The hydroxide ions are expected to have their protons directed outward from the

cluster, and they will tend to form hydrogen bonds to the surrounding perchlorate ions. Evidently such bonding or some other packing force prevents exact symmetry for the cluster. Each hydroxide ion has one or two perchlorate-oxygen neighbors at distances between 2.94 and 3.15 Å to which it could form weak hydrogen bonds. We cannot make any unique assignment of hydrogen bonds on the basis of our results. The low accuracy of oxygen-oxygen distances (ca. 0.08 Å) tends to obscure the distinction between bonds and non-bonds, and the bonds may involve disorder or bifurcation.

The perchlorate ions are not significantly coordinated, the closest distance from a lead to a perchlorate oxygen being 2.9 Å. This is in accord with the Raman and infrared spectra,[17] which show bands characteristic of unbound ClO_4^-. The observed distortions of perchlorate geometry are within the rather large standard deviations of the oxygen positions (see Table VI).

On the basis of its Raman spectrum the hexanuclear unit was predicted to have octahedral geometry.[2b] The main evidence was the occurrence of three Raman bands in the metal-metal stretching region, analogous to those found for the known octahedral species $Bi_6(OH)_{12}^{6+}$. The actual geometry revealed here (idealized point symmetry C_{2v}, lowered by the deviations in the Pb-O distances, and in the Pb-Pb distances around the base of the complex) requires twelve Raman active vibrational modes in the metal-metal region. Evidently there is a good deal of accidental degeneracy in these frequencies. Preliminary calculations[18] show that this is a plausible consequence of the observed geometry.

An interesting question is whether the rather unusual structure found here for the hexameric complex is intrinsically more stable than others which

can be envisaged, or whether it is stabilized by crystal forces. Preliminary results of solution X-ray scattering studies by Johannson[19] point to the former conclusion. The Pb-Pb peak in the radial distribution function, which occurs at 3.83 Å in solutions containing tetrahedral $Pb_4(OH)_4^{4+}$, simply broadens without change in height as the OH/Pb ratio is increased toward 1.33. Weak next nearest neighbor peaks are found at 6.40 and 7.05 Å. (Non-adjacent Pb-Pb distances in $Pb_6O(OH)_6^{4+}$, occur at 6.36 and 7.14 Å.) These observations rule out an octahedral complex in solution, and are entirely consistent with the structure reported here.

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Footnotes and References

(1) a) Work done under auspices of the Atomic Energy Commission. Supported in part by a Public Health Service Research Grant, GM13498, to T.G.S.
b) Princeton University. c) University of California.

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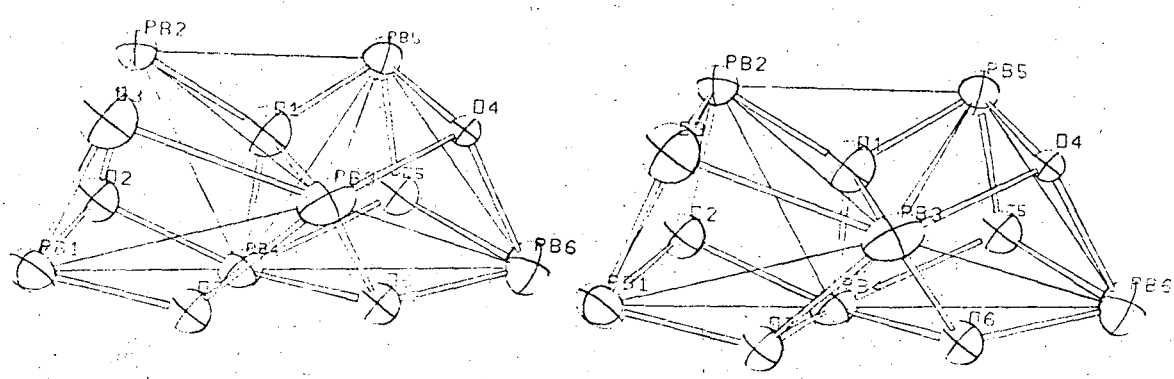
Figure Captions

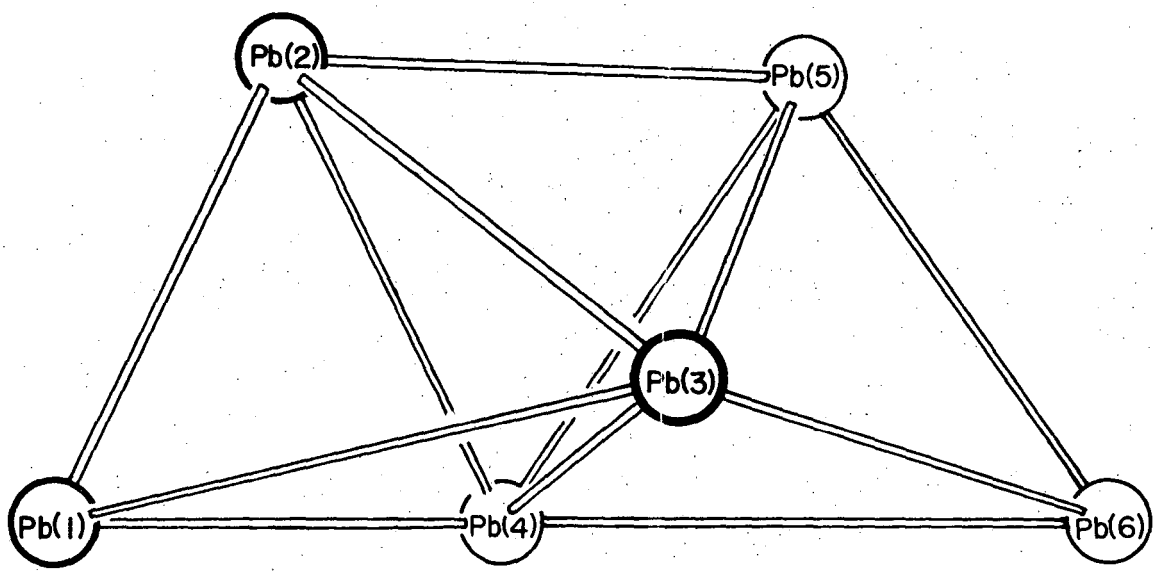
Fig. 1. Stereoscopic view of the $Pb_6O(H)_6^{4+}$ complex. The stick bonds connect oxygen and lead atoms; the lines define the lead polyhedra. Interatomic distances are given in Table V and angles in Table VIII.

Fig. 2. The three face-sharing tetrahedra of Pb atoms in the $Pb_6O(OH)_6^{4+}$ cluster.



XBL 681-13

Fig. 1



XBL 6810-6059

Fig. 2

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