and AB_2Te_4. The observation that $NiCr_2S_4$ and $NiCr_2Se_4$ are semiconductors, not metals,[13] is another indication that metal–metal bonding is not a prerequisite for the formation of an NiAs-type phase. In addition, the *relatively* small c/a and c/b values found in certain AB_2Se_4 compounds suggest that the occurrence of metallic conductivity may best be treated as a phenomenological observation rather than a structural determinant.

Acknowledgments.—The assistance of J. L. Gillson, who measured the resistivity, and J. F. Weiher, who measured the magnetic susceptibility, is gratefully acknowledged. Thanks are given to C. T. Prewitt, who provided the computer program and considerable assistance in its use. A. W. Sleight is thanked for his help in this respect. Discussions with D. B. Rogers are also appreciated.

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[13] R. J. Bouchard and A. Wold, *J. Phys. Chem. Solids*, **27**, 591 (1966).

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

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Received April 26, 1968

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, $Z = 8$, $a = 10.814 \pm 0.005$ Å, $b = 16.706 \pm 0.006$ Å, $c = 26.273 \pm 0.008$ Å, $d_x = 4.973$ g/cm^3, $d_m = 5.07 \pm 0.03$ 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[2] 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 mol 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

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

[2] V. A. Maroni and T. G. Spiro, *Inorg. Chem.*: (a) **7**, 183 (1968); (b) **7**, 188 (1968); (c) **7**, 193 (1968).

[3] A. Olin, *Acta Chem. Scand.*, **14**, 126, 814, 1999 (1960); *Svensk Kem. Tidskr.*, **73**, 482 (1961).

[4] O. E. Esval and J. S. Johnson, *J. Phys. Chem.*, **69**, 959 (1965).

[5] H. H. Willard and J. L. Kassner, *J. Am. Chem. Soc.*, **52**, 2395 (1930).

[6] C. Brosset, *Arkiv Kemi*, **1**, 353 (1949); *Arkiv Kemi, Mineral. Geol.*, **A20**, No. 7 (1945).

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 Cu Kα radiation) and counter techniques (Mo Kα radiation, λ 0.71069 Å). 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 kV 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 $2\theta = 35°$. Some difficulty was encountered with overlapping reflections, and we made some adjustments as best as 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} (Mo Kα), 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 is the net counts, B is the background, p is the fraction of I which is included to represent nonstatistical errors (0.10 in this case), and q is 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

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

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 $\exp(-{}^1/_4\Sigma\Sigma B_{ij}b_ib_jh_ih_j)$, 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 ($0kl$, $k = 2n + 1$; $h0l$, $l = 2n + 1$; and $hk0$, $h = 2n + 1$) indicate space group Pbca, with eightfold 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 $a = 10.814 \pm 0.005$, $b = 16.706 \pm 0.006$, and $c = 26.273 \pm 0.008$ Å (23°). For eight formula units of $Pb_6O(OH)_6(ClO_4)_4 \cdot H_2O$ 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, $sE_h \approx s\Sigma_k E_k E_{h-k}$, 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.

TABLE I

STARTING REFLECTIONS FOR Σ_2 PROCEDURE

Sign	*hkl*	Sign	*hkl*
+	289	a	473
+	1,5,14	b	154
+	5,10,8	c	127
		d	1,9,11

An E map (Fourier synthesis) was computed using the signs from the most consistent set. It showed six

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(7) W. L. Bond in "International Tables for X-Ray Crystallography," Vol. II, J. S. Kasper and K. Lonsdale, Ed., The Kynoch Press, Birmingham, England, 1959, p 302.

(8) D. T. Cromer and J. T. Waber, *Acta Cryst.*, **18**, 104 (1965); D. T. Cromer, *ibid.*, **18**, 17 (1965).

(9) I. L. Karle and J. Karle, *ibid.*, **16**, 969 (1963).

(10) R. E. Long, Thesis, University of California at Los Angeles, 1965.

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)	0.3391 (4)	−0.0421 (3)	0.2050 (2)	5.2 (3)	3.2 (2)	4.4 (2)	0.3 (2)	0.2 (2)	0.8 (2)
Pb(2)	0.2347 (4)	0.1505 (3)	0.1530 (2)	2.9 (2)	3.4 (2)	5.0 (2)	0.0 (2)	0.1 (2)	0.3 (2)
Pb(3)	0.5672 (4)	0.1527 (3)	0.1990 (2)	3.9 (2)	5.4 (3)	3.2 (2)	0.7 (2)	−0.2 (2)	−0.9 (2)
Pb(4)	0.5078 (4)	0.0543 (3)	0.0866 (2)	3.3 (2)	4.1 (2)	4.0 (2)	0.4 (2)	0.0 (2)	−1.2 (2)
Pb(5)	0.4734 (4)	0.2794 (3)	0.0863 (2)	3.4 (2)	3.8 (2)	4.3 (2)	−0.1 (2)	−0.2 (2)	1.1 (2)
Pb(6)	0.7958 (4)	0.2123 (3)	0.0935 (2)	3.6 (2)	5.8 (3)	4.2 (2)	−0.7 (2)	0.4 (2)	−0.5 (2)

[a] Standard deviations are given in parentheses and refer to the least significant digit. [b] Thermal parameter units are Å².

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, 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⁻/Å³) 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% of its estimated standard deviation. A final synthesis of ΔF showed a maximum value of 1.6 e⁻/Å³ and 28 other peaks higher than 1.0 e⁻/Å³. 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–VII. Some angles in the $Pb_6O(OH)_6^{4+}$ cluster are listed in Table VIII.

TABLE III

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

Atom	x	y	z	B, Å²
O(1)	0.440 (6)	0.166 (4)	0.133 (2)	6 (2)
O(2)	0.301 (5)	0.025 (3)	0.129 (2)	3 (1)
O(3)	0.309 (6)	0.096 (4)	0.222 (2)	6 (2)
O(4)	0.630 (4)	0.267 (3)	0.141 (2)	2 (1)
O(5)	0.605 (5)	0.192 (3)	0.054 (2)	4 (1)
O(6)	0.689 (5)	0.111 (3)	0.136 (2)	4 (1)
O(7)	0.519 (5)	0.012 (3)	0.176 (2)	4 (1)
O(8)	0.388 (7)	0.116 (5)	0.482 (3)	9 (2)
Cl(1)	0.890 (2)	0.296 (2)	0.233 (1)	5.0 (7)
Cl(2)	0.978 (3)	−0.002 (2)	0.162 (1)	4.9 (6)
Cl(3)	0.241 (3)	0.099 (2)	−0.002 (1)	5.5 (6)
Cl(4)	0.107 (2)	0.335 (2)	0.084 (1)	4.5 (6)
O(11)[b]	0.820 (6)	0.359 (4)	0.208 (2)	7 (2)
O(12)	0.884 (5)	0.222 (3)	0.207 (2)	5 (2)
O(13)	0.833 (7)	0.275 (4)	0.276 (3)	8 (2)
O(14)	0.028 (7)	0.315 (4)	0.235 (3)	7 (2)
O(21)	0.853 (7)	−0.033 (4)	0.174 (3)	7 (2)
O(22)	0.056 (8)	−0.065 (5)	0.136 (3)	10 (3)
O(23)	−0.022 (6)	0.067 (4)	0.134 (3)	7 (2)
O(24)	0.044 (6)	0.016 (4)	0.207 (2)	6 (2)
O(31)	0.315 (6)	0.028 (4)	−0.013 (2)	6 (2)
O(32)	0.135 (7)	0.074 (4)	0.026 (3)	8 (2)
O(33)	0.197 (6)	0.138 (4)	−0.044 (3)	7 (2)
O(34)	0.317 (8)	0.152 (5)	0.024 (3)	9 (2)
O(41)	0.141 (7)	0.398 (5)	0.045 (3)	9 (2)
O(42)	0.090 (6)	0.258 (4)	0.064 (2)	5 (1)
O(43)	0.000 (5)	0.365 (3)	0.109 (2)	3 (1)
O(44)	0.194 (7)	0.335 (4)	0.120 (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 $Pb_6O(OH)_6(ClO_4)_4 \cdot H_2O$ [FCA(0, 0, 0) = 2645]

```
    L FOB 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
   15 113-122
   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
   10 273-287
H,K=  0, 14
    0 202 212
    3 246 258
H,K=  1,  0
    2 105-129
    4 336 371
    6  65 -38
    8 257-288
   10 109-103
   12 304 311
   14  68  47
   16 129-121
   18 104  82
   20 151-161
H,K=  1,  1
    1 244-255
    2 315 308
    3 189 175
    4  60  65
    6 118  85
    7 449 471
    8 242-220
    9 178-184
   10 204-225
   11 191-194
   12 129 114
   13  73  60
   15 157-141
   16 249 247
   17 216 210
   20 142-152
H,K=  1,  2
    2 268-232
    4  87  68
    5 122-108
    6 213-197
    7 481-502
    8 396 410

    9 222 234
   11 203 212
   12 168-173
   13 280-278
   14  82  88
   15 118 104
   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
    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
    2 182-189
    3 254-251
    6 266 258
    7 217-213
    8 156-173
    9 118 111
   11 154 146
   12 131 139
   13  93  87
   14 164-165
   17 248-254
   19 150 148
H,K=  1,  7
    1 175-166
    2  61  68

    3 126 133
    4 117 109
    6  78 -56
    7 144 140
    9 131-130
   10 101 -99
   11 148-140
   12  87  90
   13 113 114
   15  76 -79
   17 109 127
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
    1  79  86
    2 305 293
    4  93 -97
    7 123-126
    9  75  81
   14 123 116
H,K=  1, 11
    2  82 -79
    3  90 -96
    4  90  86
    5 140 142
    6 132-132
    7  76 -71
H,K=  1, 12
    2  77 -71
    4 158-165
    6 168 165
    7 173 168
    9  96-125
   11 125-123
H,K=  1, 13
    1 109 101
    2 133-126
    8 136 150
H,K=  2,  0
    0 140 131
    2  93  74
    6 459-517
    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
    6 264-275
    8 204 206
   11 105 103
   12 219 227
   14 101 -92
   16 148-151
   20  88 -90
H,K=  2,  2
    0 134 128
    2  91  90
    3 210 213
    4 312-318
    5 254-256
    6  59 -44
    7 127-117
    9 316 322
   11 313-309
   12 236 221
   13 149 141
   14 107 -95
   15 129 121
   16 206-190
   17 196-190
H,K=  2,  3
    0 447-467
    1 351 358
    2 160 153
    3 384-374
    6 158 149
    7 224 230
    8 189 172
    9 197-188
   10 306-294
   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

   17  76  87
   19 217 225
H,K=  2,  5
    0  85  97
    1  77  70
    3  95  93
    4 130-133
    9  78 -69
   12  96 109
H,K=  2,  6
    0 145-143
    2 162-162
    3 129 137
    4 288 279
    5 170 167
    6  92  96
    7 174-165
    9 189-170
   10 185 187
   11  70  71
   12 210-207
   13 136 131
   14 108-106
   16 152 166
H,K=  2,  7
    0 289-282
    2 225 222
    3 119 111
    4 108 -91
    5 104  95
    7 108 -96
    8 218 217
    9 175 167
   10 242-229
   11 168-166
   12 117 113
   13  96  86
   14  91 -88
H,K=  2,  8
    1 260-264
    3 218-208
    5 318-302
    6  83 101
    7 235 224
    9 564 563
   11 246-242
   12 125-132
   13 151-140
   15 102-106
H,K=  2,  9
    0 301-296
    2 207 206
    8 112 108
   10 168-160
H,K=  2, 10
    1 111 109
    3 331 318
    6 297 292
    7 179-180
    9 215-190
   13 139 136
H,K=  2, 11
    0 205 204
    3  83  79

   10 102 102
H,K=  2, 12
    2 100-101
    3  86-101
    5 102 105
H,K=  2, 13
    1 171-173
    3 104  97
H,K=  3,  0
    2 141 126
    4 565-663
    6 142 153
    8 340 348
   10  82  86
   12 144-145
   14 179-181
   20 117 104
H,K=  3,  1
    1 145-122
    2 504 569
    3 147-147
    4 219 236
    5 354 395
    8 424-464
    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
   12 114 102
   14 210 211
   15 160 159
   17 215-200
   19 109 102
   20 104-108
H,K=  3,  3
    3 275-274
    4 220-234
    5 315 331
    6 247 246
    9  88  85
   11 125-124
   13 144-133
   14 121-134
   15 123 118
   16 110 129
   19 179 188
H,K=  3,  4

    1  63 -52
    2 362-365
    3 191 191
    4 120 126
    5 181-179
    6  79 -68
    8 107  97
    9 165 172
   10 112 108
   14  73 -59
   15 103 -94
   16 182-175
   18 169 183
H,K=  3,  5
    1  92  85
    2 344 333
    4 281 279
    6 155 154
    7  84 -83
    8 460-457
   10 170-166
   12 174 160
   13 100  80
   14 178 175
   16 169 182
   18 110-125
H,K=  3,  6
    1 113-116
    2 307 301
    3 155 158
    4 232-215
    5 104-115
    6  73  68
    7  67 -59
    8  82  83
   16 108 105
   18 118-111
H,K=  3,  7
    2 252 251
    3  86  99
    4 132-127
    5 185-171
    6 114 110
    8 222-222
   11  73  84
   13  76  61
   15 114-107
   16 127 134
H,K=  3,  8
    1 179 161
    2  76  76
    3 356-337
    4 101 -90
    5 117 114
H,K=  3,  9
    1 167 168
    4 233-213
    5 282-257
    6 175 160
    9  98 -85
   11 129 140
   13 193 205
H,K=  3, 10
    2 279-265

    4 139 139
H,K=  3, 11
    5 153-156
H,K=  3, 12
    3 185 195
H,K=  3, 13
    2 235-229
    4 112-112
H,K=  4,  0
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    2 273 286
    4 540-588
    6 224-217
   12 554 567
   14  73  57
   16 320-310
   18 115-135
H,K=  4,  1
    0 152-160
    1 317-336
    2  75  77
    3  70  90
    5 123-127
    6 103 110
    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  89 -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
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    3 124 140
    5 152 132
    9 231-243
   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
   10 211 202
   11 119-115
   12 163 152
   14 121-107
   15  99 -84
   19 113 101

H,K=  4,  5
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    1 205-195
    2 278-279
    3 222-232
    4 220 213
    5  66 -45
    7 178 168
    8 268-273
    9 245 224
   10 345 320
   12 251-232
   13 130-123
   14 105  85
   15  78 -92
   18 130-138
H,K=  4,  6
    1 131-133
    2 156-167
    5 127-128
    6 312 316
    7  96  97
    8  97  85
    9 214 198
   10 286-259
   11 166-168
   12  75 -83
H,K=  4,  7
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    2 128-130
    3 351 355
    7 262-239
    9  74 -87
   11 154-159
   12  99 -98
   13 216 214
   15 191 196
H,K=  4,  8
    1 262-267
    2 145-133
    3 146-143
    5  80  76
    6 178 186
    9 121 113
   10  84 -73
   12  86-100
   15 219-222
H,K=  4,  9
    3 292-271
    4  82 -73
    7 198 201
   11 169 164
   13 189-179
H,K=  4, 10
    0  98 -96
    3 171 158
    4 172 155
   10 154 159
   12 119-134
H,K=  4, 11
    1 163 180
    8 123-113
    9 226-218
H,K=  4, 12

    2 145-157
    4 109 116
    6 202 197
H,K=  5,  0
    4 215-231
    6 417 429
    8 278-285
   10  92  89
   12 256 250
   14 338-315
   16 101 117
H,K=  5,  1
    2 122-122
    4 190 196
    5  90  87
    7 130 125
    9 107-104
   11  87 -80
   12 107 -91
   14  76  83
   18 112 139
H,K=  5,  2
    2 260 277
    7 282-280
    8 129-121
    9 113 107
   11 167 152
   13 149-150
   14 111 102
   16  95 119
   18  90-105
H,K=  5,  3
    1 377-383
    2 130 124
    3 203 196
    4 241 235
    5 154 148
    6 122-117
    7 268 259
    8 117-109
   10  93 -77
   11 251-234
   12  96  86
   13 104-100
   14 156 145
   17 237 240
H,K=  5,  4
    3  74  59
    4 130-136
    5 193-187
    6 120-120
    7 336 329
    8 200 198
    9 188-180
   11 129-118
   12 153-142
   13 147 143
   15 151-146
H,K=  5,  5
    1 264 269
    2 282 280
    5 260-254
    7 201-209
    8 116-108

    9  88  78
   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
   14 118 108
H,K=  5,  8
    1 170-162
    2  89 -90
    3 167 158
    5 149 134
   13 182-185
H,K=  5,  9
    1 238 232
    4 184 161
    5 275-285
    7 221-235
   11 218 234
H,K=  5, 10
    5 147-151
    6 205-220
    8 287 284
H,K=  5, 11
    4 173-193
H,K=  6,  0
    0 201 197
    2 115 128
    6 391-402
    8 100 -78
   10 287 280
   12 111  98
   16 130-133
H,K=  6,  1
    0 161 163
    1 154-149
    2 270 260
    4 202-204
    6 368-363
    7  72 -64
    9 118 113
   10 213 194

   12 222 202
H,K=  6,  2
    0 332 330
    1 283 283
    2 175-165
    3 185-179
    5 185-170
    6  79  61
    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
    5 153-136
    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
    8 114-112
    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
H,K=  6,  6
    0 291-292
    2  74  84
    3 163-160
    4 134 119
    5  83  69
    8 129 119
H,K=  6,  7
    1 149-129
H,K=  6,  8
    1 235 239
    3 203-211
    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

    4 286 265
    6 250-229
    7 110  94
   10 130-146
   13 117-128
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H,K=  7,  2
    1 180 181
    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
H,K=  7,  4
    2 191-192
    3  76  54
    5 147 125
H,K=  7,  5
    2 160 159
    4 173 180
    8 255-264
   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
    3 123-139
    4 118-134
    5 178 198
H,K=  8,  0
   10 156-183
H,K=  8,  1
    7 109 133
H,K=  8,  2
    9 105-110
   10 131 145
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 PERCHLORATE 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	Atoms	Distance
O(8)–Pb(6)	2.74 (7)	O(8)–O(31)	3.25 (9)
O(8)–O(32)	2.77 (9)	O(8)–O(23)	3.29 (10)
O(8)–O(41)	3.15 (10)		

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 Figure 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 Figure 2. The structure of this cluster is related to that[11] of $Pb_4(OH)_4^{4+}$, in which the lead atoms form a

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(11) O. E. Esval, Thesis, University of North Carolina, 1963.

Table VIII

Some Angles (in deg) 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°, respectively.

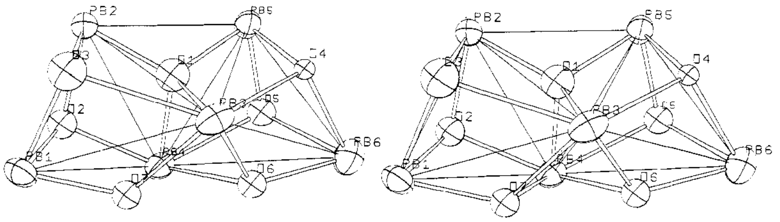

Figure 1.—Stereoscopic view of the $Pb_6O(OH)_6^{4+}$ complex. The stick bonds connect oxygen and lead atoms; the lines define the lead polyhedra. Interatomic distances are given in Table V and angles in Table VIII.

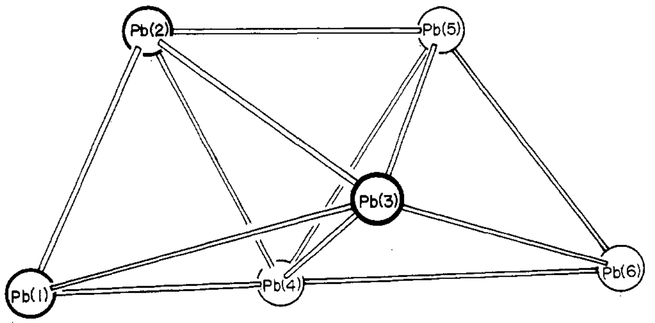

Figure 2.—The three face-sharing tetrahedra of Pb atoms in the $Pb_6O(OH)_6^{4+}$ cluster.

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.

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 noncentral 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

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(12) G. Wernfors, *Acta Chem. Scand.*, **15**, 1007 (1961).

(13) W. T. Moore and L. Pauling, *J. Am. Chem. Soc.*, **63**, 1392 (1941).

(14) A. F. Wells, "Structural Inorganic Chemistry," 3rd ed, 1962, Oxford, p 403.

(15) G. Stucky and R. E. Rundle, *J. Am. Chem. Soc.*, **86**, 4821 (1964).

(16) J. A. Bertrand, *Inorg. Chem.*, **6**, 495 (1967).

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 3.85 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 nonbonds, 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 12 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. The results of a solution X-ray scattering study by Johannson and Olin[19] point to the former conclusion. The Pb–Pb peak in the radial distribution function, which occurs at 3.85 Å in solutions containing tetrahedral $Pb_4(OH)_4^{4+}$, simply broadens without change in position as the OH:Pb ratio is increased toward 1.33. Weak next nearest neighbor peaks are found at 6.37 and 7.14 Å. (Nonadjacent 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. In fact a radial distribution function calculated on the basis of our structure is in quantitative agreement with the solution scattering data.[19]

Acknowledgments.—We wish to thank Dr. Michael G. B. Drew and Dr. Barry DeBoer for valuable assistance during the course of this work. We also thank Dr. Georg Johannson for communicating to us the results of his solution scattering experiments in advance of their publication.

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(17) V. A. Maroni and T. G. Spiro, *J. Am. Chem. Soc.*, **89**, 45 (1967).

(18) V. A. Maroni and T. G. Spiro, to be submitted for publication.

(19) G. Johannson and Å. Olin, *Acta Chem. Scand.*, in press.