

On the Structures of the Dominating Hydrolysis Products of Lead (II) in Solution

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The X-ray scattering from concentrated hydrolyzed and non-hydrolyzed solutions of lead(II) perchlorate has been measured. In solutions with an OH:Pb ratio of about 1 the scattering data indicate a tetrahedral arrangement of the lead atoms in the dominating polynuclear hydrolysis complex. For an OH:Pb ratio of 1.33, the highest value obtainable without precipitation, the results are consistent with a structure for the dominating complex which is closely related to that of a discrete six-nuclear complex found by Spiro⁵ in a crystal structure determination of the basic lead(II) perchlorate $\text{Pb}_6\text{O}(\text{OH})_6(\text{ClO}_4)_4$.

Precise emf data on hydrolyzed lead perchlorate solutions over a broad concentration range have been explained by the two complexes $\text{Pb}_4(\text{OH})_4^{4+}$ and $\text{Pb}_8(\text{OH})_8^{4+}$, and the agreement between observed and calculated data is still somewhat improved by assuming small amounts of other complexes.¹ The percentage of lead bound in the different complexes as a function of n_{OH} — the average number of OH groups per lead atom (written as Z in Ref. 1) — is shown in Fig. 1. The calculation is based on the stability constants given by Olin,¹ assuming the solution to be 2 M in Pb(II).

For a solution with $n_{\text{OH}}=1.33$, where $\text{Pb}_8(\text{OH})_8^{4+}$ is the dominating complex, the largest concentration of Pb(II), which can be obtained, is about 1.5 M. For $n_{\text{OH}}=0.97$, where $\text{Pb}_4(\text{OH})_4^{4+}$ dominates, more concentrated solutions can be prepared. The large concentrations and the high atomic number of lead make it likely that information on the structures of the complexes can be obtained by an X-ray investigation of the hydrolyzed solutions.

The X-ray scattering has been measured from three solutions of approximately the same lead concentration but with different n_{OH} values: 0, 0.97, and 1.33 (Table 1). The solutions were prepared from PbO and HClO_4 and analyzed as described in Ref. 1. The diffractometer used for these measurements was the same as described in a previous paper.² $\text{MoK}\alpha$ radiation ($\lambda=0.7109 \text{ \AA}$) was used. The hydrolyzed solutions had to be protected from

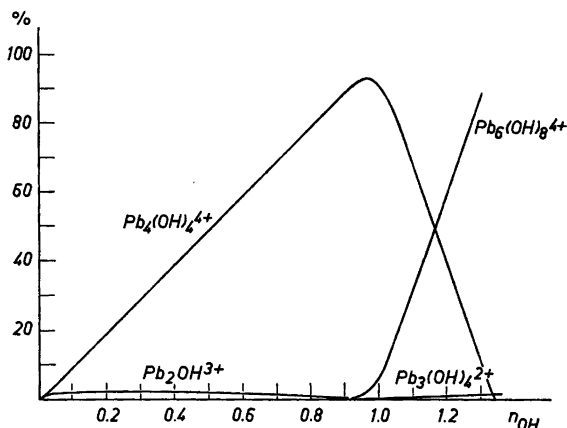


Fig. 1. The percentage of lead in a 2 M lead(II) perchlorate solution, bound in the different hydrolysis complexes, as a function of n_{OH} .

the carbon dioxide of the air and the measurements were made in a nitrogen atmosphere. The treatment of the experimental data was made in essentially the way described previously.²

The radial distribution functions ($D(r) - 4\pi r^2 \rho_0$) for the three solutions are shown in Fig. 2. They are all referred to a stoichiometric unit of solution containing one lead atom and, therefore, are directly comparable, although the concentrations differ slightly (Table 1). Peaks at about 2.6 Å, corresponding to Pb—O distances, occur in all the curves. Less pronounced maxima at about 1.5 Å, the expected Cl—O distances in the ClO_4 group, are also present. The two hydrolyzed solutions also give rise to sharp peaks at 3.85 Å, which obviously correspond to the shortest Pb—Pb distances in the polynuclear complexes. The most hydrolyzed solution shows two more peaks at 6.37 Å and 7.14 Å, which probably represent longer Pb—Pb distances within the complexes.

The reduced intensity functions, $i(s)$, obtained by subtracting the coherent scattering, $\sum n_i f_i^2$, from the scaled observed intensity values corrected for polarization and incoherent radiation, were analyzed by comparison with intensity values calculated for a single Pb—Pb interaction $i(s)_{\text{calc}} = \sum f_{\text{Pb}}^2 \cdot \exp(-bs^2) \cdot \sin(rs)/(rs)$. This comparison was made as a least-squares refinement in which the average number of nearest neighbors around each Pb atom, m , the Pb—Pb distance, r , and the temperature factor, b , were

Table 1. Compositions of the solutions in gatoms/l.

n_{OH}	Pb	Cl	O	H
0	1.86	3.99	62.3	92.8
0.973	1.86	1.91	58.8	100.4
1.33	1.64	1.09	56.9	102.9

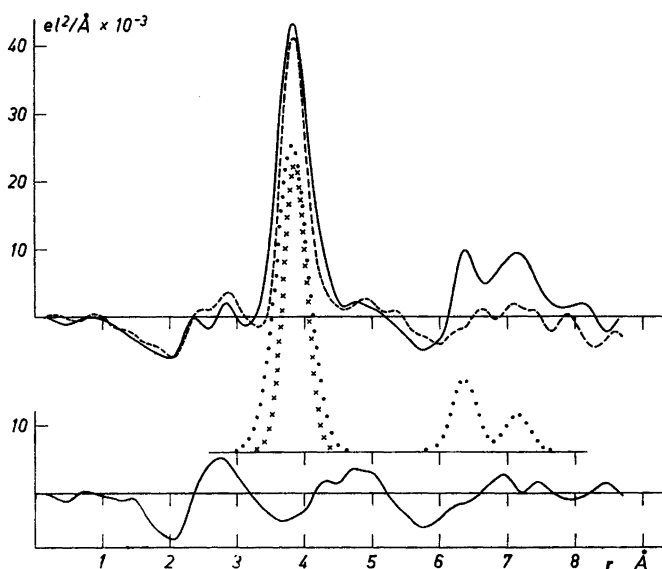


Fig. 2. Radial distribution functions $D(r) - 4\pi r^2 \rho_0$. The lower full-drawn curve is calculated for the solution with $n_{\text{OH}} = 0$. The two upper curves are calculated for the solutions with $n_{\text{OH}} = 0.97$ (dashed line) and $n_{\text{OH}} = 1.33$ (full-drawn line). Also shown are calculated peaks for a tetrahedral Pb_4 complex (crosses) using parameter values from a least squares refinement of the $i(s)$ curve, and for a six-nuclear Pb_6 complex (dots) using parameter values from the crystal structure determination⁵ of $\text{Pb}_6\text{O}(\text{OH})_6(\text{ClO}_4)_4$.

varied until a minimum was obtained for the least-squares error sum, $\sum(|s \cdot i(s)_{\text{obs}}| - |s \cdot i(s)_{\text{calc}}|)^2$, and until all shifts in the parameters were negligible in comparison with the calculated standard deviations (σ). Only values for $s (=4\pi \sin\theta/\lambda)$ larger than about three were used for this refinement, as the contribution from the Pb—Pb interactions within a complex may be expected to be dominating at these larger s values.

For the solution with $n_{\text{OH}} = 0.97$ the least squares refinement lead to the following results: $r = 3.854$ ($\sigma = 0.005$) Å, $m = 2.74$ ($\sigma = 0.10$) $b = 0.007$ ($\sigma = 0.001$). The peak calculated from these values is in close agreement with the corresponding peak in the radial distribution function (Fig. 2). Thus each lead atom in the complexes has about three nearest neighbors all at the same distance, 3.85 Å. Since no other peaks corresponding to Pb—Pb interactions seem to occur in this solution the only possible model for the polynuclear complex is a tetrahedral arrangement of the lead atoms. This is in agreement with the results of the emf data, which indicate the $\text{Pb}_4(\text{OH})_4^{4+}$ complex. Taking into account that not all of the lead is bound in this complex (Fig. 1) an average number of about 2.88 nearest neighbors around each Pb atom is expected, which agrees well with the value of 2.74 found from the least-squares refinement of the scattering curve.

Similar results and conclusions have previously been obtained by Esval³ from X-ray scattering measurements on a hydrolyzed lead perchlorate solution about 5 M in lead(II) and with an hydroxyl number of 0.93.

In the solution with $n_{\text{OH}}=1.33$ the 3.85 Å peak is considerably broadened. The area under the peak (Fig. 2) is about 35 % larger than that of the peak for the solution with $n_{\text{OH}}=0.97$. Thus the average number of nearest neighbors around each Pb atom has increased to about four. An attempt to fit a single Pb—Pb interaction to the experimental $i(s)$ values, as was done for the less hydrolyzed solution, was not successful. The results obtained in the least squares refinement lead to a calculated peak which is smaller than the observed peak in the distribution function. This indicates that the broadening of the peak is not the result of an increased temperature factor but can only be explained by assuming non-equal distances from one Pb atom to its nearest neighbors.

If it is assumed that in the solution one complex predominates as is indicated by the emf data (Fig. 1), then a model for this complex must have the following characteristics: each lead atom is surrounded by an average number of four other Pb atoms at a distance of about 3.85 Å. These distances are not equal, however, and may differ by several tenths of an Ångström. Two more distances, of lower frequencies, must occur at 6.37 Å and 7.14 Å. These characteristics exclude the possibility of an octahedral arrangement of the Pb atoms, which, as shown by Spiro,⁴ would have been compatible with the Raman spectrum of the solution. However, partly because of the splitting up of the shortest Pb—Pb distance, it is difficult to derive, in a unique way, the actual structure of the complex on the basis of the scattering data only.

From the hydrolyzed lead perchlorate solutions, crystals with n_{OH} values of 1.0 or 1.33 can easily be obtained. A crystal structure determination has been carried out by Spiro⁵ for crystals of the composition $\text{Pb}_6\text{O}(\text{OH})_6(\text{ClO}_4)_4$, that is, with $n_{\text{OH}}=1.33$. According to the structure determination, the crystals contain discrete six-nuclear complexes with the Pb arrangement shown in Fig. 3. Each Pb atom has an average number of four nearest neighbors at distances varying between 3.45 Å and 4.09 Å. Two longer distances occur at 6.36 Å and one at 7.14 Å. The complex, therefore, has exactly those characteristics which were derived from the results of the solution scattering measurements and thus it seems likely that the complex in solution has the same structure as the complex in the crystals. Using the positions of the Pb atoms in the complex in the crystals, determined by Spiro, the expected peak shapes for the solution have been calculated (Fig. 2). A value of 0.007 for the temperature factor, the same as the value found for the tetrahedral complex, was used for the calculation, and all Pb atoms in the solution were assumed to be bonded

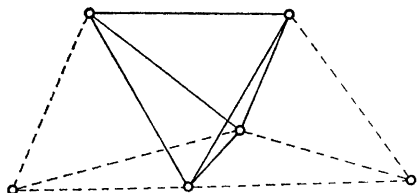


Fig. 3. The arrangement of the Pb atoms in the four- and six-nuclear hydrolysis complexes of lead. The atoms within the tetrahedral complex are joined by the full-drawn lines. The two additional atoms in the six-nuclear complex are joined to their nearest neighbors by dashed lines.

in the six-nuclear complex. Both the positions of the peaks (within about 0.02 Å) and the broadening of the 3.85 Å peak are fully explained by this model, and there seems to be little doubt that the $\text{Pb}_6(\text{OH})_8$ complex (or, according to the crystal structure determination, the $\text{Pb}_6\text{O}(\text{OH})_8$ complex) suggested by Olin on the basis of emf measurements, has the same structure as that found by Spiro in the crystals of $\text{Pb}_6\text{O}(\text{OH})_8(\text{ClO}_4)_4$.

No attempt has been made to locate the oxygen atoms in the polynuclear complexes, although the shortest Pb—O distances are clearly indicated between 2 and 3 Å in the radial distribution curves. (Fig. 2) If the oxygen positions found by Spiro in the $\text{Pb}_6\text{O}(\text{OH})_8$ group are included for the calculation of the $i(s)$ values a significant improvement of the agreement with the experimental $i(s)$ values is obtained. This indicates that not only the Pb positions but also the oxygen positions are the same in the complex in solution as they are in the crystals. The solution scattering data, however, cannot be used for more definite conclusions about the oxygen positions.

The original analysis of the emf data on dilute lead perchlorate solutions,¹ the X-ray scattering data on concentrated lead perchlorate solutions, and the crystal structure determination of a basic lead perchlorate,⁵ thus all lead to the same picture of the major hydrolysis reactions of lead(II).

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