ON THE STRUCTURE OF LEAD(II) COMPLEXES IN AQUEOUS SOLUTIONS. III. HEXANUCLEAR CLUSTERS

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Optimum geometries based on experimental structures and corresponding electronic structures of $[Pb_6(\mu_3\text{-}OH)_8]^{4+}$ and $[Pb_6O(\mu_3\text{-}OH)_6]^{4+}$ clusters as well as of their hydrated $[Pb_6(\mu_3\text{-}OH)_8(H_2O)_6]^{4+}$ and $[Pb_6O(\mu_3\text{-}OH)_6(H_2O)_6]^{4+}$ analogues are investigated using the semiempirical MNDO method of quantum chemistry. Direct Pb–Pb and O–O bonds are vanishing in the systems under study. Small differences in interatomic Pb–Pb and Pb–O distances between these clusters indicate that they cannot be distinguished by recent experimental techniques in solution. Both the mentioned structures are stable and might coexist in solution.

Keywords: Lead(II) clusters; Hydroxo complexes; Molecular structure; Semiempirical calculations.

The formation and precipitation of lead compounds in aqueous systems has important implications for many environmental problems. Structural characterization of these compounds in solutions is important for understanding the mechanism of lead transport in natural systems.

Precise potentiometric titration data[1–7] on the hydrolysis of lead(II) in perchlorate and nitrate solutions over a broad concentration and pH range indicate significant formation of $[Pb(OH)]^+$, $[Pb_3(OH)_4]^{2+}$, $[Pb_3(OH)_5]^+$, $[Pb_4(OH)_4]^{4+}$ and $[Pb_6(OH)_8]^{4+}$ species. The previously assumed[2–5] existence of $[Pb_2(OH)]^{3+}$ has not been confirmed in later studies[6,7].

Bengtsson and Hoffman[8] declared in their study on dilead structure units in lead halide and hydroxo/oxo species, clusters and extended structures found in molten salts, aqueous solutions and the solid state that the $[Pb_2(OH)_2]^{2+}$ clusters are stabilized by partial Pb–Pb bonding induced by bridging hydroxide ions. The strongest Pb–Pb bonds were deduced in complexes with predominantly ionic lead-anion interactions. They concluded

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that larger hydroxo/oxo clusters in aqueous solutions also seem to be stabilized by partial Pb–Pb bonding but in the solid structures of isolated hydroxo/oxo clusters Pb–O bonding predominate (only long Pb–Pb contacts have been found).

Our semiempirical quantum-chemical studies[9–11] of possible structures of trinuclear and tetranuclear lead(II) hydroxo complexes and of their hydrated analogues confirmed that the individual Pb atoms are bonded only *via* OH bridges due to vanishing Pb–Pb bonds. The stability of individual isomers increases with the number of μ_3-OH and μ_2-OH bridges. However, their stabilization mechanisms are mutually contradicting. Inclusion of additional H_2O molecules into the model system may significantly influence the relative stability of the systems even though the H_2O ligands do not serve as bridges.

X-Ray diffraction studies[12] of concentrated alkaline solutions of lead(II) perchlorate with the molar ratio OH/Pb of 4 : 3 indicate the existence of a hexanuclear hydrolysis complex of lead. The models for this complex must have the following characteristics: each lead atom is surrounded by four other Pb atoms on average, at a distance of about 3.85 Å. These distances, however, are not equal and may differ by *ca* 0.1 Å. Two more distances of lower frequencies must occur at 6.37 and 7.1 Å. In analogy with the crystal structure of the α-form[13] of $[Pb_6O(\mu_3\text{-}OH)_6](ClO_4)_4\cdot H_2O$, a boat-shaped arrangement of six lead atoms is assumed which can be considered as three face-sharing Pb_4 tetrahedra (Fig. 1). No attempt has been made to locate the oxygen atoms, although the shortest Pb–O distances between 2.0 and 3.0 Å are clearly indicated in the radial distribution curves. The $[Pb_6(OH)_8]^{4+}$ cluster indicated by potentiometric studies[1,6,7] should contain μ_3-OH bridges

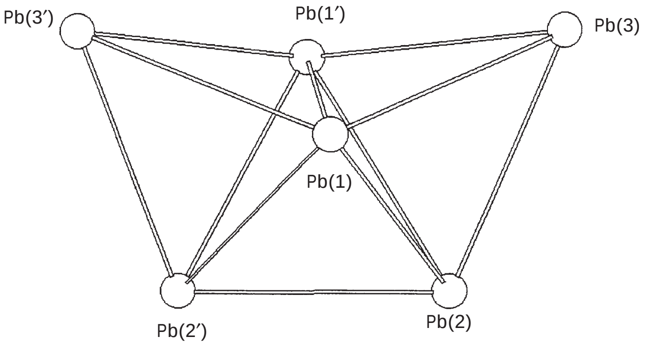

FIG. 1
Arrangement of the atoms in Pb_6 complexes

over each of the lead polyhedron faces (Fig. 2). The solution X-ray data, however, cannot be used for more definite conclusions about the oxygen positions. This model is in agreement with the rules on the OH bridges coexistence obtained by quantum-chemical treatment[9–11].

The crystal structures[13–15] of $[Pb_6O(\mu_3\text{-}OH)_6](XO_4)_4 \cdot H_2O$, X = Cl or Re, contain isolated $[Pb_6O(OH)_6]^{4+}$ units (Fig. 3, Table I) with central oxide ion inside the central Pb_4 tetrahedron and six μ_3-OH bridges over external faces of the remaining ones. Since the potentiometric measurements cannot differentiate between one O^{2-} and two OH^- groups, the presence of $[Pb_6O(\mu_3\text{-}OH)_6]^{4+}$ clusters in perchlorate solutions (from which the crystals

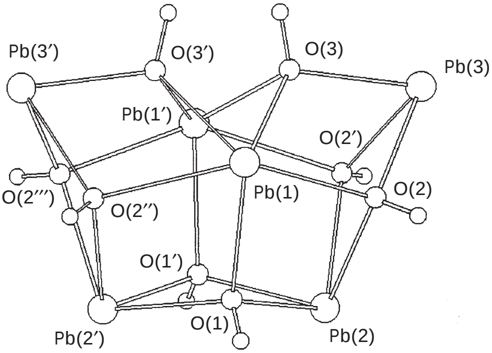

FIG. 2
Geometry of $[Pb_6(\mu_3\text{-}OH)_8]^{4+}$ cluster

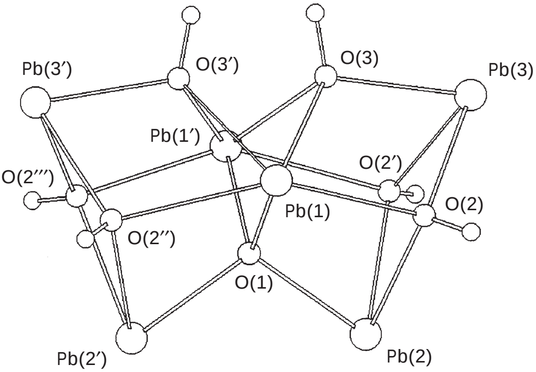

FIG. 3
Geometry of $[Pb_6O(\mu_3\text{-}OH)_6]^{4+}$ cluster

TABLE I

Interatomic distances (in Å) in perchlorate solutions and in real $[Pb_6O(\mu_3\text{-}OH)_6](XO_4)_4\cdot H_2O$ systems (standard deviations in parentheses, for atom numbering, see Fig. 3)

System	Solution[a]	Solid state			
		X = Cl α-form[b]	X = Cl β-form[c]	X = Re[d]	Average
Pb1–Pb1′	≈3.85	3.440(5)	3.462(2)	3.418(2)	3.44(2)
Pb1–Pb2	≈3.85	3.770(6)	3.841(2)	3.976(2)	3.79(7)
		3.778(5)	3.789(1)	3.740(2)	
		3.795(5)	3.732(2)	3.793(2)	
		3.786(5)	3.725(2)	3.714(2)	
Pb1–Pb3	≈3.85	3.949(6)	3.940(2)	4.081(2)	3.99(9)
		4.086(6)	3.917(2)	3.878(2)	
		3.846(5)	4.067(2)	3.942(2)	
		4.086(6)	3.983(2)	4.127(2)	
Pb2–Pb2′	≈3.85	3.790(5)	3.756(1)	3.929(2)	3.82(7)
Pb2–Pb3	≈3.85	3.674(6)	3.674(2)	3.724(1)	3.69(3)
		3.667(6)	3.650(1)	3.739(1)	
Pb2–Pb3′	≈6.37	6.378(6)	6.411(2)	6.486(2)	6.39(8)
		6.350(6)	6.245(2)	6.456(2)	
Pb3–Pb3′	≈7.14	7.144(6)	7.095(2)	7.143(2)	7.13(2)
Pb1–O1	≈2.6	2.35(6)	2.26(2)	2.26(2)	2.28(4)
		2.22(6)	2.30(2)	2.27(2)	
Pb1–O2	≈2.6	2.67(5)	2.82(2)	3.23(2)	2.7(2)
		2.53(4)	2.58(2)	2.73(2)	
		2.55(5)	2.69(2)	2.78(2)	
		3.02(6)	2.77(2)	2.61(2)	
Pb1–O3	≈2.6	2.53(6)	2.41(2)	2.55(2)	2.44(10)
		2.24(5)	2.34(2)	2.41(2)	
		2.47(5)	2.37(2)	2.43(2)	
		2.49(5)	2.62(2)	2.44(2)	
Pb2–O1	≈2.6	2.29(6)	2.33(2)	2.39(2)	2.31(5)
		2.29(6)	2.24(2)	2.31(2)	
Pb2–O2	≈2.6	2.34(5)	2.25(2)	2.23(3)	2.31(6)
		2.37(4)	2.30(2)	2.37(2)	
		2.30(5)	2.36(2)	2.32(2)	
		2.18(6)	2.30(2)	2.36(2)	
Pb3–O2	≈2.6	2.21(5)	2.31(2)	2.26(2)	2.30(5)
		2.23(4)	2.30(2)	2.28(2)	
		2.32(5)	2.33(2)	2.31(2)	
		2.36(6)	2.33(2)	2.36(2)	
Pb3–O3	≈2.6	2.33(5)	2.31(2)	2.26(3)	2.30(3)
		2.27(5)	2.30(2)	2.32(2)	
O3–O3′	–	2.69(5)	2.65(2)	2.72(3)	2.69(3)

[a] Ref.[12]; [b] ref.[13]; [c] ref.[14]; [d] ref.[15]

were obtained[13,14]) has been assumed[12–14]. Due to the width of the peaks in the radial distribution function at large interatomic distances, the X-ray measurements cannot be used to decide which of the above two clusters is most related to the species occurring in solution. The $[Pb_6O(\mu_3\text{-}OH)_6]^{4+}$ group, however, might be expected to be more symmetric in solution than in the solid phase (Table I).

The aim of our present work is to compare stable geometries and electronic structures of both the above mentioned types of clusters as well as of their hydrated forms using the quantum-chemical treatment.

CALCULATIONS

The standard semiempirical MNDO (Modified Neglect of Diatomic Overlap) method of quantum chemistry (AMPAC program package)[16–19] has been used in order to find the optimum geometries and to calculate the corresponding electronic structures of $[Pb_6(\mu_3\text{-}OH)_8]^{4+}$ (Fig. 2) and $[Pb_6O(\mu_3\text{-}OH)_6]^{4+}$ (Fig. 3) clusters as well as of their hydrated analogues $[Pb_6(\mu_3\text{-}OH)_8(H_2O)_6]^{4+}$ and $[Pb_6O(\mu_3\text{-}OH)_6(H_2O)_6]^{4+}$ with six water molecules bonded to the edges of the Pb_6 polyhedron. The results are compared using interatomic distances, ionization energy (I) and heat of formation (ΔH_f) data as well as in terms of Mulliken population analysis (bond orders, atomic charges). All calculations were performed at higher precision (keyword PRECISE) using the Davidon–Fletcher–Powell optimization procedure[20,21].

RESULTS AND DISCUSSION

The optimum geometries of $[Pb_6(\mu_3\text{-}OH)_8]^{4+}$ and $[Pb_6O(\mu_3\text{-}OH)_6]^{4+}$ complex cations obtained by the MNDO method (Table II) correspond to the highest possible C_{2v} symmetry. This skeleton symmetry is not lowered by hydration (each H_2O molecule being end-coordinated to only one of the lead atoms). It is evident that the longest Pb–OH distances are related to Pb(1) whereas the shortest ones to Pb(3) atoms (similarly to crystal structures – see Table I). Insertion of the central O(1) atom into the central Pb_4 tetrahedron causes a decrease in all Pb–Pb distances except Pb(3)–Pb(3′). An interchanged ratio of Pb(1)–Pb(1′) and Pb(2)–Pb(2′) distances in calculated and real systems might be ascribed to environmental influences. As in our previous study on tetralead(II) hydroxo complexes[9], a good agreement with experimental X-ray structures was achieved, the significantly shorter Pb(3)–Pb(3′) distance in calculated systems may be ascribed to the same reason. Small differences in interatomic Pb–Pb and Pb–O distances between $[Pb_6(\mu_3\text{-}OH)_8]^{4+}$

TABLE II
Relevant interatomic distances (in Å), electronic structure data, ionization energy (*I*), and heat of formation (ΔH_f) for the calculated model systems (for atom numbering, see Figs 2 and 3)

Model	$[Pb_6(OH)_8]^{4+}$	$[Pb_6(OH)_8(H_2O)_6]^{4+}$	$[Pb_6O(OH)_6]^{4+}$	$[Pb_6O(OH)_6(H_2O)_6]^{4+}$
		Distance		
Pb1–Pb1′	3.95	3.89	3.78	3.77
Pb1–Pb2	3.78	3.72	3.62	3.62
Pb1–Pb3	3.89	3.88	3.87	3.86
Pb2–Pb2′	3.61	3.54	3.47	3.47
Pb2–Pb3	3.84	3.82	3.83	3.82
Pb2–Pb3′	6.17	6.12	6.09	6.08
Pb3–Pb3′	6.47	6.46	6.48	6.47
Pb1–O1	2.42	2.43	2.31	2.31
Pb2–O1	2.26	2.27	2.12	2.12
Pb1–O2	2.49	2.52	2.47	2.50
Pb2–O2	2.41	2.45	2.41	2.45
Pb3–O2	2.26	2.25	2.27	2.25
Pb1–O3	2.54	2.57	2.52	2.55
Pb3–O3	2.16	2.15	2.18	2.16
O3–O3′	2.15	2.22	2.18	2.20
Pb–O(H_2O)	–	2.36–2.58	–	2.41–2.56
		Atomic charges		
Pb1	1.11	1.04	1.09	1.02
Pb2	1.07	1.06	1.13	1.05
Pb3	1.11	1.01	1.12	1.01
O1	–0.56	–0.56	–0.76	–0.79
O2	–0.57	–0.57	–0.56	–0.55
O3	–0.57	–0.56	–0.56	–0.55
		Bond orders		
Pb1–O1	0.34	0.30	0.40	0.38
Pb1–O2	0.29	0.26	0.26	0.24
Pb1–O3	0.27	0.24	0.27	0.26
Pb2–O1	0.41	0.39	0.59	0.54
Pb2–O2	0.35	0.30	0.42	0.38
Pb3–O2	0.47	0.47	0.45	0.46
Pb3–O3	0.53	0.54	0.54	0.54
Pb–O(H_2O)	–	0.12–0.27	–	0.13–0.21
		Energy parameters		
I, eV	25.3	21.8	25.3	20.6
ΔH_f, kcal/mol	616	177	691	118

and $[Pb_6O(\mu_3\text{-}OH)_6]^{4+}$ complex cations as well as between their hydrated analogues indicate that these systems cannot be distinguished by X-ray experiments in solution.

The influence of six water molecules causes the decrease in all Pb–Pb and increase in Pb–O distances (except O(1)–Pb(1,2) in $[Pb_6O(\mu_3\text{-}OH)_6]^{4+}$ and Pb(3)–O(2,3) in both complexes). However, it is an artifact of the MNDO method used (known from our previous studies[9–11]) that the additional H_2O inclusion causes an undesirable Pb–Pb shortening probably due to extremely short Pb–OH_2 bond (comparable with the Pb–OH one) and the solvent effect is overestimated[9]. The charge of the central O(1) oxide atom is significantly higher than that of O in the OH bridges. In all the systems under study, direct Pb–Pb and O–O bonds are vanishing (bond order values below 0.02).

The hydration affects the charges of Pb atoms more than those of O atoms. Pb–O(H_2O) bonds are relatively weak, μ_3-OH bridges are bonded a little stronger (especially with Pb(3) atoms) and are comparable with the oxide O(1)–Pb(1,2) bonds. These data well correlate with corresponding bond lengths (a shorter bond length corresponds to a stronger one and *vice versa*).

Small differences in ionization energies between $[Pb_6(\mu_3\text{-}OH)_8]^{4+}$ and $[Pb_6O(\mu_3\text{-}OH)_6]^{4+}$ complex cations as well as between their hydrated analogues indicate that these systems cannot be distinguished by electrochemical experiments. Ionization energies are lower in hydrated models than in their non-hydrated analogues, which is associated with the increasing size of the model systems. The equilibrium between the above mentioned complex cations may be described by the equation

$$[Pb_6(\mu_3\text{-}OH)_8]^{4+} \rightleftharpoons [Pb_6O(\mu_3\text{-}OH)_6]^{4+} + H_2O. \qquad (1)$$

An attempt to compare their relative stabilities using Eq. (*1*) and the MNDO value of the heat of formation of water ($\Delta H_f(H_2O)$ = –61 kcal/mol) gives opposite results to those for their hydrated analogues. Only chemical intuition based on stronger Pb(1,2)–O(1) bonds, lower dimensions of the central OPb_4 than those of empty Pb_4 tetrahedron and the non-existence of the $[Pb_6(\mu_3\text{-}OH)_8]^{4+}$ structures in real crystals suggests that the equlibrium in Eq. (*1*) is shifted to the right hand. The opposite relation for hydrated systems might be explained by overestimation of the solvent effect as an artifact of the MNDO method used (see above).

Our results indicate that $[Pb_6(\mu_3\text{-}OH)_8]^{4+}$ and $[Pb_6O(\mu_3\text{-}OH)_6]^{4+}$ clusters in real solutions are indistinguishable using recent experimental techniques. It is very probable that both forms exist simultaneously in a broad range of concentrations. In this connection a question on the mechanism of their interconversion arises.

It is well known that only the tetralead complexes of $[Pb_4(\mu_3\text{-}OH)_4]^{4+}$ (without central oxide atom) are present in solution[12] as well as in the solid $[Pb_4(\mu_3\text{-}OH)_4]_3(CO_3)(ClO_4)_{10}\cdot 6H_2O$ and $[Pb_4(\mu_3\text{-}OH)_4](ClO_4)_4\cdot 2H_2O$ structures[22,23]. Hexalead(II) solid structures[13–15] of α- and β-forms of $[Pb_6O(\mu_3\text{-}OH)_6](ClO_4)_4\cdot H_2O$ or $[Pb_6O(\mu_3\text{-}OH)_6](ReO_4)_4\cdot H_2O$ contain central oxo-centered OPb_4 as well as lateral empty Pb_4 tetrahedra. On the other hand, some solid crystals obtained from alkaline lead(II) solutions contain infinite $[O_2Pb_3]$ double chains of exclusively oxo-centered OPb_4 tetrahedra (each tetrahedron has two topologically distinct Pb vertices: two “outer” Pb atoms are shared by two OPb_4 tetrahedra, whereas the other two “inner” Pb ones are shared by four OPb_4 tetrahedra). These chains may be bonded by μ_2-OH bridges (as in $[Pb_6O_4](OH)(NO_3)(CO_3)$ and $[Pb_3O_2](OH)(NO_3))$[24,25] or are not interconnected (like in $[Pb_3O_2](CO_3))$[26]. Similarly, the isolated $[Pb_{13}O_8(OH)_6]^{4+}$ cluster (built from six μ_2-OH bridges and eight OPb_4 tetrahedra sharing a common Pb vertex and three edges) is the principal unit[27] of $[Pb_{13}O_8(OH)_6](NO_3)_4$. This implies that the Pb_4 tetrahedra sharing two and more faces are not stabilized by “outside” μ_3-OH bridges and one of these bridges is converted to “inner” oxide anion. The resulting OPb_4 tetrahedra cannot contain any additional μ_3-OH bridges. This might be explained by their mutually contradictory stabilization mechanisms similarly to the case of μ_2-OH and μ_3-OH bridges[9–11].

The mechanism of building larger $Pb_kO_n(OH)_m$ clusters has not been studied yet. Our calculations indicate that both $[Pb_6(\mu_3\text{-}OH)_8]^{4+}$ and $[Pb_6O(\mu_3\text{-}OH)_6]^{4+}$ clusters may be stable. The energy parameters of their interconversion according to Eq. (*1*) might enable their coexistence in solution. On the other hand, the mechanism of their building from smaller lead(II) structures is unknown. It is possible that the hexalead clusters are formed from pairs of $[Pb_3(OH)_4]^{2+}$ cations (as indicated by common maximum on pH dependences of their concentrations[1,6,12]) or by consecutive addition of $[Pb(OH)]^+$ to $[Pb_4(OH)_4]^{4+}$ (as indicated by extraordinarily strong Pb(3)–O(2,3) bonds in $[Pb_6(OH)_8]^{4+}$ and $[Pb_6O(OH)_6]^{4+}$ clusters, see Table II) or utilizing any unstable intermediate structures not detected in measurable concentrations. Further theoretical as well as experimental studies in this field are desirable.

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