ON THE STRUCTURE OF LEAD(II) COMPLEXES IN AQUEOUS SOLUTIONS. I. TRINUCLEAR CLUSTERS

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Using semiempirical MNDO method of quantum chemistry the optimal geometries and corresponding electronic structures of $[\mathrm{Pb_3(OH)}_n]^{6-n}$ model systems as well as of their hydrated $[\mathrm{Pb_3(OH)}_n\mathrm{(H_2O)}_{8-n}]^{6-n}$ analogues (n = 4, 5) are investigated. The most stable trinuclear lead(II) complexes present in aqueous solutions correspond to *cyclo*-$(\mu_3\text{-OH})(\mu_2\text{-OH})_3\mathrm{Pb}_3^{2+}$, $\mathrm{Pb}(\mu\text{-OH})_2\mathrm{Pb}(\mu\text{-OH})_2\mathrm{Pb}^{2+}$, *cyclo*-$(\mu_3\text{-OH})_2(\mu_2\text{-OH})_3\mathrm{Pb}_3^{+}$, $\mathrm{Pb(OH)}(\mu\text{-OH})_2\mathrm{Pb}(\mu\text{-OH})\mathrm{Pb(OH)}^{+}$ and $\mathrm{Pb(OH)}(\mu\text{-OH})_2\mathrm{Pb}(\mu\text{-OH})_2\mathrm{Pb}^{+}$ systems. The key role of OH bridges (by vanishing direct Pb–Pb bonds) on the stability of individual isomers is discussed.

Statistical analysis of potentiometric titration data[1,2] on the hydrolysis of lead(II) indicates the formation of the species $[\mathrm{Pb(OH)}]^{+}$, $[\mathrm{Pb_3(OH)_4}]^{2+}$, $[\mathrm{Pb_3(OH)_5}]^{+}$, $[\mathrm{Pb_4(OH)_4}]^{4+}$ and $[\mathrm{Pb_6(OH)_8}]^{4+}$.

The dominant hydrolytic species[1,2] at low lead(II) concentrations is $[\mathrm{Pb(OH)}]^{+}$. Other monomeric species as $[\mathrm{Pb(OH)_2}]$ and $[\mathrm{Pb(OH)_3}]^{-}$ are not produced at pH values lower than 8.5.

Among the dimeric species $[\mathrm{Pb_2(OH)}]^{3+}$ was not considered as making any measurable contribution to total lead concentration in aqueous solution[1]. The absence of the species $[\mathrm{Pb_2(OH)_2}]^{2+}$ is possibly the result of dimerization reaction being heavily forwarded to $[\mathrm{Pb_4(OH)_4}]^{4+}$ formation.

The species $[\mathrm{Pb_3(OH)_4}]^{2+}$ is present in aqueous solution to a considerable extent[1]. Its contribution to total lead concentration in solution is more important than this contribution of $[\mathrm{Pb_4(OH)_4}]^{4+}$ and $[\mathrm{Pb_6(OH)_8}]^{4+}$ species at any pH where all three exist. At high pH the concentration of $[\mathrm{Pb_3(OH)_5}]^{+}$ species becomes one of the highest ones, even at low total lead concentrations.

There are no experimental data on the structure of the above mentioned trinuclear lead(II) clusters in aqueous solution (on the contrary to tetra- and hexanuclear ones)[2]. Their structure may be deduced from analogies with similar compounds but some questions remain unresolved. Consequently, the systematic study of the structure of above mentioned lead(II) clusters by means of quantum chemistry is desirable. The aim of this study is to determine the structure of $[Pb_3(OH)_4]^{2+}$ and $[Pb_3(OH)_5]^+$ clusters present in aqueous solution.

EXPERIMENTAL

Method Used

The standard semiempirical MNDO (Modified Neglect of Diatomic Overlap) method of quantum chemistry (AMPAC program package)[3–5] has been used in order to find the optimal geometries and to calculate the corresponding electronic structures of $[Pb_3(OH)_4]^{2+}$ (models $\mathbf{A}_{mn}$ and $\mathbf{B}_{pq}$) $[Pb_3(OH)_5]^+$ (models $\mathbf{E}_{mn}$ and $\mathbf{F}_{pq}$) clusters as well as of their hydrated analogs $[Pb_3(OH)_4(H_2O)_4]^{2+}$ (models $\mathbf{C}_{mn}$ and $\mathbf{D}_{pq}$) and $[Pb_3(OH)_5(H_2O)_3]^+$ (models $\mathbf{G}_{mn}$ and $\mathbf{H}_{pq}$). In the cyclic $\mathbf{A}_{mn}$, $\mathbf{C}_{mn}$, $\mathbf{E}_{mn}$ and $\mathbf{G}_{mn}$ models (triangular Pb_3 geometry – see Figs 1, 2) the m and n indices denote the numbers of μ_3- and μ_2-OH bridges, respectively. In the acyclic $\mathbf{B}_{pq}$, $\mathbf{D}_{pq}$, $\mathbf{F}_{pq}$ and $\mathbf{H}_{pq}$ (quasi-linear Pb_3 geometry – see Figs 3, 4, 5) the p and q indices denote the numbers of μ_2-OH bridges on different Pb–Pb bonds, respectively. The results are compared in terms like heat of formation (ΔH_f), geometry changes, ionisation energy (I) as well as in terms of Mulliken population analysis – bond orders (BO) and atomic charges (Q). All calculations were performed in higher precision (keyword PRECISE) using Davidon–Fletcher–Powell optimization procedure[6,7].

RESULTS AND DISCUSSION

Due to the large number of the studied model systems, some results for the stable systems only are presented in Tables I – IV. Geometries of the most stable model systems are presented in Figs 1 – 5 (H_2O molecules are omitted) and selected characteristics of corresponding electronic structures are described in Tables V – VII. It is evident that individual Pb atoms must be connected by OH bridges in order to produce stable structures. In principle, the increasing stability of the system with the number of OH bridges may be explained by increasing number of stabilizing Pb–O bonds. In cyclic systems, however, the stabilization by μ_2-OH and μ_3-OH bridges are in contra-

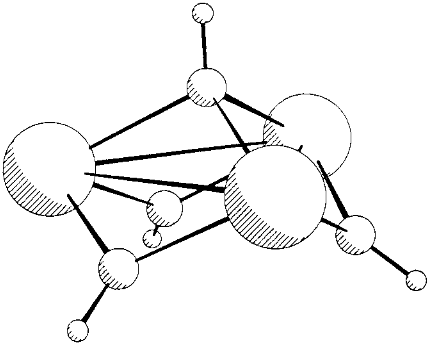

FIG. 1
Stable geometry of *cyclo*-$(\mu_3\text{-OH})(\mu_2\text{-OH})_3Pb_3^{2+}$ (model $\mathbf{A}_{13}$)

diction (compare stable $\mathbf{A}_{20}$ and unstable $\mathbf{A}_{21}$ models in Table I or $\mathbf{E}_{20}$ and less stable $\mathbf{E}_{21}$ ones in Table III). Really, μ_2-OH bridges cause the increasing Pb–Pb interatomic distances whereas the μ_3-OH ones cause, in general, the decrease of this distance (see the Pb–Pb distances in Tables I – IV). As a consequence the model systems $\mathbf{A}_{13}$ and $\mathbf{C}_{13}$ are more stable than their $\mathbf{A}_{22}$ and $\mathbf{C}_{22}$ analogues. Additional OH bridge in acyclic model systems causes the shortening of Pb–Pb distances (see Tables I – IV). The decrease of the total cluster charge (rising electron density) causes the shortening of Pb–Pb distances, too.

TABLE I
Heat of formation, ΔH_f, and mutual Pb–Pb distances, d(Pb–Pb), of stable $Pb_3(OH)_4^{2+}$ systems

Model	Cluster	ΔH_f, kJ/mol	d(Pb–Pb), 10^{-10} m
	Cyclic models		
$\mathbf{A}_{02}$	*cyclo*-$(\mu_2\text{-}OH)_2Pb_3(OH)_2^{2+}$	+1 077.7	3.87, 3.40, 3.92
$\mathbf{A}_{03}$	*cyclo*-$(\mu_2\text{-}OH)_3Pb_3(OH)^{2+}$	+858.6	4.26 (2 ×), 4.04
$\mathbf{A}_{12}$	*cyclo*-$(\mu_3\text{-}OH)(\mu_2\text{-}OH)_2Pb_3(OH)^{2+}$	+896.6	3.70, 3.87, 3.55
$\mathbf{A}_{13}$	*cyclo*-$(\mu_3\text{-}OH)(\mu_2\text{-}OH)_3Pb_3^{2+}$	+567.9	3.62 (3 ×)
$\mathbf{A}_{20}$	*cyclo*-$(\mu_3\text{-}OH)_2Pb_3(OH)_2^{2+}$	+1 042.5	3.52, 3.53, 3.95
$\mathbf{A}_{22}$	*cyclo*-$(\mu_3\text{-}OH)_2(\mu_2\text{-}OH)_2Pb_3^{2+}$	+680.4	3.32, 3.49 (2 ×)
	Acyclic models		
$\mathbf{B}_{11}$	$Pb(OH)(\mu\text{-}OH)Pb(\mu\text{-}OH)Pb(OH)^{2+}$	+760.5	4.00 (2 ×), 7.69
$\mathbf{B}_{21}$	$Pb((\mu\text{-}OH)_2Pb(\mu\text{-}OH)Pb(OH)^{2+}$	+639.8	3.55, 3.96, 6.79
$\mathbf{B}_{22}$	$Pb(\mu\text{-}OH)_2Pb(\mu\text{-}OH)_2Pb^{2+}$	+595.6	3.59 (2 ×), 6.21

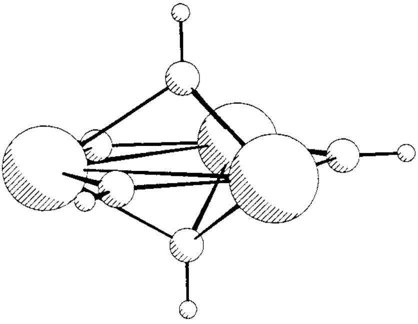

FIG. 2
Stable geometry of $Pb(\mu\text{-}OH)_2Pb(\mu\text{-}OH)_2Pb^{2+}$ (model $\mathbf{B}_{22}$)

Inclusion of additional H_2O molecules into the model may significantly influence the stability of the systems under study (compare relative stabilities of **A**, **B**, **E** and **F** models in Tables I and III with their hydrated **C**, **D**, **G** and **H** analogues in Tables II and IV). Here it must be mentioned that the influence of polar H_2O molecules on the acyclic systems is greater than on cyclic ones (due to higher polarity). More complex models (accounting a greater number of H_2O molecules) may cause larger stability differences between cyclic and acyclic systems. Due to this reason the most stable systems for both the model types are presented in Tables V – VII. Geometry investigations of **C**, **D**, **G** and **H** models (due to space shortage not presented in details) indicate that H_2O ligands

TABLE II
Heat of formation, ΔH_f, and mutual Pb–Pb distances, *d*(Pb–Pb), of stable $Pb_3(OH)_4(H_2O)_4^{2+}$ systems

Model	Cluster	ΔH_f, kJ/mol	*d*(Pb–Pb), 10^{-10} m
	Cyclic models		
$\mathbf{C}_{02}$	*cyclo*-$(\mu_3\text{-}H_2O)_2(\mu_2\text{-}OH)_2Pb_3(OH)_2(H_2O)_2^{2+}$	–424.9	4.10, 4.20, 3.99
$\mathbf{C}_{12}$	*cyclo*-$(\mu_3\text{-}OH)(\mu_3\text{-}H_2O)(\mu_2\text{-}OH)_2(\mu_2\text{-}H_2O)Pb_3(OH)(H_2O)_2^{2+}$	–271.1	3.47, 3.67, 3.45
$\mathbf{C}_{13}$	*cyclo*-$(\mu_3\text{-}OH)(\mu_3\text{-}H_2O)(\mu_2\text{-}OH)_3Pb_3(H_2O)_3^{2+}$	–573.5	3.74 (2 ×), 3.72
$\mathbf{C}_{20}$	*cyclo*-$(\mu_3\text{-}OH)_2Pb_3(OH)_2(H_2O)_4^{2+}$	–114.6	3.53, 3.54, 3.92
$\mathbf{C}_{22}$	*cyclo*-$(\mu_3\text{-}OH)_2(\mu_2\text{-}OH)_2(\mu_2\text{-}H_2O)Pb_3(OH)(H_2O)_3^{2+}$	–439.7	3.32, 3.43 (2 ×)
	Acyclic models		
$\mathbf{D}_{11}$	$Pb(OH)(H_2O)(\mu\text{-}OH)Pb(H_2O)_2(\mu\text{-}OH)Pb(OH)(H_2O)^{2+}$	–519.4	4.00 (2 ×), 7.78
$\mathbf{D}_{21}$	$Pb(H_2O)_2(\mu\text{-}OH)_2Pb(H_2O)(\mu\text{-}OH)Pb(OH)(H_2O)^{2+}$	–599.9	3.59, 3.92, 6.85
$\mathbf{D}_{22}$	$Pb(H_2O)_2(\mu\text{-}OH)_2Pb(\mu\text{-}OH)_2Pb(H_2O)_2^{2+}$	–635.5	3.62 (2 ×), 6.28

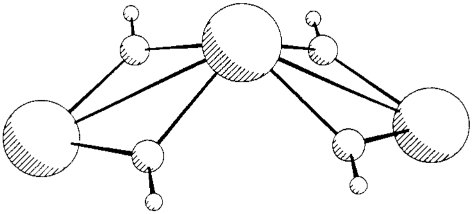

FIG. 3
Stable geometry of *cyclo*-$(\mu_3\text{-}OH)_2(\mu_2\text{-}OH)_3Pb_3^+$ (model $\mathbf{E}_{23}$)

do not serve as bridges, their distance from Pb atoms is over 2.4 . 10^{-10} m (compare with metalic Pb, covalent Pb(II) and ionic Pb^{2+} radii of 1.75 . 10^{-10} m, 1.44 . 10^{-10} m and 1.21 . 10^{-10} m, respectively)[2]. The number of H_2O ligands bonded to Pb atoms is restricted so that the number of Pb–O bonds (including OH ligands) is limited to four. The remaining H_2O molecules are bonded in a second coordination sphere.

TABLE III
Heat of formation, ΔH_f, and mutual Pb–Pb distances, *d*(Pb–Pb), of stable $Pb_3(OH)_5^+$ systems

Model	Cluster	ΔH_f, kJ/mol	*d*(Pb–Pb), 10^{-10} m
	Cyclic models		
$\mathbf{E}_{02}$	*cyclo*-$(\mu_2\text{-OH})_2\text{Pb}_3(\text{OH})_3^+$	–204.0	2.72 (2 ×), 3.40
$\mathbf{E}_{03}$	*cyclo*-$(\mu_2\text{-OH})_3\text{Pb}_3(\text{OH})_2^+$	–193.9	4.02 (2 ×), 4.12
$\mathbf{E}_{11}$	*cyclo*-$(\mu_3\text{-OH})(\mu_2\text{-OH})\text{Pb}_3(\text{OH})_3^+$	–125.2	3.26 (2 ×), 3.29
$\mathbf{E}_{12}$	*cyclo*-$(\mu_3\text{-OH})(\mu_2\text{-OH})_2\text{Pb}_3(\text{OH})_2^+$	–166.1	3.51, 3.17, 3.70
$\mathbf{E}_{13}$	*cyclo*-$(\mu_3\text{-OH})(\mu_2\text{-OH})_3\text{Pb}_3(\text{OH})^+$	–254.4	3.81 (2 ×), 3.58
$\mathbf{E}_{20}$	*cyclo*-$(\mu_3\text{-OH})_2\text{Pb}_3(\text{OH})_3^+$	–114.4	3.55 (3 ×)
$\mathbf{E}_{21}$	*cyclo*-$(\mu_3\text{-OH})_2(\mu_2\text{-OH})\text{Pb}_3(\text{OH})_2^+$	–90.5	3.24 (2 ×), 3.64
$\mathbf{E}_{22}$	*cyclo*-$(\mu_3\text{-OH})_2(\mu_2\text{-OH})_2\text{Pb}_3(\text{OH})^+$	–309.4	3.66 (2 ×), 3.10
$\mathbf{E}_{23}$	*cyclo*-$(\mu_3\text{-OH})_2(\mu_2\text{-OH})_3\text{Pb}_3^+$	–493.8	3.48 (3 ×)
	Acyclic models		
$\mathbf{F}_{11}$	$\text{Pb(OH)}(\mu\text{-OH})\text{Pb(OH)}(\mu\text{-OH})\text{Pb(OH)}^+$	–428.7	3.90 (2 ×), 6.81
$\mathbf{F}_{21}$	$\text{Pb(OH)}(\mu\text{-OH})_2\text{Pb}(\mu\text{-OH})\text{Pb(OH)}^+$	–521.1	3.54, 3.90, 6.61
$\mathbf{F}_{22}$	$\text{Pb(OH)}(\mu\text{-OH})_2\text{Pb}(\mu\text{-OH})_2\text{Pb}^+$	–508.7	3.59, 3.62, 5.75

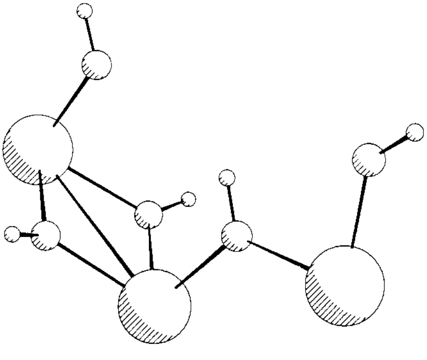

FIG. 4
Stable geometry of $\text{Pb(OH)}(\mu\text{-OH})_2\text{Pb}(\mu\text{-OH})\text{Pb(OH)}^+$ (model $\mathbf{F}_{21}$)

The geometry of the most stable cyclic systems (due to space shortage not presented in details) corresponds to the highest possible symmetry (C_{3v}) symmetry group for $\mathbf{A}_{13}$ and $\mathbf{C}_{13}$ models, D_{3h} for $\mathbf{E}_{23}$ and $\mathbf{G}_{23}$ ones). On the contrary, this rule does not hold for the acyclic systems where the Pb–Pb–Pb angle is near 120° (non-linear systems). Non-bridging Pb–O bonds (under $2.1 \cdot 10^{-10}$ m) are shorter than the bridging ones, the

TABLE IV
Heat of formation, ΔH_f, and mutual Pb–Pb distances, d(Pb–Pb), of stable $\text{Pb}_3(\text{OH})_5(\text{H}_2\text{O})_3^+$ systems

Model	Cluster	ΔH_f, kJ/mol	d(Pb–Pb), 10^{-10} m
	Cyclic model		
$\mathbf{G}_{02}$	*cyclo*-$(\mu_3\text{-H}_2\text{O})_2(\mu_2\text{-OH})_2(\mu_2\text{-H}_2\text{O})\text{Pb}_3(\text{OH})_3^+$	–1 007.1	3.70 (2 ×), 3.39
$\mathbf{G}_{03}$	*cyclo*-$(\mu_3\text{-H}_2\text{O})_2(\mu_2\text{-OH})_3\text{Pb}_3(\text{OH})_2(\text{H}_2\text{O})^+$	–990.0	3.94 (2 ×), 4.02
$\mathbf{G}_{11}$	*cyclo*-$(\mu_3\text{-OH})(\mu_3\text{-H}_2\text{O})(\mu_2\text{-OH})(\mu_2\text{-H}_2\text{O})_2\text{Pb}_3(\text{OH})_3^+$	–930.4	3.27 (3 ×)
$\mathbf{G}_{12}$	*cyclo*-$(\mu_3\text{-OH})(\mu_3\text{-H}_2\text{O})(\mu_2\text{-OH})_2(\mu_2\text{-H}_2\text{O})\text{Pb}_3(\text{OH})_2(\text{H}_2\text{O})^+$	–988.1	3.44, 3.13, 3.61
$\mathbf{G}_{13}$	*cyclo*-$(\mu_3\text{-OH})(\mu_3\text{-H}_2\text{O})(\mu_2\text{-OH})_3\text{Pb}_3(\text{OH})(\text{H}_2\text{O})_2^+$	–1 104.8	3.78, 3.80, 3.64
$\mathbf{G}_{20}$	*cyclo*-$(\mu_3\text{-OH})_2\text{Pb}_3(\text{OH})_3(\text{H}_2\text{O})_3^+$	–911.5	3.54 (3 ×)
$\mathbf{G}_{21}$	*cyclo*-$(\mu_3\text{-OH})_2(\mu_2\text{-OH})(\mu_2\text{-H}_2\text{O})_2\text{Pb}_3(\text{OH})_2(\text{H}_2\text{O})_2^+$	–896.9	3.23 (2 ×), 3.60
$\mathbf{G}_{22}$	*cyclo*-$(\mu_3\text{-OH})_2(\mu_2\text{-OH})_2(\mu_2\text{-H}_2\text{O})\text{Pb}_3(\text{OH})(\text{H}_2\text{O})_2^+$	–1 107.0	3.64 (2 ×), 3.11
$\mathbf{G}_{23}$	*cyclo*-$(\mu_3\text{-OH})_2(\mu_2\text{-OH})_3\text{Pb}_3(\text{H}_2\text{O})_3^+$	–1 226.3	3.51 (3 ×)
	Acyclic model		
$\mathbf{H}_{21}$	$\text{Pb}(\text{OH})(\text{H}_2\text{O})(\mu\text{-OH})_2\text{Pb}(\text{H}_2\text{O})(\mu\text{-OH})\text{Pb}(\text{OH})(\text{H}_2\text{O})^+$	–1 369.8	3.58, 3.90, 6.64
$\mathbf{H}_{22}$	$\text{Pb}(\text{OH})(\text{H}_2\text{O})(\mu\text{-OH})_2\text{Pb}(\mu\text{-OH})_2\text{Pb}(\text{H}_2\text{O})_2^+$	–1 348.4	3.60, 3.62, 5.92

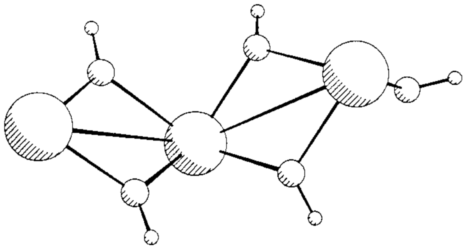

FIG. 5
Stable geometry of $\text{Pb}(\text{OH})(\mu\text{-OH})_2\text{Pb}(\mu\text{-OH})_2\text{Pb}^+$ (model $\mathbf{F}_{22}$)

TABLE V
Electronic structure of the most stable $Pb_3(OH)_4^{2+}$ and $Pb_3(OH)_4(H_2O)_4^{2+}$ systems

Model	**A**$_{13}$	**C**$_{13}$	**B**$_{22}$	**D**$_{22}$
I, eV	20.0	16.9	19.0	17.1
		Atom charges		
Pb	1.07 (3 ×)	0.97 (2 ×) 0.94	0.95^a 1.16 (2 ×)	0.87^a 0.95 (2 ×)
O	–0.56 (3 ×)^b –0.53	–0.56 (3 ×)^b –0.52	–0.55 (4 ×)	–0.56(4 ×)
H	0.25 (3 ×)^b 0.24	0.23 (3 ×)^b 0.19	0.24 (4 ×)	0.21 (4 ×)
		Bond orders		
Pb–Pb	0.02 (3 ×)	0.01 (3 ×)	0.02 (2 ×)	0.02 (2 ×)
Pb–O	0.56 (3 ×)^b 0.40 (3 ×)	0.52 (3 ×)^b 0.36 (3 ×)	0.42 (4 ×)^a 0.68 (4 ×)	0.45 (4 ×)^a 0.58 (4 ×)
O–H	0.91 (3 ×)^b 0.93	0.93 (3 ×)^b 0.95	0.92 (4 ×)	0.93 (4 ×)

^{a} Related to central Pb; ^{b} related to μ_2-OH.

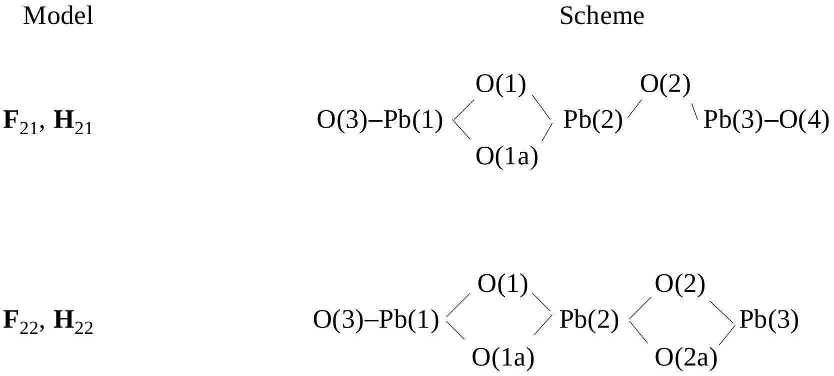

FIG. 6
Atom numbering for central part of acyclic models of stable $Pb_3(OH)_5^+$ and $Pb_3(OH)_5(H_2O)_3^+$ systems

μ_2-ones (ca 2.2 . 10^{-10} m) shorter than the μ_3-ones (ca 2.4 . 10^{-10} m). The influence of H_2O molecules on the symmetry of optimal geometries is of lower importance.

On the other hand, the electronic structure of these optimal model geometries (Tables V – VII) is more influenced by H_2O molecules. Ionisation potentials and polarity of atoms (especially Pb charges) are higher in simple **A**, **B**, **E** and **F** models than in their **C**, **D**, **G** and **H** analogues including additional H_2O ligands. Inclusion of H_2O influence especially the Pb–O bonds and diminish the bond orders in cyclic models as well as in the Pb–O bonds related to central Pb atom of acyclic models. Here it must be mentioned that the Pb–O(H_2O) bond is relatively weak (bond orders ca 0.2 – 0.3), μ_3-OH bridges in cyclic systems are bonded a little bit stronger (bond orders ca 0.4). The strongest Pb–O bonds correspond to non-bridging OH in acyclic models (bond orders over 0.8). These data well correlate with corresponding bond lengths (shorter bond length corresponds to stronger bond and vice versa).

Due to vanishing Pb–Pb bond order values the individual Pb atoms are bonded only via OH bridges. The increase of ionisation potential values with the positive charge of the system may be explained by increasing polarity of the system. By the same way is explainable the difference between cyclic and acyclic models. The decrease of ionisation potential values in hydrated models is, moreover, partly connected with the in-

TABLE VI
Electronic structure of the most stable cyclic $Pb_3(OH)_5^+$ and $Pb_3(OH)_5(H_2O)_3^+$ systems

Model	**E**$_{23}$	**G**$_{23}$
I, eV	14.5	13.1
	Atom charges	
Pb	0.90 (3 ×)	0.85 (3 ×)
O	–0.59 (3 ×)[a] –0.50 (2 ×)	–0.59 (3 ×)[a] –0.50 (2 ×)
H	+0.22 (3 ×)[a] +0.21 (2 ×)	+0.20 (3 ×)[a] +0.18 (2 ×)
	Bond orders	
Pb–Pb	0.01 (3 ×)	0.01 (3 ×)
Pb–O	0.49 (3 ×)[a] 0.38 (2 ×)	0.47 (3 ×)[a] 0.36 (2 ×)
O–H	0.93 (3 ×)[a] 0.94 (2 ×)	0.94 (3 ×)[a] 0.95 (2 ×)

[a] Related to μ_2-OH.

TABLE VII
Electronic structure of the most stable acyclic $Pb_3(OH)_5^+$ and $Pb_3(OH)_5(H_2O)_3^+$ systems (see Fig. 6 for atoms numbering)

Model	**F**$_{21}$	**F**$_{22}$	**H**$_{21}$	**H**$_{22}$
I, eV	13.5	13.0	13.2	12.6
		Atom charges		
Pb(1)	0.97	0.77	0.84	0.73
Pb(2)	0.89	0.86	0.88	0.83
Pb(3)	0.83	1.05	0.81	0.92
O(1)	–0.53 (2 ×)	–0.53 (2 ×)	–0.52 (2 ×)	–0.53 (2 ×)
O(2)	–0.52	–0.53 (2 ×)	–0.52	–0.55 (2 ×)
O(3)	–0.58	–0.60	–0.60	–0.59
O(4)	–0.61	–	–0.61	–
H(1)	0.22 (2 ×)	0.23 (2 ×)	0.22 (2 ×)	0.20 (2 ×)
H(2)	0.24	0.21 (2 ×)	0.23	0.22 (2 ×)
H(3)	0.22	0.18	0.20	0.17
H(4)	0.18	–	0.19	–
		Bond orders		
Pb(1)–Pb(2)	0.02	0.02	0.02	0.02
Pb(2)–Pb(3)	0.03	0.02	0.03	0.02
Pb(1)–O(1)	0.62 (2 ×)	0.51 (2 ×)	0.56 (2 ×)	0.55 (2 ×)
Pb(2)–O(1)	0.61 (2 ×)	0.35 (2 ×)	0.57 (2 ×)	0.42 (2 ×)
Pb(2)–O(2)	0.52	0.54 (2 ×)	0.61	0.50 (2 ×)
Pb(3)–O(2)	0.48	0.76 (2 ×)	0.49	0.66 (2 ×)
Pb(1)–O(3)	1.02	0.87	0.89	0.86
Pb(3)–O(4)	0.86	–	0.90	–
O(1)–H(1)	0.93 (2 ×)	0.94 (2 ×)	0.93 (2 ×)	0.93 (2 ×)
O(2)–H(2)	0.92	0.92 (2 ×)	0.92	0.94 (2 ×)
O(3)–H(3)	0.92	0.95	0.94	0.95
O(4)–H(4)	0.86	–	0.95	–

creasing size of the model systems. The above mentioned differences may indicate the possibility of verification of our results by electrochemical experiments.

Finally, it may be concluded that the most probable trilead(II) complexes in aqueous solutions correspond to *cyclo*-$(\mu_3\text{-OH})(\mu_2\text{-OH})_3\text{Pb}_3^{2+}$, $\text{Pb}(\mu\text{-OH})_2\text{Pb}(\mu\text{-OH})_2\text{Pb}^{2+}$, *cyclo*-$(\mu_3\text{-OH})_2(\mu_2\text{-OH})_3\text{Pb}_3^{+}$, $\text{Pb(OH)}(\mu\text{-OH})_2\text{Pb}(\mu\text{-OH})\text{Pb(OH)}^{+}$, and $\text{Pb(OH)}(\mu\text{-OH})_2\text{Pb}(\mu\text{-OH})_2\text{Pb}^{+}$ systems. The key role of configuration of OH bridges on the stability of individual isomers is explained.

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