

ON THE STABILITY OF HYDROXO–DILEAD(II) COMPLEX CATIONS

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Dedicated to Professor Rudolf Zahradník on the occasion of his 75th birthday.

Using Hartree–Fock, B3LYP and MP2 treatments, the optimal geometries and corresponding electronic structures of various isomers of $[\text{Pb}_2(\text{OH})_n]^q$ complex cations with total charges $q = 4 - n$, $n = 1, 2, 3$, are investigated. $[\text{Pb}(\mu\text{-OH})\text{Pb}]^{3+}$ seems to be the most stable whereas $[\text{Pb}(\mu\text{-OH})\text{Pb}(\text{OH})]^{2+}$ and $[\text{Pb}(\mu\text{-OH})\text{Pb}(\text{OH})_2]^+$ are unstable (because additional non-bridging hydroxyl weakens the neighboring $\text{Pb}-\text{O}_\mu$ and $\text{O}_\mu-\text{H}_\mu$ bonds). Direct $\text{Pb}-\text{Pb}$ and $\text{O}_\mu-\text{O}_\mu$ interactions are weakly antibonding in all the systems under study. The clusters are held together exclusively by relatively weak $\text{Pb}-\text{O}$ bonds. Non-measurable concentrations of $[\text{Pb}(\mu\text{-OH})\text{Pb}]^{3+}$ in aqueous solutions might be explained by its reaction with OH^- yielding preferably unstable $[\text{Pb}(\mu\text{-OH})\text{Pb}(\text{OH})]^{2+}$ species.

Keywords: Lead(II) clusters; Hydroxo complexes; Molecular structure; Geometry optimization; *Ab initio* calculations; HF; DFT.

The structure and bonding characterization of lead compounds in aqueous systems is important for understanding the mechanism of lead transport in natural systems. Precise potentiometric titration data¹ on the hydrolysis of lead(II) in perchlorate and nitrate solutions over a broad concentration and pH range indicate significant formation of $[\text{Pb}(\text{OH})]^+$, $[\text{Pb}_3(\text{OH})_4]^{2+}$, $[\text{Pb}_3(\text{OH})_5]^+$, $[\text{Pb}_4(\text{OH})_4]^{4+}$ and $[\text{Pb}_6(\text{OH})_8]^{4+}$ species. The previously assumed^{1b-1e} existence of $[\text{Pb}_2(\text{OH})]^{3+}$ has not been confirmed in later studies^{1f,1g}.

Dilead structural units in lead halide and hydroxo/oxo molecules, clusters and extended structures found in molten salts, aqueous solutions and the solid state have been studied by various methods including very simple quantum-chemical modeling². It has been concluded that the $[\text{Pb}_2(\text{OH})_2]^{2+}$ clusters are stabilized by partial $\text{Pb}-\text{Pb}$ bonding induced by bridging hydroxide ions. The strongest $\text{Pb}-\text{Pb}$ bonds have been deduced in complexes with predominantly ionic lead–anion interactions. Larger lead hydroxo/oxo

clusters in aqueous solutions also seem to be stabilized by partial Pb–Pb bonding but the structures of hydroxo/oxo clusters isolated in the solid state are dominated by Pb–O bonding. The existence of long Pb–Pb contacts only is explained by lack of stabilizing ionic medium². The concept of direct Pb–Pb bonding is also used in chemistry textbooks³.

On the other hand, semiempirical quantum-chemical studies⁴ of possible structures of trinuclear, tetranuclear and hexanuclear lead(II) hydroxo complexes indicate 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 OH bridges. There is only one *ab initio* MP2 study on such systems but this is restricted to the structure and vibrational spectra of $[\text{Pb}_4(\text{OH})_4]^{4+}$ clusters⁵.

The aim of this study is the *ab initio* investigation of stable geometries and corresponding electronic structures of possible dilead(II) clusters with hydroxyl bridges. This might be helpful for explanation of their absence in aqueous solutions.

CALCULATIONS

Using Gaussian 94 program package⁶, the optimal geometries of $[\text{Pb}_2(\mu\text{-OH})_n]^q$ with total charges $q = 4 - n$, $n = 1-4$, are investigated within standard restricted Hartree–Fock, B3LYP and MP2 treatments^{7,8} using standard accuracy parameters. Dunning's correlation consistent cc-pVDZ basis sets have been used for O and H atoms⁹ whereas LANL2DZ effective core potential and (3s,4p,1d)/[2s,3p,1d] basis set^{10,11} with diffuse and polarization functions^{11,12} have been used for Pb atoms. Electron structure parameters have been evaluated in terms of Mulliken population analysis (gross atomic charges, overlap populations).

RESULTS AND DISCUSSION

Lead atoms in $[\text{Pb}_2(\text{OH})_n]^q$ complex cations may be, in principle, linked by:

1. single $\mu\text{-OH}$ bridge like in $[\text{Pb}(\mu\text{-OH})\text{Pb}]^{3+}$, $[\text{Pb}(\mu\text{-OH})\text{Pb}(\text{OH})]^{2+}$, $[\text{Pb}(\mu\text{-OH})\text{Pb}(\text{OH})_2]^+$ and $[(\text{HO})\text{Pb}(\mu\text{-OH})\text{Pb}(\text{OH})]^+$,
2. two $\mu\text{-OH}$ bridges like in $[\text{Pb}(\mu\text{-OH})_2\text{Pb}]^{2+}$ and $[\text{Pb}(\mu\text{-OH})_2\text{Pb}(\text{OH})]^+$,
3. three $\mu\text{-OH}$ bridges like in $[\text{Pb}(\mu\text{-OH})_3\text{Pb}]^+$.

According to our results, $[\text{Pb}(\mu\text{-OH})\text{Pb}(\text{OH})]^{2+}$ and $[\text{Pb}(\mu\text{-OH})\text{Pb}(\text{OH})_2]^+$ are unstable (possible reasons will be discussed later). The total energies, structures and selected electronic parameters of the remaining stable complex cations are described in Tables I–III and Figs 1–5. The energy trend observed

TABLE I
Selected characteristics of dilead systems with a single hydroxyl bridge (subscript μ denotes bridging OH atoms, see Figs 1, 2)

Characteristics	[Pb(μ -OH)Pb] ³⁺			[(HO)Pb(μ -OH)Pb(OH)] ⁺		
	HF	B3LYP	MP2	HF	B3LYP	MP2
E_{tot} , a.u.	-81.05502	-81.60672	-81.31718	-232.93362	-234.31330	-233.62947
Distance ($\times 10^{-10}$ m)						
Pb-O $_{\mu}$	2.289	2.313	2.298	2.214	2.234	2.232
Pb-O	-	-	-	1.929	1.961	1.972
Pb-Pb	4.461	4.494	4.485	4.208	4.210	4.195
O $_{\mu}$ -H $_{\mu}$	0.963	0.984	0.988	0.954	0.976	0.976
O-H	-	-	-	0.946	0.968	0.969
Angles, °						
Pb-O $_{\mu}$ -Pb	154.1	152.6	154.8	143.7	140.9	140.0
Pb-O $_{\mu}$ -H $_{\mu}$	103.0	103.6	102.6	108.2	109.5	110.0
Pb-O-H	-	-	-	145.7	137.2	130.6
O-Pb-O $_{\mu}$	-	-	-	92.9	95.9	96.0
Charge						
Pb	1.474	1.688	1.679	1.332	1.064	1.100
O $_{\mu}$	-0.778	-0.799	-0.639	-0.805	-0.609	-0.661
O	-	-	-	-0.739	-0.546	-0.568
H $_{\mu}$	0.283	0.423	0.282	0.229	0.207	0.210
H	-	-	-	0.195	0.183	0.193
Bond order						
Pb-O $_{\mu}$	0.078	0.070	0.107	0.068	0.097	0.091
Pb-O	-	-	-	0.206	0.246	0.252
Pb-Pb	-0.030	-0.041	-0.030	-0.010	-0.016	-0.011
O $_{\mu}$ -H $_{\mu}$	0.344	0.306	0.315	0.444	0.311	0.301
O-H	-	-	-	0.364	0.339	0.329

TABLE II
 Selected characteristics of dilead systems with two hydroxyl bridges (subscript μ denotes bridging OH atoms, see Figs 3, 4)

Characteristics	[Pb(μ -OH) $_2$ Pb] $^{2+}$			[Pb(μ -OH) $_2$ Pb(OH)] $^+$		
	HF	B3LYP	MP2	HF	B3LYP	MP2
E_{tot} , a.u.	-157.13996	-158.13176	-157.62059	-232.91730	-234.30370	-233.61809
Distance ($\times 10^{-10}$ m)						
Pb-O $_{\mu}$	2.176	2.194	2.192	2.724/2.047	2.643/2.076	2.645/2.078
Pb-O	-	-	-	1.947	1.975	1.972
Pb-Pb	3.591	3.600	3.615	3.917	3.849	3.864
O $_{\mu}$ -H $_{\mu}$	0.957	0.976	0.979	0.950	0.972	0.972
O-H	-	-	-	0.945	0.967	0.966
O $_{\mu}$ -O $_{\mu}$	2.459	2.507	2.479	2.684	2.702	2.687
Angle, $^{\circ}$						
Pb-O $_{\mu}$ -Pb	111.2	110.3	111.1	109.5	108.7	109.2
O $_{\mu}$ -Pb-O $_{\mu}$	68.8	69.7	68.9	59.0/81.9	61.5/81.1	61.1/80.6
O-Pb-O $_{\mu}$	-	-	-	150.5	149.3	149.5
Pb-O $_{\mu}$ -H $_{\mu}$	124.4	124.9	124.4	129.7/120.8	131.8/119.5	133.3/117.5
Pb-O-H	-	-	-	180.0	180.0	180.0
Charge						
Pb	1.526	1.412	1.389	1.375/1.287	1.077/1.053	1.132/1.086
O $_{\mu}$	-0.796	-0.820	-0.657	-0.762	-0.584	-0.626
O	-	-	-	-0.733	-0.524	-0.560
H $_{\mu}$	0.271	0.407	0.268	0.202	0.195	0.202
H	-	-	-	0.189	0.172	0.189
Bond order						
Pb-O $_{\mu}$	0.080	0.074	0.108	0.005/0.154	0.029/0.177	0.020/0.180
Pb-O	-	-	-	0.148	0.192	0.198
Pb-Pb	-0.039	-0.063	-0.040	-0.025	-0.038	-0.027
O $_{\mu}$ -H $_{\mu}$	0.358	0.319	0.330	0.351	0.330	0.319
O-H	-	-	-	0.361	0.335	0.330
O $_{\mu}$ -O $_{\mu}$	-0.032	-0.042	-0.029	-0.014	-0.012	-0.013

TABLE III
Selected characteristics of $[\text{Pb}_2(\mu\text{-OH})_3]^+$ (subscript μ denotes bridging OH atoms, see Fig. 5)

Characteristics	$[\text{Pb}_2(\mu\text{-OH})_3]^+$		
	HF	B3LYP	MP2
E_{tot} , a.u.	-232.99831	-234.42240	-233.69292
Distance ($\times 10^{-10}$ m)			
Pb-O $_{\mu}$	2.181	2.200	2.198
Pb-Pb	3.210	3.226	3.238
O $_{\mu}$ -H $_{\mu}$	0.949	0.967	0.969
O $_{\mu}$ -O $_{\mu}$	2.557	2.592	2.574
Angle, $^{\circ}$			
Pb-O $_{\mu}$ -Pb	94.8	94.3	94.9
O $_{\mu}$ -Pb-O $_{\mu}$	71.8	72.2	71.7
Pb-O $_{\mu}$ -H $_{\mu}$	132.6	132.8	132.5
Charge			
Pb	1.340	1.184	1.143
O $_{\mu}$	-0.782	-0.810	-0.647
H $_{\mu}$	0.222	0.354	0.218
Bond order			
Pb-O $_{\mu}$	0.088	0.088	0.113
Pb-Pb	-0.034	-0.060	-0.044
O $_{\mu}$ -H $_{\mu}$	0.365	0.323	0.335
O $_{\mu}$ -O $_{\mu}$	-0.030	-0.044	-0.028

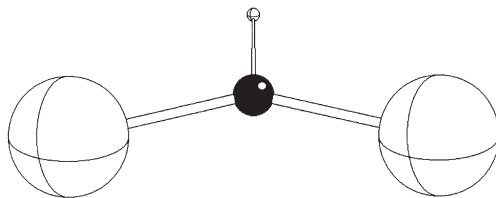


FIG. 1
Structure of $[\text{Pb}(\mu\text{-OH})\text{Pb}]^{3+}$

in the series $[\text{Pb}(\mu\text{-OH})_3\text{Pb}]^+ < [(\text{HO})\text{Pb}(\mu\text{-OH})\text{Pb}(\text{OH})]^+ < [\text{Pb}(\mu\text{-OH})_2\text{Pb}(\text{OH})]^+$ is not in full agreement with the conclusion of semiempirical quantum-chemical studies^{4a-4c} on trilead(II) and tetralead(II) hydroxo complexes that stability of individual isomers increases with the number of OH bridges. (Nevertheless, the triple bridge corresponds to the most stable system.) Our

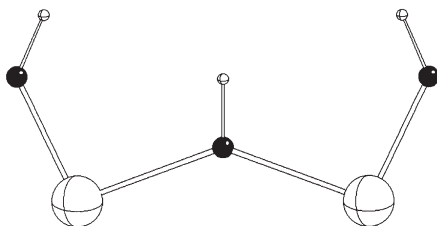


FIG. 2
Structure of $[(\text{HO})\text{Pb}(\mu\text{-OH})\text{Pb}(\text{OH})]^+$

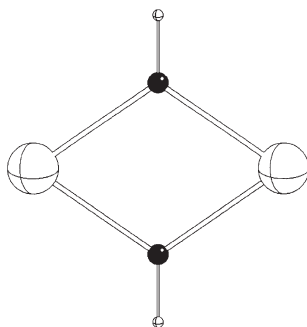


FIG. 3
Structure of $[\text{Pb}(\mu\text{-OH})_2\text{Pb}]^{2+}$

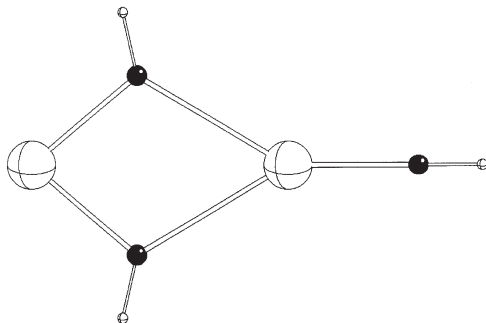


FIG. 4
Structure of $[\text{Pb}(\mu\text{-OH})_2\text{Pb}(\text{OH})]^+$

results indicate that the energy effect of OH^- addition to $[\text{Pb}_2(\text{OH})_n]^q$ decreases with increasing n . Despite being a rough approximation, the comparison of $[\text{Pb}_2(\text{OH})_n]^q$ total energies with those of OH^- within the same basis sets (-75.330856 , -75.72143 and -75.525658 a.u. at Hartree-Fock, B3LYP and MP2 levels, respectively) indicates that $[\text{Pb}(\mu\text{-OH})\text{Pb}]^{3+}$ is the most stable (its existence has been assumed in some studies^{1b-1e}). This statement is supported by the expected higher stabilizing solvent effects of cations with higher charges in polar solvents.

The optimum geometries of $[\text{Pb}_2(\mu\text{-OH})_n]^q$ clusters correspond to the highest possible C_{2v} ($[\text{Pb}(\mu\text{-OH})\text{Pb}]^{3+}$, $[(\text{HO})\text{Pb}(\mu\text{-OH})\text{Pb}(\text{OH})]^+$ and $[\text{Pb}(\mu\text{-OH})_2\text{Pb}(\text{OH})]^+$), D_{2h} ($[\text{Pb}(\mu\text{-OH})_2\text{Pb}]^{2+}$) or D_{3h} ($[\text{Pb}(\mu\text{-OH})_3\text{Pb}]^+$) symmetry point groups. The bridging hydroxide groups are coplanar with both Pb atoms in all the systems under study.

Bridging hydroxyls are more polar than the non-bridging ones, which is associated with weaker and longer $\text{O}_\mu\text{-H}_\mu$ bonds. An additional non-bridging hydroxyl weakens the neighboring Pb-O_μ and $\text{O}_\mu\text{-H}_\mu$ bonds (especially in less symmetric systems like $[\text{Pb}(\mu\text{-OH})_2\text{Pb}(\text{OH})]^+$). This implies the instability of single-bridged $[\text{Pb}(\mu\text{-OH})\text{Pb}(\text{OH})]^{2+}$ and $[\text{Pb}(\mu\text{-OH})\text{Pb}(\text{OH})_2]^+$ systems (the weakened single bridge is not strong enough to overcome the Pb-Pb repulsion).

The Pb-Pb, $\text{O}_\mu\text{-H}_\mu$ and $\text{O}_\mu\text{-O}_\mu$ distances as well as the $\text{Pb-O}_\mu\text{-Pb}$ and $\text{O}_\mu\text{-Pb-O}_\mu$ angles decrease with increasing number of hydroxyl bridges – similarly to the total cation charge. It implies the reverse trend also in $\text{Pb-O}_\mu\text{-H}_\mu$ angles.

Pb-O_μ bonds are significantly weaker than the O-H ones (in particular non-bridging). The decrease in Pb and H_μ positive charges with the number of hydroxyl bridges may be explained by decreasing positive total charge of

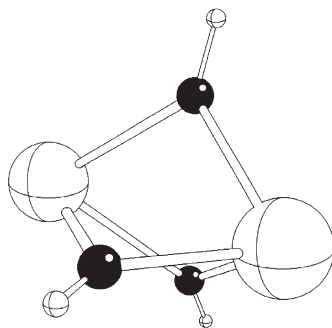


FIG. 5
Structure of $[\text{Pb}_2(\mu\text{-OH})_3]^+$

the systems under study. No such trend is observed for negative-charged O_{μ} atoms. The number of hydroxyl bridges has only a small influence on $Pb-O_{\mu}$ bond strengths in comparison with the influence of the number and symmetry of non-bridging hydroxyls. The character of $Pb-Pb$ and $O_{\mu}-O_{\mu}$ interactions is (weakly) antibonding. Thus they cannot stabilize the cluster as assumed in literature^{2,3}.

Hartree-Fock, B3LYP and MP2 treatments exhibit similar trends. Nevertheless, more sophisticated models of the solvent effect are desirable for our studies but these do not work properly under Gaussian 94 (ref.⁶) for our systems due to the effective core potentials use.

Finally it may be concluded that the highest stability of the $[Pb(\mu-OH)Pb]^{3+}$ cluster is in contradiction with the stabilizing role of a higher number of hydroxyl bridges in multinuclear lead(II) complexes⁴. This might be explained by repulsive $Pb-Pb$ and $O_{\mu}-O_{\mu}$ interactions (compare significantly longer $Pb-Pb$ distance in the single-bridged system than in the others). Non-measurable concentration of $[Pb(\mu-OH)Pb]^{3+}$ in aqueous solutions might be explained by a higher rate of the reaction (1)



which is significantly shifted to the right side due to the unstable product compared with the reaction (2)



which is shifted to the left side (*cf.* the above mentioned energy data). Nevertheless, more detailed experimental as well as theoretical studies in this field are desirable.

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