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On the structure of lead(II) complexes in aqueous solutions. Part IV. Binuclear clusters

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In the memory of Prof. Peter Pelikán (1939–2002)

Abstract

Optimal geometries and corresponding electronic structures of $[Pb_2(\mu\text{-}OH)_n]^q$ and of their hydrated $[Pb_2(\mu\text{-}OH)_n(H_2O)_2]^q$ analogues with total charges $q = 4 - n$, $n = 1 \rightarrow 4$, are investigated within Hartree-Fock, B3LYP and MP2 treatments. Direct Pb–Pb and O–O interactions are weakly antibonding in all the systems under study. The clusters are held together exclusively by Pb–O bonds that are approximately 2–4 times stronger than $Pb-OH_2$ interactions of van der Waals type.

Keywords: Lead(II) clusters; Hydroxo-complexes; Molecular structures; Geometry optimizations

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1. Introduction

Lead compounds in aqueous systems play an important role in many environmental problems. Their structural characterization 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].

Based on the study of dilead structure units in lead halide and hydroxo/oxo species, clusters and extended structures found in molten salts, aqueous solutions and the solid state, it has been assumed [8] 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. Such a conception is used in chemistry textbooks [9] too.

Semiempirical quantum-chemical studies [10–13] of possible structures of trinuclear, tetranuclear and hexanuclear lead(II) hydroxo-complexes and of their hydrated analogues 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. Inclusion of additional H_2O molecules into the model system may significantly influence the relative stability of the systems even through the H_2O ligands do not serve as bridges. There is only one ab initio MP2 study on such systems but this is restricted do the structure and vibrational spectra of $Pb_4(OH)_4^{4+}$ clusters [14].

The aim of this study is ab initio investigation of possible structures of binuclear Pb clusters with hydroxyl bridges as well as of their bonding. This might help to explain why these clusters are not observed experimentally.

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2. Experimental

2.1. Method

Using GAUSSIAN-94 program package [15], the optimal geometries of $[Pb_2(\mu\text{-}OH)_n]^q$ (Figs. 1–4) and of their hydrated $[Pb_2(\mu\text{-}OH)_n(H_2O)_2]^q$ analogues with total charges $q = 4-n$, $n = 1 \rightarrow 4$, are investigated within standard restricted Hartree-Fock, B3LYP [16] and MP2 [17] treatments using standard accuracy parameters. Dunning's correlation consistent cc-pVDZ basis sets have been used for O and H atoms [18] whereas LANL2DZ effective core potential and (3s,4p,1d)/[2s,3p,1d] basis set [19,20] with diffuse and polarization functions [20,21] have been used for Pb atoms. Electron structure parameters have been evaluated in terms of Mulliken population analysis (gross atomic charges, overlap populations).

3. Results and discussion

According to our results (Tables 1–4), the energy effect of OH^- addition decreases with increasing n more rapidly in $[Pb_2(\mu\text{-}OH)_n]^q$ clusters than in their hydrated analogs. The comparison with OH^- total energy (−75.330856, −75.72143 and −75.525658 a.u. at Hartree-Fock, B3LYP and MP2 level, respectively) might indicate decreasing exothermic effect of the hydroxylation but it is very rough approximation. Accounting for solvent effects (being higher in cations with higher charges) as well as (in lower extent) for relativistic effects should significantly influence the relative stability of the systems under study.

The optimum geometries of $[Pb_2(\mu\text{-}OH)_n]^q$ clusters correspond to the highest possible C_{2v} ($n = 1$) or D_{nh} ($n = 2, 3, 4$) symmetry point groups. This skeleton symmetry (except C_{2v}) is lowered by hydration (each H_2O molecule being end-coordinated to only one of the lead atoms) but the hydroxyl groups remain coplanar with both Pb atoms in all the systems under study. The Pb–Pb, O–H and (neighboring) O–O distances as well as of Pb–O–Pb and O–Pb–O angles decrease with increasing number of OH bridges similarly as total cluster charge. It implies the reverse trend in Pb–O–H angles, too. However, any such trend is observed for the distances between Pb and neither hydroxyl O atoms nor aqueous O(aq) atoms. Hydration lengthens the Pb–O bonds (except the single-bridged systems) which depend on H_2O orientation, too. Despite the hydration influ-

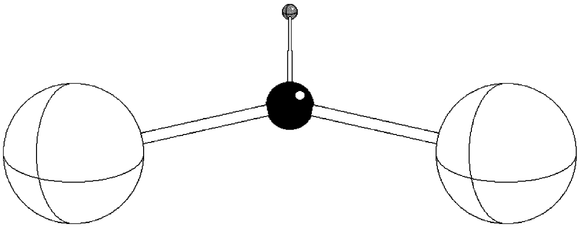
Fig. 1. Structure of $[Pb_2(\mu\text{-}OH)]^{3+}$.

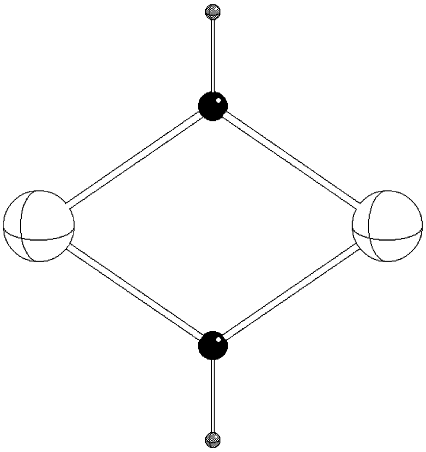
Fig. 2. Structure of $[Pb_2(\mu\text{-}OH)_2]^{2+}$.

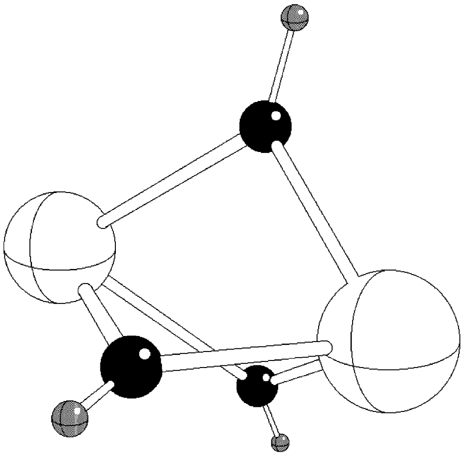
Fig. 3. Structure of $[Pb_2(\mu\text{-}OH)_3]^{+}$.

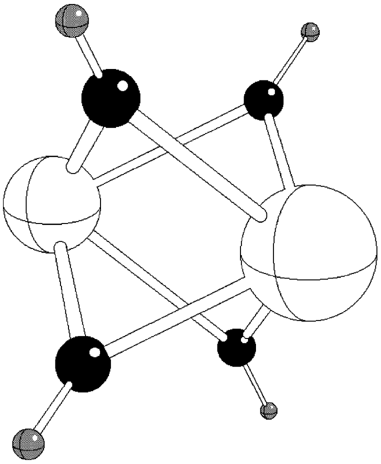
Fig. 4. Structure of $[Pb_2(\mu\text{-}OH)_4]$.

Table 1
Selected characteristics of dilead systems with a single hydroxyl bridge (Fig. 1)

System	$[Pb_2OH]^{3+}$			$[Pb_2(OH)(H_2O)_2]^{3+}$		
Method	HF	B3LYP	MP2	HF	B3LYP	MP2
E_{tot} [a.u.]	−81.05502	−81.60672	−81.31718	−233.27450	−234.62330	−233.95520
Distances [10^{-10} m]						
Pb–O	2.289	2.313	2.298	2.268	2.284	2.274
Pb–O(aq)	–	–	–	2.347	2.992	2.335
Pb–Pb	4.461	4.494	4.485	4.352	4.371	4.370
O–H	0.963	0.984	0.988	0.960	0.983	0.984
Angles [°]						
Pb–O–Pb	154.1	152.6	154.8	147.3	146.3	147.9
Pb–O–H	103.0	103.7	102.6	106.3	106.8	106.1
Charges						
Pb	1.474	1.688	1.679	1.591	1.409	1.475
O	−0.778	−0.799	−0.639	−0.791	−0.597	−0.650
H	0.283	0.423	0.282	0.267	0.257	0.260
Bond orders						
Pb–O	0.078	0.070	0.107	0.076	0.109	0.105
Pb–O(aq)	–	–	–	0.044	0.084	0.069
Pb–Pb	−0.030	−0.041	−0.030	−0.022	−0.027	−0.021
O–H	0.344	0.306	0.315	0.344	0.324	0.313

ence on bond angles (except the single-bridged system with significantly decreased Pb–O–Pb angle) is very small, increased Pb–O–Pb angles in the H_2O plane may be observed. Nevertheless, the effects of the hydration in other positions could be much stronger.

Pb–O bonds are weak, their strength (overlap population 0.08–0.12) is comparable with Pb–O(aq) bonds of van der Waals type (0.03–0.08) rather than with the O–H ones (0.31–0.36). The decrease of Pb and H positive charges as well as of Pb–O(aq) interaction

Table 2
Selected characteristics of dilead systems with two hydroxyl bridges (Fig. 2)

System	$[Pb_2(OH)_2]^{2+}$			$[Pb_2(OH)_2(H_2O)_2]^{2+}$		
Method	HF	B3LYP	MP2	HF	B3LYP	MP2
E_{tot} [a.u.]	−157.13996	−158.13176	−157.62059	−309.25652	−311.01843	−310.15037
Distances [10^{-10} m]						
Pb–O	2.176	2.194	2.192	2.200	2.221	2.217
Pb–O(aq)	–	–	–	2.880	2.718	2.765
Pb–Pb	3.591	3.600	3.615	3.623	3.631	3.644
O–H	0.957	0.976	0.979	0.955	0.976	0.976
O–O	2.459	2.507	2.479	2.499	2.558	2.525
Angles [°]						
Pb–O–Pb	111.2	110.3	111.1	110.8	109.7	110.6
O–Pb–O	68.8	69.7	68.9	69.2	70.3	69.4
Pb–O–H	124.4	124.9	124.4	124.6	125.2	124.7
Charges						
Pb	1.526	1.412	1.389	1.476	1.234	1.309
O	−0.796	−0.820	−0.657	−0.796	−0.603	−0.656
H	0.271	0.407	0.268	0.252	0.237	0.247
Bond orders						
Pb–O	0.080	0.074	0.108	0.068	0.098	0.096
Pb–O(aq)	–	–	–	0.025	0.052	0.036
Pb–Pb	−0.039	−0.063	−0.040	−0.067	−0.089	−0.067
O–H	0.358	0.319	0.330	0.355	0.337	0.325
O–O	−0.032	−0.042	−0.029	−0.025	−0.018	−0.021

Table 3
Selected characteristics of dilead systems with three hydroxyl bridges (Fig. 3)

System	$[Pb_2(OH)_3]^+$			$[Pb_2(OH)_3(H_2O)_2]^+$		
Method	HF	B3LYP	MP2	HF	B3LYP	MP2
E_{tot} [a.u.]	−232.99831	−234.42240	−233.69292	−385.07642	−387.26475	−386.20268
Distances $[10^{-10}$ m]						
Pb–O	2.181	2.200	2.198	2.183 2.203(2 ×)	2.198 2.232(2 ×)	2.195 2.231(2 ×)
Pb–O(aq)	–	–	–	3.371	2.778	2.792
Pb–Pb	3.210	3.226	3.238	3.227	3.231	3.236
O–H	0.949	0.967	0.969	0.948	0.968 0.973(2 ×)	0.967 0.974(2 ×)
O–O	2.557	2.592	2.574	2.555(2 ×) 2.634	2.600(2 ×) 2.720	2.597(2 ×) 2.715
Angles [°]						
Pb–O–Pb	94.8	94.3	94.9	95.3 94.2(2 ×)	94.6 92.7(2 ×)	94.7 92.7(2 ×)
O–Pb–O	71.8	72.2	71.7	71.2(2 ×) 73.4	71.8(2 ×) 75.1	71.8(2 ×) 74.9
Pb–O–H	132.6	132.8	132.5	132.3 130.2(2 ×)	132.7 114.0(2 ×)	111.9 132.6(2 ×)
Charges						
Pb	1.340	1.184	1.143	1.314	0.992	1.062
O	−0.782	−0.810	−0.647	−0.785 −0.776(2 ×)	−0.610 −0.574(2 ×)	−0.666 −0.612(2 ×)
H	0.222	0.354	0.218	0.216 0.210(2 ×)	0.197 0.182(2 ×)	0.211 0.191(2 ×)
Bond orders						
Pb–O	0.088	0.088	0.113	0.081 0.082(2 ×)	0.108 0.123(2 ×)	0.103 0.122(2 ×)
Pb–O(aq)	–	–	–	0.023	0.037	0.026
Pb–Pb	−0.034	−0.060	−0.044	−0.060	−0.053	−0.038
O–H	0.365	0.323	0.335	0.364 0.359(2 ×)	0.345 0.321(2 ×)	0.334 0.510(2 ×)
O–O	−0.030	−0.044	−0.028	−0.026(2 ×) −0.027	−0.020(2 ×) −0.026	−0.021(2 ×) −0.028

with the number of OH^- bridges may be explained by decreasing positive total charge of the systems under study. No such trend is observed for negative-charged O atoms. The number of bridges has only small influence on bond strengths. The character of Pb–Pb and (neighboring) O–O interactions is (weakly) antibonding. Thus they cannot stabilize the cluster as supposed in [8,9]. Hydration diminishes Pb charges but its influence on other electronic structure characteristics is very small (except B3LYP data).

Hartree-Fock and MP2 treatments exhibit the same trends but the B3LYP one differs in some characteristics, especially in electronic structure of hydrated systems (such as overestimated Pb–H_2O electron transfer). More sophisticated models of solvent effect are desirable for our studies but they do not work properly under GAUSSIAN-94 [15] for our systems (probably due to effective core potential use).

Finally it may be concluded that the non-measurable concentration of binuclear Pb clusters with hydroxyl bridges in aqueous solutions might be explained by their high reactivity. Insufficient accounting for solvent and relativistic effects in our study decreases the accuracy of our results on the relative stability of our systems as well as (in lower extent) on their geometries and bonding. Nevertheless, the qualitative conclusions could be correct. More detailed experimental as well as theoretical studies in this field are necessary.

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Table 4
Selected characteristics of dilead systems with four hydroxyl bridges (Fig. 4)

System	$[Pb_2(OH)_4]$			$[Pb_2(OH)_4(H_2O)_2]$		
Method	HF	B3LYP	MP2	HF	B3LYP	MP2
E_{tot} [a.u.]	−308.54364	−310.40719	−309.45400	−460.60115	−463.18798	−461.91773
Distances $[10^{-10}$ m]						
Pb–O	2.270	2.298	2.283	2.279	2.301	2.293
				2.282	2.305	2.296
Pb–O(aq)	–	–	–	3.982	3.507	3.652
Pb–Pb	2.973	3.006	3.003	2.984	3.021	3.016
O–H	0.944	0.963	0.964	0.944	0.965	0.963
O–O opposing	3.431	3.476	3.439	3.444	3.471	3.454
O–O neighboring	2.426	2.458	2.432	2.438	2.458	2.446
Angles [°]						
Pb–O–Pb	81.8	81.7	82.3	81.8	82.1	82.3
				81.7	81.9	82.1
O–Pb–O opposing	98.2	98.3	97.7	98.2	97.9	97.7
				98.3	98.1	97.9
O–Pb–O neighboring	64.6	64.7	64.4	64.6	64.5	64.4
Pb–O–H	139.1	139.2	138.9	139.1	139.0	138.9
				139.2	139.1	139.0
Charges						
Pb	1.184	0.991	0.943	1.178	0.832	0.928
O	−0.754	−0.785	−0.627	−0.755	−0.572	−0.630
H	0.161	0.290	0.156	0.157	0.134	0.150
				0.156	0.133	0.149
Bond orders						
Pb–O	0.091	0.090	0.110	0.086	0.108	0.105
Pb–O(aq)	–	–	–	0.017	0.036	0.026
Pb–Pb	−0.049	−0.072	−0.075	−0.060	−0.121	−0.089
O–H	0.362	0.317	0.328	0.362	0.332	0.325
O–O neighboring	−0.050	−0.068	−0.048	−0.047	−0.040	−0.045

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