

**ON THE RELIABILITY OF THE STRUCTURES OF LEAD(II) HYDROXO COMPLEXES OBTAINED BY MNDO METHOD**Martin BREZA<sup>a,\*</sup> and Alena MANOVÁ<sup>b</sup><sup>a</sup> Department of Physical Chemistry, Slovak Technical University, SK-812 37 Bratislava, Slovak Republic; e-mail: breza@cvtstu.cvt.stuba.sk<sup>b</sup> Department of Analytical Chemistry, Slovak Technical University, SK-812 37 Bratislava, Slovak Republic; e-mail: manova@chelin.chtf.stuba.sk

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Optimum geometry of *tetrahedro*-Pb<sub>4</sub>[(μ<sub>3</sub>-OH)<sub>4</sub>]<sup>4+</sup> cluster obtained by the semiempirical MNDO method corresponds to T<sub>d</sub> symmetry. The calculated Pb-Pb (3.70 · 10<sup>-10</sup> m) and Pb-O (2.33 · 10<sup>-10</sup> m) distances are in reasonable agreement with experimental X-ray data. Additional H<sub>2</sub>O inclusion makes the agreement worse.

**Key words:** Lead(II) clusters; Hydroxo complexes; Molecular structure; MNDO calculations; Semiempirical calculations.

Precise potentiometric titration data<sup>1,2</sup> on the hydrolysis of lead(II) indicate the significant formation of the species [Pb(OH)]<sup>+</sup>, [Pb<sub>3</sub>(OH)<sub>4</sub>]<sup>2+</sup>, [Pb<sub>3</sub>(OH)<sub>5</sub>]<sup>+</sup>, [Pb<sub>4</sub>(OH)<sub>4</sub>]<sup>4+</sup> and [Pb<sub>6</sub>(OH)<sub>8</sub>]<sup>4+</sup>. Our previous quantum-chemical study by MNDO method on possible structures of trinuclear lead(II) hydroxo complexes and of their hydrated analogues<sup>3</sup> 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<sub>3</sub>-OH and μ<sub>2</sub>-OH bridges. However, their stabilization mechanisms are contradictory. Inclusion of additional H<sub>2</sub>O molecules into the model system may significantly influence the relative stability of the systems despite the H<sub>2</sub>O ligands do not serve as bridges.

Unfortunately, the second part of this series concerning all the possible structures of tetranuclear lead(II) hydroxo complexes and of their tetrahydrated analogues had to be published elsewhere<sup>4</sup> because one of the referees doubted of the reliability of the semiempirical MNDO method used. Fortunately, there are some X-ray structure data on [Pb<sub>4</sub>(OH)<sub>4</sub>]<sup>4+</sup> species that make it possible to verify the MNDO results and this is the aim of our study.

The hexagonal crystals of  $[\text{Pb}_4(\text{OH})_4]_3(\text{CO}_3)(\text{ClO}_4)_{10} \cdot 6 \text{H}_2\text{O}$  (**A**), space group  $P6_3/m$ , contain two formula units in the unit cell<sup>5</sup>. The monoclinic crystals of  $[\text{Pb}_4(\text{OH})_4](\text{ClO}_4)_4 \cdot 2 \text{H}_2\text{O}$  (**B**), space group  $P2_1/c$ , contain four formula units in the unit cell<sup>6</sup>. The lead atoms and the hydroxide groups form  $[\text{Pb}_4(\text{OH})_4]^{4+}$  units in both the compounds (Fig. 1). The lead atoms are at the vertices of a slightly distorted tetrahedron and the hydroxide oxygens are outside the faces of this tetrahedron. The metal atoms are thus linked by double hydroxide bridges. The oxygen atoms form another, slightly distorted, tetrahedron. The two tetrahedra are positioned with respect to each other in such a way, that the lead and oxygen atoms are at the alternate vertices of a distorted cube.

The interatomic distances vary more in **A** than in **B**. In **A** the Pb–Pb distances range between  $3.76 \cdot 10^{-10}$  and  $3.85 \cdot 10^{-10}$  m, and in **B** between  $3.72 \cdot 10^{-10}$  and  $3.95 \cdot 10^{-10}$  m. The mean values are almost the same (Table I).  $[\text{Pb}_4(\text{OH})_4]^{4+}$  group possesses a plane of symmetry in **A**. This plane is almost retained by the  $\text{Pb}_4$  tetrahedron in **B** but is lost when the hydroxide oxygens are added. The Pb–O distances vary between  $2.29 \cdot 10^{-10}$  and  $2.49 \cdot 10^{-10}$  m in **A**, and  $2.34 \cdot 10^{-10}$  and  $2.54 \cdot 10^{-10}$  m in **B**. If the two groups are compared so as to minimize the differences between Pb–Pb distances, the greatest difference in a Pb–O link becomes  $0.18 \cdot 10^{-10}$  m and the mean difference  $0.07 \cdot 10^{-10}$  m.

The  $[\text{Pb}_4(\text{OH})_4]^{4+}$  units definitely occur as discrete groups since the shortest distance between a metal atom and hydroxide oxygen in an adjacent unit is  $4.51 \cdot 10^{-10}$  m in **A** and  $4.88 \cdot 10^{-10}$  m in **B**. The shortest interunit metal–metal distance is  $4.40 \cdot 10^{-10}$  m in **A** and  $4.72 \cdot 10^{-10}$  m in **B**. The closest distance between a lead atom and a perchlorate oxygen is  $2.96 \cdot 10^{-10}$  m in **A** and  $2.80 \cdot 10^{-10}$  m in **B**.

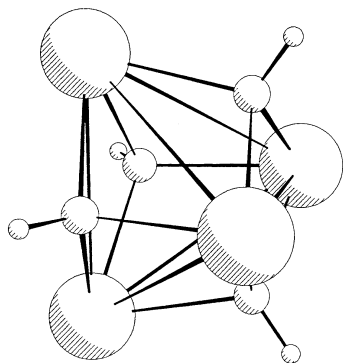


FIG. 1  
Idealized geometry of  $\text{tetrahedro-}[\text{Pb}_4(\mu_3\text{-OH})_4]^{4+}$

The water molecule in **A** may be considered attached to the  $\text{Pb}_4$  cluster through interactions with two Pb atoms, which are  $2.78 \cdot 10^{-10}$  and  $2.98 \cdot 10^{-10}$  m distant. The water molecules in **B** are coordinated to one lead atom at the distance of  $2.74 \cdot 10^{-10}$  and  $2.75 \cdot 10^{-10}$  m, the distances to another lead atom being  $2.93 \cdot 10^{-10}$  and  $3.00 \cdot 10^{-10}$  m. The carbonate oxygen in **A** coordinates two Pb atoms at  $2.91 \cdot 10^{-10}$  m.

$[\text{Pb}_4(\text{OH})_4]^{4+}$  predominates in perchlorate solutions with the molar OH : Pb ratio of about 1. The large concentrations and the high atomic number of lead make it likely that the information on the structure of the complex **C** can be obtained by an X-ray investigation of the hydrolyzed solution<sup>7</sup>. The radial distribution function exhibits an intense maximum corresponding to Pb–Pb distances as well as two lower peaks which may be ascribed to Pb–O distances (see Table I). Since no other significant peaks corresponding to Pb–Pb interactions seem to occur in this solution, a tetrahedral arrangement of the lead atoms has been deduced. Nevertheless, there are some less intense peaks at distances over  $4.9 \cdot 10^{-10}$  m.

The observed differences in bond lengths for  $[\text{Pb}_4(\text{OH})_4]^{4+}$  in the solid state and in solution may be due to the difference in environment and to a less regular  $\text{Pb}_4$  unit in the solid caused by unequal sets of the nearest neighbours of the lead atoms<sup>5,6</sup>.

TABLE I  
Relevant interatomic distances ( $10^{-10}$  m) in  $[\text{Pb}_4(\mu_3\text{-OH})_4]^{4+}$  units (mean values)

Model	System	Pb–Pb	Pb–OH	Pb–OH <sub>2</sub>	Reference
X-ray data					
A	$[\text{Pb}_4(\text{OH})_4]_3(\text{CO}_3)(\text{ClO}_4)_{10} \cdot 6 \text{H}_2\text{O}$	3.79	2.38	2.88	5
B	$[\text{Pb}_4(\text{OH})_4](\text{ClO}_4)_4 \cdot 2 \text{H}_2\text{O}$	3.81	2.41	2.86	6
C	perchlorate solution	3.85	2.4	2.9	7
MNDO data					
D	$[\text{Pb}_4(\text{OH})_4]^{+4}$	3.70	2.33	–	this work
E	$[\text{Pb}_4(\text{OH})_4(\text{H}_2\text{O})_4]^{+4}$	3.60	2.34	2.32	this work

## CALCULATIONS

The standard semiempirical MNDO method of quantum chemistry (AMPAC program package)<sup>8-10</sup> was used to find the optimum geometries of *tetrahedro*-Pb<sub>4</sub>[(μ<sub>3</sub>-OH)<sub>4</sub>]<sup>4+</sup> (D) and *tetrahedro*-[Pb<sub>4</sub>(μ<sub>3</sub>-OH)<sub>4</sub>(H<sub>2</sub>O)<sub>4</sub>]<sup>4+</sup> (E) clusters. All calculations were performed at higher precision (keyword PRECISE) using the Davidon-Fletcher-Powell optimization procedure<sup>11,12</sup>.

## RESULTS AND DISCUSSION

The optimum geometry of *tetrahedro*-[Pb<sub>4</sub>(μ<sub>3</sub>-OH)<sub>4</sub>]<sup>4+</sup> complex cation obtained by the MNDO method (Table I) corresponds to the highest possible T<sub>d</sub> symmetry. This skeleton symmetry is not lowered by hydration (each H<sub>2</sub>O molecule being end-coordinated to only one of the lead atoms). The calculated Pb-Pb and Pb-O distances are in reasonable agreement with experimental X-ray data which are <5% and <3% longer, respectively. These differences are lower than the experimental data dispersion. This fact approves the use of MNDO method for lead(II) hydroxo complexes despite the presence of heavy Pb atoms. The appropriate parametrization accounts for the main relativistic effects which is an advantage in comparison with non-relativistic *ab initio* treatments.

The more complicated problem is accounting for the environmental influences. The lead atoms bonding is not completely saturated by three μ<sub>3</sub>-OH bridges but an additional H<sub>2</sub>O molecule might be bonded too strongly. The artefact of the method used is that the inclusion of an additional H<sub>2</sub>O causes undesirable Pb-Pb shortening due to an extremely short Pb-OH<sub>2</sub> bond (comparable with Pb-OH). The MNDO method is not able to reproduce these van der Waals structures correctly.

Finally, it may be concluded that the MNDO method is suitable for studying the structures of hydroxo lead(II) complexes, though it overestimates the solvent effect.

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