CHEMISTRY
A EUROPEAN JOURNAL

DOI: 10.1002/chem.200600045

Exploring the Hydration of Pb^{2+}: Ab Initio Studies and First-Principles Molecular Dynamics

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Abstract: Even though lead is a well-known toxicant widely scattered throughout the world since antiquity, its chemistry is poorly documented at the molecular level. Here we investigate the hydration of the Pb^{2+} ion by means of first-principles molecular dynamics (Car–Parrinello molecular dynamics, CPMD). We found that the hydrated cation is heptacoordinated in a dynamically holodirected arrangement roughly corresponding to a fluxional distorted pentagonal bipyramid. The time-averaged Pb–O bond length is especially large and amounts to 2.70 Å with an associated root-mean-square deviation of 0.26 Å. This results from a dynamic exchange between short (<2.6 Å), intermediate (2.6–3.0 Å) and long (>3.0 Å) Pb–O bonds. The latter very long Pb–O distance implies that the determination of the coordination number n_c from experimental work may not necessarily yield values directly comparable to the theoretical value of $n_c = 7$, since not all experimental techniques would recognize such a long distance as a bond to the metal cation. Pronounced disorders are evidenced in the second shell, characteristic of a chaotropic cation, and exchanges between the first and second shells cannot be excluded on a timescale of a few tens of picoseconds.

Keywords: ab initio calculations · cations · ELF (electron localization function) · lead · molecular dynamics

Introduction

Manufactured for more than 6000 years, lead has become the most widely scattered toxic metal in the world.[1,2] The toxicity of lead and its compounds, together with associated clinical symptoms, have been recognized for centuries.[3] Nowadays, acute lead intoxication in adults are still reported, but children remain the most readily damageable targets of lead intoxication: among other disorders, irreversible cerebral damage can occur from chronic exposure to lead during pregnancy or infancy.

Although biochemical data on this topic have become more and more available, there have been only a few experimental studies, from the molecular physics viewpoint, devoted to understanding lead poisoning, usually called saturnism (or plumbism).

Moreover, there have been only very few theoretical investigations on lead compounds relevant to saturnism, an essential field for public health: works have been essentially devoted to species relevant to atmospheric chemistry[4–6] and thus focus mainly on issues related to environmental conservation. Except for three notable pioneering exceptions in which a large number of ligands were investigated,[7–9] lead compounds such as PbO,[10] $PbCl_4$,[10] Pb_2,[11] PbH_4[10,12] and $[Pb(CH_3)_3H]$[12] have, up to now, interested theoreticians essentially because of the relativistic effects to which the metal atom is subject.

Understanding the mechanisms of lead poisoning at a molecular level requires good knowledge of the binding properties of Pb^{2+} if the aim is to design specific and efficient chelating ligands for identification, probing, sensing, monitoring, dosing, sequestering or treatment protocols. Among the various parameters, the knowledge of which seems to be a prerequisite, rational design of chelating agents would require the following questions to be addressed:

1) As Pb^{2+} is known to exhibit n_c values ranging from 1 to 10, what is the effective coordination number n_c of Pb^{2+} in the Pb^{II} complexes of interest?[7]
2) Is the investigated Pb^{II} complex holodirected or hemidirected?[7]
3) Is the investigated Pb^{II} complex chaotropic or cosmotropic?[13,14]

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In a biological environment such knowledge begins with an in-depth understanding of the static and dynamic solvation properties of the aqueous Pb^{2+} ion.

Pb^{II} complexes exhibit wide versatility of possible coordination numbers, but it appears that the most common, as derived from X-ray structures, are four and six.[8] Surprisingly, such a naive parameter as the coordination number of solvated Pb^{2+} is very poorly documented in the literature. To the best of our knowledge, there has been only one experimental determination of n_c in water: a value of 5.7 was deduced from ^1H NMR experiments as early as 1966.[15] This value has been questioned[16] on the basis that, by using the same technique, the Mg^{2+} and Ca^{2+} ions were found to have n_c values of 3.8 and 4.3 respectively, whereas recent experimental work and theoretical calculations agree on $n_c = 6.0$ and n_c ranging between 6 and 10, respectively.[17,18] Nevertheless, to the best of our knowledge, there have been only two recent theoretical reports, which relied on hybrid HF/MM[16] and MM[19] calculations and proposed $n_c = 9.0$.

The large discrepancy between the previously reported n_c values is a clear illustration that this ion deserves further investigation.[20] X-ray diffraction, neutron scattering/diffraction and EXAFS measurements, as well as ultrafast NMR experiments, can be proposed to provide up-to-date experimental values, but a purely quantum approach can complement the previous theoretical study and deepen our understanding of the problem.

Here we report static and Car–Parrinello (CP) molecular dynamics (CPMD) simulations[21] carried out within the framework of density functional theory (DFT), a procedure successfully applied previously to the description of solvated anions,[22,23] but also to the solvation of metal cations.[24] Although the high computational cost of this method technically limits the number of water molecules used to model the bulk or the duration of the simulations,[20,25] this approach has been used to describe first and second hydration shells and has proven to be of special interest.[24] In the difficult case of the hydration of Cu^{2+}, for example, it was able to give an in-depth view of the first and second hydration shells and to suggest the possibility of fivefold coordination[24a,b] $[Cu(H_2O)_5]^{2+}$, a feature confirmed by several concomitant or later experimental works.[24a,26–28] The internal reorganization of this pentacoordinate structure, which was predicted to be subject to interconversion between square-pyramidal and trigonal-bipyramidal conformations,[24a] two structures of comparable energy,[29] has also been observed experimentally.[27]

It is thus expected that CP computations will provide insightful clues to address the above-mentioned prerequisites in the case of hydrated Pb^{2+} or complement the few available data. The present paper is structured as follows. First, static gas-phase investigations of some $[Pb(H_2O)_n]^{2+}$ clusters ($n = 6$, 8) are reported: this study is used to validate the choice of functional retained in the CP treatment and explains why a dynamic treatment must be considered. Then, dynamic gas-phase investigations allow the dynamic behaviour of Pb^{2+}–water coordination to be benchmarked. Finally, we turn to full CP simulation using periodic boundary conditions, the results of which are analyzed and discussed from a physicochemical point of view.

Computational Details

The static ab initio computations were carried out using Gaussian 03.[30] As HF calculations are in principle unable to account for hydrogen bonding due to the lack of any dispersion contribution in the intermolecular interactions,[31,32] we considered the DFT approach using the B3LYP[33] and BLYP[34–36] functionals. The B3LYP functional has been widely used to investigate metal cations interacting with organic ligands or water molecules; it is moreover expected to provide a balanced way of describing the subtle competition between metal–water bonds and the water–water interactions occurring either within the first coordination shell or between the first and second coordination spheres.[37] The quantum treatment of hydrogen bonds ideally requires diffuse atomic orbitals on oxygen atoms:[31,32] the 6-31+G** basis set was used for the O and H atoms.[38–40] Divalent lead Pb^{2+}, $[Xe]4f^{14}5d^{10}6s^2$, was described by using the large-core scalar relativistic SDD pseudopotential coupled to a double-zeta-quality basis set obtained from a (4s4p1d)/[2s,2p,1d] contraction.[41] These pseudopotential and basis set have been found reliable in reproducing four-component all-electron relativistic B3LYP calculations for the $[Pb(OH)]^+$ and $[Pb(H_2O)]^{2+}$ complexes[42] and for other monohydrates of heavy metal cations.[43] The nature of each optimised minimum was characterized by means of a vibrational analysis performed within the harmonic approximation. No scaling procedure was applied when evaluating the zero-point energy (ZPE) and thermal corrections.

The CP dynamic calculations were performed using the PINY-MD program.[44] The BLYP functional was retained as we found it able to reproduce the B3LYP energetics of a number of static $[Pb(H_2O)_n]^{2+}$ structures. This functional has long been known to provide a non-perfect[45–50] but accurate quantum description of liquid water.[22,24f,51–55]

Goedecker[56] (Pb) and Troullier–Martins[57] (O and H) pseudopotentials were used. The associated plane-wave basis set was truncated at $E_{cut} = 80$ Rydberg, the commonly used and recommended value.[51,53] The CP computations were run at a constant temperature of 300 K using Nosé–Hoover chains of length 6 on the atoms.[58] The fictitious electron kinetic energy was checked to remain small compared to that of the nuclei (adiabaticity): electronic thermostating was not required for a fictitious electronic mass of 553 amu.

A cluster simulation was first carried out with aperiodic boundary conditions[59] by using a 20 Å box. A periodic simulation was then performed in a 9.8 Å box containing one Pb^{2+} cation and 32 water molecules, a number that has recently been recognized as "an optimum compromise between system dimension and time scale given the current performance of hardware".[24d] In our case, it allows the description of the chemically relevant first hydration shell interacting with a quasicomplete second hydration shell, since they are expected to include about 33 water molecules,[16,20] and to investigate the first coordination shell and its interactions with the second for more than 12 ps with a time step of 0.125 fs. Given this number of water molecules, the box size was adjusted to reproduce the experimental density of pure water. With these values, the concentration of Pb^{2+} in the periodic dynamic simulation was $1.76\ mol\,L^{-1}$.

Results

Static calculations: First, the geometries of the hexa- and octaaqua Pb^{2+} complexes were determined. Since they were shown to properly reproduce the interaction energies obtained from all-electron four-component correlated relativistic calculations for monohydrate complexes,[42,43] the B3LYP results were taken here as reference. Moreover, B3LYP calculations have been shown to provide results comparable to MP2 computations on these systems.[16] They are then compared to those provided by the BLYP functional used in the CP studies. Binding energies per water molecule were computed for $[Pb(H_2O)_n]^{2+}$ ($n=6$ or 8, Table 1). The various structures reported differ in their n_c values; the remaining $n-n_c$ water molecules belong to the second hydration shell. Despite many attempts, the heptacoordinate compound corresponding to $n=8$ and $n_c=7$ could not be found. Even though the optimized structures appear very different when n_c is decreased for a given n, the binding energies per water molecule are surprisingly similar for given values of n: the largest difference, for a given level of calculation, is 2.1 kcal mol^{-1} and occurs for the octaaqua complex treated with BLYP. These bonding energies are also quite insensitive to the computational level (HF, BLYP or B3LYP), which confirms a previous study:[16] the lowest energies (averages over available isomers) are found for HF and are within 2.6 kcal mol^{-1} of the largest ones, obtained at the B3LYP level. These results are especially noteworthy, since the computed structures are characterized by different numbers of Pb–O or hydrogen-bonding interactions. It follows that these computational levels all report comparable results when aiming at the evaluation of Pb–O versus H-bond competition. They are thus equally suitable for studying the hydration shells of Pb^{2+}. Consequently, the description of these shells will not lose any accuracy and relevance on turning from the B3LYP to the BLYP functional when performing the forthcoming CP calculations.

The ZPE corrections lower the binding energies by about 2 kcal mol^{-1}. Free energies are about 10 kcal mol^{-1} lower than internal energies and, quite notably, increasing the number of water molecules in the second shell is not systematically favoured. The variations in free energy with respect to the number of water molecules in the second shell for a given n are within 2 kcal mol^{-1} whatever the level of calculation. Static calculations, then, cannot unambiguously predict the lowest energy structure for a given n: a number of isomers exist which are almost isoenergetic and isoenthalpic. A dynamic treatment is thus required.

Gas-phase dynamic simulation of the hexaaqua cluster: A CP simulation on the $[Pb(H_2O)_6]^{2+}$ complex was then performed. An octahedral hexacoordinate structure was taken as a starting point. As shown in Figure 1, a first water molecule moves from the first hydration shell towards the second within 1 ps. Full decoordination does not occur, however, since this molecule stays in the vicinity of Pb^{2+} (Pb–O ca. 4.5 Å) for the remainder of the simulation and becomes H-bonded to water molecule #1. A similar departure (water molecule #6) is observed for a second water molecule at 5 ps, followed by H-bonding to water molecule #5. This evolution of the coordination number at Pb^{2+} is especially encouraging, since it proves that the hydrated complex is not overly rigid and can easily rearrange. The simulation can thus be split into two well-defined periods: one during which the complex is hemidirected and pentacoordinate ($1.5 < t < 4$ ps), and one during which the complex is still hemidirected but tetracoordinate ($5 < t < 8.5$ ps). Both these coordination modes are common for Pb^{2+}.[8]

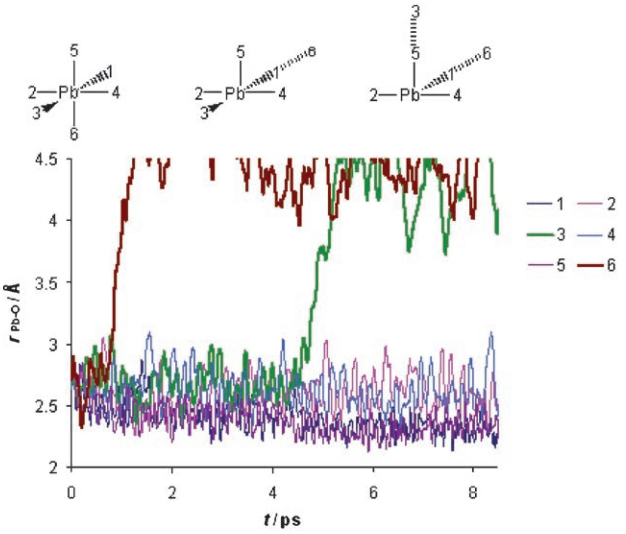

Figure 1. Pb–O distances [Å] as a function of time in the $[Pb(H_2O)_6]^{2+}$ cluster.

Table 1. Static calculations: binding energy per water molecule [kcal mol^{-1}] (first line), ZPE-corrected (second line) and free energy (third line). n.c. stands for not concerned, and N.C. for not converged.

	Number of water molecules in the second shell				
	0	1	2	3	4
hexaaqua complex, B3LYP	−36.5	−37.3	−37.9	−37.4	n.c.
	−34.8	−35.2	−35.6	−35.4	
	−27.3	−27.1	−27.0	−27.3	
hexaaqua complex, BLYP	−35.9	−36.6	−37.3	−37.0	n.c.
	−34.3	−34.6	−35.0	−35.1	
	−26.6	−26.6	−26.6	−27.0	
hexaaqua complex, HF	−34.6	−35.0	−35.1	−33.9	n.c.
	−32.9	−32.8	−32.7	−31.7	
	−24.7	−24.7	−24.2	−23.8	
octaaqua complex, B3LYP	−31.2	N. C.	−32.7	−33.2	−33.0
	−29.4		−30.5	−30.9	−30.5
	−21.1		−22.1	−22.4	−22.0
octaaqua complex, BLYP	−30.4	N. C.	−32.0	−32.5	N.C.
	−28.6		−29.9	−30.3	
	−20.3		−21.6	−21.9	
octaaqua complex, HF	−29.8	N. C.	−30.7	−30.9	−31.1
	−28.0		−28.6	−28.6	−28.7
	−20.1		−20.4	−20.2	−20.2

The four remaining water ligands which characterize the first coordination sphere are coordinated as a *cis*-divacant octahedron having shorter Pb–O distances for the water molecules *trans* to a vacant site. These distances were already shorter in the pentacoordinate species. No rearrangement of the apical ligand towards the basal positions occurs. Interestingly, even though water molecule #3 lies in a basal site during the first period of the simulation, it retains a long Pb–O bond similar to that of the apical ligands.

Table 2 reports the Pb–O bond lengths averaged over each of the two periods of the simulation. It appears that decoordination of the second water molecule does not significantly alter the structure of the complex. In particular, the basal O^1-Pb-O^5 and apical O^2-Pb-O^4 angles remain close to 90° and 150°, respectively. A major effect is observed for the small Pb–O distances: they shorten by 0.12 Å on decoordination of water molecule #3 from the metal ion.

Table 2. Dynamics performed on the $[Pb(H_2O)_6]^{2+}$ cluster (aperiodic conditions). Distances and RMSD (values in parentheses) in angstroms, angles in degrees.

	$1.5<t<4$ ps, $n=6$, $n_c=5$	$5<t<8.5$ ps, $n=6$, $n_c=4$
Pb–O "short"[a]	2.432 (0.095)	2.318 (0.075)
Pb–O "long"[b]	2.634 (0.155)	2.616 (0.147)
Pb–O "nonbonding"[c]	4.648 (0.219)	4.394 (0.252)
O^1-Pb-O^5	84.5 (8.8)	86.3 (7.5)
O^2-Pb-O^4	156.4 (9.3)	149.9 (16.9)

[a] Pb to O^1 and O^5. [b] Pb to O^2 and O^4 (and to O^3 during the first period of the simulation). [c] Pb to O^6 (and to O^3 during the second period of the simulation).

Dynamic simulation with periodic boundary conditions: Quite different results are obtained when a 32-water-molecule box and periodic boundary conditions are used to reproduce explicit hydration of Pb^{2+}.

In a first trajectory, we considered a starting nonaaqua complex having the structure obtained from HF/MM computations.[16] In less than 2 ps, two water molecules initially located in the first hydration shell are repelled toward the second shell. In the following 2 ps of the simulation, a relaxed heptaaqua complex was observed, with no trend to recover a higher coordination number. This simulation was thus not carried out further, as another trajectory had simultaneously been launched starting ($t=0$ ps) from the octahedral $[Pb(H_2O)_6]^{2+}$ cluster previously used as the starting point for the gas-phase dynamics. At $t=2$ ps, one supplementary water molecule enters the first hydration shell (Figure 2). Both investigated trajectories thus lead to a heptaaqua complex. This is especially noteworthy since it proves that using a low (6) or a high (9) coordination state as a starting point does not predispose the simulation. This heptaaqua complex is stable for the remaining 10 ps of the second simulation. This peculiar coordination number is proposed to result from the presence of second-shell water molecules, since our first optimisation of $[Pb(H_2O)_7]^{2+}$ complexes did not result in heptacoordinate systems within the static cluster approach.

Analysing in more details the corresponding dynamics give insightful clues for addressing the three important prerequisites mentioned in the Introduction (see below).

Coordination number deduced from the Pb–O radial distribution function: As seen from Figure 2 no exchange between the first and the second hydration shell is observed after the 7th water molecule has entered the first shell. It is thus meaningful to compute a time average over the seven Pb–O bonding distances (2.70 Å) and the associated root-mean-square deviation (RMSD = 0.26 Å). The fact that the averaged Pb–O bond length is larger than that observed in the previous cluster simulation reflects the ability of Pb^{2+} to reorganize in order to adopt high n_c values. Moreover, the significantly high value of the associated RMSD is the signature of a dynamic competition between 1) chelation to the metal cation, which tends to diminish the Pb–O bond lengths; 2) repulsion between the Pb^{2+} lone pair ($6s^2$) and those of the water molecules, which tends to increase the Pb–O bond lengths; and 3) H-bond formation with the

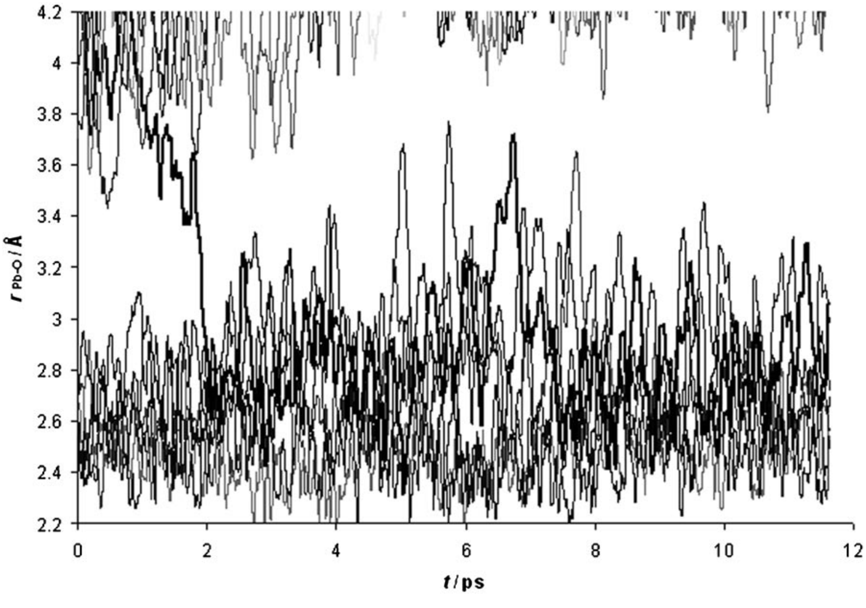

Figure 2. Pb–O distances [Å] as a function of time for the aqueous Pb^{2+} complex (periodic conditions).

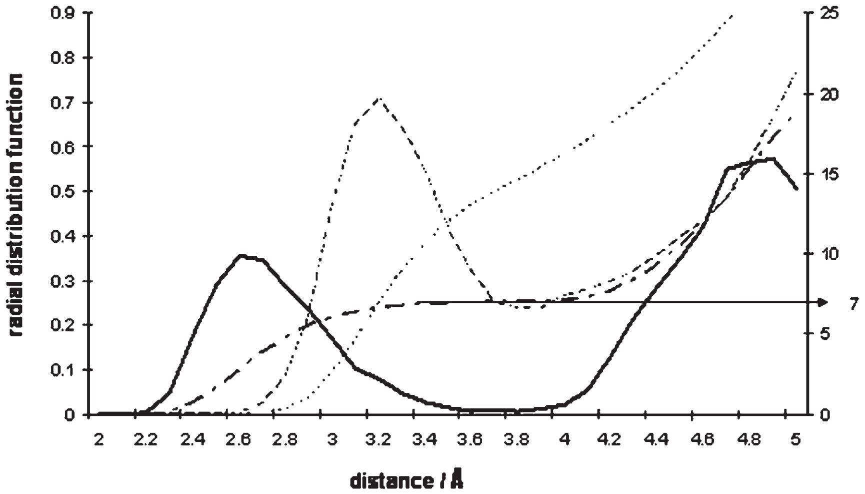

Figure 3. Radial distribution functions g(Pb–O) (bold line) and g(Pb–H) (thin line, dashed -----) and integrations (dashed lines, bold –•–• and thin ··· respectively).

second hydration shell, which tends to repel the chelated water molecules from the metal centre.

The Pb–O radial distribution function (Figure 3) reveals a nicely defined first hydration shell, as it falls to zero at r values between roughly 3.6 and 4.0 Å. Integration between 2.0 and 3.7 Å leads to $n_c = 7.0$, that is, hydrated Pb^{2+} is heptacoordinate.

Moreover, the Pb–H distribution function exhibits a first maximum at $r \approx 3.2$ Å, followed by a minimum between 3.9 and 4.4 Å. Integration of the radial function from zero to the first minimum leads to 15.4 hydrogen atoms. The existence of a nonzero minimum, together with 1.4 extra hydrogen atoms, is the clear-cut signature of hydrogen-bonding interactions between hydrogen atoms relevant to the second-sphere water molecules with oxygen atoms from the first sphere. This is another noticeable qualitative difference between the present CP dynamics and the previous HF/MM simulation,[16] in which no such nonzero minimum was found.

The structure of aqueous Pb^{2+}: Pb–O bond lengths: The peak corresponding to the first hydration shell in Figure 3 is large and asymmetric; this is characteristic of long and short Pb–O distances coexisting in the complex (Figure 4). Careful inspection of Figure 2 reveals that the coordinating water molecules can be split into three different groups: 1) a set of water molecules having short Pb–O lengths ranging roughly between 2.4 and 2.6 Å, 2) other water molecules associated with intermediate Pb–O lengths amounting of about 2.8 Å, and 3) at least one water molecule associated with a long Pb–O length exceeding 3.0 Å.

The snapshot shown in Figure 4 gives an instantaneous view of the structure, which appears as a distorted pentagonal bipyramid. One long bond is observed (3.54 Å), together with three short ones (2.43, 2.45 and 2.51 Å) and three intermediate ones (2.77, 2.82, and 2.83 Å). The radial distribution function between 0 and 3.0 Å, a chemically meaningful truncation radius, integrates to 6.1: this is a clear illustration that one water molecule (integration to 0.9), even though it is bonded to Pb^{2+} and does not yet belong to the second hydration sphere, can exhibit a large Pb–O distance. Numerous crossings between short, intermediate and long Pb–O bond lengths occur within the first hydration shell during the simulation time. Moreover, numerous lengthenings of some Pb–O bonds, up to 3.7 Å, are observed: the distal water molecule is thus subject to exchange with the proximal ones.

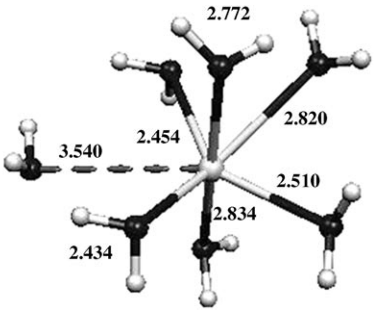

Figure 4. Instantaneous structure (snapshot) of the aqueous Pb^{2+} complex. The Pb–O distances are in Å.

The structure of aqueous Pb^{2+}: O-Pb-O angular distributions: Figure 5 shows the angular distribution of the 21 O-Pb-O angles for the water molecules involved in the first hydration sphere. Three peaks are observed, consistent with a pentagonal-bipyramidal structure. In such an ideal arrangement, two successive basal water molecules induce five angles of 72°, whereas one basal and one apical water molecule induce ten angles amounting to 90°. In contrast, the

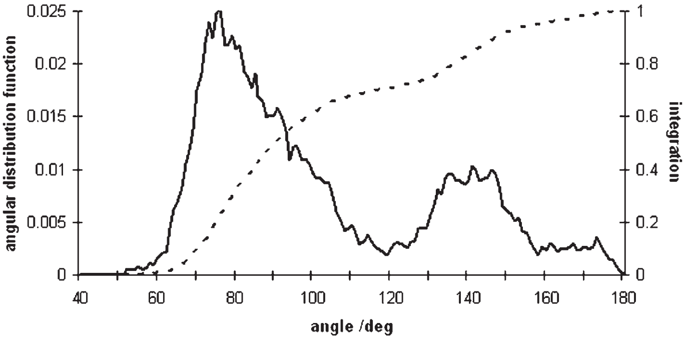

Figure 5. Angular distribution function for O-Pb-O angle (full line) and integration (dotted line) in the aqueous Pb^{2+} complex.

first peak observed in Figure 5 ranges between 30 and 120°, is centred at about 80° and integrates for 15 angles. This can be accounted for if the thermal fluctuations of these angles are large and prevent discrimination between the different types of angles characterising the ideal pentagonal-bipyramidal structure. As far as angles larger than 120° are concerned, the two apical molecules would ideally define an angle of 180° and the basal ligands would be associated with five angles of 144°. This corresponds exactly to the distribution found (Figure 5): a second peak arises between 120 and 160°, with a corresponding mean value of about 140°, and integrates for five angles, and the remainder of the angular distribution corresponds to one angle and extends beyond 160°.

Holo- or hemidirected? An interpretation from the ELF function: The electron localization function (ELF)[60,61] was used to investigate the origin of preserving one long Pb–O bond throughout the simulation. Topological analysis of the ELF[62,63] was performed with the TopMod package.[64,65] Within the framework of the topological analysis of ELF, space is partitioned into basins of attractors, each of which has a chemical meaning.[65] These basins are classified as core basins surrounding nuclei and valence basins, which are characterized by their synaptic order.

A core basin C(X) where X stands for a nucleus, is representative of electrons not involved in chemical bonding: they correspond to nonvalence internal-shell electrons ("core electrons"). The valence basins are discriminated according to the number (synaptic order) of core basins with which they share a common boundary. A valence basin V(X) is monosynaptic and corresponds to lone pairs or nonbonding regions. A V(X,Y) basin is disynaptic: it links the cores of two nuclei X and Y and thus corresponds to a bonding region between X and Y.

In the present case, the ELF analysis (Figure 6) performed on the geometrical arrangement presented in Figure 4 shows that the $6s^2$ lone pair of Pb^{2+} is not exactly spherically distributed around the metal centre. It points toward the distal water molecules. Thus, it appears that the repulsion between the lone pairs of these water molecules and the directional lone pair of Pb^{2+} is associated with increased Pb–O bond lengths and a slightly hemidirected character of the resulting complex as perceived from a static point of view. However, the numerous changes occurring within the simulation time between short and long bonds result in averaging of this phenomenon: even on such a small timescale as picoseconds, the complex is dynamically holodirected.

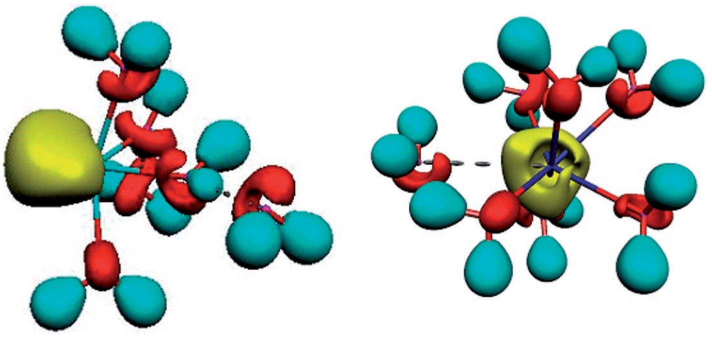

Figure 6. ELF localization domains ($\eta = 0.85$) on an instantaneous structure (snapshot) issued from the dynamics performed on the $[Pb(H_2O)_6]^{2+}$ complex (left) and on the aqueous Pb^{2+} complex (right). The X–H disynaptic basins are in blue, the monosynaptic valence basins (lone pairs) are in red, and the core basins in magenta. For the sake of better visibility, the monosynaptic basin associated with the $6s^2$ lone pair of Pb^{2+} is represented by shaded yellow.

This is at variance with the structure obtained from the cluster dynamic approaches: in the hexaaqua structure, more precisely the tetraaqua structure with two water molecules in the second hydration shell, the hemidirected character is clearly identified (Figure 6) and is retained throughout the cluster simulation performed under aperiodic conditions.

Chaotropic or cosmotropic? Figure 7 shows the angular distribution of the Pb-O-H-H dihedral angles for the $[Pb(H_2O)_6]^{2+}$ complex obtained from the cluster dynamic simulation and in the complex obtained by means of the periodic simulation (restrained to the seven water molecules bonded to Pb^{2+}).

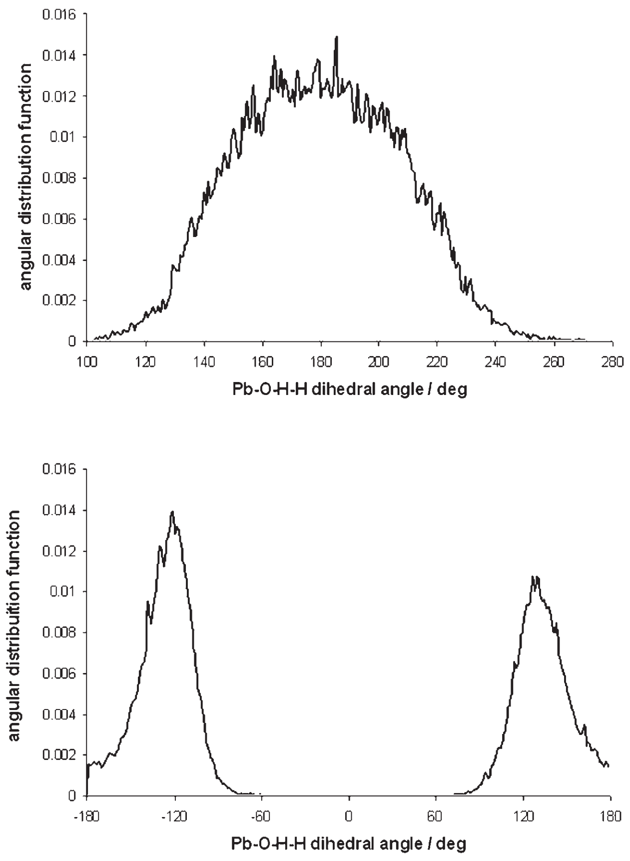

Figure 7. Pb-O-H-H dihedral angle distribution functions in the $[Pb(H_2O)_6]^{2+}$ cluster (top) and in the aqueous Pb^{2+} complex (bottom, only the seven water molecules of the first hydration shell have been retained).

These two distributions are obviously different. In the cluster simulation, the dihedral angle distribution is centred at 180° with a RMSD of 27.5°. It is noteworthy that this orientation is also that observed for the two water molecules coordinated in the second shell of the cluster. This is consistent with the static results, where the dihedral angles all lie between 160 and 180°, whatever the distance between the water molecules and Pb^{2+}.

In contrast, in the periodic simulation, the Pb-O-H-H dihedral angles of the water species of the inner shell split into two symmetric peaks centred at 133.0° (RMSD = 18.6°) and −127.5° (RMSD = 18.6°). At least one inversion of this dihedral angle is observed for each water molecule. Furthermore, and at variance with the results obtained from dynamics performed within the cluster framework, no organisation of the second coordination sphere is observed.

A clear-cut conclusion about the chaotropic or cosmotropic character of the solvated cation would require consideration of more water molecules in a larger simulation box, and maybe a longer simulation time (see, however, ref. [22]). Nevertheless, the fact that only seven water molecules enter the first hydration shell for a radius of 3.7 Å, that flips are observed for the Pb-O-H-H angles within this shell and that no angular organisation is associated with the second coordination sphere seem to constitute a set of converging clues that hydrated Pb^{2+} might be rather chaotropic.

Conclusion

From the current 12-ps simulation performed within the CP scheme, the hydrated Pb^{2+} ion is found to be heptacoordinated in a dynamically holodirected, but statically hemidirected arrangement corresponding roughly to a distorted pentagonal bipyramid. Such fluxional coordination seems reasonable when confronted with statistical analyses of the coordination numbers of Pb^{II} compounds, which established that heptacoordination is quite commonly observed.[8]

This value of n_c (7.0) is lower than those found in previous theoretical studies ($n_c = 8.5$ or 9.0), which report a holodirected structure,[16,19] but slightly larger than that reported in the sole experimental study available at that time, namely, $n_c = 5.7 \pm 0.2$,[15] deduced from ^{1}H NMR measurements. In fact, as described previously and evidenced in Figures 2 and 3, a time average of 0.9 water molecules exhibit a Pb−O distance larger than 3.0 Å and are thus loosely coordinated to Pb^{2+}. It is expected that, for such a long distance and high coordination number, the relevant remote protons will not be subject to the influence of the metal cation: they may not have been taken into account as coordinated in the first shell in the pioneering NMR study.[15]

Timescale is a well-known difficulty for first-principles molecular dynamics in comparison to most experimental results and might be considered as a matter of debate. The present study shows that the first hydration shell of Pb^{2+}, though well defined, is very diffuse, so that a problem of definition arises: according to the Pb−O distances, some molecules in the first shell would indeed be better considered as chemically unbound entities. Indeed, different experimental techniques may lead to different values of n_c, as the most remote solvent molecules will be accounted for or not, depending on the physicochemical properties probed. Thus, the description of the coordination sphere is not a straightforward process: it must rely on clearly specified and understood definitions directly derived from the experimental technique used. It follows that a clear distinction should always be made between the primary coordination shell, defined as the set of solvent molecules that form short bonds with the metal cation and that act as true ligands, and the first solvation shell, defined as those solvent molecules for which the M−O bond length is shorter than that corresponding to the first minimum of the metal–oxygen radial distribution function. These two notions, closely related but different, do sometimes match and overlap, but sometimes do not, as demonstrated here in the case of Pb^{2+}.

The notions of holo/hemi-directionality of the Pb^{II} complexes, which has been exposed in the present contribution as a dynamic concept together with the notions of chaotropy/cosmotropy, should moreover not be seen as purely theoretical/academic problems: the former is directly related to the chemical availability of the nucleophilic $6s^2$ lone pair of the Pb^{2+} ion engaged in a Pb^{II} complex, while the latter is strongly related to the behaviour of proteins towards the Pb^{2+} cation.

Keeping these warnings in mind, it is hoped that the present calculations will stimulate the necessary high-level experiments and acute interpretations[27b] needed to recover the insightful information required for a better understanding of the bio- and environmental chemistry of lead compounds, as most of them evolve into Pb^{II} species in aqueous media. Another point that should be kept in mind for further investigations of the properties of lead in biologically relevant environments is the coordination of counteranions in the first solvation shell. This point is currently under study.

Acknowledgements

This research was supported by IDRIS (F. 91403, Orsay - France) and CINES (F. 34000 Montpellier - France) national supercomputing centers. The static computations were performed at the CCRE of the University Pierre et Marie Curie - Paris 6 (F. 75252, Paris - France).

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Received: January 12, 2006