Ab Initio Calculations on the Electronic Structure of the Divalent Lead−Water Complex

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We studied the electronic structure of the $Pb^{2+}-4H_2O$ system. Analysis of the complex orbital evidenced no mixing between the 6s lone pair orbital of the lead and the 6p orbital components. Moreover, we found that the HOMO is widely described by the mixture of the 6p components with the 7s valence orbital of the lead. This orbital shows an important elliptical electron charge density around the lead ion and opposite the direction of the short lead−water bonds. From these results, we demonstrated that the hemidirected conformation of the $Pb^{2+}-4H_2O$ system could be easily explained by the shape of the electron charge density distribution of the HOMO rather than by the stereochemically active character of the $6s^2$ lone pair of lead electrons.

Introduction

Non-transition metals are known to both take various coordination numbers and lead to complexes with diverse structures.[1] Thanks to the numerous studies about lead in the divalent ion state, Pb(II), this metal can be used as a didactic example to highlight the role of the metal valence electrons not only in reactions with ligands, but also in the determination of the geometric structures of a compound under study. The geometry taken by complexes involving Pb(II) is either holodirected or hemidirected. The holodirected geometry is found in compounds containing lead ions with high coordination numbers and can be understood in terms of the crowding effect. On the other hand, the hemidirected geometry is generally observed in compounds involving lead ions with small coordination numbers and associated with the impact of the stereochemical activity of the $6s^2$ lone pair of lead electrons on the geometry conformation of the lead−ligand complex.[2] According to Shimoni-Livny and co-workers,[2] when the coordination number is small (2−5), the 6s lone pair orbital mixes with the 6p subshell and then takes a nonspherical distributed electron charge density around Pb(II); i.e., the layout of the ligands around the cation results in an identifiable void. By carrying out an ab initio study at the MP2 level of theory for compounds involving Pb(II) with four coordinating ligands, these authors showed that the hemidirected structure is the most widespread. The obtained geometric properties provided evidence of the presence of two short Pb(II)−ligand bonds at an angle below 110° and that of two longer Pb(II)−ligand bonds forming an outer angle varying between 160° and 220°. The analysis of the complex electronic structure indicated that the 6s lone pair orbital of the lead cation was always polarized by a small contribution of the 6p orbital. In addition, these authors also found that the contribution of the 6s orbital of lead was important in the natural bond orbital (NBO) associated with the pair of shorter Pb(II)−ligand bonds and that the character of this NBO was markedly covalent. In contrast, the smaller contribution by the 6s orbital to the NBO associated with the pair of longer Pb(II)−ligand bonds explains its somewhat ionic character. However, the holodirected structure can only occur with soft halogen anion ligands (Cl^-, Br^-, and I^-). For such systems, the four Pb(II)−ligand bonds were found to be of equal length and positioned as a regular tetrahedron; moreover, the 6s lone pair orbital of lead is not polarized with the p components, and all four NBOs are of ionic character.[6–8]

Recent investigations by Yakami and Nobusada[3] were focused on the electronic structure of the Pb(II)−porphyrin complex, where the lead is in divalent ion state and coordinated to four nitrogen atoms. Their ab initio calculations were performed at a B3LYP level of theory. Optimization of the geometry showed that the lead atom was out of the four-nitrogen plane; i.e., the lead atom is positioned at the top of a square-pyramidal structure, whereas the nitrogen atoms are set at the bottom. Moreover, according to this study, the 6s lone pair orbital of Pb(II) was not involved in the formation of the Pb(II)−porphyrin bonds and remained almost distributed spherically around the lead ion. This means that the p character of the 6s orbital is nonexistent, which disagrees with the results obtained by Shimoni-Livny et al.[2] from calculations on the Pb(II) complexes with four coordination numbers. On the other hand, the bond between Pb(II) and the porphyrin ring is mainly of covalent type and is constructed exclusively from the $6p_z$ and 7s orbitals of lead and the $2p_x$ and $2p_y$ orbitals of nitrogen atoms.[3]

This paper deals with ab initio calculations made on a divalent lead−water complex. It relies on analyses of the complex molecular orbitals and of the Mulliken populations of the optimized geometry performed to gain a better insight into the role of the s and p shells in the reactivity of the Pb(II) and concomitantly in the determination of the complex geometric properties. The results obtained for Pb(II)−water should be of great help to have more insight into the hemidirected geometry, which is observed in complexes involving VA and VIA ligands. The next section presents the method of calculation. It is followed by the report of the obtained results, and then with our conclusions.

Method of Calculation

Ab initio molecular orbital optimizations of the $Pb^{2+}-4H_2O$ complex were performed at three levels of theory, i.e., HF, MP2,

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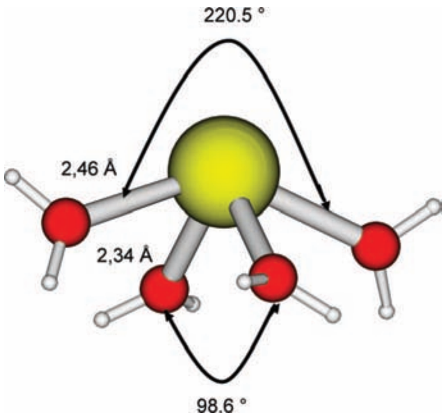


Figure 1. Ab initio optimized geometry of the $Pb^{2+}-4H_2O$ complex. The indicated parameters were obtained at the HF level of theory.

and B3LYP, by using the Gaussian 98 package of programs[4] at the IDRIS center. The LanL2DZ[5] basis set was used for all elements.

Unless otherwise noted, the geometric structure optimizations were carried out with no symmetry constraints. Harmonic frequencies were also obtained for the optimized structure to confirm its association with local minima (not transition states). Therefore, energy calculations were corrected from zero point vibration energy.

Results

After optimization of the geometry parameters of the $Pb^{2+}-4H_2O$ complex, at equilibrium the molecules of water took hemidirected positions around the lead ion. Moreover, the water bonds were found to be oriented within only a small region around the lead atom, which constitutes a remarkable signature of their distribution. The gap observed in the water bond coordination sphere had been previously identified by Shimoni-Livny et al.[2] in their studies of a series of complexes containing lead in the divalent state. For lead, these authors analyzed this fact as evidence of the stereochemical activation of the 6s lone pair orbital induced by its mixture with a few percent of the 6p lead atomic orbital component. They also considered that this process disturbs the original spherical charge distribution of the $6s^2$ lone pair of electrons around the Pb(II) ion and concomitantly affects the layout of the ligand species. Figure 1 presents the optimized geometry for the system under study and shows a structure with two short $Pb-OH_2$ bonds separated by a relatively small $A_1(O-Pb-O)$ angle. The two other $Pb-OH_2$ bonds are slightly longer and form a large $A_2(O-Pb-O)$ outer angle; i.e., the five heavy atoms constitute a structure belonging to the C_{2v} point group symmetry. Table 1 compares the geometric parameters calculated at the HF, MP2, and B3LYP levels of theory against those given by Shimoni-Livny et al.[2]

According to our calculations, the interparticle distances in HF and MP2 are quite alike, but higher than those at the B3LYP level. The angle between the two short lead−water bonds obtained at B3LYP (103.4°) is greater than those at HF and MP2 (98.6 and 100.4°, respectively). In our opinion, this difference results from the enhancement of the mutual water−water repulsion induced by the shortening of the interparticle distance obtained in the B3LYP calculation. We also attribute the difference between our MP2 geometric parameters and those calculated by Shimony-Livny et al.[2] to the effect by the contribution of the polarization component that was considered by these authors in the basis sets of the heavier atoms, but not taken into account in our calculations.

TABLE 1: Optimized Geometric Parameters for the $Pb^{2+}-4H_2O$ Complex Obtained at HF, MP2, and B3LYP Levels of Theory[a]

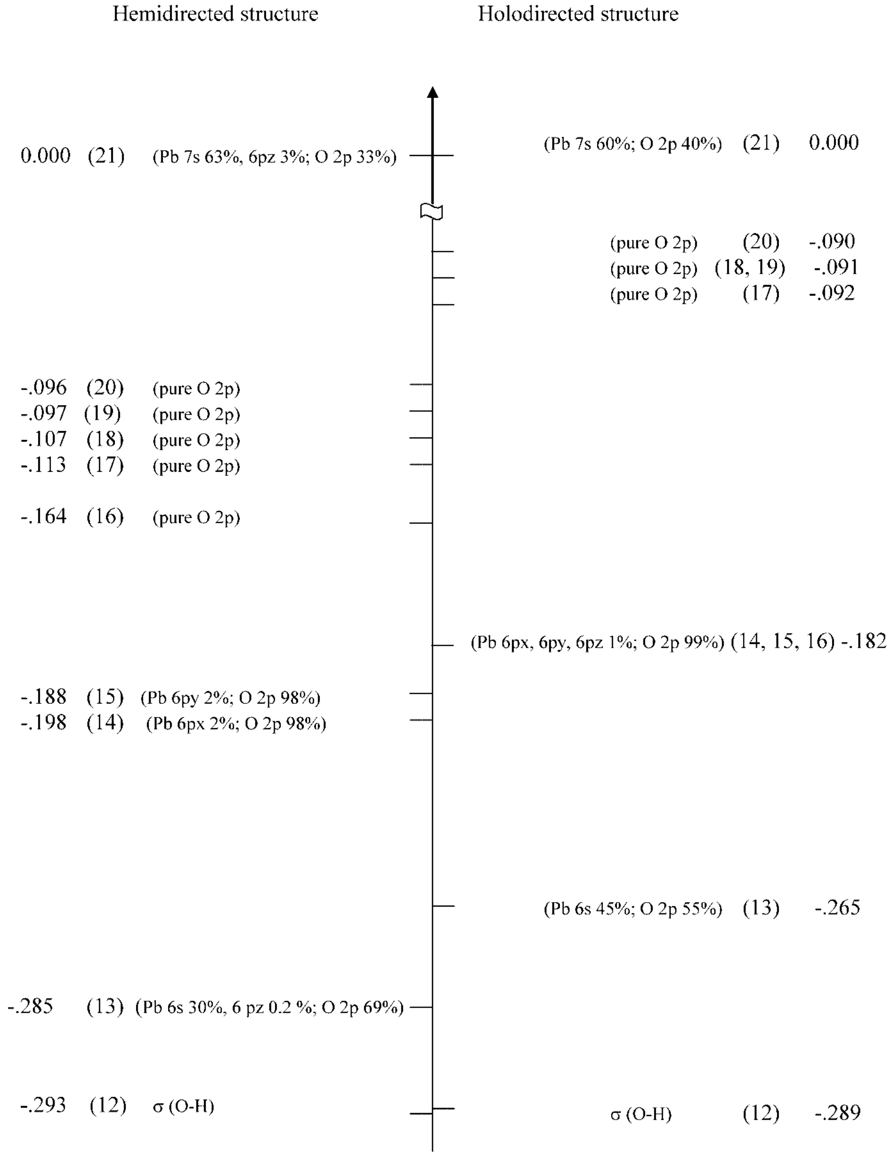
	ref 2	this study		
geometric parameters	MP2	HF	MP2	B3LYP
$R_1(Pb-OH_2)$ (Å)	2.36	2.34	2.34	2.32
$A_1(H_2O-Pb-OH_2)$ (deg)	98.4	98.6	100.4	103.4
$R_2(Pb-OH_2)$ (Å)	2.46	2.46	2.46	2.43
$A_2(H_2O-Pb-OH_2)$ (deg)	222.6	220.5	221.5	223.2

[a] A minor difference is observed between our MP2 results and those by Shimoni-Livny et al.;[2] this is attributed to the role of the polarization d component, which was taken into account in the basis sets for the heavy atoms.

Figure 2. Contour plot of the 13th orbital. This orbital was built by a mixture of the $6s^2$ lone pair of electrons of the lead with the nonbonding (O, 2p) lone pairs of the water molecules.

For the three HF, B3LYP, and MP2 levels of theory, it sounded to us worth calculating the bonding energy of the system, which is defined as the difference between the energy of the optimized complex and the sum of the respective energies of the separated constituents, i.e., the four free water molecules and the divalent lead ion. These calculations led, at first, to -208.6 kcal mol^{-1} (HF), -230.1 kcal mol^{-1} (B3LYP), and -216.8 kcal mol^{-1} (MP2), and then to -198.0 kcal mol^{-1} (HF), -219.4 kcal mol^{-1} (B3LYP), and -206.0 kcal mol^{-1} (MP2) after inclusion of the zero point vibration energy. The binding energy can be decomposed into two components: (i) the attraction energy between the Pb^{2+} and the four adjacent water molecules and (ii) the energy required to maintain the corresponding water molecules in the optimized geometric configuration, i.e., confined within a solid angle of less than 140°. The first corresponds to the energy needed to extract the lead ion without altering the positions of the four ligand water molecules. The second can be considered as the bonding energy of the system when the lead ion is replaced with a dummy atom. In both calculations, the system is considered in its optimized geometry. Application of this decomposition led us to conclude that the lead divalent ion was bound to the four water molecule system by 230.9 kcal mol^{-1} (HF), 247.3 kcal mol^{-1} (B3LYP), and 235.4 kcal mol^{-1} (MP2). The energy required to keep the molecules of water in this specific geometric configuration was found to be 22.2 kcal mol^{-1} (HF), 17.2 kcal mol^{-1} (B3LYP), and 18.6 kcal mol^{-1} (MP2). These energies correspond to the mutual repulsion potential existing between the four water molecules; it systematically includes the predicted stereochemical activity of the $6s^2$ lone pair of electrons. According to the molecular orbital scheme by Shimoni-Livny et al.,[2] it concerns the Coulomb repulsion potential that must exist between the elliptical shape component induced by the stereochemical activation of the $6s^2$ lone pair of electrons and the four water

TABLE 2: Energy and the Atomic Character of the External Orbitals That We Optimized at the MP2 Level When the Geometric Structure of the $Pb^{2+}-4H_2O$ Complex Is either Holo- or Hemidirected[a]



[a] In both structures, the energy scales were normalized to zero for the upper molecular orbital (HOMO).

electron clouds. It is worth recalling that this quantity was evaluated by these authors as the difference between the energies of the optimized hemidirected structure and those of the tetrahedral geometry. It led us to reoptimize the geometry of the complex issued from the tetrahedral layout of the four water molecules, all set at the same distance around the Pb(II) ion. They found an energy difference of 7.7 kcal mol^{-1} between the two geometric configurations. By using the same approach, we got 9.19 kcal mol^{-1} (HF), 7.01 kcal mol^{-1} (B3LYP), and 8.13 kcal mol^{-1} (MP2).

To understand the primary origin of the hemidirected structure of the $Pb^{2+}-4H_2O$ complex, it appeared to us worth focusing, at first, on the stereochemistry of the 6s lone pair orbital of the lead at the three HF, B3LYP, and MP2 levels of theory. All of our calculations indicated that the 6s orbital was never mixed with the 6p orbital components; on the other hand, it was exclusively involved in the building of the 13th orbital found to be mainly lead−water bonding (Figure 2). Table 2 gives the energy and atomic character of the external orbitals when the geometric structure of the $Pb^{2+}-4H_2O$ complex is either holo- or hemidirected. In both structures, the energy scales were normalized to 0 for the upper molecular orbitals (HOMOs). These results suggest that the contribution of the $6p_z$ in the 13th orbital is quasi-null in both configurations. On the other hand, this contribution was found to be null in the holodirected structure and is only equal to 0.2% in the hemidirected one. In a recent study about the electronic structure of Pb(II)−porphyrin, Yakami and Nobusada[3] observed a lack of polarization of the 6s orbital of lead with the p components; it ensues that this orbital is spherically distributed around the lead atom. Furthermore, they argued that because the radius of the Pb^{2+} ion is larger than that of the central metal in other common metalloporphyrins, the lead bonds are not formed in the nitrogen plane. When considering the results of Shimoni-Livny et al.[2] supporting the concept of polarization of the 6s lone pair orbital with the 6p components, we found that the contribution of the 6p component never exceeds a few percent of the lone pair total density. In our opinion, this contamination is likely too small to disturb the spherical electron charge density of the primarily $6s^2$ shell. In addition, one should note that the 7s valence orbital of the lead was not considered in the analysis by Shimoni-Livny et al.[2] This orbital is likely a key parameter in the determination of the complex molecular structures and even in the reactivity between the ion metal and ligands (6, 7, and 8). Further in these considerations, the 6s lone pair orbital has no p character and thus cannot play a prominent role in the determination of the position geometry of the ligands around the lead atom, i.e., holo- or hemidirected geometry. An analysis of the optimized complex orbitals and especially of those containing the 6p and 7s components of lead is liable to provide important data. In the $Pb^{2+}-4H_2O$ system, the charge on lead found by calculation is +1.63 (HF), +1.41 (B3LYP), and +1.63 (MP2). The variation of the electron charge on the metal can result from the well-known processes of donation and back-donation.[9,10] In the present case study, the donation process, which is usually considered as the important part of the transfer, allows charge transit from water molecules to the divalent lead. It is also responsible for the population of the 6p and 7s orbitals of the lead atom. The back-donation can be considered as the counterpart to the previous process and corresponds, usually, to the transfer of only a small amount of charge from the lead atom to the molecules of water, where the $6s^2$ lead orbital is involved. Our analysis of the Mulliken charge on the lead 6p components showed (i) that $6p_x$ and $6p_y$ were both equally populated with −0.09 (HF), −0.17 (B3LYP), and −0.09 (MP2) and (ii) an enhancement of the charge on the $6p_z$ component: −0.18 (HF), −0.23 (B3LYP), and −0.18 (MP2). Moreover, $6p_x$ and $6p_y$ both slightly contributed to the 14th (O 2p, 98%; Pb $6p_x$, 2%) and 15th (O 2p, 98%; Pb $6p_y$, 2%) quasi-degenerate orbitals found to be of nonbonding character and mainly constructed by the water lone pairs. By mixing with the 7s orbital, the $6p_z$ component contributes to the antibonding HOMO numbered 21 in the orbital energy scale. Because the $6p_z$ is largely populated by charge transfer from the water molecules to the lead atom, its mixture with the 7s produces an important elliptical orbital lobe oriented along the O *z*-axis and opposite the direction of the short lead → water bonds. Comparison of the percentage of the $6p_z$ in the HOMO from Table 2 shows dependence on the geometry. The percentage of the $6p_z$ component, which is equal to 0 in the holodirected structure, is increased to 3% in the hemidirected one. This change testifies to the predominant role of this component in the determination of the geometric structure of the $Pb^{2+}-4H_2O$ complex. Figure 3 shows the contour plot of the HOMO. This analysis drives us to think that the HOMO orbital is responsible for the hemidirectional orientation of the four water molecules set around the lead cation. The analysis of the Mulliken charge for the three components of the 6p subshell gives clues about the nature of the geometry of the lead complexes: indeed, when the three 6p subshell components are equally populated, the geometric structure is likely holodirected, otherwise it is hemidirected.

To get general information about the reactivity of the lead atom in the four coordination systems, it is worth analyzing the electronic structure of the metal cation in complexes involving water molecules and porphyrin. This gives insight into the mechanisms by which the 6s, 6p, and 7s valence orbitals are involved in the interaction with the ligands. In contrast to the previous results by Shimoni-Livny et al.,[2] this study shows that the 6s lone pair orbital is never polarized through mixture with the 6p subshell and thus cannot be involved in the determination of the geometric conformation of the complex system. On the other hand, in the case of the $Pb^{2+}-4H_2O$ complex, we established that the interaction between the lead atom and water mainly occurs through a pure 6s orbital. Thus, this orbital is stabilized conversely to the ($6p_z$ + 7s) orbital mixture found at a higher energy and assigned to the HOMO (as shown in Figure 3). The morphology of the ($6p_z$ + 7s) mixture orbital gives rise to an electron lobe, which extends outside the molecular complex and favors the hemidirected structure. The scenario in the case of the Pb(II)−porphyrin complex is different. Following the results by Yakami and Nobusada,[3] the interaction between the lead atom and the four nitrogen ones results from an orbital overlap between the lead (7s + $6p_z$) mixture and the $2p_x$ and $2p_y$ orbitals of the four nitrogen atoms. Furthermore, the $6s^2$ orbital of lead exhibited an inert pair character with no interaction with the porphyrin. Presumably, this situation is induced in response to a pure geometric constraint and because the radius of Pb^{2+} ion is longer than that of the center metal in other common metalloporphyrins. As a corollary, the ($6p_z$ + 7s) bonding orbital mixture is stabilized conversely to the 6s lone pair orbital.

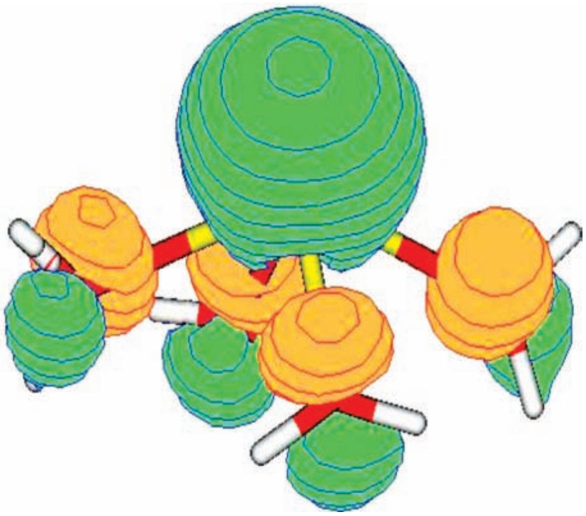


Figure 3. Contour plot of the HOMO for the $Pb^{2+}-4H_2O$ complex. This orbital was built mainly by the mixture of the $6p_z$ component with the 7s valence orbital of the lead.

Conclusion

This study of the orbital electron density for $Pb^{2+}-4H_2O$ showed that the 6s lone pair orbital is not polarized by a mixture of the 6p subshell components. Moreover, it highlighted the presence of a second orbital constructed by the mixture of the ($6p_z$ + 7s) orbitals induced by electron transfer from the water to the lead cation. It also evidenced an interaction between the metal cation and the four molecules of water via a pure $6s^2$ electron pair of electrons. Finally, we attributed the hemidirected structure mainly to the morphology of the HOMO characterized by the presence of an electron lobe set along the O *z*-axis. In our opinion, the geometric structures of complexes involving lead in divalent ions can be easily explained by an analysis of the Mulliken population of the lead subshell 6p components. When the three components are equally populated, the geometric structure of the complex is likely holodirected; it is hemidirected under other conditions.

We performed additional calculations with different basic sets. At first, we used the sdd basis sets (the Stuttgart relativistic pseudopotential)[11] for all elements. Then, we employed the sdd basis set for the lead ion, and 6-31G** for the hydrogen and oxygen atoms. According to Salpin et al.[12,13] the sdd basis sets, which correspond to the (4s,4p,1d)/[2s,2p,1d] basis set and contains d polarization, can be directly used, for geometry optimization, in conjunction with the standard 6-31G(d,p) People basis set for O and H.[12,13] These authors also demonstrated that the use of this basis set in DFT calculations leads to an accurate estimation of binding enthalpies[12] and activation energies[13] in the case of systems where the divalent lead ion is involved.

The descriptions we obtained for the electronic structure of lead, when using these two supplementry basis sets, were similar to the one produced by the LanL2DZ which is in favor of the minor role of the d orbital in the reactivity of lead cation. Moreover, by proving its ability to correctly describe the valence shell of lead, the LanL2DZ basis set showed its ability to take into account the general processes governing the interaction of lead cation with ligands.

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