Introduction

Hydrated metal ions abound in nature. Examinations of microhydrated metal ions permit insight into metal ion chemistry in solution. In fact, the study of metal ion hydration has been among the classical pursuits in physical chemistry for many decades. An early technique is to grow metal hydrates from the bare metal ions by allowing them to collide with water molecules in vacuo.1 This works well with singly charged metals, but fails for the majority of doubly charged metals (M^{2+}), including most alkaline earths. This is because the second ionization energies (IEs) of most metals are much higher than the first IE of water (12.6 eV), and efficient electron transfer from water to the doubly charged metal occurs, resulting in M^{4+} and H_2O^-. The fascinating chemistry of doubly charged ions and their solvation properties have prompted many studies.2–6 Paradoxically, many doubly charged metals do obviously exist in solution.7

The creation of microsolvated doubly charged metals has proven to be challenging, and whether some of these exist has been hotly debated.8–10 In the past decade, M^{2+}(H_2O)_m, where m is typically >5, have been produced by electrospraying aqueous solutions of many M^{2+}.11–15 In addition, recent experiments on dehydrating M_2^+{(H_2O)_n} by collisional heating have demonstrated that, for most doubly charged metals, the monohydrates, M^{2+}(H_2O), do exist, at least within the tens of microseconds observation windows of these experiments.14,15,17 Theory established that, although the separated M^{4+} and H_2O^- may be thermodynamically more stable than M^{2+}(H_2O), the latter can be kinetically stable, provided the barrier against electron transfer is larger than a few kcal/mol and the monohydrate is formed with minimal vibrational excitation.8,9,11,16,18 Indeed, the monohydrate of the divalent metal that has the highest known second IE, copper, as well as those of many other metals that have high second IEs have all recently been identified.14,15,17 A notable exception is lead.5

Lead is known to hydrolyze in solution to form polymeric hydroxide species.7 However, as shown in Table 1, the most abundant Pb species in solution at a pH of 7 is Pb^{2+} at 53.1%, while the most abundant hydroxide species is [Pb(OH)_3]^{3+} at 22.9%. By comparison, the most abundant Cu species at pH 7 is [Cu_2(OH)_2]^{3+} at 65.6%, while Cu^{2+} is at 26.9%. Despite this high abundance of Pb^{2+} in solution, and in contrast to the

Table 1. Aqueous Solution Composition of Cu^{2+}(NO_3)_2 and Pb^{2+}(NO_3)_2 at pH 7

<table>
<thead>
<tr>
<th>Pb(NO_3)_2</th>
<th>Cu(NO_3)_2</th>
</tr>
</thead>
<tbody>
<tr>
<td>rel. concn (%)</td>
<td>species</td>
</tr>
<tr>
<td>53.1</td>
<td>Pb^{2+}</td>
</tr>
<tr>
<td>22.9</td>
<td>[Pb(OH)_3]^{2+}</td>
</tr>
<tr>
<td>10.6</td>
<td>PbOH^-</td>
</tr>
<tr>
<td>8.9</td>
<td>[Pb(OH)_3]^{3+}</td>
</tr>
<tr>
<td>3.8</td>
<td>[Pb(OH)_4]^{3-}</td>
</tr>
</tbody>
</table>

* Calculations were performed using COMICS^2 using stability constants available from ref 7.

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behavior of most metal ions, electrospraying lead (II) salt solutions fails to produce any \( \text{Pb}^{2+} (\text{H}_2\text{O})_n \). Attempts to produce hydrated \( \text{Pb}^{2+} \) by first solvating \( \text{Pb} \) atoms with water and then ionising the lead hydrates in argon clusters using electron ionization (the "pick-up" technique) were also unsuccessful, although they were effective for \( \text{Pb} \) clusters with propan-1-ol and butan-1-ol (but not those with methanol and ethanol).\(^{22}\)

These results were taken to indicate that alcohols that are softer (propan-1-ol and butan-1-ol)\(^{23}\) are better matches for \( \text{Pb}^{2+} \), a soft cation, and they confer stability to the solvated complex; harder, shorter alcohols and water do not have the same stabilizing effect.\(^{22}\) It has been suggested that \( \text{Pb}^{2+} \) is among "a select group of doubly charged metal ions that will not form stable complexes in the gas phase with water, irrespective of how many molecules are present".\(^{5}\) Calculated energy differences between proton-transfer products and \( [\text{Pb}(\text{H}_2\text{O})_4]^{2+} \) were used to justify the absence of \( [\text{Pb}(\text{H}_2\text{O})_4]^{2+} \) in experiments.\(^{22}\)

Here we report the first observation of \( [\text{Pb}(\text{H}_2\text{O})_2]^{2+} \). This complex was observed in the gas phase as a minor product in the reaction of \( [\text{Pb}(\text{CH}_3\text{CN})]^{2+} \) with water. Results of a density functional theory (DFT) examination on the energetics of dissociation reactions of doubly charged lead hydrates and those of reactions between \( [\text{Pb}(\text{CH}_3\text{CN})]^{2+} \) and \( \text{H}_2\text{O} \) are also presented.

**Experimental Method**

Experiments were performed on an MDS Sciex (Concord, ON) hybrid quadrupole/time-of-flight mass spectrometer, the Centaur, which is a prototype of the commercially available QSTAR (AB/MDS Sciex). This ion was mass-selected by the first quadrupole mass filter and analyzed. 58% in the second quadrupole at a pressure of typically 6 mTorr, and \( 1 \mu \text{L/min} \). The lens voltages were optimized to produce \( [\text{Pb}(\text{CH}_3\text{CN})]^{2+} \). This ion was mass-selected by the first quadrupole mass filter and allowed to collide with room air (23–25 °C, relative humidity = 50–58%) in the second quadrupole at a pressure of typically 6 mTorr, and the product ions were mass-analyzed by the time-of-flight mass analyzer.

**Computational Method**

Geometry optimizations and energy calculations were performed with Gaussian 98\(^{24}\) using the B3LYP exchange-correlation functional\(^{22,25}\) with the sdd relativistic core potential and basis set\(^{26}\) for lead and the 6-311++G** doubly split-valuation basis set\(^{27,28}\) for the other atoms. All stationary points were characterized by harmonic vibrational frequency calculations.

**Results and Discussion**

Prior to showing the results that establish \( [\text{Pb}(\text{H}_2\text{O})_2]^{2+} \) to be a minor product in the gas-phase reaction of \( [\text{Pb}(\text{CH}_3\text{CN})]^{2+} \) with water, we will begin by examining the intrinsic stability of doubly charged lead hydrates. Contrary to an earlier prediction,\(^3\) DFT calculations (Figure 1) suggest that \( [\text{Pb}(\text{H}_2\text{O})_2]^{2+} \) is stable against both dissociative proton and charge transfers. \( [\text{Pb}(\text{H}_2\text{O})_2]^{2+} \) is lower in energy than the dissociation products of three possible channels (\( \text{Pb}^{2+} + \text{H}_2\text{O}^+, \text{Pb}^{2+} + \text{H}_2\text{O}, \) and \( \text{PbOH}^+ + \text{H}^+ \)) by a minimum of 22.5 kcal/mol in free energy at 298 K. \( [\text{Pb}(\text{H}_2\text{O})_2]^{2+} \) and \( [\text{Pb}(\text{H}_2\text{O})_3]^{2+} \) are thermodynamically stable with respect to charge transfer but are only kinetically stable regarding proton transfer; detection will require that they be formed with minimal excitation. Charge transfer to water becomes increasingly more endoergic in \( [\text{Pb}(\text{H}_2\text{O})_n]^{2+} \) as \( n \) increases, from 22.5 kcal/mol for \( n = 1 \), 39.7 kcal/mol for \( n = 2 \), to 54.7 kcal/mol for \( n = 3 \). These energies should, however, be considered with caution as spin–orbit coupling (SOC) may lower the energy levels of radical cations significantly. The B3LYP/sdd method underestimates the second IE of lead by 1.1 eV (13.9 eV versus the experimental second IE of 15.0 eV).\(^{33}\) Assuming that this error is due mostly to the lack of SOC consideration in Pb*\(^+\) (there is no SOC in Pb*\(^+\)), the charge-transfer reaction for \( n = 1 \) may become almost thermoneutral. For \( n = 2 \) and 3, charge-transfer reactions that are less endoergic than those shown in Figure 1b and c may also be anticipated. However, charge-transfer dissociations must proceed via substantial barriers as there is considerable Coulombic repulsion between the two separating positive charges.\(^2\) Locating the relevant transition structures is a theoretical challenge involving multireference electronic states beyond the scope of this study. Dissociative proton transfer to water is exoergic, but has substantial free-energy barriers. For \( [\text{Pb}(\text{H}_2\text{O})_2]^{2+} \), the barrier against the first, water-dissociation step accompanied by proton transfer is 14.0 kcal/mol in free energy; the second step in which the complex dissociates is slightly lower in barrier at 13.8 kcal/mol. For \( [\text{Pb}(\text{H}_2\text{O})_3]^{2+} \), the barrier against proton transfer and loss of \( \text{H}_2\text{O}^+ \) is even higher at 19.7 kcal/mol in free energy. \( \text{PbOH}^+ \) and \( \text{H}_2\text{O} \) are lower in free energy than \( [\text{Pb}(\text{H}_2\text{O})_2]^{2+} \) by 45.0 kcal/mol, whereas \( \text{PbOH}(\text{H}_2\text{O})^+ \) and \( \text{H}_2\text{O}^+ \) are lower than \( [\text{Pb}(\text{H}_2\text{O})_3]^{2+} \) by 30.9 kcal/mol. The proton-transfer results are in line with the expectation that \( [\text{Pb}(\text{H}_2\text{O})_n]^{2+} \) for large \( n \) values must be thermodynamically stable with respect to dissociation (hydrated \( \text{Pb}^{2+} \) is stable in solution). Thus, contrary to earlier conclusions,\(^2\) \( [\text{Pb}(\text{H}_2\text{O})_2]^{2+} \) and probably \( [\text{Pb}(\text{H}_2\text{O})_3]^{2+} \), once formed, should at least be kinetically stable and experimentally observable.

As electrospraying an aqueous solution of Pb\(^{2+}\), addition of water to Pb\(^{2+}\), and ionization of Pb(\( \text{H}_2\text{O} \)) in argon clusters (the pick-up technique) all fail to produce any lead (II) hydrates,\(^{22}\) we decided to attempt producing \( [\text{Pb}(\text{H}_2\text{O})_n]^{2+} \) \( n \geq 2 \) via ligand-
exchange reaction of water and \([\text{Pb(CH}_3\text{CN)}]^{2+}\); the latter ion is facilely produced by electrospraying \(\text{Pb}^{2+}\) in acetonitrile. Figure 2 shows the products of colliding (a) \([^{208}\text{Pb(CH}_3\text{CN)}]^{2+}\) and (b) \([^{206}\text{Pb(CH}_3\text{CN)}]^{2+}\) with approximately 6.3 mTorr of room air (50% relative humidity) at a laboratory energy of 35 eV. Figure 3 shows details of the mass spectral windows 101–115 Th. Mass selection was performed using the first quadrupole, which was operated under nominally unit mass-to-charge resolution at half peak-height. The characteristics were that ions within \(+0.5\) Th from the mass-selected ion were more efficiently

Figure 1. Relative energies (in kcal/mol) for lead hydrates calculated with the B3LYP/6-31++G** method: (a) \([\text{Pb(H}_2\text{O)}]^{2+}\), (b) \([\text{Pb(H}_2\text{O)}^2]\), and (c) \([\text{Pb(H}_2\text{O)}^3]\). The top values are relative enthalpies at 0 K \(\Delta H_0^\circ\); the bottom values (italics) are relative free energies at 298 K \(\Delta G_{298}^\circ\).

\[\Delta H_0^\circ = 60.4\quad \Delta G_{298}^\circ = 54.9\]
\[79.0\quad 74.4\]
\[28.8\quad 22.5\]

\[\Delta H_0^\circ = 106.2\quad \Delta G_{298}^\circ = 92.7\]
\[49.3\quad 39.7\]
\[12.4\quad 13.8\]
\[12.4\quad 13.8\]

\[\Delta H_0^\circ = 143.3\quad \Delta G_{298}^\circ = 122.0\]
\[64.0\quad 54.7\]
\[5.9\quad 9.5\]
\[5.7\quad 5.8\]

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transmitted than those within ~0.5 Th. A manifestation of this transmission characteristic is that the abundance of the $^{207}\text{Pb}^{2+}$ ion is lower in Figure 3a than it is in Figure 3b. As the following discussion of the fragmentation chemistry applies to all Pb isotopes, reference to specific Pb isotopes will be dropped from now on. The products observed in Figures 2 and 3 are: Pb$^{+}$, CH$_3$CN$^{+}$, PbOH$^{+}$, [CH$_3$CN + H]$^{+}$, PbNC$^{+}$, O$_2^{+}$, Pb$^{2+}$, and [Pb(H$_2$O)]$^{2+}$; the last two are minor and at approximately 2% and 0.4% of the total abundance, respectively. The presence of ions of all three major Pb isotopes in Figure 3b serves as a convenient confirmation of the assignments of Pb$^{2+}$ and [Pb-(H$_2$O)]$^{2+}$. At a laboratory collision energy of 10 eV, the only discernible products are PbOH$^{+}$ and [CH$_3$CN + H]$^{+}$ (spectrum not shown). At 35 eV (Figures 2 and 3), the following reaction channels are apparent: (1) dissociative charge transfer, [Pb-(CH$_3$CN)]$^{2+}$ + H$_2$O $\rightarrow$ [Pb(CH$_3$CN)(H$_2$O)]$^{2+}$* (vibronically excited) $\rightarrow$ PbOH$^{+}$ + [CH$_3$CN + H]$^{+}$; (4) ligand dissociation, [Pb(CH$_3$CN)]$^{2+}$ + M $\rightarrow$ Pb$^{2+}$ + CH$_3$CN + M; and (5) ligand exchange, [Pb(CH$_3$CN)]$^{2+}$ + H$_2$O $\rightarrow$ [Pb(CH$_3$CN)(H$_2$O)]$^{2+}$* $\rightarrow$ [Pb(H$_2$O)]$^{2+}$ + CH$_3$CN. O$_2^{+}$ is probably formed via charge transfer as a special case of (1) [Pb(CH$_3$CN)]$^{2+}$ + O$_2$ $\rightarrow$ Pb$^{2+}$ + CH$_3$CN + O$_2^{+}$; the ionization energy of O$_2$ (12.07 eV) is lower than that of CH$_3$CN (12.19 eV).$^{35,36}$ By comparison, the ionization energies of H$_2$O (12.62 eV), N$_2$ (15.58 eV), and Pb$^{2+}$ (i.e. the second ionization energy of Pb, 15.0 eV) are all

(35) Ionization energies are from http://webbook.nist.gov/chemistry.

(36) The lower abundance of O$_2^{+}$ relative to CH$_3$CN$^{+}$ probably reflects the collisional frequency with O$_2$ versus other molecules (~20%) and geometric effects. The acetonitrile is in close proximity with Pb$^{2+}$, whereas O$_2$ needs to approach Pb$^{2+}$ from directions that are not shielded by the acetonitrile for electron transfer from O$_2$ to take place.
higher. Other routes in forming $O_2^+$, e.g. by charge transfer between $\text{Pb}^{2+}$ and $O_2$ or between $\text{CH}_3\text{CN}^+$ and $O_2$, are also possible.

At 25 °C, air at a pressure of 6 mTorr contains $1.9 \times 10^{20}$ molecules per cubic meter. Using an estimate of 100 Å² for the collision cross section of $[\text{Pb(CH}_3\text{CN)}]^2+$ in air\(^{(37)}\) gives a mean free path of $1000/(100 \times 10^{−20})(1.9 \times 10^{20})$ mm = 5.3 ~ 5 mm. For an ion that has a straight ion path paralleling the quadrupole axis (possible only for an ion that suffers no collision and is not under the influence of rf voltage) and a second quadrupole length of 20 cm, there are 200/5 or 40 collisions. As the mole percent of water is 1.65%, in 40 collisions, 0.7 or ~1 collision will be with water. Of course in reality, the ion path is never straight. Furthermore, the ion loses its kinetic energy in collisions with air. This, coupled with the lack of an imposed axial electric field within the second quadrupole, means that in reality there are many more collisions (in fact, an injected ion will stop within an ideal quadrupole that has a pressure of a few mTorr and will only begin to exit, after a considerable number of ions have been accumulated within the quadrupole, because of ion/ion repulsion).\(^{(38)}\)\(^{(39)}\) In other words, ligand-exchange reaction between $[\text{Pb(CH}_3\text{CN)}]^2+$ and water is feasible insofar as the number of collisions is concerned.

Figure 4 shows the energy profiles of reactions between $[\text{Pb(CH}_3\text{CN)}]^2+$ and water. For energies, the upper values are $\Delta H^\circ$ and the lower values $\Delta G^\circ$. The reactions on the right-hand half of the figure have water as a mere spectator or

collision partner (M). Those on the left-hand half require formation of \([\text{Pb(CH}_3\text{CN})(\text{H}_2\text{O})]^2+\), which then dissociates to products. Reaction channel 1 (vide supra), dissociative charge transfer, is endoergic by 35.0 kcal/mol. Reaction channel 2, ligand fragmentation to \(\text{PbNC}^+\) and \(\text{CH}_3\text{CN}^+\), is endoergic by 31.6 kcal/mol. The free-energy barrier of the reaction, 72.5 kcal/mol, is sizable. Reaction channel 4, ligand dissociation, is barrierless and the most endoergic at 84.9 kcal/mol. Reaction channel 3, complexation followed by dissociative proton transfer, yields the lowest-energy products of \(\text{PbOH}^+\) and \([\text{CH}_3\text{CN}^+\text{H}^+]\). At higher collision energies, other reaction channels open. At a laboratory collision energy of 35 eV, products of dissociative charge transfer (\(\text{Pb}^+\) and \(\text{CH}_3\text{CN}^+\)), ligand fragmentation (\(\text{PbNC}^+\)), and ligand dissociation (\(\text{Pb}^{2+}\)) are observed (Figures 2 and 3). Observation of \([\text{Pb(H}_2\text{O})]^2+\), the charged ligand-exchange product, also requires higher collision energies (higher vibronically excited states for \([\text{Pb(CH}_3\text{CN})(\text{H}_2\text{O})]^2+\)). Multiple collisions in the second quadrupole facilitates vibronic excitation by collisionally activating cooler \([\text{Pb(CH}_3\text{CN})(\text{H}_2\text{O})]^2+\) or activating \([\text{Pb(CH}_3\text{CN})]^2+\) before its complexation with \(\text{H}_2\text{O}\). However, as formation of \([\text{Pb(H}_2\text{O})]^2+\) requires collision with \(\text{H}_2\text{O}\), whereas formation of the other product ions can result from collisions with any of the other more plentiful molecules from air, the relative abundance of \([\text{Pb(H}_2\text{O})]^2+\) is necessarily low (only 1.65% collisions are with water). In addition to this factor, the lower-energy dissociation pathway for vibronically excited \([\text{Pb(CH}_3\text{CN})(\text{H}_2\text{O})]^2+\) is dissociative proton transfer, which is an effective competition against ligand exchange. These factors combine to result in a low abundance \([\text{Pb(H}_2\text{O})]^2+\) ion. The observation of \([\text{Pb(H}_2\text{O})]^2+\), however, was reproducible over a span of weeks on the hydrid quadrupole/time-of-flight mass spectrometer as well as on a triple quadrupole mass spectrometer. \([\text{Pb(H}_2\text{O})]^2+\) was also apparent in a set of experiments in which the collision gas was wet nitrogen (moisture content unknown).

**Conclusions**

We have provided proof that doubly charged lead monohydrate does exist and can be synthesized, albeit in low yield, from ligand exchange that results in energized collisions between \([\text{Pb(CH}_3\text{CN})]^2+\) and \(\text{H}_2\text{O}\) in the gas phase. DFT calculations suggest that \([\text{Pb(CH}_3\text{CN})(\text{H}_2\text{O})]^2+\) is stable, while \([\text{Pb(H}_2\text{O})]^2+\) and \([\text{Pb(H}_2\text{O})_2]^2+\) are metastable against dissociative proton transfer. All three hydrated ions are stable against dissociative charge transfer.

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**Supporting Information Available:** Tables 1S and 2S, enthalpies and free energies of relevant ions and neutrals; Table 3S, total energies and Cartesian coordinates for all structures reported. This material is available free of charge via the Internet at http://pubs.acs.org.

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