

Existence of Doubly Charged Lead Monohydrate: Experimental Evidence and Theoretical Examination

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Abstract: Despite reports to the contrary, doubly charged lead monohydrate is a stable species against both proton and charge transfers. $[\text{Pb}(\text{H}_2\text{O})]^{2+}$ has been observed as a minor product in the ligand-exchange reaction of $[\text{Pb}(\text{CH}_3\text{CN})]^{2+}$ with H_2O after collisional activation. Density functional theory has been used to examine reaction profiles of $[\text{Pb}(\text{H}_2\text{O})_n]^{2+}$ where $n = 1, 2,$ and 3 .

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^{+} 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.^{8–18} In the past decade, $\text{M}^{2+}(\text{H}_2\text{O})_m$, where

Table 1. Aqueous Solution Composition of $\text{Cu}^{\text{II}}(\text{NO}_3)_2$ and $\text{Pb}^{\text{II}}(\text{NO}_3)_2$ at pH 7^a

$\text{Pb}^{\text{II}}(\text{NO}_3)_2$		$\text{Cu}^{\text{II}}(\text{NO}_3)_2$	
rel. concn (%)	species	rel. concn (%)	species
53.1	Pb^{2+}	65.6	$[\text{Cu}_2(\text{OH})_2]^{2+}$
22.9	$[\text{Pb}_4(\text{OH})_4]^{4+}$	26.9	Cu^{2+}
10.6	PbOH^+	5.4	CuOH^+
8.9	$[\text{Pb}_3(\text{OH})_4]^{2+}$	1.7	$\text{Cu}(\text{OH})_2$
3.8	$[\text{Pb}_6(\text{OH})_8]^{4+}$		

^a Calculations were performed using COMICS²¹ using stability constants available from ref 7.

m is typically >5 , have been produced by electrospraying aqueous solutions of many M^{2+} .^{19,20} In addition, recent experiments on dehydrating $\text{M}^{2+}(\text{H}_2\text{O})_m$ by collisional heating have demonstrated that, for most doubly charged metals, the monohydrates, $\text{M}^{2+}(\text{H}_2\text{O})$, do exist, at least within the tens of microseconds observation windows of these experiments.^{14,15,17} Theory established that, although the separated M^{+} and H_2O^{+} may be thermodynamically more stable than $\text{M}^{2+}(\text{H}_2\text{O})$, 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 polynuclear 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 $[\text{Pb}_4(\text{OH})_4]^{4+}$ at 22.9%. By comparison, the most abundant Cu species at pH 7 is $[\text{Cu}_2(\text{OH})_2]^{2+}$ at 65.6%, while Cu^{2+} is at 26.9%. Despite this high abundance of Pb^{2+} in solution, and in contrast to the

- (1) Spears, K. G.; Fehsenfeld, F. C. *J. Chem. Phys.* **1972**, *56*, 5698–5705.
- (2) Price, S. D. *J. Chem. Soc., Faraday Trans.* **1997**, *93*, 2451–2460.
- (3) Schröder, D.; Schwarz, H. *J. Phys. Chem. A* **1999**, *103*, 7385–7394.
- (4) Stace, A. J. *J. Phys. Chem. Chem. Phys.* **2001**, *3*, 1935–1941.
- (5) Stace, A. J. *J. Phys. Chem. A* **2002**, *106*, 7993–8005.
- (6) Price, S. D. *J. Phys. Chem. Chem. Phys.* **2003**, *5*, 1717–1729.
- (7) Smith, R. M.; Martell, A. E. *Critical Stability Constants; Inorganic Complexes*, Vol. 4; Plenum: New York, 1981.
- (8) Beyer, M.; Williams, E. R.; Bondybej, V. E. *J. Am. Chem. Soc.* **1999**, *121*, 1565–1573.
- (9) El-Nahas, A. M.; Tajima, N.; Hirao K. *Chem. Phys. Lett.* **2000**, *318*, 333–339.
- (10) Stace, A. J.; Walker, N. R.; Wright, R. R.; Firth, S. *Chem. Phys. Lett.* **2000**, *329*, 173–175.
- (11) El-Nahas, A. M. *Chem. Phys. Lett.* **2000**, *329*, 176–178.
- (12) Walker, N.; Dobson, M. P.; Wright, R. R.; Barran, P. E.; Murrell, J. N.; Stace, A. J. *J. Am. Chem. Soc.* **2000**, *122*, 11138–11145.
- (13) Wright, R. R.; Walker, N.; Firth, S.; Stace, A. J. *J. Phys. Chem. A* **2001**, *105*, 54–64.
- (14) Shvartsburg, A. A.; Siu, K. W. M. *J. Am. Chem. Soc.* **2001**, *123*, 10071–10075.
- (15) Schröder, D.; Schwarz, H.; Wu, J.; Wesdemiotis, C. *Chem. Phys. Lett.* **2001**, *343*, 258–264.
- (16) El-Nahas, A. M. *Chem. Phys. Lett.* **2001**, *345*, 325–330.
- (17) Stone, J. A.; Vukomanovic, D. *Chem. Phys. Lett.* **2001**, *346*, 419–422.

- (18) El-Nahas, A. M. *Chem. Phys. Lett.* **2001**, *348*, 483–490.
- (19) Jayaweera, P.; Blades, A. T.; Ikononou, M. G.; Kebarle, P. *J. Am. Chem. Soc.* **1990**, *112*, 2452–2454.
- (20) Cheng, Z. L.; Siu, K. W. M.; Guevremont, R.; Berman, S. S. *J. Am. Soc. Mass Spectrom.* **1992**, *3*, 281–288.

behavior of most metal ions, electrospraying lead (II) salt solutions fails to produce any $\text{Pb}^{2+}(\text{H}_2\text{O})_m$. Attempts to produce hydrated Pb^{2+} by first solvating Pb atoms with water and then ionizing the lead hydrates in argon clusters using electron ionization (the “pick-up” technique) were also unsuccessful, although they were effective for 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 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 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 $[\text{Pb}(\text{H}_2\text{O})]^{2+}$. 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 H_2O 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). The time-of-flight analyzer incorporates a reflectron; the typical resolution achieved for ions of the m/z range examined in this study is 10 000. The sample was 200 μM lead (II) nitrate in acetonitrile. It was introduced into the ion source by electrospraying at a flow rate of 3 $\mu\text{L}/\text{min}$. 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 98²⁴ using the B3LYP exchange-correlation functional^{25–27} with the sdd relativistic core potential and basis set²⁸ for lead and the 6-31++G** doubly split-valence basis set^{29–32} for the other atoms.

All stationary points were characterized by harmonic vibrational frequency calculations.

Results and Discussion

Prior to showing the results that establish $[\text{Pb}(\text{H}_2\text{O})]^{2+}$ 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,⁵ DFT calculations (Figure 1) suggest that $[\text{Pb}(\text{H}_2\text{O})]^{2+}$ is stable against both dissociative proton and charge transfers. $[\text{Pb}(\text{H}_2\text{O})]^{2+}$ is lower in energy than the dissociation products of three possible channels ($\text{Pb}^{+} + \text{H}_2\text{O}^{+}$, $\text{Pb}^{2+} + \text{H}_2\text{O}$, 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^{2+}), 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.^{2–6,9,11,16,18} 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 H_3O^{+} is even higher at 19.7 kcal/mol in free energy. PbOH^{+} and H_3O^{+} are lower in free energy than $[\text{Pb}(\text{H}_2\text{O})_2]^{2+}$ by 45.0 kcal/mol, whereas $[\text{Pb}(\text{OH})(\text{H}_2\text{O})]^{+}$ and H_3O^{+} 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 Pb^{2+} is stable in solution). Thus, contrary to earlier conclusions,⁵ $[\text{Pb}(\text{H}_2\text{O})]^{2+}$ and probably $[\text{Pb}(\text{H}_2\text{O})_{2,3}]^{2+}$, 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 $\text{Pb}(\text{H}_2\text{O})_n$ in argon clusters (the pick-up technique) all fail to produce any lead (II) hydrates,^{5,22} we decided to attempt producing $[\text{Pb}(\text{H}_2\text{O})]^{2+}$ via ligand-

- (21) Perrin, D. D.; Sayce, I. G. *Talanta* **1967**, *14*, 833–842.
 (22) Akibo-Betts, G.; Barran, P. E.; Puskar, L.; Duncombe, B.; Cox, H.; Stace, A. J. *J. Am. Chem. Soc.* **2002**, *124*, 9257–9264.
 (23) Parr, R. G.; Pearson, R. G. *J. Am. Chem. Soc.* **1983**, *105*, 7512–7516.
 (24) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Salvador, P.; Dannenberg, J. J.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, Rev. A.11; Gaussian, Inc.: Pittsburgh, PA, 2001.
 (25) Becke, A. D. *Phys. Rev.* **1988**, *A38*, 3098–3100.
 (26) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648–5652.
 (27) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev.* **1988**, *B37*, 785–789.
 (28) Wedig, U.; Dolg, M.; Stoll, H.; Preuss, H. In *Quantum Chemistry: The Challenge of Transition Metals and Coordination Chemistry*; Veillard, A., Ed.; NATO Advanced Study Institute Series, Series C, Mathematical and Physical Sciences, Vol. 176; Reidel: Dordrecht, 1986; p 79.

- (29) Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257–2261.
 (30) Hariharan, P. C.; Pople, J. A. *Chem. Phys. Lett.* **1972**, *16*, 217–219.
 (31) Chandrasekhar, J.; Andrade, J. G.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1981**, *103*, 5609–5612.
 (32) Clark, T.; Chandrasekhar, J.; Spitznagel, G. W.; Schleyer, P. v. R. *J. Comput. Chem.* **1983**, *4*, 294–301.
 (33) Lide, D. R. *CRC Handbook of Chemistry and Physics*, 71st ed.; CRC Press: Boca Raton, FL, 1990; pp 210–211.

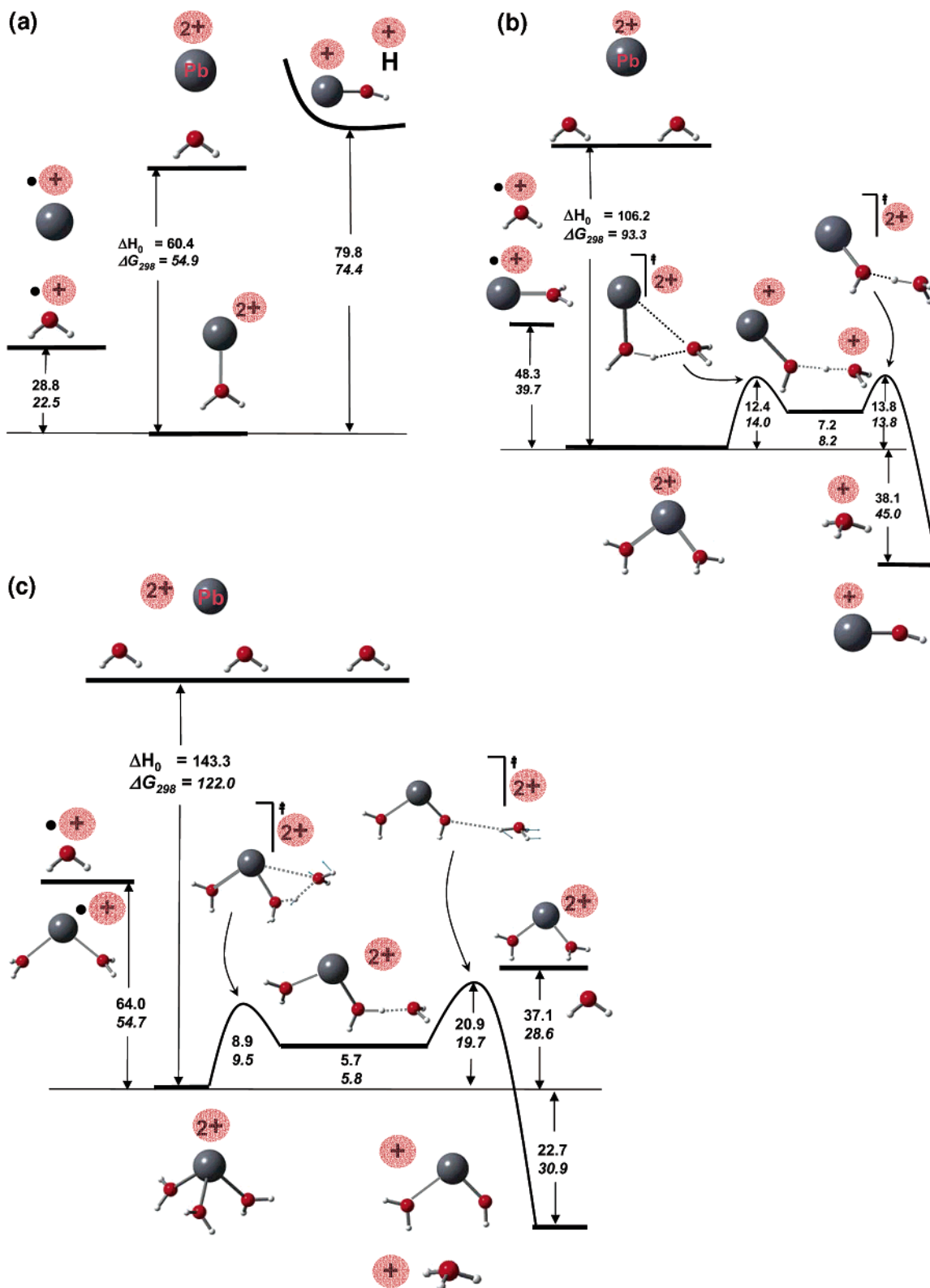


Figure 1. Relative energies (in kcal/mol) for lead hydrates calculated with the B3LYP/sdd/6-31++G** method: (a) $[\text{Pb}(\text{H}_2\text{O})]^{2+}$, (b) $[\text{Pb}(\text{H}_2\text{O})_2]^{2+}$, and (c) $[\text{Pb}(\text{H}_2\text{O})_3]^{2+}$. The top values are relative enthalpies at 0 K (ΔH_0°); the bottom values (*italics*) are relative free energies at 298 K (ΔG_{298}°).

exchange reaction of water and $[\text{Pb}(\text{CH}_3\text{CN})]^{2+}$; the latter ion is readily produced by electro spraying Pb^{2+} in acetonitrile.³⁴ Figure 2 shows the products of colliding (a) $^{208}\text{Pb}(\text{CH}_3\text{CN})]^{2+}$ and (b) $^{206}\text{Pb}(\text{CH}_3\text{CN})]^{2+}$ 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

(34) Cheng, Z. L.; Siu, K. W. M.; Guevremont, R.; Berman, S. S. *Org. Mass Spectrom.* **1992**, *27*, 1370–1376.

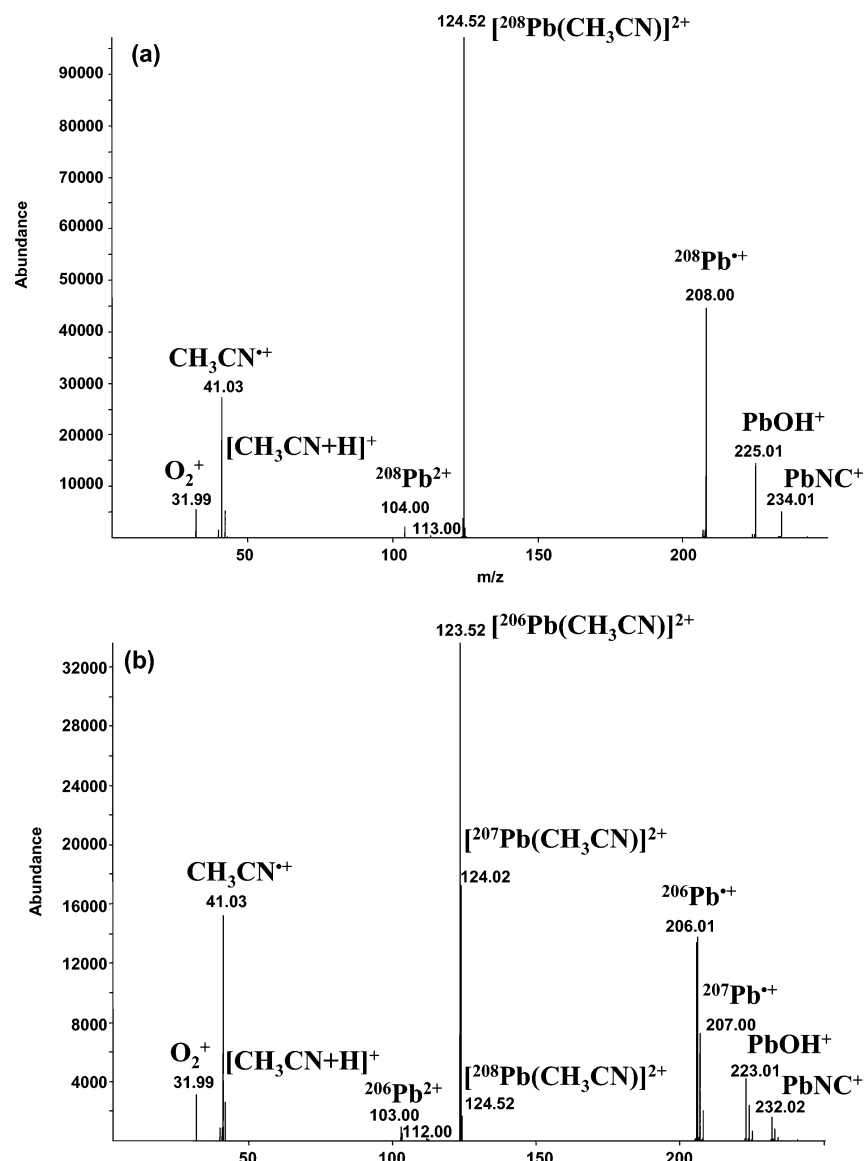


Figure 2. Collisional activation of (a) $[^{208}\text{Pb}(\text{CH}_3\text{CN})]^{2+}$ and (b) $[^{206}\text{Pb}(\text{CH}_3\text{CN})]^{2+}$ by, and reaction with, room air at 50% relative humidity: laboratory collision energy, 35 eV; air pressure, 6.3 mTorr. The precursor ions were mass-selected by the first quadrupole operating at nominally unit mass-to-charge resolution at half peak-height.

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_3CN^{+} , PbOH^{+} , $[\text{CH}_3\text{CN} + \text{H}]^{+}$, PbNC^{+} , O_2^{+} , Pb^{2+} , and $[\text{Pb}(\text{H}_2\text{O})]^{2+}$; 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 $[\text{Pb}(\text{H}_2\text{O})]^{2+}$. At a laboratory collision energy of 10 eV, the only discernible products are PbOH^{+} and $[\text{CH}_3\text{CN} + \text{H}]^{+}$ (spectrum not shown). At 35 eV (Figures 2 and 3), the following reaction channels are apparent: (1) dissociative charge transfer, $[\text{Pb}(\text{CH}_3\text{CN})]^{2+} + \text{M}$ (M is a collision partner, N_2 , O_2 , or H_2O) $\rightarrow \text{Pb}^{+} + \text{CH}_3\text{CN}^{+} + \text{M}$; (2) ligand fragmentation, $[\text{Pb}(\text{CH}_3\text{CN})]^{2+} + \text{M} \rightarrow \text{PbNC}^{+} + \text{M} + \text{CH}_3^{+}$ (CH_3^{+} is not observed in Figure 2 because of enhanced scattering losses relative to other heavier fragment ions; it is, however, observable after

prolonged spectral accumulation. Some PbNC^{+} may isomerize to PbCN^{+} , which is 0.7 kcal/mol lower in ΔG°_{298} than the former; the barrier against isomerization is also low at 7.7 kcal/mol in free energy); (3) complexation followed by dissociative proton transfer, $[\text{Pb}(\text{CH}_3\text{CN})]^{2+} + \text{H}_2\text{O} \rightarrow \{[\text{Pb}(\text{CH}_3\text{CN})(\text{H}_2\text{O})]^{2+}\}^*$ (vibronically excited) $\rightarrow \text{PbOH}^{+} + [\text{CH}_3\text{CN} + \text{H}]^{+}$; (4) ligand dissociation, $[\text{Pb}(\text{CH}_3\text{CN})]^{2+} + \text{M} \rightarrow \text{Pb}^{2+} + \text{CH}_3\text{CN} + \text{M}$; and (5) ligand exchange, $[\text{Pb}(\text{CH}_3\text{CN})]^{2+} + \text{H}_2\text{O} \rightarrow \{[\text{Pb}(\text{CH}_3\text{CN})(\text{H}_2\text{O})]^{2+}\}^* \rightarrow [\text{Pb}(\text{H}_2\text{O})]^{2+} + \text{CH}_3\text{CN}$. O_2^{+} is probably formed via charge transfer as a special case of (1) $[\text{Pb}(\text{CH}_3\text{CN})]^{2+} + \text{O}_2 \rightarrow \text{Pb}^{+} + \text{CH}_3\text{CN} + \text{O}_2^{+}$; the ionization energy of O_2 (12.07 eV) is lower than that of CH_3CN (12.19 eV).^{35,36} By comparison, the ionization energies of H_2O (12.62 eV), N_2 (15.58 eV), and Pb^{+} (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_3CN^{+} probably reflects the collisional frequency with O_2 versus other molecules ($\sim 20\%$) 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.

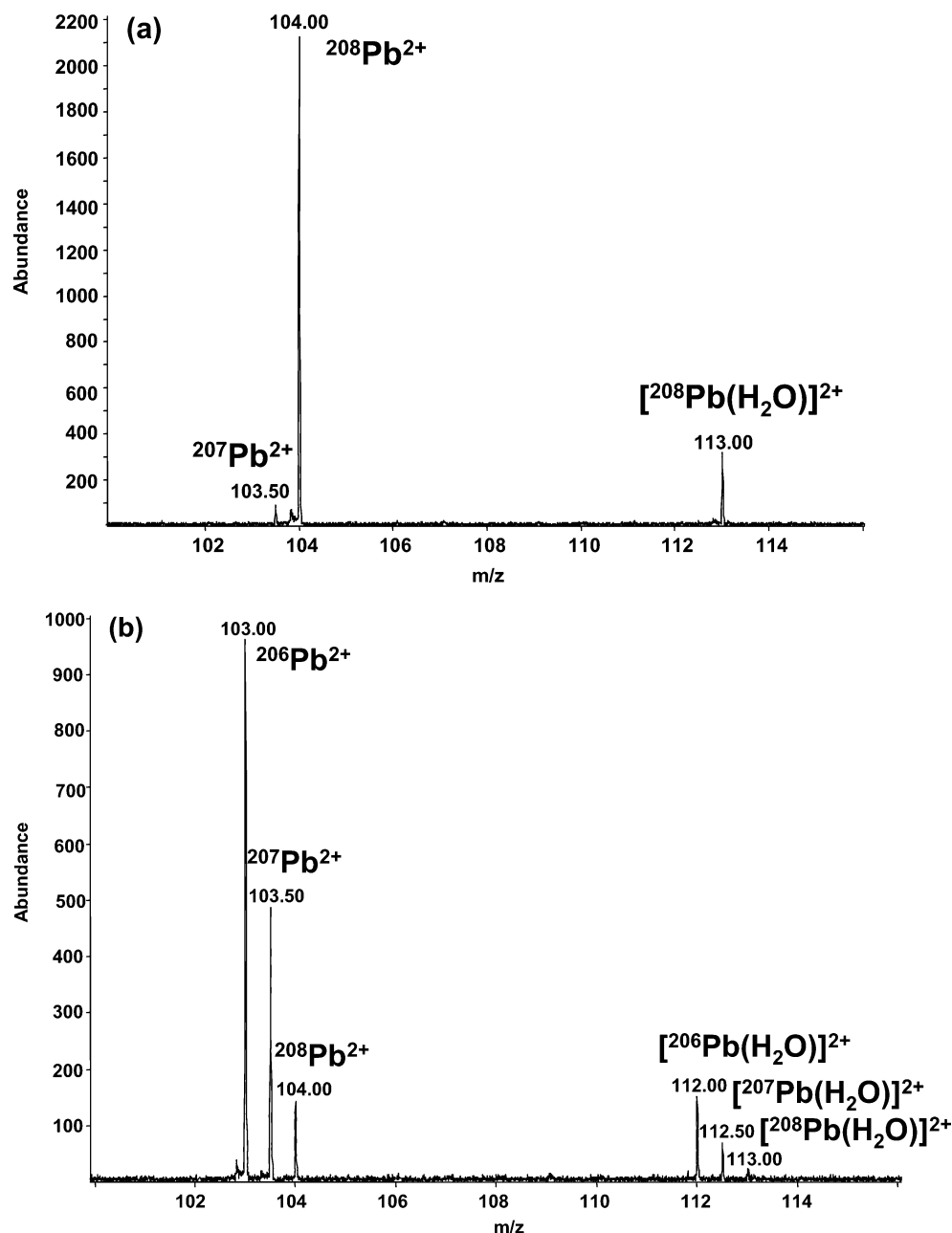


Figure 3. Collisional activation of (a) $[^{208}\text{Pb}(\text{CH}_3\text{CN})]^{2+}$ and (b) $[^{206}\text{Pb}(\text{CH}_3\text{CN})]^{2+}$ by, and reaction with, room air at 50% relative humidity: laboratory collision energy, 35 eV; air pressure, 6.3 mTorr. Mass spectral windows 101–115 Th from Figure 2 are shown.

higher.^{33,35} Other routes in forming O_2^+ , e.g. by charge transfer between 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 1.9×10^{20} molecules per cubic meter. Using an estimate of 100 \AA^2 for the collision cross section of $[\text{Pb}(\text{CH}_3\text{CN})]^{2+}$ in air³⁷ gives a mean free path of $1000/[(100 \times 10^{-20})(1.9 \times 10^{20})] \text{ mm} = 5.3 \sim 5 \text{ mm}$. 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 $[\text{Pb}(\text{CH}_3\text{CN})]^{2+}$ and water is feasible insofar as the number of collisions is concerned.

Figure 4 shows the energy profiles of reactions between $[\text{Pb}(\text{CH}_3\text{CN})]^{2+}$ and water. For energies, the upper values are ΔH_0° and the lower values ΔG_{298}° . The reactions on the right-hand half of the figure have water as a mere spectator or

(37) Berant, Z.; Karpus, Z. *J. Am. Chem. Soc.* **1989**, *111*, 3819–3824.

(38) Douglas, D. J.; French, J. B. *J. Am. Soc. Mass Spectrom.* **1992**, *3*, 398–408.

(39) Covey, T.; Douglas, D. J. *J. Am. Soc. Mass Spectrom.* **1993**, *4*, 616–623.

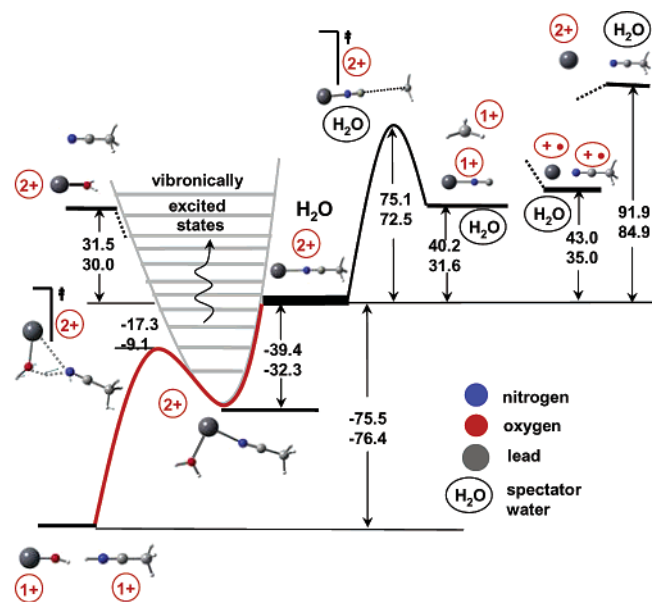


Figure 4. Energy profiles of reactions between $[\text{Pb}(\text{CH}_3\text{CN})]^{2+}$ and water at B3LYP/sdd/6-31++G**^{*}: the spectator H_2O participates as a collision partner. The top values are relative enthalpies at 0 K (ΔH_0°); the bottom values are relative free energies at 298 K (ΔG_{298}°). All energies are in kcal/mol. The energy levels shown for vibrionically excited $[\text{Pb}(\text{CH}_3\text{CN})(\text{H}_2\text{O})]^{2+}$ are arbitrary and are intended as an aid for discussion.

collision partner (M). Those on the left-hand half require formation of $\{[\text{Pb}(\text{CH}_3\text{CN})(\text{H}_2\text{O})]^{2+}\}^*$, 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 PbNC^+ and CH_3^+ , 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 PbOH^+ and $[\text{CH}_3\text{CN} + \text{H}]^+$ and is exoergic by 76.4 kcal/mol. The intermediate of this reaction, $[\text{Pb}(\text{CH}_3\text{CN})(\text{H}_2\text{O})]^{2+}$, readily dissociates as the entrance channel is exoergic by 32.3 kcal/mol, which is well above the free-energy barrier against dissociation of 23.2 kcal/mol. Reaction channel 5, ligand exchange, is endoergic by 30.0 kcal/mol. According to Figure 4, the only viable reaction at low collision energies is complexation followed by dissociative proton transfer, which is exoergic and effectively barrierless as the $[\text{Pb}(\text{CH}_3\text{CN})(\text{H}_2\text{O})]^{2+}$ complex is formed in a vibrionically excited state. Indeed, as mentioned above, the only observable fragment ions at a laboratory collision energy of 10 eV (center-of-mass energy of

~ 1 eV for the first collision) and lower are the final products of this reaction, 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 (Pb^{2+} and CH_3CN^+), ligand fragmentation (PbNC^+), and ligand dissociation (Pb^{2+}) are observed (Figures 2 and 3). Observation of $[\text{Pb}(\text{H}_2\text{O})]^{2+}$, the charged ligand-exchange product, also requires higher collision energies (higher vibrionically excited states for $[\text{Pb}(\text{CH}_3\text{CN})(\text{H}_2\text{O})]^{2+}$). Multiple collisions in the second quadrupole facilitates vibronic excitation by collisionally activating cooler $[\text{Pb}(\text{CH}_3\text{CN})(\text{H}_2\text{O})]^{2+}$ or activating $[\text{Pb}(\text{CH}_3\text{CN})]^{2+}$ before its complexation with H_2O . However, as formation of $[\text{Pb}(\text{H}_2\text{O})]^{2+}$ requires collision with H_2O , 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 $[\text{Pb}(\text{H}_2\text{O})]^{2+}$ is necessarily low (only 1.65% collisions are with water). In addition to this factor, the lower-energy dissociation pathway for vibrionically excited $[\text{Pb}(\text{CH}_3\text{CN})(\text{H}_2\text{O})]^{2+}$ is dissociative proton transfer, which is an effective competition against ligand exchange. These factors combine to result in a low abundance $[\text{Pb}(\text{H}_2\text{O})]^{2+}$ ion. The observation of $[\text{Pb}(\text{H}_2\text{O})]^{2+}$, however, was reproducible over a span of weeks on the hybrid quadrupole/time-of-flight mass spectrometer as well as on a triple quadrupole mass spectrometer. $[\text{Pb}(\text{H}_2\text{O})]^{2+}$ 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 $[\text{Pb}(\text{CH}_3\text{CN})]^{2+}$ and H_2O in the gas phase. DFT calculations suggest that $[\text{Pb}(\text{H}_2\text{O})]^{2+}$ is stable, while $[\text{Pb}(\text{H}_2\text{O})_2]^{2+}$ and $[\text{Pb}(\text{H}_2\text{O})_3]^{2+}$ 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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