Evidence of asymmetric cation solvation from the instability of [Pb(H$_2$O)$_n$]$^{2+}$ complexes†

Keri McQuinn,[a] Fraser Hof,*[a] J. Scott McIndoe,*[a] Xiaojing Chen,[b] Guohua Wu[b] and Anthony J. Stace*[b]

Experiments on [Pb(H$_2$O)$_n$]$^{2+}$ complexes show that they require an unusually large number of water molecules (eleven) to stabilize the Pb^{2+} ion against charge (proton) transfer.

There has been considerable debate in recent years as to why doubly charged metal–ligand complexes should be stable in the gas phase.[1–3] Attention has frequently focused on water as a ligand,[2] and of particular interest recently has been the series [Pb(H$_2$O)$_n$]$^{2+}$, and why two quite disparate experimental methods have both failed to provide any evidence of these ions in the gas phase.[4–6] Since the electron affinity of Pb^{2+} is 15.02 eV and the ionization energy of water is 12.6 eV, it is easy to appreciate that, in the absence of any additional stabilizing interactions, contact between the two will result in immediate charge transfer. In an elegant series of ligand exchange experiments, Siu and co-workers were able to form the monohydrate [Pb(H$_2$O)]$^{2+}$, which calculations showed to be stable with respect to the asymptotes Pb^{2+} + H$_2$O, Pb$^+$ + H$_2$O$^+$ and PbOH$^+$ + H$^+$.[5,6] Their calculations also showed that the reaction pathway leading to the latter hydrolysis product only becomes exothermic in the presence of two and three water molecules; however, [Pb(H$_2$O)$_{2,3}$]$^{2+}$ ions are still metastable with respect to this asymptote and, as noted by Siu and co-workers, the presence of a kinetic barrier should make them open to experimental observation.[5] Reported here are the results recorded from two separate experimental techniques that have each succeeded in forming [Pb(H$_2$O)$_n$]$^{2+}$ ions. From the combined observations, it is possible to show that these complexes exhibit a much higher degree of instability than any other metal dication–water complex to have been observed previously. In the condensed phase an equivalent degree of instability could be responsible for the anomalously low pK_a of water when in the presence of Pb^{2+}.

[Pb(H$_2$O)$_n$]$^{2+}$ complexes were first prepared from a solution of Pb(NO$_3$)$_2$ using ESI-MS (electrospray ionization mass spectrometry) (ESI-MS) under conditions of low temperature, high flow rate and high cone voltage,† previously employed to observe [M(H$_2$O)$_n$]$^{3+}$ (M = Ln, Tb, Lu).[7] A mass spectrum is

obtained from which lead isotope profiles corresponding to three series of ions can be identified: [Pb(NO$_3$)(H$_2$O)$_n$]$^+$, [Pb(OH)(H$_2$O)$_n$]$^+$, and [Pb(H$_2$O)$_n$]$^{2+}$ (see ESI†). For the latter, the lowest value observed for n was eight. Confirmation of this minimum stable size has been obtained from ED (energy dependent) ESI-MS/MS[8] experiments,† where large (e.g. n = 48) ions have been selected for collisional activation. The results show doubly charged fragments of all sizes down to n = 8, but loss of water eventually leads to charge separation and formation of the series [Pb(OH)(H$_2$O)$_n$]$^+$ and weak signals for [H(H$_2$O)$_k$]$^+$ (k = 3, 4) (see Fig. 1; note that k = 1 and 2 fall below the m/z range of the instrument).

In a second series of experiments the pick-up technique[3] has also been successful at generating [Pb(H$_2$O)$_n$]$^{2+}$ complexes and has been able to confirm the observation that [Pb(H$_2$O)$_8$]$^{2+}$ is the minimum size. However, because these experiments have been undertaken on a double focusing mass spectrometer (VG ZAB-E), it has been possible to use the MIKES (mass analyzed ion kinetic energy spectra) technique[9] to study the unimolecular (metastable) fragmentation patterns of some of the smaller [Pb(H$_2$O)$_n$]$^{2+}$ complexes. Ions with a given m/z value have been selected using a magnet and following unimolecular fragmentation in a field-free region,
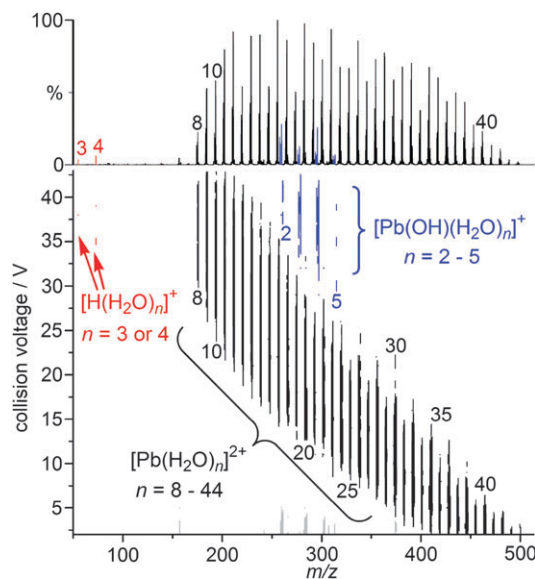

Fig. 1 Positive ion EDESI-MS/MS of [Pb(H$_2$O)$_{48}$]$^{2+}$. Water molecules are sequentially removed through multiple collisions, producing [Pb(H$_2$O)$_n$]$^{2+}$ (n = 8–47). No n < 8 dications are observed; instead, charge separation occurs.

[a] Department of Chemistry, University of Victoria, PO Box 3065, Victoria, Canada BC V8W3V6. E-mail: fhof@uvic.ca, mcindoe@uvic.ca
[b] Department of Physical Chemistry, School of Chemistry, The University of Nottingham, University Park, Nottingham, UK NG7 2RD. E-mail: anthony.stace@nottingham.ac.uk
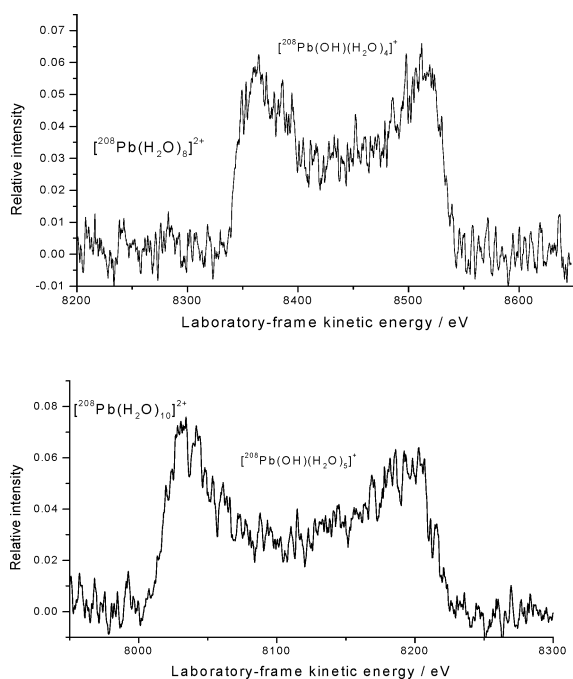
Fig. 2 Examples of kinetic energy profiles recorded following the metastable decay of the complexes $[Pb(H_2O)_8]^{2+}$ and $[Pb(H_2O)_{10}]^{2+}$.

any charged products were identified by scanning an electrostatic analyzer to record their laboratory-frame kinetic energies. The advantage of this approach is that the experiments can be performed in the absence of any collision gas and so evidence of fragmentation reflects the inherent instability of a particular complex.

Fig. 2 shows evidence of charge separation reactions recorded for $[Pb(H_2O)_8]^{2+}$ and $[Pb(H_2O)_{10}]^{2+}$ and where, for example, it can be determined that $[Pb(H_2O)_{10}]^{2+}$ has undergone the reaction: $[Pb(H_2O)_{10}]^{2+} \rightarrow [Pb(OH)(H_2O)_5]^+ + [H(H_2O)_4]^+$. Similar behaviour has also been recorded from $[Pb(H_2O)_9]^{2+}$, and for each case, the kinetic energy profile exhibits the classic shape of a fragmentation process that is accompanied by rapid charge separation.[9] A disadvantage of this type of scan is that, because of instrumental discrimination, it can be difficult to detect the counter ion, $[H(H_2O)_4]^+$. Being lighter these ions carry a greater fraction of the kinetic energy release and so experience increased scattering and instrumental discrimination. Hence, there is the possibility that the fragments could take the form $H_3O^+ + 3H_2O$; however, confirmation of $[H(H_2O)_4]^+$ as a product is provided by the EDESI-MS/MS experiments (Fig. 1).

Table 1 summarizes fragmentation patterns recorded for the three ions that exhibit metastability. Each of the $[Pb(H_2O)_n]^{2+}$ complexes exhibits a very specific reaction pathway, which, in part, appears to be driven by the formation of the stable ion

Table 1 Summary of unimolecular (metastable) fragmentation pathways observed for $[Pb(H_2O)_n]^{2+}$ complexes

n in $[Pb(H_2O)_n]^{2+}$	$PbOH^+$ fragment	Counter ion
8	$[PbOH(H_2O)_4]^+$	$[H(H_2O)_3]^+$
9	$[PbOH(H_2O)_4]^+$	$[H(H_2O)_4]^+$
10	$[PbOH(H_2O)_5]^+$	$[H(H_2O)_4]^+$

$[H(H_2O)_4]^+$. However, the most remarkable feature of the data is the fact that a $[Pb(H_2O)_n]^{2+}$ complex requires the presence of 11 water molecules in order for it to be stable with respect to proton transfer (charge separation). If, for example, these data are compared with strontium (Sr^{2+}), which has a similar ionic radius/charge density to Pb^{2+} at all coordination numbers,[10] then $[Sr(H_2O)_n]^{2+}$ complexes are stable at all values of n (see ESI†). Similarly, if the results are compared with observations on Mg^{2+}–water complexes, where Mg^{2+} has a similar electron affinity to Pb^{2+}, then the former complexes require just 4 water molecules to achieve stability.[11] The only example that comes close to the behaviour exhibited by Pb^{2+} is $[Cu(H_2O)_n]^{2+}$, where 8 water molecules are required to suppress metastable decay;[12] however, Cu^{2+} has an electron affinity ~ 6 eV larger than that of Pb^{2+}. What is very evident from the experimental results is that $[Pb(H_2O)_n]^{2+}$ complexes behave very differently from all other systems studied to date.

Although Fig. 2 shows that the proton transfer reaction is clearly exothermic, the delay in reaction time for $n = 8$–10 ($\sim 10^{-5}$ s) is caused by the presence of a Coulomb barrier for the reverse reaction.[5,13] Passage across the barrier is then determined by a combination of statistical energy partitioning and the probability of crossing potential energy surfaces.[14] The fact that $[Pb(H_2O)_n]^{2+}$ ions below $n = 8$ are not observed would suggest that, for these ions, the barrier is low and that surface crossing occurs early in the reaction coordinate (see Fig. 5 of ref. 15). As the number of water molecules increases, the barrier both increases in magnitude and shifts further along the reaction coordinate, until at $n = 11$, evaporative loss of water becomes the lowest energy reaction pathway (see Fig. 3 of ref. 7).

The experiments show that eleven water molecules are required to stabilize Pb^{2+} in the gas phase, which suggests a fundamental difference between this dication and how other metal dications interact with water. In particular, eleven molecules constitute more than a primary solvation shell, and this is larger than any coordination number determined for a Pb(II) complex.[16] One possibility, based on an extensive analysis of X-ray data,[16] is that $[Pb(H_2O)_n]^{2+}$ ions adopt a hemidirected geometry. In such a configuration ligands would occupy just one half of the space surrounding Pb^{2+}, and beyond $n = 3$ or 4, only hydrogen bonded sites would be available to accommodate further molecules.[16] Although Pb(II) has an outer electron configuration of $6s^2$, relativistic effects cause this lone pair to become chemically inert but, at the same time, stereochemically active through mixing with a vacant 6p orbital. Properties of water that would favour the formation of a hemidirected geometry include: hardness (low polarizability), hydrogen bond strength; and minimal electron transfer to Pb^{2+}.[16] However, a recent DFT calculation by Wander and Clark [17] suggested an alternative scenario, whereby low coordinate hemidirected Pb^{2+}–water structures result from lone pair electron donation by ligands into the vacant 6p orbital. Structures calculated by Wander and Clark for $[Pb(H_2O)_6]^{2+}$ and above were primarily holodirected.[17] These static calculations contrast with the results of Car–Parrinello molecular dynamics simulations by Gourlaouen et al.[18] A dynamic simulation of isolated $[Pb(H_2O)_6]^{2+}$ lasting 8.5 ps

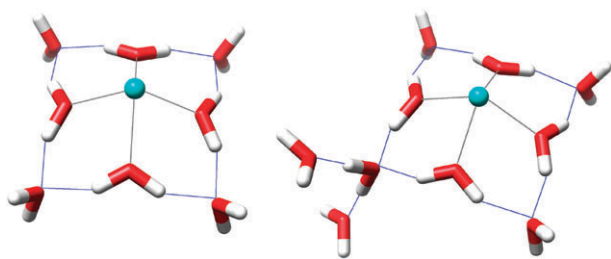**Fig. 3** Geometry optimized structures of $[Pb(H_2O)_8]^{2+}$ (left) and $[Pb(H_2O)_{10}]^{2+}$ (right) using DFT B3LYP/LANL2DZ 6-31G*. See ESI† for other structures close in energy to these.

showed a structure that evolved towards hemidirected coordination through the promotion of water molecules from the primary to the secondary solvation shell. A similar simulation of aqueous Pb^{2+} gave evidence of instantaneous hemidirected character, but averaged over time, coordination to solvated Pb^{2+} was dynamically holodirectional.

Neither of the calculations on $[Pb(H_2O)_6]^{2+}$ showed any evidence of the instability detected in these experiments,[17,18] and it is also clear that to help interpret the results presented here, additional calculations are required on complexes where $n > 6$. Therefore, minimum energy structures have been calculated for $[Pb(H_2O)_n]^{2+}$ complexes ($n = 8$, 10–12) using DFT/B3LYP functional and the 6-31G*/lanl2DZ basis set.† Fig. 3 shows examples of the structures obtained for $[Pb(H_2O)_8]^{2+}$ and $[Pb(H_2O)_{10}]^{2+}$ and further examples can be found in the ESI†. These static lowest energy structures are all found to be hemidirected. As noted earlier,[15] this type of geometry places water molecules in a configuration that is ideally suited to the promotion of proton loss. However, what is required of the structures in Fig. 3 (and especially of the larger complexes with 8–10 water molecules) is that they should be able to facilitate the loss of either $[H(H_2O)_3]^+$ or $[H(H_2O)_4]^+$.

As part of the hemidirectionality displayed by Pb^{2+}, water molecules are accumulated preferentially on one side of the ion. As a result, the solvated ion is effectively preorganized for the elimination of $[H(H_2O)_k]^+$ ($k = 3$, 4); both being considerably lower in energy than isolated H_3O^+. In contrast, dications *without* a stereochemically active lone pair (*e.g.* Sr^{2+}) can delocalize charge more uniformly because a larger number of water molecules are coordinated directly to a central cation. However, when the number of water molecules is reduced sufficiently for proton transfer to be favourable, it then becomes necessary for molecules to move from the primary shell over an energy barrier to the secondary solvation shell.[13,15]

The $[Pb(H_2O)_n]^{2+}$ ($n = 8$, 10–12) structures calculated in Spartan[19] using the lanl2DZ basis set all exhibit hemidirected geometries (see ESI†), for which the charge separation process would only require proton transfer and the breaking of hydrogen bonds. Once beyond the primary solvation shell, the difference in energy between the structures is small as are the barriers to reorganization[13] (see ESI†). Hence, secondary solvent shells could readily adopt configurations that allow the

elimination of $[H(H_2O)_k]^+$ ($k = 3$, 4) ions during the 10^{-5} s prior to Coulomb explosion.

The observed instability of $[Pb(H_2O)_n]^{2+}$ complexes has revealed a unique example of a dication system where solvent geometry has a greater influence than charge density in promoting proton transfer. The stereochemical influence of the $6s^2$ electrons on Pb^{2+} forces solvent molecules into asymmetric configurations that are unable to stabilize the $2+$ charge on the metal ion to the same degree that is seen, for example, in other dications of similar size and charge density. Similar considerations could easily be responsible for the unexpectedly high acidity of the Pb(II) cation in aqueous solution. Calculated evidence of a similar asymmetry in ion solvation is seen in the recent molecular dynamics simulations of Beret *et al.*[20] These authors found that the square-planar primary solvation shells of Pt(II) and Pd(II), in a model aqueous solution, were surrounded by secondary shells of 10 water molecules located predominantly in the equatorial plane. Axial sites were occupied, but the interactions were very weak. As with Pb(II), water also exhibits a low pK_a when both Pt(II) and Pd(II) are in aqueous solution.

Notes and references

1 A. T. Blades, P. Jayaweera, M. G. Ikonomou and P. Kebarle, *Int. J. Mass Spectrom. Ion Processes*, 1990, **102**, 251.
2 A. A. Shvartsburg and K. W. M. Siu, *J. Am. Chem. Soc.*, 2001, **123**, 10071.
3 A. J. Stace, *J. Phys. Chem. A*, 2002, **106**, 7993.
4 G. Akibo-Betts, P. E. Barran, L. Puskar, B. Duncombe, H. Cox and A. J. Stace, *J. Am. Chem. Soc.*, 2002, **124**, 9257.
5 T. Shi, G. Orlova, J. Guo, D. K. Bohme, A. C. Hopkinson and K. W. M. Siu, *J. Am. Chem. Soc.*, 2004, **126**, 7975.
6 T. Shi, J. Zhao, A. C. Hopkinson and K. W. M. Siu, *J. Phys. Chem. B*, 2005, **109**, 10590.
7 K. McQuinn, F. Hof and J. S. McIndoe, *Chem. Commun.*, 2007, 4099.
8 S. L. G. Husheer, O. Forest, M. A. Henderson and J. S. McIndoe, *Rapid Commun. Mass Spectrom.*, 2005, **19**, 1352.
9 R. G. Cooks, J. H. Beynon, R. M. Caprioli and G. R. Lester, *Metastable Ions*, Elsevier, Amsterdam, 1973.
10 R. D. Shannon, *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Cryst.*, 1976, **32**, 751.
11 B. Wu, *Gas-phase studies of multiply charged metal-ligand complexes*, PhD thesis, University of Nottingham, 2007.
12 B. J. Duncombe, K. Duale, A. Buchanan-Smith and A. J. Stace, *J. Phys. Chem. A*, 2007, **111**, 5158.
13 M. Beyer, E. R. Williams and V. E. Bondybey, *J. Am. Chem. Soc.*, 1999, **121**, 1565.
14 J. N. Harvey, *Phys. Chem. Chem. Phys.*, 2007, **9**, 331.
15 H. Cox and A. J. Stace, *J. Am. Chem. Soc.*, 2004, **126**, 3939.
16 L. Shimoni-Livny, J. P. Glusker and C. W. Bock, *Inorg. Chem.*, 1998, **37**, 1853.
17 M. C. F. Wander and A. E. Clark, *Inorg. Chem.*, 2008, **47**, 8233.
18 C. Gourlaouen, H. Gérard and O. Parisel, *Chem.–Eur. J.*, 2006, **12**, 5024.
19 Spartan '06, Wavefunction, Irvine, CA (USA), 2006.
20 E. C. Beret, J. M. Martínez, R. R. Pappalardo, E. S. Marcos, N. L. Doltsinis and D. Marx, *J. Chem. Theory Comput.*, 2008, **4**, 2108.