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Is There a Minimum Size for Aqueous Doubly Charged Metal Cations?

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Abstract: A major feature of the chemistry of multiply charged solvated metal ions is dissociative charge transfer. It happens because the second ionization potential (IP) of a metal atom usually exceeds the first IP of a solvent molecule. This raises the issue of whether there is a minimum number of ligands below which the species would charge-separate spontaneously. To elucidate this, doubly charged aqueous cations of most common divalent metals (group 2 elements Mn, Fe, Co, Ni, Zn, Cd, and Cu) have been generated using electrospray and examined by collision-induced dissociation in a triple-quadrupole mass spectrometer. We have clearly observed the monoaqua complexes for all aforementioned doubly charged metal ions, except Be for which the smallest complex found is the dihydrate. We have also systematically revisited the matter of critical size—the maximum number of ligands at which dissociative charge transfer is competitive with simple ligand loss.

Introduction

The study of ion solvation has been among the classical pursuits in physical chemistry since its early beginnings. Solvation of multiply charged metal ions is of special interest because of the rich chemistry that is often associated with it, involving charge transfer and formation of specific well-defined complexes and solvation shells.[1,2] A recent new angle here is that similar patterns may be exhibited in the coordination of metal ion hemes in proteins and other biological molecules (self-solvation).[3] This aspect attracts further attention to the solvation of metal ions in finite systems.[4] These processes can suitably be investigated by mass spectrometry, which allows one to clearly elucidate the thermodynamic and other properties of stepwise solvation. Another major advantage of finite systems is that close connection with reasonably accurate theory can be made.

However, dissociative charge transfer has for a long time limited the research on solvated metal ions to singly charged ions. Indeed, the second ionization potentials (IPs) of metal atoms are, with few exceptions, above 12 eV (see Table 1), while the first IPs of most common solvent molecules lie in the 9−12-eV range (for example, 9.1 eV for dimethyl sulfoxide, 9.2 eV for tetrahydrofuran and pyridine, 9.4 eV for diethyl ether, 9.7 eV for acetone, 10.8 eV for methanol, 12.2 eV for acetonitrile, and 12.6 eV for water). Hence, electron transfer from a neutral ligand to a multiply ionized metal atom is typically energetically favorable and should occur spontaneously on contact, with the dissociation driven by Coulomb repulsion:

Table 1. Critical and Minimum Sizes for Dissociative Charge Transfer in $M^{2+}(H_2O)_n$ versus the Second Ionization Potential of M

		$n_{\min}$		n_{crit}[e]	
element	second IP, eV	previous	this work	previous	this work
Ba	10.0	1[a]	1	0[a]	2
Sr	11.0	f	1	2[a]	2
Ca	11.9	1[a]	1	2[a]	2
Mg	15.0	2[b]	1	3[a]	4
Mn	15.6	2[a]	1	3[a]	4
Fe	16.2	4[a]	1	5[a]	5
Cd	16.8	≤7[c]	1	f	4
Co	17.1	3[a]	1	4[a]	5
Zn	18.0	f	1	5[a]	6
Ni	18.2	3[a]	1	4[a]	5
Be	18.2	7[a]	2	7[a]	8
Cu	20.3	3,[b] 2[d]	1	6[d]	6

[a] Kebarle and co-workers.[21−23,25] [b] Stace and co-workers.[15−18] [c] Cheng et al.[27] [d] Stone and Vukomanovic.[30] [e] As discussed in the text, n_{crit} is the largest complex size for which dissociative proton transfer (5) was observed. [f] No published data available.

$$M^{2+} + H_2O \Rightarrow M^{+} + H_2O^{+} \tag{1}$$

Furthermore, sequential hydration has proven to be not feasible even for some metals that have second IPs below the first IP of water, in which case reaction 1 is endothermic. This is because of a competing proton-transfer reaction that produces the metal hydroxide and the hydronium ion:

$$M^{2+} + 2H_2O \Rightarrow MOH^{+} + H_3O^{+} \tag{2}$$

This phenomenon (instead of sequential hydration) was observed in the experiments of Spears and Fehsenfeld[5] when a beam of Ca^{2+} was passed through water vapor. In fact, the only doubly charged metal ion that underwent a straightforward sequential hydration[5] was that of Ba, which has the lowest second IP of all elements (Table 1). Thus, while clusters of multiply charged

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(1) Marcus, Y. *Ion Solvation*; John Wiley: New York, 1985.

(2) Castleman, A. W., Jr. *J. Phys. Chem.* **1996**, *100*, 12911 and references therein.

(3) Karlin, K. D. *Science* **1993**, *261*, 701. Siegbahn, P. E. M.; Blomberg, M. R. A. *Chem. Rev.* **2000**, *100*, 421.

(4) Pavlov, M.; Siegbahn, P. E. M.; Sandström, M. *J. Phys. Chem. A* **1998**, *102*, 219.

(5) Spears, K. G.; Fehsenfeld, F. C. *J. Chem. Phys.* **1972**, *56*, 5698.

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metal ions with many water molecules must evidently be stable, they generally could not be formed by sequential ligation of the metal ion, a standard procedure for singly charged ions.

There was an ingenious proposal[6] to create doubly charged metal−ligand clusters via photoionization of singly charged species that are readily available through stepwise ligation, for example, $Zn^{2+}H_2O$ from $Zn^{+}H_2O$. This idea has never been implemented in its original form; however, a fundamentally analogous "pickup" technique has recently been established by Stace and co-workers.[7−20] In this method, a beam of neutral solvent clusters is passed through a metal vapor, solvation occurs, and the resulting complexes are ionized by electron impact. This approach is successful because a multiply charged metal ion with the desired number of ligands is derived via evaporation of "excess" solvent molecules from a large solvent cluster embedding the metal ion, rather than by ligand addition to a bare multiply charged metal ion. This avoids the small size range where competing electron-transfer (1) and proton-transfer (2) reactions would occur.

Another prominent method that follows the same paradigm of "shrinking from above" is electrospray ionization (ESI), in which a multiply charged metal ion is transferred into the gas phase directly from solution as a solvated species. The utility of an ESI source for the production of various multiply charged metal ions ligated by water and alcohols has clearly been demonstrated by Kebarle's group.[21−25] This method was subsequently adopted by several groups,[27−35] notably Williams and co-workers,[33−35] who measured the sequential metal−water binding energies in these complexes using blackbody infrared radiative dissociation. ESI has been successfully employed to generate doubly charged hydrated cations for most divalent metals, including Be,[25] Mg,[22,23,25,28,34,35] Ca,[22,23,25,28,33−35] Sr,[22,23,26,34,35] Ba,[22,23,28,34,35] Zn,[23,25,27,28] Cd,[27,28] Mn,[22,23,28] Fe,[23] Co,[21−23] Ni,[23,33] and Cu.[27,28,30] The experimental difficulty tends to increase with increasing second ionization potential of the metal atom. For instance, the first $M^{2+}(H_2O)_{\boldsymbol{n}}$ reported was for M = Sr,[26] while early efforts[21−23] to produce $Cu^{2+}(H_2O)_{\boldsymbol{n}}$ and $Be^{2+}(H_2O)_{\boldsymbol{n}}$ had failed as these were formed only under mild conditions in the supersonic expansion (lens) region.[24,27,28,30] The obvious question then is, at and below which critical *n* value (n_{crit}) would an $M^{2+}(H_2O)_{\boldsymbol{n}}$ complex dissociate not solely by simple ligand evaporation

$$M^{2+}(H_2O)_{\boldsymbol{n}} \Rightarrow M^{2+}(H_2O)_{\boldsymbol{n}-1} + H_2O \qquad (3)$$

but also experience, in analogy to processes 1 and 2, electron-transfer (4), proton-transfer (5), or both processes:

$$M^{2+}(H_2O)_{\boldsymbol{n}} \Rightarrow M^{+}(H_2O)_{\boldsymbol{n}-1} + H_2O^{+} \qquad (4)$$

$$M^{2+}(H_2O)_{\boldsymbol{n}} \Rightarrow M^{+}OH(H_2O)_{\boldsymbol{n}-\boldsymbol{k}-2} + H_3O^{+}(H_2O)_{\boldsymbol{k}} \qquad (5)$$

This issue has been studied in detail by Kebarle and collaborators,[21−23,25] who determined the values of n_{crit} for most divalent metals (Table 1) using collision-induced dissociation (CID). For $n \leq n_{\text{crit}}$, channels 3 and 5 compete, and the fractional yield of (5) swiftly increases with decreasing *n*. Channel 4 has not been reported, except for $Mg^{2+}(H_2O)_{\boldsymbol{n}}$ with certain *n* values.[15] Recent theoretical modeling[36] also suggests that the proton transfer (5) would generally be preferred over the electron transfer (4).

The other issue that has received much attention recently is the following: at what minimum $n = n_{\text{min}}$ would $M^{2+}(H_2O)_{\boldsymbol{n}}$ remain stable against a spontaneous decay along pathway 4, pathway 5, or both (which have been described as "Coulomb explosions")? This matter was particularly disputed for copper: high-level theory[37,38] predicted $Cu^{2+}H_2O$ and $Cu^{2+}(H_2O)_2$ to exist as stable species, but the smallest complex found in experiments of Stace and collaborators[9,17,18] was $Cu^{2+}(H_2O)_3$. For Mg, $n_{\text{min}} = 2$ was claimed.[15,17] Although no specific searches for the smallest hydrated complexes of other metals have been reported, some of these values may be gleaned from published tandem mass spectrometry (MS/MS) spectra.[21−23,25] Here we report a comprehensive investigation of the critical (n_{crit}) and especially minimum (n_{min}) sizes for hydrated divalent metal cations.

Experimental Section

Experiments were performed using a Sciex TAGA 6000E triple-quadrupole mass spectrometer (MDS Sciex, Concord, ON, Canada) modified for electrospray ionization.[27,28] Doubly charged hydrated metal cations were produced by electrospraying 1−10 mM aqueous solutions

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(6) Marcos, E. S.; Pappalardo, R. R.; Barthelat, J. C.; Gadea, F. X. *J. Phys. Chem.* **1992**, *96*, 516.

(7) Dobson, M. P.; Stace, A. *J. Chem. Commun.* **1996**, 1533.

(8) Woodward, C. A.; Dobson, M. P.; Stace, A. J. *J. Phys. Chem.* **1996**, *100*, 5605.

(9) Stace, A. J.; Walker, N. R.; Firth, S. *J. Am. Chem. Soc.* **1997**, *119*, 10239.

(10) Woodward, C. A.; Dobson, M. P.; Stace, A. J. *J. Phys. Chem. A* **1997**, *101*, 2279.

(11) Dobson, M. P.; Stace, A. J. *Int. J. Mass Spectrom. Ion Processes* **1997**, *165/166*, 5.

(12) Walker, N. R.; Firth, S.; Stace, A. J. *Chem. Phys. Lett.* **1998**, *292*, 125.

(13) Walker, N. R.; Wright, R. R.; Stace, A. J. *J. Am. Chem. Soc.* **1999**, *121*, 4837.

(14) Walker, N. R.; Wright, R. R.; Barran, P. E.; Stace, A. J. *Organometallics* **1999**, 18, 3569.

(15) Barran, P. E.; Walker, N. R.; Stace, A. J. *J. Chem. Phys.* **2000**, *112*, 6173.

(16) Walker, N. R.; Dobson, M. P.; Wright, R. R.; Barran, P. E.; Murrell, J. N.; Stace, A. J. *J. Am. Chem. Soc.* **2000**, *122*, 11138.

(17) Stace, A. J.; Walker, N. R.; Wright, R. R.; Firth, S. *Chem. Phys. Lett.* **2000**, *329*, 173.

(18) Wright, R. R.; Walker, N. R.; Firth, S.; Stace, A. J. *J. Phys. Chem. A* **2001**, *105*, 54.

(19) Walker, N. R.; Wright, R. R.; Barran, P. E.; Cox, H.; Stace, A. J. *J. Chem. Phys.* **2001**, *114*, 5562.

(20) Puskar, L.; Barran, P. E.; Wright, R. R.; Kirkwood, D. A.; Stace, A. J. *J. Chem. Phys.* **2000**, *112*, 7751.

(21) Jayaweera, P.; Blades, A. T.; Ikonomou, M. G.; Kebarle, P. *J. Am. Chem. Soc.* **1990**, *112*, 2452.

(22) Blades, A. T.; Jayaweera, P.; Ikonomou, M. G.; Kebarle, P. *J. Chem. Phys.* **1990**, *92*, 5900.

(23) Blades, A. T.; Jayaweera, P.; Ikonomou, M. G.; Kebarle, P. *Int. J. Mass Spectrom. Ion Processes* **1990**, *102*, 251.

(24) Peschke, M.; Blades, A. T.; Kebarle, P. *J. Phys. Chem. A* **1998**, *102*, 9978.

(25) Peschke, M.; Blades, A. T.; Kebarle, P. *Int. J. Mass Spectrom.* **1999**, *185/186/187*, 685.

(26) Schmelzeisen-Redeker, G.; Bütfering, L.; Röllgren, F. W. *Int. J. Mass Spectrom. Ion Processes* **1989**, *90*, 139. A thermospray ionization source has been used in this work.

(27) Cheng, Z. L.; Siu, K. W. M.; Guevremont, R.; Berman, S. S. *J. Am. Soc. Mass Spectrom.* **1992**, *3*, 281.

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

(29) Seto, C.; Stone, J. A. *Int. J. Mass Spectrom. Ion Processes* **1998**, *175*, 263.

(30) Stone, J. A.; Vukomanovic, D. *Int. J. Mass Spectrom.* **1999**, *185/186/187*, 227.

(31) Nielsen, S. B.; Bojesen, G. *Chem. Commun.* **1998**, 613.

(32) Andersen, U. N.; Bojesen, G. *Int. J. Mass Spectrom. Ion Processes* **1996**, *153*, 1.

(33) Rodriguez-Cruz, S. E.; Jockusch, R. A.; Williams, E. R. *J. Am. Chem. Soc.* **1998**, *120*, 5842.

(34) Rodriguez-Cruz, S. E.; Jockusch, R. A.; Williams, E. R. *J. Am. Chem. Soc.* **1999**, *121*, 1986.

(35) Rodriguez-Cruz, S. E.; Jockusch, R. A.; Williams, E. R. *J. Am. Chem. Soc.* **1999**, *121*, 8898.

(36) Beyer, M.; Williams, E. R.; Bondybey, V. E. *J. Am. Chem. Soc.* **1999**, *121*, 1565.

of appropriate metal salts (typically nitrates) and fragmented by multicollisional low-energy CID with Ar as the collision gas at a pressure of 0.3−1 mTorr. The collision energy (***E***) was typically 100−190 eV (laboratory frame) to maximize the abundance of desired products. In accordance with previous observations,[24,27,28,30] efficient production of multiply charged ions requires "mild" source conditions, where the potential drop in the lens region is small, thus resulting in minimal collisional heating of the ions. Otherwise (under "harsh" conditions), charge reduction via process 5 takes place in the source. However, this also causes dissociation along channel 3, thus shifting the maximum of the $M^{2+}(H_2O)_n$ distribution toward lower n values. When searching for the smallest possible $M^{2+}(H_2O)_n$, it was expedient to fragment the smallest precursor ion with a reasonably high abundance. For this reason, we have sometimes adopted source conditions harsher than the mildest limit.

Results and Discussion

We have investigated all divalent metal cations that yield doubly charged hydrates (Table 1). Several metals, including Sn and Hg, assume a formal oxidation state of (2+) in aqueous solutions but do not exhibit $M^{2+}(H_2O)_n$ ions when they are electrosprayed.[27,28] The second IPs of these elements are not unusually high (14.6 eV for Sn and 18.8 eV for Hg); hence, it is most unlikely that $M^{2+}(H_2O)_n$ complexes involving them would be fully destroyed by spontaneous dissociative charge transfer at any observable n. We have calculated the equilibrium metal-containing species' concentrations in solutions using COMICS.[39] At pH 7, the relative abundances (in 2 mM solutions) for Sn are as follows: $[Sn_3(OH)_4]^{2+}$, 99.4%; $SnOH^+$, 0.5%; Sn^{2+}, 0.0002%. Those for Hg are as follows: $Hg(OH)_2$, 100.0%; Hg^{2+}, 2×10^{-6}% only. Thus, the principal species in aqueous solutions of Sn^{2+} and Hg^{2+} salts are metal hydroxides, while doubly charged metal ions are virtually nonexistent. As ESI transfers into the gas phase the ions already present in solution, the failure to observe doubly charged metal hydrates for these elements is hardly surprising.

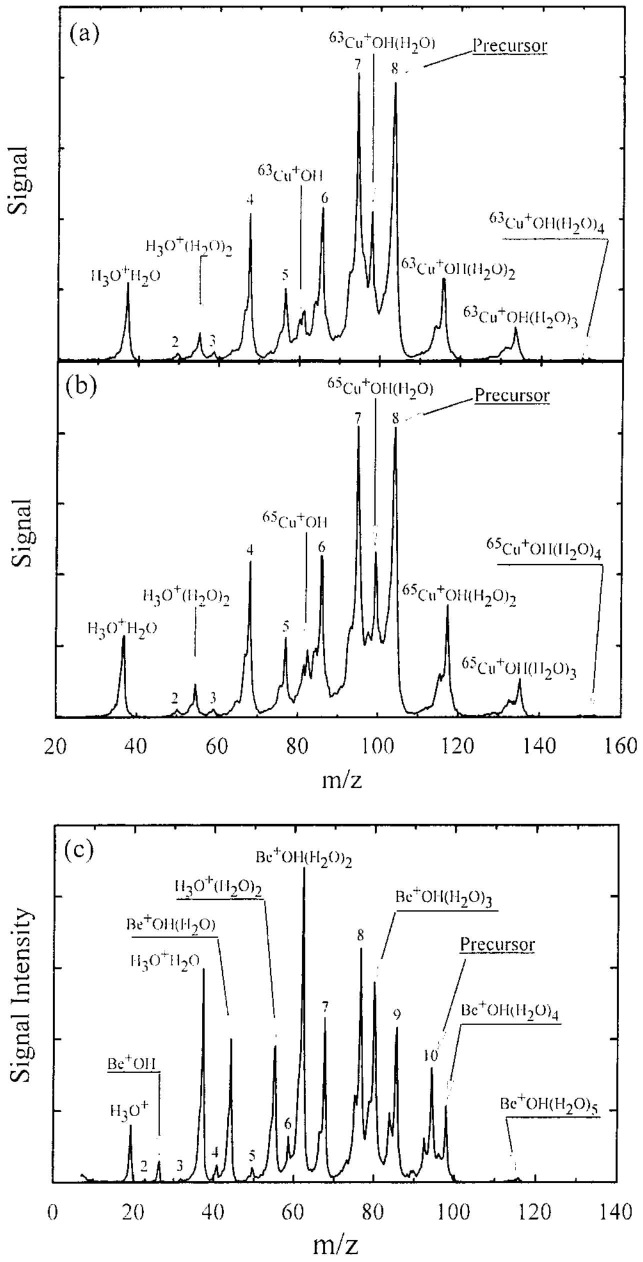

Figure 1. Product ion spectra for (a) $^{63}Cu^{2+}(H_2O)_8$, $E = 188$ eV; (b) $^{65}Cu^{2+}(H_2O)_8$, $E = 188$ eV; (c) $Be^{2+}(H_2O)_{10}$, $E = 158$ eV. The numbers indicate n in $M^{2+}(H_2O)_n$.

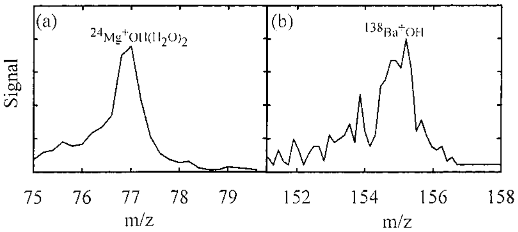

Figure 2. CID spectral windows showing the largest singly charged cations observed from the Coulomb explosion of $M^{2+}(H_2O)_n$: (a) Mg with $n_{crit} = 4$, $E = 108$ eV; (b) Ba with $n_{crit} = 2$, $E = 168$ eV. Precursor ions were $^{24}Mg^{2+}(H_2O)_6$ and $^{138}Ba^{2+}(H_2O)_6$, respectively.

Product ion spectra for Cu and Be are presented in Figure 1 as examples. These elements with high second IPs exhibit the most complex spectra due to extensive proton transfer; the spectra for other metals are simpler. Wherever possible, ion assignments were verified by separate MS/MS for every abundant metal isotope, as demonstrated for ^{63}Cu and ^{65}Cu in Figure 1a,b. For all metal ions studied, only proton transfer (5) rather than electron transfer (4) was observed. We have carefully searched for the largest singly charged hydrated metal ions produced via proton transfer by varying the collision energy and the size of the precursor ion; the resulting n_{crit} values are listed in Table 1. Our data broadly agree with previous findings, but the present values are often larger by 1. A reason for this difference may simply be that we accumulated a larger number of scans (had better signal-to-noise ratios), often facilitated by focusing more narrowly on only the relevant *m/z* ranges (a typical example of Mg is shown in Figure 2a). Also, for these tests, we deliberately selected doubly charged precursor ions with *m/z* below that of the singly charged fragments being monitored, which ensured minimal background levels. We, of course, cannot rule out that some proton transfer might proceed in precursor ions with $n > n_{crit}$. (Reaction 5 is exothermic; therefore, the $M^+OH(H_2O)_m$ product may be vibrationally excited. This hot product could cool by evaporation of one or more water molecules. This conceivably could eliminate the $M^+OH(H_2O)_m$ fragment ions with the largest values of $\boldsymbol{m}$ before they are detected. For this reason, measured n_{crit} should be viewed as the lower limits for true values. However, the values found for all M^{2+} studied were independent of both the precursor size, as long as $n \geq n_{crit}$, and the collision energy within the range used. This means that the n_{crit} quantity is a significant property of $M^{2+}(H_2O)_n$ complexes and not merely an artifact of specific experimental conditions.) We emphasize that the determination of n_{crit} requires MS/MS to be performed: merely observing $M^+OH(H_2O)_n$ in a single-stage MS experiment is no proof that the ion is produced via proton transfer from an M^{2+} associated with ($n + 2$) or more water molecules; the $M^+OH(H_2O)_{\boldsymbol{n}}$ ion may be generated by hydration of $M^+OH(H_2O)_{\boldsymbol{l}}$ ($l < n$) in the supersonic jet following adiabatic cooling. For instance, the electrospray mass spectrum of $CuSO_4$ features[30] $Cu^+OH(H_2O)_{\boldsymbol{n}}$ with $n = 5$ and 6, yet the highest n found in the CID spectra is 4.

Overall, the dependence of n_{crit} on the second IP of corresponding metal deduced by Kebarle and co-workers[22,23] is manifested clearly, although Be remains an anomaly. The n_{crit} for cadmium not reported previously fits nicely in the trend. Furthermore, our present data eliminate the abnormal drop[23] of n_{crit} from Fe to Co and Ni. The situation with barium is of particular interest. It has been thought[22,23] that, because of the exceptionally low second IP of Ba, Ba^{2+} is the only multiply charged metal cation that does not charge transfer to water, and hence, unlike other hydrated divalent metal ions, $Ba^{2+}(H_2O)_{\boldsymbol{n}}$ fragments exclusively by sequential water loss (3) all the way to naked Ba^{2+}. While this channel does indeed dominate, we have clearly observed the proton-transfer channel (5) producing Ba^+OH (Figure 2b). In this regard, Ba resembles Sr and Ca for which charge reduction to M^+OH from $M^{2+}(H_2O)_2$ has been reported.[5] Calculations[36] favor water loss from $Ba^{2+}(H_2O)_2$ over proton transfer by 20 kJ/mol.

We now proceed to the findings for the minimum size, n_{min}. A painstaking examination of MS/MS data has allowed us to prove the *existence of $M^{2+}H_2O$ and all immediately larger hydrates for all divalent metals listed in Table 1 with the exception of Be*. While in a few cases the yield of $M^{2+}H_2O$ was less than 1%, the evidence was unambiguous, including that from all abundant metal isotopes. For example, the much debated[17,37,38] existence or nonexistence of $Cu^{2+}H_2O$ is addressed in Figure 3a,b. Calculations[37,38] performed using both density functional theory (B3LYP) and highly correlated ab initio CCSD(T) methods find this species' potential energy to lie above that of separated Cu^+ and H_2O^+ by 3.2−3.3 eV, with the barrier to electron transfer and subsequent dissociation being just ~0.3 eV. If these values are accurate, then the observation of $Cu^{2+}H_2O$ in a standard triple-quadrupole apparatus is remarkable. We have also observed the $Cu^{2+}(H_2O)_2$ ion first reported by Stone and Vukomanovic.[30] Although calculations[37,38] showed the electron-transfer process (4) to be exothermic, this reaction is unlikely to be prominent as the activation barrier is above 1 eV. However, the lowest pathway for dissociation of $Cu^{2+}(H_2O)_2$ is probably via proton transfer (5); unfortunately, competitive fragmentation of $M^{2+}(H_2O)_2$ has so far been modeled[36] for group 2 elements only. Similarly, the smallest aqua complex heretofore found for Mg^{2+} was the dihydrate.[16] In the present experiments, $Mg^{2+}H_2O$ has clearly been identified; see Figure 3c−e.

Other noteworthy examples of $M^{2+}H_2O$ are $Fe^{2+}H_2O$ in Figure 4 and $Ni^{2+}H_2O$ and $Co^{2+}H_2O$ in Figure 5a,b. The predominant natural isotope of iron is ^{56}Fe, with an abundance of 92%. Unfortunately, $^{56}Fe^{2+}H_2O$ ($m/z = 37$) is isobaric with $H_3O^+H_2O$, a ubiquitous ion produced in reaction 5 for $n \geq 3$. Nevertheless, the existence of iron(II) monohydrate can still be established using a minor ^{54}Fe isotope (5% abundance); this is illustrated in Figure 4. The $^{54}Fe^{2+}H_2O$ ion is isobaric with $(H_2O)_2^+$; however, no peak at $m/z = 36$ has appeared in any MS/MS spectra of any other $M^{2+}(H_2O)_{\boldsymbol{n}}$ complex studied here, including those for $^{56}Fe^{2+}$, $^{58}Ni^{2+}$, $^{60}Ni^{2+}$, or Co^{2+} (Figures 4 and 5a,b). The existence of zinc monohydrate, considered by Marcos et al.,[6] is documented in Figure 5c,d. Zinc and copper are two cases in which the fractional yield of $M^{2+}H_2O$ is sufficiently low (~0.1%) to render this peak invisible on the linear scales of full MS/MS spectra. It is hardly a coincidence that the second IPs of Cu and Zn are the highest and third highest among the metals examined. For other divalent metals studied here (except Be below), the yields of $M^{2+}H_2O$ are typically on the order of 1% or higher.

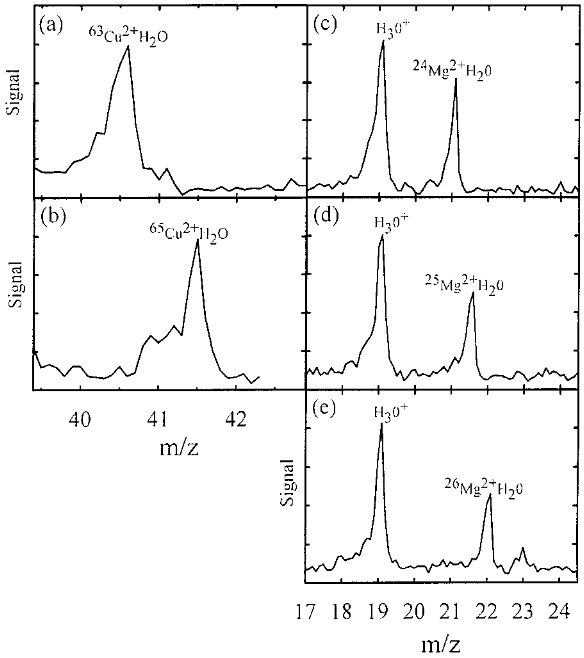

Figure 3. CID spectral windows establishing $n_{min} = 1$ for Cu and Mg. Precursors were heptahydrates for (a) $^{63}Cu^{2+}$ and (b) $^{65}Cu^{2+}$ ($E = 128$ eV) and octahydrates for (c) $^{24}Mg^{2+}$, (d) $^{25}Mg^{2+}$, and (e) $^{26}Mg^{2+}$ ($E = 108$ eV). Fractional yields were on the order of 0.1% for $Cu^{2+}H_2O$ and 1% for $Mg^{2+}H_2O$.

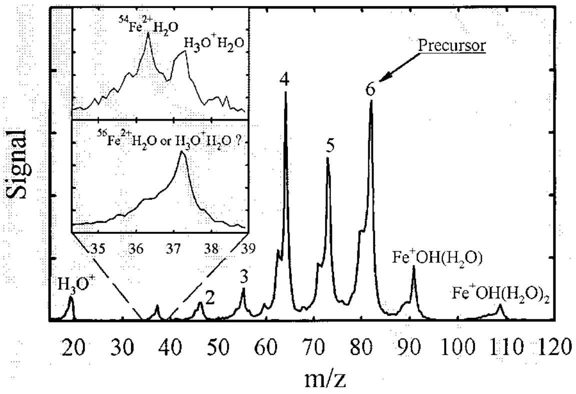

Figure 4. Product ion spectrum ($E = 188$ eV) for $^{56}Fe^{2+}(H_2O)_6$. The numbers indicate $\boldsymbol{n}$ in $Fe^{2+}(H_2O)_{\boldsymbol{n}}$. Insets show the expanded $Fe^{2+}H_2O$ peaks for ^{56}Fe (lower panel) and ^{54}Fe (upper panel).

Beryllium is the only element we investigated for which not a trace of doubly charged monohydrate could be found despite a focused effort; the smallest hydrate of Be^{2+} observed was the dihydrate (Figure 6). Considering that the value of n_{crit} gauges the charge-transfer propensity from M^{2+} to a water molecule and that n_{crit} for Be is the highest of all metals in Table 1, it fits that the production of $M^{2+}H_2O$ would be toughest for Be among all divalent metals. (Notably the smallest Be^{2+} hydrate reported

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(37) El-Nahas, A. M.; Tajima, N.; Hirao, K. *Chem. Phys. Lett.* **2000**, *318*, 333.

(38) El-Nahas, A. M. *Chem. Phys. Lett.* **2000**, *329*, 176.

(39) Perrin, D. D.; Sayce, I. G. *Talanta* **1967**, *14*, 833. We used the stability constants from: Smith, R. M.; Martell, A. E. ***Critical Stability Constants***. Vol. 4. ***Inorganic Complexes***; Plenum: New York, 1981.

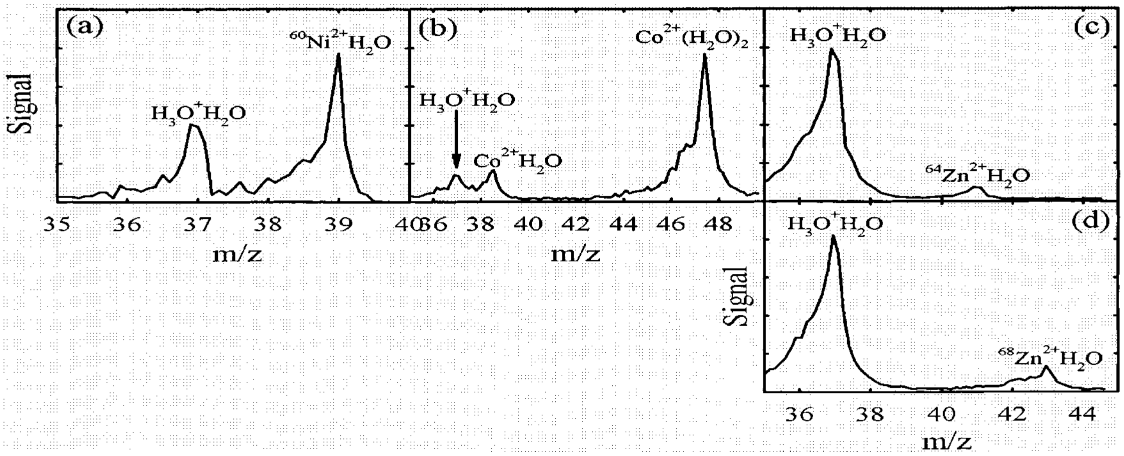

Figure 5. MS/MS spectral windows showing $M^{2+}H_2O$ produced from larger hydrates of divalent metals: (a) $^{60}Ni^{2+}(H_2O)_6$ ($E = 108$ eV), (b) $Co^{2+}(H_2O)_6$ ($E = 188$ eV), (c) $^{64}Zn^{2+}(H_2O)_8$ ($E = 188$ eV), and (d) $^{68}Zn^{2+}(H_2O)_6$ ($E = 188$ eV). Fractional yields were on the order of 0.1% for $Zn^{2+}H_2O$ and 1% for $Ni^{2+}H_2O$ and $Co^{2+}H_2O$.

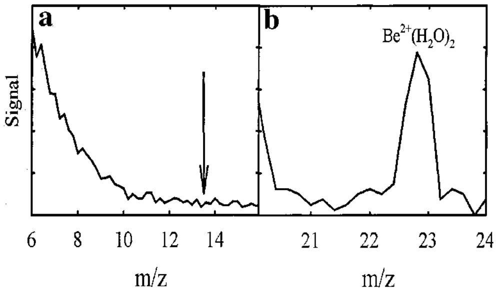

Figure 6. CID spectral windows ($E = 158$ eV) for $Be^{2+}(H_2O)_{10}$ demonstrating (a) the absence of $Be^{2+}H_2O$ ($m/z = 13.5$) and (b) the existence of $Be^{2+}(H_2O)_2$ (fractional yield on the order of 1%). $Be^{2+}H_2O$ was absent in the fragmentation of all $Be^{2+}(H_2O)_n$ examined.

previously[25] was $Be^{2+}(H_2O)_7$). Of course, an absence of evidence is not an evidence of absence. Dated calculations[40] suggested that the barrier to electron transfer in and dissociation of $Be^{2+}H_2O$ was several electronvolts. Had this been the case, observing this ion in our experiment would have been routine. It should be noted that the second IP of Be is not the highest of divalent metals: it is 2 eV below that of Cu and equal to that of Ni, for which $M^{2+}H_2O$ is readily observed.

Summarizing, we have used tandem mass spectrometry to study the fragmentation of and charge transfer in doubly charged hydrated metal ions. We revisited the issue of critical sizes (the largest coordination number at and below which proton transfer followed by charge separation is competitive with neutral water loss). These sizes are strongly correlated with the second ionization potential of the metal, though the size for Be is anomalously high. One significant result here is the observation of proton transfer and charge reduction in Ba^{2+} hydrates—barium was reported to be the only divalent metal that did not charge transfer because of its very low second ionization potential. We have carefully searched for the minimum sizes—the coordination numbers of the smallest doubly charged hydrates below which dissociative charge transfers occur spontaneously. For all divalent metals studied except Be, $n_{\min} = 1$; i.e., all hydrates including the monohydrates are stable, at least on the time scale of our MS/MS experiment ($\sim$10 μs). The stable species include $Cu^{2+}H_2O$ and $Cu^{2+}(H_2O)_2$, the existence of which has been debated recently. The smallest hydrate that we found for beryllium is $Be^{2+}(H_2O)_2$. In conjunction with an abnormal critical size, this larger minimum size denotes a peculiar propensity of Be^{2+} to charge transfer to water beyond what the second IP of Be would suggest. What is most impressive to us in this study is that single water molecules form stable complexes with metal ions in which differences in ionization energies that are released by dissociative charge transfer can be up to 8 eV, or 2 eV per constituent atom.

The results presented here prompt a question on the relative merits of the pickup technique and electrospray as sources of solvated metal ions for physical chemistry studies. A distinct advantage of the former is its ability[13,16,18,19] to access exotic complexes with ligands that are not easily available as solvents, such as Ar, NO, or CO_2. It appears, however, that a relatively high level of background noise and spurious peaks associated with the present implementation of the pickup technique make ESI a more robust choice when searching for novel solvated ions.

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[40] Cossi, M.; Persico, M. *Theor. Chim. Acta* **1991**, *81*, 157.