Fragmentation and charge transfer in gas-phase complexes of divalent metal ions with acetonitrile

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Abstract

The development of electrospray has enabled generation of gas-phase multiply charged metal ion complexes with various solvent molecules. These species exhibit rich fragmentation chemistry, involving competition among neutral ligand loss, ligand cleavage, and dissociative electron and proton transfer. Acetonitrile is a common aprotic solvent. Here we present a comprehensive MS/MS study on acetonitrile complexes of divalent metal cations. We measured the critical sizes below which dissociation channels other than the trivial neutral evaporation become operative and minimum sizes at which dications remain stable against charge reduction. For all sizes between the two, low-energy fragmentation patterns have been elucidated in detail. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

Solvation of ions in liquids has been at the core of physical chemistry since its inception [1]. Lately, the focus has shifted to finite systems, which can be conveniently studied by mass spectrometry [2]. This allows one to investigate the process one step at a time while making a connection to high-level theoretical modeling. Solvation of metal ions has been particularly topical, especially in view of the critical function that their coordination has in many proteins. Another aspect is that metalated organic and biological molecules in the gas phase often dissociate along pathways that materially differ from those of protonated molecules [3,4]. This is of advantage in protein identification using peptide sequencing by tandem mass spectrometry (MS/MS) [5]. This technology is presently developed for automated sequencing.

These factors have precipitated a substantial interest in metal ion–ligand complexes. However, most early work was limited to singly charged systems because solvated multiply charged metal ions had not been experimentally accessible until recently. Indeed, the ionization potentials (IPs) of most common organic ligands are in the range of 8–12 eV, while the second IPs (IP2s) of metals...
(except alkaline-earths) lie above 12 eV. Hence, charge transfer between a metal cation with charge of 2+ or higher and a neutral ligand is typically exothermic and occurs spontaneously on contact followed by dissociation (‘Coulomb explosion’) [6]. This precludes most sequential ligation of multiply charged metal ions in the fashion standard for singly charged ones – by passage through a vapor of the desired ligand.

A decade ago, ligated multiply charged metal ions were successfully produced by electrospray ionization (ESI) [7–9]. This method directly transfers existing solvated ions into the gas phase, with the extent of ligation controllable by thermal or collisional heating in the source prior to mass-spectrometric analysis. This route obviously circumvents the smallest complexes in which spontaneous dissociative charge transfer would occur. Most subsequent work has concentrated on aqueous metal ions [7–13]. However, ESI can generate complexes involving other protic and aprotic solvents, such as alcohols [11,14], acetone [11], dimethyl sulfoxide (DMSO) [7–9,11], dimethyl formamide (DMF) [9], pyridine [15], and acetonitrile [11,15–17]. A recently introduced alternative ‘pick-up’ technique [18–22] generates multiply charged ligated ions by electron-impact ionization of pre-solvated neutral metal atoms. This method has produced complexes of metal di- and tri-cations with a variety of ligands, including water, alcohols, ketones, ethers, tetrahydrofuran, ammonia, carbon dioxide, benzene, pyridine, and acetonitrile.

Except for hydrated ions, greatest attention was devoted to metal ions solvated by acetonitrile and DMSO, presumably because these are common aprotic solvents. Nevertheless, knowledge was limited to only a few metal complexes. Collision-induced dissociation of multiply charged metal–acetonitrile complexes was first investigated by Kohler and Leary [15,16], who determined the low-energy fragmentation pathways for M2(CH3CN) and M2(CH3CN)2, where M was Ca, Sr, Mn, or Co. Seto and Stone [17] reported the CID of Cu2(CH3CN)n, where n = 2–4. Their findings differed from those in [15,16], and it was unclear whether this revealed an element-specific chemistry or simply reflected different collision energies in the two experiments [17]. Stace and coworkers observed the fragmentation of acetonitrile-ligated Mg2+ [21], Cu2+ [22], Ag2+ [23], and Au2+ [24] for some n, but the pathways and associated critical sizes were not researched systematically.

Here we present a comprehensive MS/MS study of dications of divalent metals solvated by acetonitrile. We examined in detail the dissociation of M2(CH3CN)n for M = Be, Mg, Ca, Sr, Ba, Zn, Cd, Mn, Fe, Co, Ni, and Cu. All data were collected under the same source conditions, CID energy, and collision gas pressure, which ensured that all the results were directly comparable. A special effort was made to detect and identify even minor dissociation channels.

2. Experimental methods

Experiments were performed using a SCIEX 6000E triple-quadrupole mass spectrometer (MDS SCIEX, Concord, Ontario) fitted with a custom ESI source [10,11]. As is standard for SCIEX instruments, the atmospheric pressure (API) source and vacuum region interface via a pinhole crossed by an orthogonal flow of curtain gas for desolvation of ions. Some data were reproduced employing the TSQ 7000 MS/MS system (Thermo Finnigan) where the API source connects to the vacuum region via a heated capillary. For either instrument, no nebulizing gas flow was used. We have typically set the ESI needle voltage to 4 kV, although the results were largely insensitive to this value as long as the ion current was established. Metal–acetonitrile complex dications were produced by electrospraying 1–10 mM solutions of appropriate metal salts (typically nitrates) in acetonitrile or acetonitrile/water and fragmented by low-energy CID with argon as the collision gas at a pressure of 0.3–1.3 mTorr. To investigate a possible dependence of fragmentation chemistry on collision energy, we used laboratory collision energies (E) of 10–160 eV.

In agreement with earlier work, the overall production of multiply charged ions is optimum under ‘mild’ source conditions, where the potential drop in the lens region is minimal, thus avoiding
excessive collisional heating and dissociation of ions. However, the abundance distribution of ions appearing under these conditions tends to peak sharply at \( n = 4 - 6 \). The actual value depends on the particular metal, the examples of extraordinarily pronounced (over 99% abundance) magic numbers of five (Cu) and six (Ni) are presented in Fig. 1. Hence, generation of ions with only one or two acetonitrile ligands requires enhancing the desolvation in the source. This is achieved by changing to ‘harsher’ conditions, with the voltage drop in the lens region typically in the 30–60 V range. To confirm the assignments, we repeated most experiments with \( d_2 \)-acetonitrile and \( D_2 \)O substituted for CH\(_3\)CN and H\(_2\)O, respectively. For metals that have more than one stable isotope, MS/MS spectra were collected for all isotopes.

3. Results

The specific questions that we posed were as follows. First, what is the smallest dication acetonitrile complex for each metal studied; in other words, for what minimum \( n \) \( (n_{\text{min}}) \) would \( M^{2+}(\text{CH}_3\text{CN})_n \) remain stable against spontaneous dissociative charge transfer? This issue gained prominence in the work on aqueous metal dications, where the experimental data [24,25] seemed to contravene the theoretical predictions [26,27]. The point here is that, when the IP2 of the metal exceeds the IP of the ligand \( L \), the \( M^{2+}L \) complex is not thermodynamically stable (although it could be metastable). However, as \( M^{2+} \) survives in the bulk solution, there must be some \( n_{\text{min}} \) at which \( M^{2+}L_n \) still exists. Recently it has been shown [28,29] that \( n_{\text{min}} \leq 1 \) for all hydrated \( M^{2+} \), except \( \text{Be}^{2+} \) for which \( n_{\text{min}} = 2 \). Second, what is the largest \( n \) \( (n_{\text{crit}}) \) at and below which \( M^{2+}(\text{CH}_3\text{CN})_n \) decomposes not solely by neutral evaporation but via charge (electron and/or proton) transfer as well? As a macroscopic droplet evidently ‘dissociates’ by solvent evaporation only, \( n_{\text{crit}} \) must always be finite. The \( n_{\text{crit}} \) values for \( M^{2+}(\text{H}_2\text{O})_n \) have been measured: as expected, they increase with increasing IP2 of the metal [28] ranging from 2 to 6–8. Third, what are the possible dissociation channels for \( M^{2+}(\text{CH}_3\text{CN})_n \)? We aimed to elucidate all low-energy fragmentation channels for \( M^{2+}(\text{CH}_3\text{CN})_n \) with \( n_{\text{min}} \leq n \leq n_{\text{crit}} \). Our findings on the above three issues are discussed below for specific elements, and the summary is presented in Table 1.

3.1. Alkaline-earth metals

The simplest fragmentation patterns were observed for alkaline-earth elements that have low IP2s and thus charge-transfer to ligands minimally. Our findings for Ca, Sr, and Ba resemble in general those reported previously for Ca and Sr [15,16]. The primary dissociation channel for \( M^{2+}(\text{CH}_3\text{CN})_n \) is the evaporation of neutral acetonitrile all the way to bare \( M^{2+} \):

\[
M^{2+}(\text{CH}_3\text{CN})_n = M^{2+}(\text{CH}_3\text{CN})_{n-1} + \text{CH}_3\text{CN}
\]
This is not a surprise considering that the IP2s for Ca, Sr, and Ba are all under 12 eV, whereas the IP of acetonitrile is 12.2 eV. Thus electron transfer from ligand to M\(^{2+}\) is endothermic. Similar to [16], we observed some Ca\(^+\)CN and Sr\(^+\)CN that arise from a heterolytic cleavage

\[
M^{2+}(CH_3CN)_n = M^+CN(CH_3CN)_{n-1} + CH_3^+ \tag{2}
\]

The methyl radical cation (not reported in [16]) was clearly present in our data. The heaviest singly charged product of Ca\(^{2+}\)(CH\(_3\)CN)\(_n\) that we identified was Ca\(^+\)CN(CH\(_3\)CN), apparently resulting from (2); no Ca\(^+\)CN(CH\(_3\)CN)\(_2\) fragments were observed from any Ca\(^{2+}\)(CH\(_3\)CN)\(_n\) precursors tried. We could not find M\(^+\)(CH\(_3\)CN)\(_n\) or M\(^+\)CH\(_2\)CN(CH\(_3\)CN)\(_n\) products for any \(n\), in agreement with [16]. Then no complementary CH\(_3\)CN\(^+\) and HCH\(_3\)CN\(^+\) fragments reported in [16] were expected, and none were seen. However, a trace of Ca\(^+\) was observed, originating presumably from the breakdown of Ca\(^+\)CN. The MS/MS spectra of the Ba\(^{2+}\) and Sr\(^{2+}\) complexes were analogous, except that no M\(^+\)CN(CH\(_3\)CN) was produced from any precursor.

3.2. Manganese, cobalt, iron, and nickel

As pointed out in [15,16], acetonitrile complexes of metals with IP2 > 12.2 eV, such as Mn (15.6 eV) and Co (17.1 eV), exhibit more diverse fragmentation patterns. We similarly found Co\(^{2+}\)CH\(_3\)CN to break up, in addition to (2), via electron transfer

\[
M^{2+}(CH_3CN)_n = M^+(CH_3CN)_{n-1} + CH_3CN^+ \tag{3}
\]

Dissociation of Co\(^{2+}\)CH\(_3\)CN produces, in addition to CH\(_3^+\), some CH\(_2^+\) (Fig. 2a). Also, complete evaporation (1) to bare Co\(^{2+}\), not noted in [16], was observed. For Co\(^{2+}\)(CH\(_3\)CN)\(_2\), one more channel involving intraligand proton transfer opened [16]

\[
M^{2+}(CH_3CN)_n = M^+CH_2CN(CH_3CN)_{n-2} + H^+CH_3CN \tag{4}
\]

This is analogous to the dissociative proton transfer well known for hydrated metal dications [28]

\[
M^{2+}(H_2O)_n = MOH^+(H_2O)_m + H_3O^+(H_2O)_{n-m-2} \tag{4'}
\]
Fig. 2. CID spectral windows addressing aspects in fragmentation of the acetonitrile complexes with Co$^{2+}$: (a) observation of the CH$_2^+$ product and (b) observation of both electron (3) and proton (4) transfer channels yielding, respectively, Co$^{+}$CH$_2$CN and Co$^{-}$CH$_2$CN. Fractional yields were on the order of 1%. All data were measured on TAGA at $E = 40$ eV for both regular acetonitrile (solid lines) and $d_3$-acetonitrile (dashed lines). Precursors were Co$^{2+}$CH$_3$CN (a) and Co$^{2+}$(CH$_3$CN)$_2$ (b). The results for Mn$^{2+}$ were similar.

We also observed the electron transfer (3) not reported in [16], see Fig. 2b. Remarkably, reaction (4) occurred in a significant yield, despite CH$_3$CN being classified as an ‘aprotic’ solvent. Still, the proton transfer here was comparatively less facile than for protic solvents: electron (3) and proton (4) transfers were more frequent for acetonitrile complexes, whereas for aprotic complexes electron transfer is non-competitive and is not encountered for any metal, with any number of ligands [28]. The reasons for that became clear from recent calculations [30]. The dissociation of Co$^{2+}$(CH$_3$CN)$_3$ was dominated by acetonitrile evaporation (1), but also exhibited the ligand cleavage (2) and electron (3) and proton (4) transfers missed in [16]. For $n = 4$, only evaporation was observed, hence for Co $n_{crit} = 3$. Our findings for Mn$^{2+}$ complexes are identical to those for Co$^{2+}$. So our results for the dissociation of Mn$^{2+}$CH$_3$CN and Mn$^{2+}$(CH$_3$CN)$_2$ differ from those reported in [16] in observations of CH$_2^+$ among the fragments and of electron transfer (3) for $n = 2$.

The most significant difference between our and Kohler and Leary’s [15,16] results for the MS/MS of Mn$^{2+}$CH$_3$CN and Mn$^{2+}$(CH$_3$CN)$_2$ (where M = Mn and Co) is perhaps not in the raw data, but in interpretation. This pertains to the identity of the peak at $m/z = 40$. This was assigned [15,16] as Ar$^+$, produced by charge transfer to the argon collision gas. However, when deuterated acetonitrile was used in our experiments, this feature in-varily and completely shifted to $m/z = 42$ (Fig. 3). Our interpretation is that this ion is not Ar$^+$ but CH$_2$CN$^+$. As no M$^+$H(CH$_3$CN)$_n$ ions were ever observed, CH$_2$CN$^+$ likely originates from the breakdown of M$^+$CH$_3$CN, a product of proton transfer (4). This is consistent with the feature appearing at higher $E$ only (Fig. 2). It was argued in [16] that the ion in question was Ar$^+$ because it was not among the products of Ca$^{2+}$(CH$_3$CN)$_n$ or Sr$^{2+}$(CH$_3$CN)$_n$ and the IP2s of Ca (11.9 eV) and Sr (11.0 eV) are too low for Ar (IP = 15.8 eV) to transfer an electron to M$^{2+}$. Our data instead show that this CH$_2$CN$^+$ peak was not observed when M = Ca or Sr simply because proton transfer (4) was inoperative and the putative MCH$_2$CN$^+$ precursor was therefore unavailable.

Fig. 3. CID spectral windows (at $E = 40$ eV on TAGA) for Co$^{2+}$CH$_3$CN (solid line) and Co$^{2+}$CD$_3$CN (dashed line) proving the assignment of the peak at $m/z = 40$ as CH$_2$CN$^+$. Same situation was observed for other metals examined.
Nothing has been reported on the acetonitrile complexes of iron and nickel. For Fe$^{2+}$ complexes, we found the chemistry to follow that of Mn$^{2+}$. For nickel complexes, no bare Ni$^{2+}$ was observed despite our focused efforts. This is likely a consequence of the higher IP2 for Ni (Table 1), which favors electron transfer (3) over acetonitrile evaporation (2) in Ni$^{2+}$CH$_3$CN.

3.3. Copper

The dissociation of Cu$^{2+}$(CH$_3$CN)$_2$ was investigated by Seto and Stone [17]. They emphasized its difference from that of Mn$^{2+}$ and Co$^{2+}$ complexes as reported in [15,16] in that no CH$_3^+$, Cu$^{+}$CN, or Cu$^{+}$CN(CH$_3$CN) ions were observed. Also, no Cu$^{+}$CH$_2$CN(CH$_3$CN) were reported for any $n$, though H$^+$CH$_2$CN found from the Cu$^{2+}$(CH$_3$CN)$_3$ precursor [17] would require it. It appeared then that channels (2) and (4) were inoperative for any Cu$^{2+}$(CH$_3$CN)$_n$; that is Cu$^{2+}$ could not induce the cleavage of the C–C bond in CH$_3$CN or proton transfer between two acetonitrile ligands. It was unclear whether these discrepancies were due to different collision energies or reflected chemical differences between copper and cobalt/manganese [17]. We did find Cu$^+$CH$_2$CN and Cu$^+$CH$_2$CN(CH$_3$CN) in addition to Cu$^+$CH$_3$CN and Cu$^+$CH$_3$CN$_2$ (Fig. 4a,b), indicating a competition between electron (3) and proton (4) transfers as in the cases of Co and Mn complexes. However, the yield of M$^+$CH$_3$CN relative to that of M$^+$CH$_2$CN for Cu complexes was indeed smaller than that for Mn or Co studied in [15,16]. This explains why CH$_3$CN$^+$ was not found among the products for any Cu$^{2+}$(CH$_3$CN)$_n$ precursor [17]. That said, the [M$^+$CH$_3$CN]/[M$^+$CH$_2$CN] yield ratio for Cu is close to that for Ni complexes, hence Cu is not special in that regard.

We also found CH$_3^+$ and Cu$^+$CN(CH$_3$CN) (Fig. 4c,d), though their yields were below those of their Co$^{2+}$ and Mn$^{2+}$ equivalents. In agreement with [17], no Cu$^+$CN(CH$_3$CN)$_2$ or any charge-transfer products arising from Cu$^{2+}$(CH$_3$CN)$_n$ with $n \geq 4$ were observed. The Cu$^+$CN was encountered in trace amounts only. This apparently is because the immediate precursor, Cu$^{2+}$CH$_3$CN, was present only in minute quantities [17] compared to Mn$^{2+}$CH$_3$CN or Co$^{2+}$CH$_3$CN. This is due to a much higher IP2 of Cu, which promotes dissociative charge transfer rather than acetonitrile elimination in Cu$^{2+}$(CH$_3$CN)$_2$. The fact that Cu$^+$CN(CH$_3$CN) and CH$_3^+$ were produced shows that Cu$^{2+}$ is not as inert in forcing heterolytic cleavage (and not altogether different from Co$^{2+}$ or Mn$^{2+}$) as appeared previously [17]. Rather, competing reactions reduce Cu$^{2+}$ before the complex is small enough for this cleavage to yield Cu$^+$CN.

Seto and Stone [17] reported Cu$^{2+}$CH$_3$CN among the fragments of Cu$^{2+}$(CH$_3$CN)$_2$, however Wright et al. [22] found $n_{\text{min}} = 2$ for acetonitrile complexes of Cu$^{2+}$. We have now verified the existence of Cu$^{2+}$CH$_3$CN, Fig. 4e.

3.4. Beryllium, magnesium, zinc, and cadmium

No acetonitrile complexes of these metals have been studied previously. We found their fragmentation chemistry to resemble that of the Mn$^{2+}$, Fe$^{2+}$, Ni$^{2+}$, and Co$^{2+}$ complexes, whose transition metals have IP2s in the same 15–18 eV range. It, however, differs from that of the other Group 2 elements, Ca$^{2+}$, Sr$^{2+}$, and Ba$^{2+}$ that have low IP2s. This confirms that the CID behavior of M$^{2+}$(CH$_3$CN)$_n$ is determined primarily by the IP2 of the metal, rather than by its electronic configuration. Bare M$^{2+}$ was observed among the fragmentation products for the complexes of Mg (IP2 = 15.0 eV) and Cd (IP2 = 16.8 eV), but not those of Be (IP2 = 18.2 eV) or Zn (IP2 = 18.0 eV). This is similar to the case of Ni versus Fe or Co mentioned above, and further demonstrates the critical importance of the IP2 value. We note that M$^{2+}$CH$_3$CN were observed for all metals, including Be for which no M$^{2+}$H$_2$O could be produced [28]. However, the extent of dissociative charge transfer is determined not only by the value of IP2. For example, $n_{\text{crit}} = 4$ for Be is above $n_{\text{crit}} = 3$ for Cu, although the IP2 of Be is 2 eV below that of Cu. This tracks the trend for hydrated ions, where $n_{\text{crit}} = 8$ for Be and 6 for Cu [28].
3.5. Competition between electron and proton transfer

Unlike hydrated M$^{2+}$ that yield ubiquitous protonated water clusters in MS/MS [28], acetonitrile complexes of any metal produce no H$^+$-(CH$_3$CN)$_n$ or (CH$_3$CN)$_n^+$ for $n > 1$. Hence M$^+$CH$_2$CN and M$^+$CH$_3$CN fragments must originate only from M$^{2+}$(CH$_3$CN)$_2$, and M$^+$CH$_2$CN(CH$_3$CN) and M$^+$CH$_3$CN$_2$ only from M$^{2+}$(CH$_3$CN)$_3$. Thus dissociative charge transfer is evident in complexes containing two and three ligands for all M$^{2+}$ studied except Ca$^{2+}$, Sr$^{2+}$, and Ba$^{2+}$ (Table 1). The partition of this process between electron and proton transfer may depend on the collision energy. For some metals studied here, MS/MS fragment intensity ratios of M$^+$CH$_2$CN to M$^+$CH$_3$CN and of M$^+$CH$_2$
CN(\text{CH}_3\text{CN}) to \text{M}^+\text{(CH}_3\text{CN)}_2 both increased with increasing \( E \) at any collision gas pressure, suggesting that the activation barrier for electron transfer is lower in both \( n = 2 \) and \( 3 \) (Fig. 5a,b). In other cases however, those fragment ratios were roughly energy-independent, suggesting similar energy barriers for two processes.

Under identical conditions, \( \frac{[\text{M}^+\text{CH}_3\text{CN}(\text{CH}_3\text{CN})]}{[\text{M}^+(\text{CH}_3\text{CN})_2]} \) ratio normally exceeds \( \frac{[\text{M}^+\text{CH}_2\text{CN}]}{[\text{M}^+\text{CH}_3\text{CN}]} \) one, indicating a generally easier proton transfer for \( n = 3 \). In particular for Ni and Cu, \text{M}^+\text{CH}_2\text{CN} fragment is minor compared to \text{M}^+\text{CH}_3\text{CN} under any conditions tried, while \text{M}^+\text{CH}_2\text{CN}(\text{CH}_3\text{CN}) often dominates \text{M}^+\text{(CH}_3\text{CN)}_2. This might be due to a larger spatial separation of ligands in \text{M}^{2+}(\text{CH}_3\text{CN})_2 than in \text{M}^{2+}(\text{CH}_3\text{CN})_3. However, for the same \text{M}^{2+}(\text{CH}_3\text{CN})_n precursor \((n \geq 3)\), CID of \text{M}^{2+}(\text{CH}_3\text{CN})_2 intermediate is in reality less energetic than that of \text{M}^{2+}(\text{CH}_3\text{CN})_3 one, as the latter produces the former via endothermic ligand loss. Since the propensity for electron transfer often increases at lower \( E \), its higher prevalence for \( n = 2 \) may be partly an experimental artifact. The identity of the metal also matters (Fig. 5c). For example, at medium \( E \) the \text{M}^+\text{CH}_3\text{CN} product is preferred for Mn and Fe, \text{M}^+\text{CH}_3\text{CN} dominates for Ni and Cu, and the two channels are close in intensity for Mg, Zn, Cd, and Co.

4. Conclusions

We have extensively studied the fragmentation of acetonitrile complexes of dication of divalent metals. Large complexes dissociate solely via \text{CH}_3\text{CN} evaporation. In small complexes \((n = 1–4)\), heterolytic cleavage, and electron and proton transfers followed by ‘Coulomb explosion’ become operative. This diapason of threshold sizes is smaller than that of \( n = 2–8 \) for aqua complexes [28], presumably due to the shorter range of intermolecular interactions in aprotic solvents that lack hydrogen bonding propagating long-range structure in protic media. Also, while the ionization potential of acetonitrile (12.2 eV) is slightly
below that of water (12.6 eV), it has a much higher dipole moment (3.9 D vs. 1.8 D) and polarizability (4.40 Å^3 vs. 1.4 Å^3) that stabilize the metal (2+) charge. Metal–CH3CN dication exists for all metals studied, including Be^{2+} for which no monohydrate could be produced [28].

Unlike in aqua complexes, in acetonitrile complexes electron and proton transfer channels compete. Data suggest that the barriers to electron transfer are similar to those for proton transfer or slightly lower, but the actual branching ratio depends on the metal and the collision energy. However, this ratio is largely insensitive to the value of the second IP of the metal, not surprising as both reactions eventually reduce the metal charge. The second IP affects the critical number of ligands below which either electron or proton transfer occurs: this number shifts from 0 to 4 as the IP2 increases from 10 to 20 eV. Beryllium exhibits an anomalously high critical number. It behaves in the same way in aqua complexes [28]; future work should reveal whether this is a systematic ligand-independent property. The IP2 also determines whether the solvent evaporation could proceed all the way to bare M^{2+} ion: this happens only for metals with second IP below 17–18 eV. Conversely, the IP2 of a metal does not clearly correlate with the largest complex size for which heterolytic cleavage takes place. This would be expected for a process not initiated by charge transfer.

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References