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Chemistry in aldol complexes of metal dications: dehydration of the bisligand species

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Abstract

The advent of electrospray has enabled the generation of microsolvated multiply charged metal ions. For dications, these had been produced for most common organic ligand classes including simple alcohols and ketones, but not aldols. Solution-phase aldol chemistry is reknown for dehydration and retro-aldol reactions. One of the simplest aldols is the acetone dimer, known as diacetone alcohol (DAA). It has recently been shown to coordinate gas-phase metal trications—the first precedent thereof for any protic solvent. Here we report on the formation and collisional fragmentation of DAA complexes for dications of divalent metals ($M = Mg$, Ca, Ba, Mn, Ni, Co, Fe, and Cu). Both retro-aldol and dehydration processes were observed in these species. Most notable is the extreme size-specificity of dehydration. Sequential loss of two waters dominates the dissociation of $M^{2+}(DAA)_2$ for all metals studied, yielding extraordinary M^{2+}(mesityl oxide)$_2$ peaks. However, $M^{2+}(DAA)_3$ essentially do not dehydrate. This suggests a geometry of complexes with two DAA in the first solvation shell, perhaps in a bidentate arrangement involving both carbonyl and hydroxyl. Similarly to their simple alcohol analogs, charge-reduction of $M^{2+}(DAA)_n$ proceeds via proton transfer, except in the case of Cu where proton and electron transfers compete. A comparison of the critical and minimum sizes for $M^{2+}(DAA)_n$ and $M^{3+}(DAA)_n$ reveals a major intrinsic gap between the stabilities of metal di- and trications in protic solvent complexes.

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1. Introduction

Aldol condensation is a classic of organic chemistry [1]. This is an addition of the α-carbon of one aldehyde or ketone to the carbonyl carbon of another. This process can be catalyzed by either acid or base, and the reverse retrograde aldol reaction is generally important. Aldol products routinely dehydrate, particularly in acidic media [1]. One of the simplest, most frequently encountered aldols is diacetone alcohol (DAA), $(CH_3)_2C(OH)CH_2COCH_3$, resulting from the dimerization of acetone. Dehydration of DAA yields mesityl oxide, $(CH_3)_2C{=}CHCOCH_3$, abbreviated as “mox”.

Thorough understanding of chemical processes generally benefits from their microscopic study in finite systems, where elementary reactions can be followed stepwise and experimental data related to tractable theoretical models. This opportunity is provided by free molecular clusters, often solvating various ions. While these systems were researched for several decades,

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most work has been on singly charged species. This is because gas-phase solvated monocations are readily produced by a variety of experimental methods, most commonly sequential ligation of bare ions in the vapor of relevant ligand. Complexes of multiply charged cations are essentially inaccessible by this route, because of dissociative charge transfer. That is, the 2nd and 3rd ionization energies (IE) of all elements except alkaline earths are above 14 eV, while the IE of almost all organic ligands lie in the 8–13 eV range. Hence an electron transfer from a neutral ligand (L) to a bare metal (M) polycation is exothermic. It usually occurs on contact, with the Coulomb repulsion forcing an immediate charge separation [2]. Often, even dications with 2nd IE (IE2) below the ligand IE that do not undergo electron transfer still cannot be ligated by addition, because of other charge reduction processes. This is particularly common for protic ligands, which exhibit a facile proton transfer [2].

The route to ligated multiply charged cations has been opened by the advent of electrospray ionization (ESI) source a decade ago. ESI transfers ions existing in solution into the gas phase, inside large native solvation shells. These shells are partly removed by thermal/collisional heating in the desolvation region, prior to mass spectrometric analysis. This change of paradigm for generation of complexes from “building up” by sequential ligation of bare ions to “shrinking down” of microscopic droplets allows one to circumvent the small size regime in which charge reduction via separation would take place. Since the pioneering work of Kebarle’s group [3–5], dication complexes of most divalent metals have been formed in ESI for water and various organic solvents, including alcohols, ketones, dimethyl sulfoxide, ethers, amides, acetonitrile, and nitrogen-containing heterocycles such as pyridine [6–30]. More recently, Stace and coworkers have developed a novel “pick-up” technique, where first a neutral metal atom is embedded into a cluster of desired solvent, then the charge state is raised by electron-impact ionization [31]. This method has successfully produced complexes of doubly and triply charged metal ions with most above mentioned ligands, and also some not easily amenable to ESI, such as argon and carbon dioxide [31–43]. Ligated metal polycations can also be generated via charge-stripping, a procedure conceptually analogous to the pick-up technique that starts from monocations [44,45].

The hallmark property of ligated metal polycations is charge reduction, which increases in prominence with decreasing complex size. While the detailed reduction pathways depend on the ligand, two universal parameters have been introduced to characterize the stability of microsolvated multiply charged ions. One is the minimum size (n_{min}), giving the smallest n for which $M^{k+}L_n$ could still survive in their original charge state. Since an electron transfer from L to M^{k+} is normally exothermic as described above, n_{min} may well be greater than 1. For some ligated ions, n_{min} values as high as eight have been established [46]. However, n_{min} could equal one even when the relevant metal IE exceeds the ligand IE, often by a huge margin. For example, $Nd^{3+}CH_3CN$ does exist [24], even though it lies 10 eV above the separated Nd^{2+} and CH_3CN^+ (the 3rd IE of Nd is 22 eV and the IE of acetonitrile is 12 eV). Such metastable complexes are held together by activation barriers to charge transfer [47–49]. The other parameter is critical size (n_{crit}), defined as the largest precursor dissociating via either electron or proton transfer in competition with the trivial neutral ligand loss. However, cleavage processes, whether accompanied by charge reduction or not, could occur in complexes with $n > n_{\text{crit}}$. Those reactions could be characterized by their own “critical sizes”.

No complexes between any doubly charged metal ion and aldols have been studied previously. While some of their properties would be expected to resemble those of regular alcohol complexes, the presence of a carbonyl group and the ease of retro-aldol and dehydration reactions could create major differences. Here we report on the ESI formation of DAA complexes with dications of nine common divalent metals (Ba, Ca, Mg, Zn, Mn, Fe, Co, Ni, Cu). Fragmentation chemistry of these species is elucidated using low-energy collision-induced dissociation (CID). To set a benchmark for the general effect of double charge, we probe the behavior of DAA complexes for two singly charged cations, K^+ and Ag^+, representative of the alkali and Group 11 metals, respectively. Recently, DAA has been shown to coordinate triply charged rare-earth metal ions, the precedent of gas-phase trications in protic solvent complexes [46]. This allows us to directly compare the stability of doubly and triply charged complexes, something that had heretofore been possible for aprotic ligands only.

2. Experimental methods

Experiments were performed using a Finnigan TSQ 7000 tandem mass spectrometry apparatus. In Finnigan instruments, the API source and vacuum region are connected via a heated capillary. The ESI needle voltage was about 4 kV. There was a moderate nebulizing gas flow, but no auxiliary gas. Some data were acquired with nebulizing gas switched off. This diminished the signal by more than an order of magnitude, but did not affect the results otherwise. $M^{2+}(DAA)_n$ complexes were produced by electrospraying dilute solutions of divalent metal nitrates in aqueous DAA. (Since no nitrate is available for Fe^{2+}, $FeSO_4$ was substituted.) Mass-selected precursors were fragmented by CID with argon at the laboratory collision energy (E) of 10–160 eV and pressure of $P = 1.3$ mTorr. This pressure corresponds to a

Table 1
Fragmentation products of the DAA complexes of divalent metal dications[a]

M	IE2 (eV)	Dication products[b]			Monocation products, M^+ ligated by					
		Retro[c]	Dehydration[d]	Other[e]	$(A_n\text{–}H)$[f,g]	$(mox_n\text{–}H)A_n$[h]	CH_3A_n	OHA_n	$CHCOA_n$[i]	Other[j]
Ba	10.0	1.5, 2.5	1.5′, 2″, 2′, 3′, 4′, 5″	2, 4	1–4	0, 1	0, 1	0, 1		1, 2
Ca	11.9	1.5, 2.5	1.5′, 2″, 2′, 3′, 4′, 5″, 5′	1, 2, 4, 6	1–4, 6	0, 1	0, 1	0–2		1, 4
Mg	15.0	2.5	2″, 2′, 3″, 3′, 4′, 5″, 5′	1, 3–6	1–4, 6, 8	0, 1	0	0–2		1, 2, 4
Mn	15.6	1.5, 2.5, 3.5	1.5′, 2″, 2′, 3′, 4′	1, 4–8	1–4, 6	0, 1	0–2	0–2	1, 2	1–5
Fe	16.2	1.5, 2.5	1.5′, 2″, 2′, 3″, 3′, 4″, 4′, 5″, 5′	1, 4–8	1–4, 6, 8	0–2	0–2	0–2	1–3	1–4
Co	17.1	1.5, 2.5	2″, 2′, 4′	1, 6–8	1–4, 6, 8	0, 2	0, 1	0–2	2, 3	1, 2, 5
Zn	18.0	1.5	2″, 2′, 3′, 4′, 5′	1	1–4, 6	0	0–2	0–2		1–3
Ni	18.2	2.5, 3.5	2″, 2′, 3″, 3′, 4″, 5″	1	1–4, 6, 8	0	0	0–2	1	1, 2, 5
Cu	20.3		2″, 2′, 3′	1	1–4, 6					5

[a] General abbreviations throughout the table match those in the text and figures: "M" for the metal, "L" for DAA ligand, "mox" for mesityl oxide, and "A" for acetone.

[b] The minimum $M^{2+}(DAA)_n$ sizes observed ($n_{\min}$) are 1 for Ba and 2 for all other metals.

[c] Products of the retro-aldol reaction (3) with $M^{2+}(\text{acetone})(DAA)_{n-0.5}$ stoichiometry. (Some peaks at m/z of $M^{2+}(DAA)_n$ that we treat as derived from simple ligand loss may conceal $M^{2+}(\text{acetone})_{2n}$ isomers resulting from retro-aldol processes. Present methods do not gauge the extent of this happening.)

[d] Products of dehydration (4). Numbers n designate the $M^{2+}(DAA)_n$ precursor, one or two apostrophes indicate the number of waters lost. Except for 1.5′, 2″, and 2′, these appear in trace amounts only.

[e] Other doubly charged fragments: $M^{2+}(CH_3)_2CL_2$ (1), $M^{2+}CHCOCH_3$ (2), $M^{2+}(CHCOCH_3)_2$ (3), $M^{2+}(mox)$ (4), $M^{2+}CO(mox)$ (5), $M^{2+}CHCOCH_3(mox)$ (6), $M^{2+}CHCOCH_3(mox)L$ (6), and $M^{2+}CHCOCH_3(mox)L_2$ (7).

[f] These mostly result from the dissociative proton transfer (processes (7) and (8)) in either original DAA complexes or dications derived therefrom via a retro-aldol reaction. Critical sizes (n_{crit}) equal ($n/2 + 1$): 4 (Ca), 5 (Mg), 4 (Mn), 5 (Fe), 5 (Co), 4 (Zn), and 5 (Ni). In the case of Cu, $H^+(DAA)_2$ complementary fragment was observed, hence $n_{\text{crit}} = n/2 + 2 = 5$. The value for Ba could not be determined because of uncertainty regarding the identity of precursors as purely DAA or acetone/DAA complexes.

[g] Complexes of Cu^{2+} also exhibit a dissociative electron transfer, yielding the Cu^+A_n stoichiometry for $n = 1$–4.

[h] These species mostly arise from the dissociative proton transfer in dication complexes with mesityl oxide (reaction (10)).

[i] See footnote 2.

[j] $M^+CH_3(CH_2)_2C$ (1), $M^+CH_3(CH_2)_2C(mox)$ (2), $M^+CH_3(mox)$ (3), $M^+CH_3CO(mox)$ (4), $M^+(mox)$ (5).

multicollisional dissociation, necessary to induce extensive fragmentation of large precursor ions at reasonable collision energies. High energies needed to reach the same depth of fragmentation in a single collision substantially degrade the instrumental mass resolution and accuracy, which would be a particular problem for multiply charged ions. The heated capillary was at 150 °C in most cases, with some data collected at 250 °C to verify reproducibility. It has been widely noted that the overall relative yield of multiply charged ions maximizes at the "mildest" source conditions, meaning an essentially flat potential in the lens region [21–23]. This minimizes the collisional excitation of field-accelerated ions that would promote their charge reduction. Unfortunately, the total ion signal under these conditions is low, most likely because of a wide spatial divergence of slow ion beams. So the optimum absolute intensity of dications is usually attained at a small voltage drop, in this case 7 V.

DAA is a large and intricate ligand, and the dissociation chemistry of metal–DAA cluster dications turned out to be rich. To verify the peak assignments and deconvolute certain mass overlaps, we repeated selected experiments for perdeuterated complexes generated using the d_{12}-DAA/D_2O mixed solvent. Whenever possible, CID spectra have been collected for several metal isotopes. While those checks assure the integrity of all assignments made, some minor peaks could not be identified conclusively; these are not labeled in the figures. The large number of observed products precludes our mentioning them all, and only major ones or those of specific relevance are marked in the figures and/or discussed in the text. All fragments identified are listed in Table 1.

3. Results

For divalent metal salts, source mass spectra exhibited $M^{2+}(DAA)_n$ features for n in the 4–8 range, with no stand-out peaks ("magic sizes"). The case of Fe is presented in Fig. 1. For monovalent K and Ag, $M^+(DAA)_n$ with $n = 1$–3 were present in the Q1 spectra.

3.1. Dissociation of monocation DAA complexes

First, we studied the decomposition of $K^+(DAA)_2$ and $Ag^+(DAA)_2$. As one would expect for monocation complexes, these mostly desolvated to bare metal ions by ligand loss (Fig. 2). This was the sole pathway found for K^+ complexes of any size. In silver complexes, ligand loss was the only breakdown channel for $Ag^+(DAA)_2$, but $Ag^+(DAA)$ exhibited an intense retro-aldol reaction yielding Ag^+(acetone) and a minor dehydration channel producing Ag^+(mox) (Fig. 2B). Traces of $Ag^+(CH_2)_2C$ and $Ag^+(CH_3)_2C$ were also observed. These probably result from, respectively, the dehydration of Ag^+(acetone) (1) and scission in Ag^+(mox) at the site of double bond in (mox) (2), viz:

$$M^+(CH_3COCH_3) \Rightarrow M^+(CH_2)_2C + H_2O \qquad (1)$$

$$M^+(CH_3)_2C{=}CHCOCH_3 \Rightarrow M^+(CH_3)_2C + CHCOCH_3 \qquad (2)$$

Though one might expect metals to attach to the oxygen in mesityl oxide, no $Ag^+CHCOCH_3$ was produced in competition to (2). The richer chemistry of silver complexes relative to those of potassium is consistent with a higher IE of Ag (7.6 eV) compared to that of K (4.3 eV).

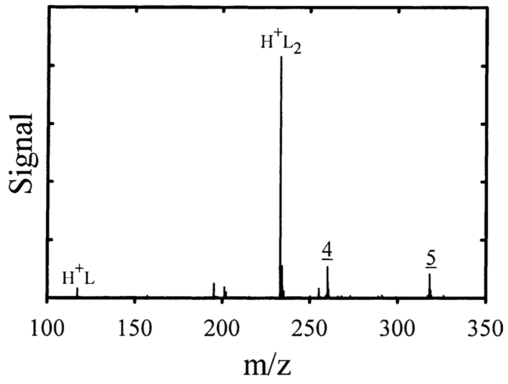

Fig. 1. ESI/MS (Q1) spectrum of $FeSO_4$ dissolved in aqueous DAA. Numerals n are for $M^{2+}(DAA)_n$, dications are underlined. Symbol L stands for the aldol ligand.

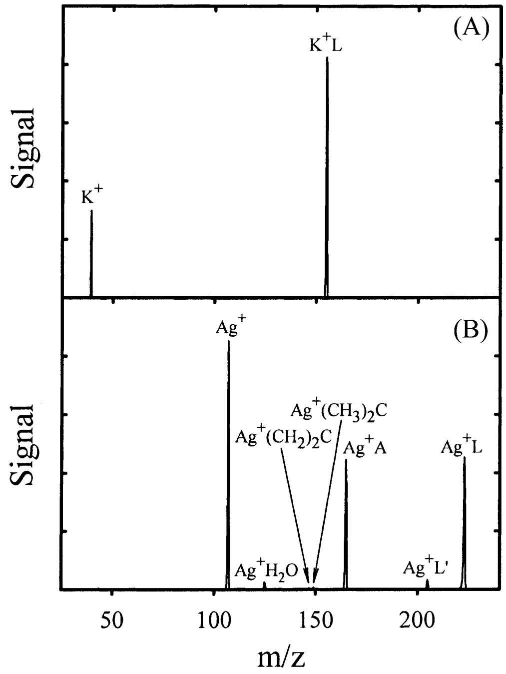

Fig. 2. CID spectra for $^{39}K^+(DAA)_2$ (panel A) and $^{107}Ag^+(DAA)_2$ (panel B) at $E = 20$ and 40 eV, respectively. Symbol A stands for acetone ($m/z = 58$), and L for the aldol ligand ($m/z = 116$). An apostrophe on any symbol codes for single water loss: L′ and A indicate, respectively, a dehydrated DAA (i.e., mesityl oxide, $m/z = 98$) and dehydrated acetone ($m/z = 40$). Assignments for silver complexes were verified using the data for ^{109}Ag.

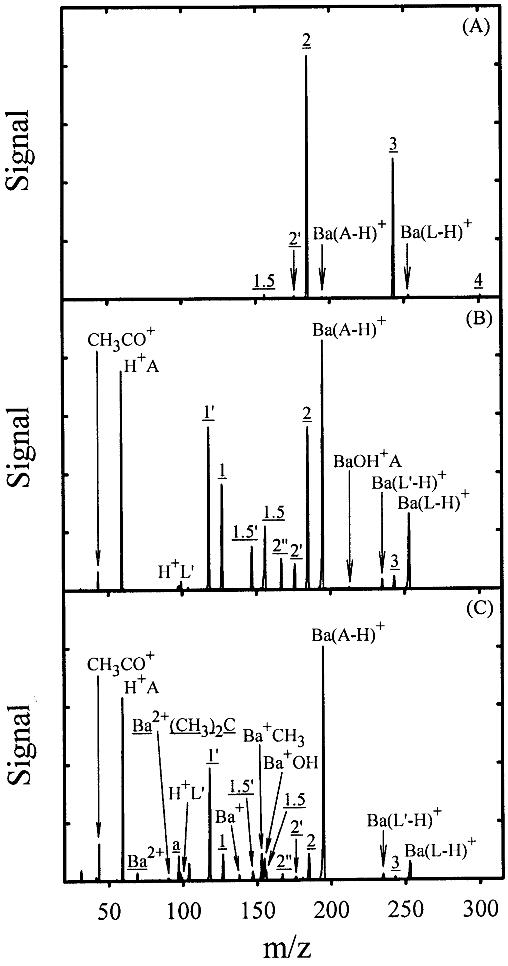

Fig. 3. CID of $^{138}Ba^{2+}(DAA)_5$ as a function of collision energy, at $E = 40$ eV (A), 80 eV (B), and 120 eV (C). Symbol "a" stands for $M^{2+}CHCOCH_3$, numerals n are for $M^{2+}(DAA)_n$ (half-integers mark $M^{2+}(acetone)(DAA)_{n-0.5}$). All dications are underlined. Other notation is as in Fig. 2, including the numerals with apostrophes (e.g., 2″ stands for $[M^{2+}(DAA)_2–2H_2O] = M^{2+}(mox)_2$; 1.5′ stands for $[M^{2+}(acetone)(DAA)–H_2O] = M^{2+}(acetone)(mox)$). All assignments were confirmed by the data for ^{136}Ba analogues.

3.2. *General picture of $M^{2+}(DAA)_n$ dissociation: the Ba case*

The lowest IE2 of all elements (10.0 eV) belongs to barium, thus, we started the investigation of dication DAA complexes from this metal (Fig. 3). $Ba^{2+}(DAA)_n$ species shrink almost solely by ligand loss until the bisligand complex is reached (Fig. 3A). Exceptions are a minor retro-aldol channel (3) for $n = 3$ yielding $Ba^{2+}(acetone)(DAA)_2$:

$$M^{2+}(DAA)_n = M^{2+}(acetone)(DAA)_{n-1} + \text{acetone} \tag{3}$$

and minute traces of water and methanol loss from $Ba^{2+}(DAA)_n$ with $n = 3–5$. The latter are exemplified and discussed below for Mg^{2+} complexes. The fragmentation pattern changes drastically once $Ba^{2+}(DAA)_2$ is the precursor: the ligand loss to $Ba^{2+}(DAA)$ closely competes with several other channels (Fig. 3B). One is an intense retro-aldol reaction (3). Another is the sequential double dehydration (4) producing Ba^{2+} bisligated by mesityl oxide:

$$M^{2+}(DAA)_2 = M^{2+}(mox)_k(DAA)_{2-k} + kH_2O \quad (k = 1, 2) \tag{4}$$

Since acetone may dehydrate as per reaction (1), in principle both water eliminations could be from the same DAA molecule. This is, however, highly unlikely considering that absolutely no third dehydration of $M^{2+}(DAA)_2$ was encountered, for Ba or any other dication studied here. Further, Ba^{2+}(acetone)(DAA) product of (3) and Ba^{2+}(DAA) also dehydrate readily, but only one water could be lost from either (Fig. 3B). Two remarkable high-energy products (Fig. 3C) are $Ba^{2+}CHCOCH_3$ and a trace of $Ba^{2+}(CH_3)_2C$. These clearly result from a homolytic cleavage in Ba^{2+}(mox) at the site of double bond in (mox), with Ba^{2+} coordinating to either end:

$$M^{2+}(CH_3)_2C{=}CHCOCH_3 \Rightarrow M^{2+}CHCOCH_3 + (CH_3)_2C \qquad (5)$$

$$M^{2+}(CH_3)_2C{=}CHCOCH_3 \Rightarrow M^{2+}(CH_3)_2C + CHCOCH_3 \qquad (6)$$

Finally, Ba^{2+} was observed.

All channels (3)–(6) described above conserve the (+2) charge state of metal complexes. Singly-charged products are dominated by those of $[Ba(acetone–H)]^+(acetone)_{n-1}$ stoichiometry observed for $n = 1$–4. For $n = 2$ and 4, these species can be written as $[Ba(DAA–H)]^+(DAA)_{n/2-1}$. One might assume that those come from dissociative proton transfer, which is ubiquitous for the complexes of metal dications with protic ligands such as water and simple alcohols:

$$M^{2+}L_n \Rightarrow [M(L–H)]^+L_{n-2} + H^+L \qquad (7)$$

However, no H^+(DAA) at $m/z = 117$ was observed. That and a huge yield of H^+(acetone) suggest that the proton transfer actually occurs in the products of retro-aldol reaction (3):

$$M^{2+}(\text{acetone})_n \Rightarrow [M(\text{acetone–H})]^+(\text{acetone})_{n-2} + H^+(\text{acetone}) \qquad (8)$$

In agreement with this mechanism, the biggest fragment of this type is $[Ba(DAA–H)]^+$(DAA) while the biggest product of (3) is $Ba^{2+}(acetone)(DAA)_2$. It is unclear why the process (7) is closed; it could be that the retro-aldol reaction (3) has a significantly lower activation barrier. In that case, dissociative proton transfer would proceed only once DAA is converted to acetone.

Less intense singly-charged products are $[Ba(mox–H)]^+(acetone)_n$ for $n = 0$ and 1 (Fig. 3B). These could not originate from DAA or acetone/DAA complexes of Ba^{2+} since no $H_3O^+(acetone)_k$ complementary ions were found for any k. Likely, proton transfer operates in the products of dehydration (4):

$$M^{2+}(\text{mox})(\text{DAA}) = [M(\text{mox–H})]^+(\text{acetone}) + H^+(\text{acetone}) \qquad (9)$$

$$M^{2+}(\text{mox})_2 = [M(\text{mox–H})]^+ + H^+(\text{mox}) \qquad (10)$$

$$M^{2+}(\text{mox})(\text{acetone}) = [M(\text{mox–H})]^+ + H^+(\text{acetone}) \qquad (11)$$

where H^+(mox), the complementary fragment in (10), is prominent. Notably, the largest product of this series is $[Ba(mox–H)]^+$ and the largest product of (4) is Ba^{2+}(mox)(DAA), exactly as reactions (9)–(11) would predict. An alternative dehydration of $[Ba(DAA–H)]^+$ yielding $[Ba(mox–H)]^+$ cannot be ruled out, but is implausible considering a low first IE of Ba (5.2 eV). Higher energies induce further decay to $[BaOH]^+$(acetone), $[BaOH]^+$, Ba^+CH_3, and, ultimately, Ba^+ (Fig. 3C).

3.3. Ca^{2+} and Mg^{2+} complexes

Overall, $Ca^{2+}(DAA)_n$ fragment similarly to $Ba^{2+}(DAA)_n$. The key difference is the domination of double dehydration in the dissociation of bisligand precursor: at some energies the $Ca^{2+}(mox)_2$ peak towers over the CID spectrum (Fig. 4A). The yield of Ca^{2+}(acetone)(DAA) via (3) is low, and no or almost no Ca^{2+}(DAA) product emerges. The IE2 of Ca (11.9 eV) lies above that of Ba (10.0 eV). In general, a higher IE2 of the metal favors charge reduction, thus, destabilizing small ligated dications. This is commonly manifested in the minimum size of doubly charged metal complexes shifting up with increasing metal IE2. This is absolutely not the

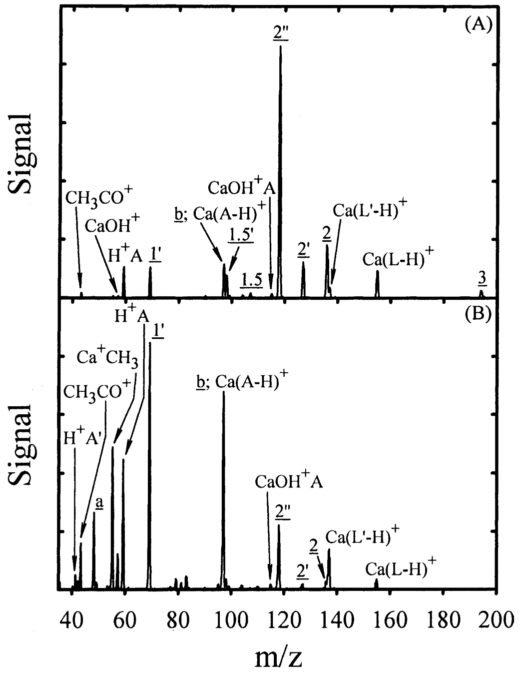

Fig. 4. CID of $^{40}Ca^{2+}(DAA)_5$ at $E = 80\,eV$ (A) and 120 eV (B). Symbol "b" stands for $M^{2+}CHCOCH_3(mox)$, other notation copies that in Fig. 3. All assignments are supported by the data for ^{44}Ca analogues.

case here: $Ca^{2+}(mox)$ and $Ca^{2+}CHCOCH_3$ fragments, both smaller than $Ca^{2+}(DAA)$, are abundant (Fig. 4B). Hence the reason for (virtual) absence of $Ca^{2+}(DAA)$ must be that the bisligand complex dehydrates nearly quantitatively to $Ca^{2+}(mox)_2$. This species then evaporates a mesityl oxide yielding $Ca^{2+}(mox)$ or cleaves at the double bond site (5) to produce $Ca^{2+}CHCOCH_3(mox)$. The $Ca^{2+}CHCOCH_3$ product emerges at higher collision energies (Fig. 4B), deriving by either homolytic cleavage in $Ca^{2+}(mox)$ or from $Ca^{2+}CHCOCH_3(mox)$. Process (6) opens for precursors as large as $Ca^{2+}(DAA)_3$, generating $Ca^{2+}(CH_3)_2C(DAA)_2$. In line with the prevalence of $Ca^{2+}(mox)_2$, a precursor in proton transfer (10), charge-reduced $[Ca(mox–H)]^+$ is intense (Fig. 4B). Among the fragments of $[M(acetone–H)]^+(acetone)_{n-1}$ stoichiometry (8), the largest has $n = 6$ rather than $n = 4$ as found in the Ba case. Since the product with $n = 5$ is missing, we conclude that the ion at the mass of $[Ca(acetone–H)]^+(acetone)_5$ is, in fact, $[Ca(DAA–H)]^+(DAA)_2$ resulting from the dissociative proton transfer in original aldol complexes:

$$M^{2+}(DAA)_n \Rightarrow [M(DAA–H)]^+(DAA)_{n-2} + H^+(DAA) \qquad (12)$$

The opening of this new channel is probably connected with a higher IE2 of Ca.

Dissociation of $Mg^{2+}(DAA)_n$ presented in Fig. 5 further augments the trend favoring the two-step dehydration (4) of bisligand complexes: the domination of intermediate-energy MS/MS spectra by $Mg^{2+}(mox)_2$ is remarkable (Fig. 5B), and neither $Mg^{2+}(acetone)(DAA)$ nor $Mg^{2+}(DAA)$ fragments appear. Again, this is not due to those species being unstable against charge reduction: a smaller $Mg^{2+}(mox)$

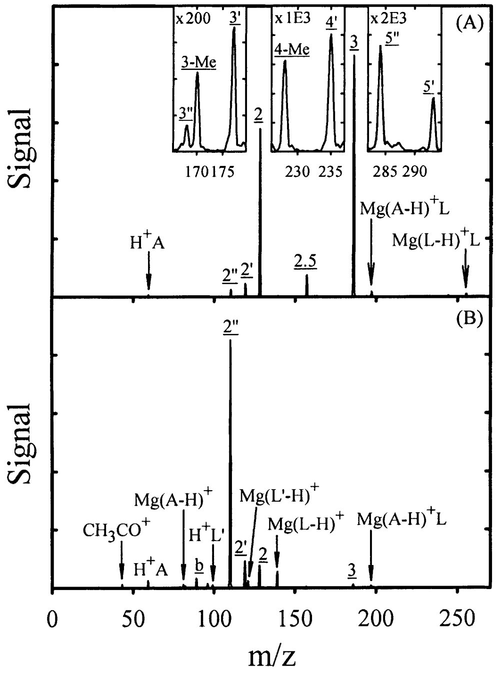

Fig. 5. CID of $^{24}Mg^{2+}(DAA)_5$ at low (A) and intermediate (B) collision energies. Insets in A, show how minute are water or methanol losses from $Mg^{2+}(DAA)_n$ for $n = 3–5$. In A, $E = 40\,eV$ for the main graph and 40, 20, and 10 eV for the insets (left to right); in B, $E = 80\,eV$. In the insets, Me stands for CH_3OH (methanol); other notation is as in Fig. 4. All assignments were confirmed by comparisons with the spectra for perdeuterated and ^{26}Mg-containing precursors.

ion is abundant at high collision energies. No $Mg^{2+}CHCOCH_3$ product has been found, but $M^{2+}(CHCOCH_3)_2$ absent for Ca and Ba is observed: apparently Mg^{2+} cuts both double bonds in $M^{2+}(mox)_2$. We also found a small amount of $Mg^{2+}CO(mox)$. As the metal IE2 increases, proton transfer in $M^{2+}(DAA)_n$ occurs at larger sizes: here the largest product found for (12) is[1] $[Mg(DAA–H)]^+(DAA)_3$. There also are new monocation fragments that require cleaving single C–C bonds in mesityl oxide, such as $Mg^+CH_3CO(mox)$, Mg^+CH_3(acetone–H_2O)(mox), and Mg^+CH_3(acetone–H_2O). As stated above, Ba^{2+} and Ca^{2+} complexes with 3–5 DAA ligands exhibit truly minute losses of water and/or methanol. For Mg^{2+} complexes, this is demonstrated in Fig. 5A. For all three metals, there is a double dehydration for $n = 5$, but a single loss of water or methanol for both $n = 3$ and 4. ($Mg^{2+}(DAA)_3$ experiences a two-step dehydration as well.)

3.4. Transition metals: Mn, Fe, Co, Ni, Zn, Cu

The IE2 of these metals except Cu are 16–18 eV, which exceeds the values for Ba, Ca, and Mg. Hence dication complexes of those transition metals should charge-reduce more easily, with smaller species becoming less stable. This is indeed the case, with a greater yield of monocation fragments at the expense of $M^{2+}(DAA)_2$ dehydration (Fig. 6). No $M^{2+}CHCOCH_3$ or $M^{2+}(CHCOCH_3)_2$ products could be found for any of these metals (presumably because of instability to charge reduction), but $M^{2+}CHCOCH_3(mox)$ and the new $M^{2+}CHCOCH_3(mox)(DAA)_n$ ($n = 1$, 2) product are registered for Mn, Fe, and Co. (No dications of these series appear for Ni^{2+} and Zn^{2+} complexes.) Traces of $M^{2+}(mox)$ and $M^{2+}CO(mox)$ have been registered for Mn and Fe, but not Co, Ni, or Zn; probably again because of the charge reduction favored by increasing IE2. Another development is the increase of dehydration relative to methanol loss in $M^{2+}(DAA)_n$ ($n = 3$, 4) precursors, though absolute yields remains miniscule. For example, $M^{2+}(DAA)_4$ exhibit a double dehydration for Fe and Ni, and show no methanol loss for Co, Ni, and Zn. For monocation

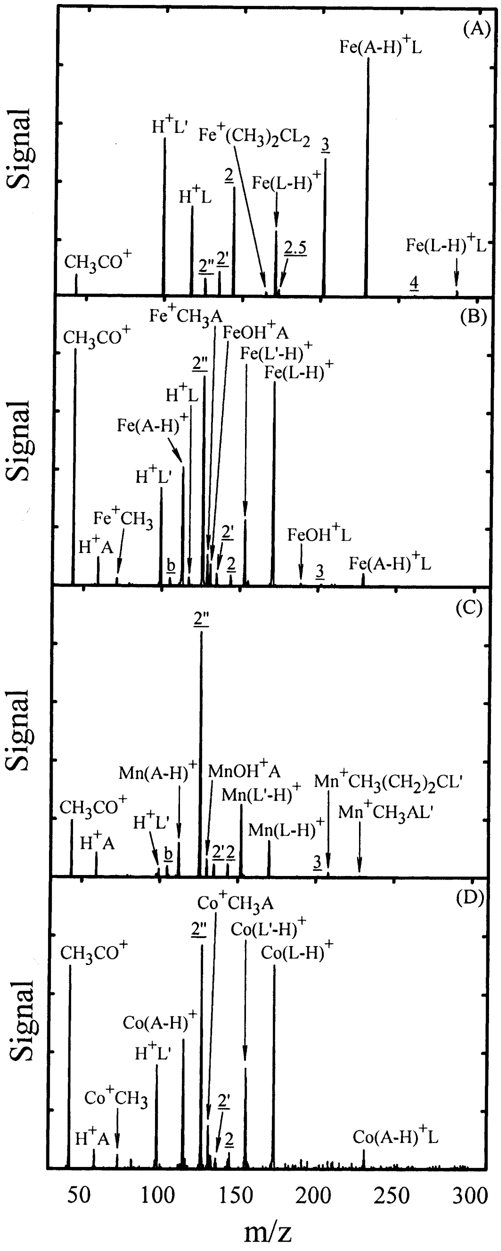

Fig. 6. CID of $^{56}Fe^{2+}(DAA)_5$ at $E = 40$ eV (A) and 80 eV (B), $Mn^{2+}(DAA)_5$ at 80 eV (C), and $Co^{2+}(DAA)_5$ also at $E = 80$ eV (D). Notation is as in Fig. 4.

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[1] No $[Mg(acetone–H)(acetone)_6]^+$ is produced, so the feature at $m/z = 371$ is probably not due to $[Mg(acetone–H)(acetone)_7]^+$.

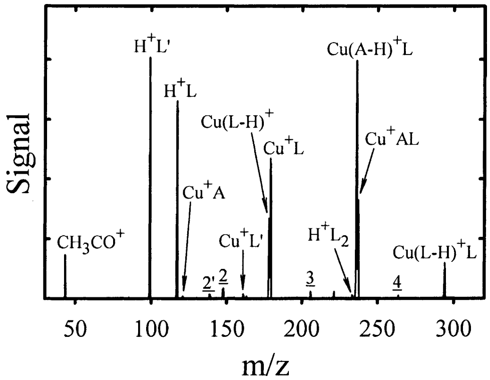

Fig. 7. CID of $^{63}Cu^{2+}(DAA)_5$ at $E = 40$ eV. Notation is as in Fig. 4.

products, there is a richer diversity of species with cut C–C bonds (Table 1). In addition to those observed for Ca^{2+} and Mg^{2+} complexes, there are ions based on M^+CH_3 ($M^+CH_3(mox)$ and $M^+CH_3(DAA)$) and, except for Zn^{2+} complexes, on M^+CHCO, such as $M^+CHCO(acetone)$ and $M^+CHCO(DAA)$.[2]

Copper has the highest IE2 for all divalent metals stable in protic media.[3] Not surprisingly, complexes of Cu^{2+} are easiest to charge-reduce, and the intensity of ligand loss leading to $Cu^{2+}(DAA)_2$ is relatively small (Fig. 7). Still, both $Cu^{2+}(mox)(DAA)$ and $Cu^{2+}(mox)_2$ dehydration products are observed. A distinct feature of $Cu^{2+}(DAA)_n$ fragmentation is a close competition between dissociative proton transfer (7) and electron transfer:

$$M^{2+}L_n \Rightarrow M^+L_{n-1} + L^+ \tag{13}$$

This process is ubiquitous in the charge-reduction of metal dication and trication complexes with aprotic ligands, such as DMSO [23] and acetonitrile [22,24], but unusual for protic solvent complexes. By inspection of Fig. 7, the relative intensity of electron transfer (13) increases for smaller complexes: the abundance of $Cu^+(DAA)$ is comparable to that of $[Cu(DAA–H)]^+$, while $Cu^+(DAA)_2$ is not even found. Further, other proton transfer products such as $[M(acetone–H)]^+(acetone)_2$ and $[M(mox–H)]^+$ are fully or partially supplanted by corresponding electron transfer products, such as $M^+(acetone)_3$ and $M^+(mox)$.[4] In those series, electron transfer is likewise favored by smaller complex size. For example, the yield of $[Cu(acetone–H)]^+(acetone)_2$ is about twice that of $Cu^+(acetone)_3$, while no $[Cu(acetone–H)]^+$ is produced (Fig. 7). The retro-aldol reaction (3), common for the complexes of all other metals studied here, is not encountered: apparently facile proton and electron transfers render it noncompetitive. Perhaps for the same reason, Cu^{2+} complexes are the only ones yielding no singly-charged fragments involving the cleavage of C–C bonds (Table 1).

4. Discussion

Since the discovery that electrospray produces microsolvated multiply charged metal cations, complexes with molecules belonging to most major organic compound classes have been generated. These included a number of simple alcohols and ketones, but no aldol condensation products (aldols). While aldols feature both hydroxyl and carbonyl functional groups, and thus, exhibit similarities to both alcohols and ketones, they also react in ways that are unusual for either, including by dehydration and retro-aldol cleavage. Here complexes of metal dications with a common aldol (DAA) were formed using ESI of appropriate metal salt solutions. We studied nine representative divalent metals: Ba, Ca, Mg, Mn, Fe, Co, Ni, Zn, and Cu. Under the conditions used, $M^{2+}(DAA)_n$ with $n = 4$–8 were produced. The dissociation chemistry of those complexes was elucidated using CID.

In a similarity to those with water and regular alcohols, DAA complexes of metal dications (except possibly Ba^{2+}) exhibit a dissociative proton transfer.

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[2] These species might instead contain both $CHCOCH_3$ and CH_3CO ligands, e.g., $M^+CHCO(DAA)$ could be represented as $M^+(CHCOCH_3)(CH_3CO)(acetone)$.

[3] The 2nd IEs of Ag (21.5 eV) and Au (20.5 eV) are above that of Cu, and that of Ag is the highest of all metals. However, neither Ag^{2+} nor Au^{2+} survives in protic media.

[4] The $M^+(mox)$ product of electron transfer appears also for Mn, Co, and Ni. However, complexes of those metals undergo proton transfer yielding $M^+(mox–H)$ as well.

The critical size at and below which this occurs equals four or five, with no apparent correlation to the metal IE2 (Table 1). However, the proton transfer in smaller precursors clearly intensifies with increasing IE2. Minimum sizes for $M^{2+}(DAA)_n$ do not significantly depend on the IE2 either: n_{min} is 1 for Ba and 2 for all other metals studied. For Cu^{2+} complexes only, proton transfer competes with the electron transfer, which is unusual for protic solvents. An increasing relative yield of the latter with increasing IE2 (3rd IE for trications) of the metal has been seen for complexes with some aprotic solvents, e.g., acetonitrile [22,24] and DMSO [50]. Analogously to the pattern in those species, the intensity ratio of electron to proton transfer increases with decreasing complex size.

A rigorous quantitation of the propensity of ligated metal polycations to charge-reduce would involve measuring the thermochemistry of those processes. In the absence of that, characteristic sizes furnish a useful approximate gauge. One topical question has been whether there is an intrinsic gap between the stabilities of doubly and triply charged species, once the difference in IE is adjusted for. By inspection of minimum and critical sizes for acetonitrile and DMSO complexes of numerous metal di- and trications, this gap is either minor or non-existent [24,50]. This would be expected for aprotic solvent complexes: they dissociate mostly by electron transfer, which is controlled by IE values. The situation for protic solvent analogs differs greatly: water and simple alcohols readily coordinate Cu^{2+} (IE2 of Cu is 20.3 eV), but not trications of any metal, including La (3rd IE = 19.2 eV) and Ce (3rd IE = 20.2 eV). Those species normally charge-reduce by proton transfer, a process not directly governed by IE. The recent finding [46] of diacetone alcohol ligating rare-earth trications allows us to make the first comparison of characteristic sizes for protic solvent complexes across charge states (Fig. 8). There is a large gap of about four units between both minimum and critical sizes for dications and trications.

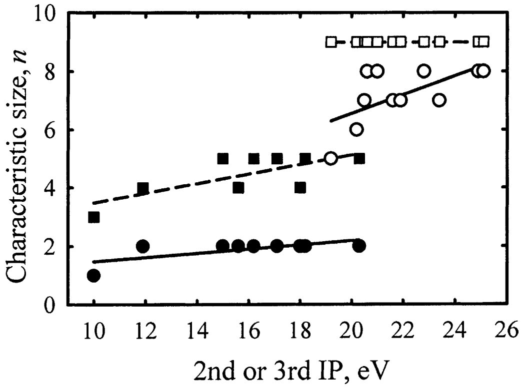

Fig. 8. Characteristic sizes for the DAA complexes of metal dications (filled symbols) and trications [46] (open symbols). Circles and squares stand for minimum and critical sizes, respectively. Lines are first-order regressions through the data for each charge state: solid for minimum and dashed for critical sizes.

While the proton and electron transfer are universal to ligated polycations, DAA complexes of M^{2+} also exhibit two specific reactions, both conserving the double charge. One is the retro-aldol process followed by neutral acetone evaporation. This results in $M^{2+}(acetone)_n$ stoichiometry with n in the 3–7 range depending on the metal, except for Cu^{2+} complexes, which yield no retro-aldol products. Perhaps of greatest interest is the dehydration of $M^{2+}(DAA)_n$. For any metal, it occurs as a trace channel, at most, when $n > 2$, but abruptly becomes the major process for bisligand precursors. For those, two waters are lost sequentially, often resulting in a dominant M^{2+}(mesityl oxide)$_2$ peak. In cases of Ba, Ca, Mn, and Fe, where the retro-aldol reaction yields M^{2+}(acetone)(DAA), it dehydrates once to M^{2+}(acetone)(mesityl oxide). In contrast, dehydration is absent or minor for DAA-ligated monocations of any size. For dication complexes, it is least intense (though still major) for $Ba^{2+}(DAA)_2$, the metal with the lowest IE2. These facts clearly indicate the importance of double charge and sufficiently high metal IE for the initiation of dehydration in aldol complexes. What causes the dramatic jump from no or virtually no ($\ll$1%) dehydration for $M^{2+}(DAA)_3$ to nearly 100% double water loss for $M^{2+}(DAA)_2$? Since this transition is independent of the metal IE2 over the whole 10–20 eV range, it has to be associated with the common geometry of complexes. Specifically, the first solvation shell bound to the metal center could consist of two DAA, with further ligands building external shell(s) that do not coordinate the metal directly. If this is true, the metal binding of internal two aldols is probably bidentate, involving both carbonyls and hydroxyl sites.

The dication mesityl oxide complexes resulting from dehydration mostly fragment further via the proton transfer analogous to that occurring for aldol complexes. We also observed a homolytic cleavage of mesityl oxide $(CH_3)_2C{=}CHCOCH_3$ at the double bond position, with metal attaching to either $(CH_3)_2C$ (except for Ba) or $CHCOCH_3$ (for Ba, Ca, Mg, Mn, Fe, and Co). In the case of Mg, both ligands in the complex can be cleaved, producing $Mg^{2+}(CHCOCH_3)_2$. Finally, in all cases except Cu, a number of singly-charged fragments with severed carbon–carbon bonds arise. These consist of M^+OH, M^+CH_3, M^+CH_3CO, and M^+CHCO residues, possibly ligated by acetone, DAA, or mesityl oxide. Species based on M^+CHCO appear for open-shell transition metals only (Mn, Fe, Co, Ni). A greater proficiency of those dications compared to main group ones in cleaving covalent bonds of coordinating ligands has been noted for DMSO complexes [23].

5. Conclusions

There are two key novel aspects to this contribution. One is the first comparison of metal polycations coordinated with protic ligands across charge states. This reveals a sizable gap between the intrinsic stabilities of doubly and triply charged species after adjusting for the difference in ionization energies, which has not been observed for aprotic solvents. The other is the finding of dehydration for bisligand and smaller precursors only, yielding mesityl oxide complexes. This suggests the complex geometry with two aldol molecules in the first solvation shell, perhaps in a bidentate arrangement involving both carbonyl and hydroxyl.

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