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DMSO Complexes of Trivalent Metal Ions: First Microsolvated Trications Outside of Group 3

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Abstract: The advent of electrospray ionization source opened the door to generation of multiply charged metal ions complexed with organic molecules. A significant amount of work on ligated dications has appeared over the past decade. In contrast, only several microsolvated tripositive ions have been reported, involving solely the few rare earths with the lowest third ionization energies (IEs) of all elements ($<$23 eV). Here trications of numerous trivalent metals outside of group 3 are shown to coordinate dimethyl sulfoxide (DMSO), an eminent aprotic solvent. These include both main group elements (Al, Ga, In, Bi) and transition metals (V, Fe, Cr) with the third IE up to 31 eV, which is 22 eV above the IE of DMSO. Fragmentation of $M^{3+}(DMSO)_n$ for these metals (plus La, Yb, and Sc) has been characterized in detail using collision-induced dissociation (CID). A rich, highly element specific dissociation chemistry is observed, including the homolytic C$-$S cleavage in (+3) charge state and various charge-reduction processes, such as dissociative electron and proton transfer and heterolytic S$=$O cleavage with and without a concomitant proton transfer. Characteristic sizes for the charge reduction in $M^{3+}(DMSO)_n$ and $M^{2+}(DMSO)_n$ have been measured as a function of the relevant elemental IE. These reveal no intrinsic gap between the stabilities of dication and trication complexes, once the IE is adjusted for. This, in particular, suggests that even microsolvated tetracations may exist.

I. Introduction

Ligated metal ions have been a front-line topic in gas-phase ion chemistry for several decades now. Motivations for this work include revealing the growth of solvation shells and long-range order in solutions,[1] elucidating the structural transitions in finite systems,[2] investigating the basic organometallic chemistry,[3] understanding the metal coordination in condensed-phase complexes[4] and biological molecules,[5] and developing the computational models of ion solvation using tractable microscopic objects.[6] More recently, differences between the fragmentation pathways of metalated and protonated organic molecules, including peptides, were found to be of analytical utility.[7−9] This research has mostly involved singly charged ions that are easily accessible by ligation of bare metal (M) cations in a molecular vapor. For multiply charged cations, this procedure generally results, instead of addition, in a charge reduction of the metal on contact with the neutral ligand.[10] This happens because the second ionization energies (IEs) of almost all metals are above 12 eV, while the first IEs of organic ligands typically range[11] between 8 and 12 eV. The situation for trications is yet worse, as the third IEs (IE3) of metals are all above 19 eV. However, microsolvated polycations are of special interest, in view of their connection to stable coordination compounds ubiquitous in inorganic and solid-state chemistry and metal ion hemes in biomolecules. Multiple charge and high IEs of metal polycations allow them to induce a plethora of reactions initiated by bond polarization and charge transfer, including some exotic high-energy processes. To accent this rich chemistry, the dissociation of dimethyl sulfoxide (DMSO) complexes of Ag^+ is exhibited in Figure 1: the only significant pathway is the trivial ligand evaporation down to bare metal. For monocations, this is typical for other metals and ligands.

The world of solvated metal polycations has been created by a new paradigm, in which these result not from the ligand adsorption on a bare cation, but by ligand elimination from large species. This happens in the electrospray ionization (ESI) source where ions in solution are lifted into the gas phase inside solvent microdroplets, which are then partly removed by heating.[11−13] Alternatively, one can generate a complex containing a metal in the charge state of (0) or (+1) and then raise it (e.g., by

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Table 1. Trication and Dication Products of the Dissociation of Triply Charged Metal−DMSO Complexes[a]

			tricationic fragments upon loss of		major dicationic product series,[e,f] M^{2+} coordinated with						
M	IE3, eV	n_{min}[b]	CH_3 only[c]	$CH_4 + CH_3$[d]	L_n(e);[g] L_{n-}H(p)	$L'L_n$	CH_3SL_n/CH_2SL_n[h]	OHL_n	$OHL'L_n$	OL_n	both[i]
La	19.2	2	2′, 3‴, 3″, 3′, 4′	a, b, c, d, e, g		0−4	1−3/1, 2	0−3			b, d
Sc	24.8	3	3″, 3′, 4′	d, e, g		1, 2	1−3/3	1−4	1, 2		
Yb[j]	25.1	3	3′, 4″, 4′	e, f	1−3(e)	0−3	2, 3/1, 2	1−3			
Bi	25.6	4			3, 4(p)		1−4	3−5			
In	28.0	4	4′	g	2−4(p)	3, 4	2, 3	3, 4			
Al	28.5	3	4″, 4′	f, g	2−5(p)	1−3	1−3	2, 3	1, 2		a, b, c
V[j]	29.3	5								3, 4	
Ga	30.7	4			2−4(p)	3, 4	2, 3	2, 3			b
Fe	30.7	4			2−5(e)	1, 2	3, 4	3, 4			
Cr	31.0	4			2−5(e)	2	3	4		2−4	

[a] Singly charged fragments are listed in the Supporting Information (Table 2S). [b] Minimum number n for which $M^{3+}(DMSO)_n$ were found among the fragmentation products. [c] Products of homolytic cleavage (1). The numeral indicates the precursor size n, the number of slanted primes equals that of sequential CH_3 eliminations. For example, 3″ stands for $M^{3+}(CH_3SO)_2(DMSO)$. No CH_3 loss was found for any metal complex with $n > 4$. [d] Products of rearrangement(s) (2) ejecting methane plus, possibly, one or more CH_3 losses (1): $M^{3+}CH_2SO(DMSO)$ (a), $M^{3+}(CH_2SO)_2CH_3SO$ (b); $M^{3+}CH_2SO(CH_3SO)_2$ (c); $M^{3+}CH_2SOCH_3SO(DMSO)$ (d); $M^{3+}CH_2SO(DMSO)_2$ (e); $M^{3+}CH_2SOCH_3SO(DMSO)_2$ (f); $M^{3+}CH_2SO(DMSO)_3$ (g). [e] In this table, L means the whole ligand (DMSO); L′ stands for CH_3SO. [f] Other products specific to few metals are the following: $M^{2+}OHCH_2SOL$ for La, Sc, and Al; $Yb^{2+}SO$, $Yb^{2+}CH_2SOCH_3SO$, and $Yb^{2+}(CH_3SO)_2$; $Al^{2+}OHCH_2SOCH_3SO$, $Al^{2+}OHCH_2SOL_2$, and $Al^{2+}OH(CH_3SO)_2L$; $Ga^{2+}CH_3SOCH_3SCH_2L$. [g] Products of electron transfer (3) marked (e) and proton transfer (4) marked (p). Critical sizes n_{crit} equal the largest of these values plus 1. [h] The route to these CH_3S-containing products is unclear, as discussed in the text. [i] Products containing both CH_3S and CH_3SO groups: $M^{2+}CH_3S(CH_3SO)_2$ (a), $M^{2+}CH_3SCH_3SOL$ (b), $M^{2+}CH_3SCH_3SOL_2$ (c), and $M^{2+}CH_3SCH_2SOL$ (d). [j] A low signal and/or unknown contamination has prevented the elucidation of all minor fragmentation channels for Yb^{3+} and V^{3+} complexes.

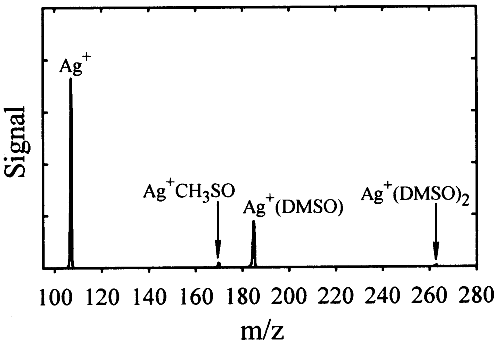

Figure 1. CID spectrum for $Ag^+(DMSO)_3$, $E = 60$ eV. Save for a trace of C−C cleavage in $Ag^+(DMSO)$, ligand evaporation to bare M^+ is the sole dissociation pathway.

laser or electron ionization). This is implemented in the "pickup"[3,4] and "charge-stripping"[14,15] techniques. Those methods have generated metal dications coordinated with various ligands,[16−29] including both protic (water and alcohols) and aprotic (aromatic hydrocarbons, ethers, ketones, sulfoxides, amides, and nitriles). Producing these species becomes more challenging as the second ionization energy (IE2) of the metal increases; still, most have been found for all M^{2+} ions up to[11,19,20,24] Cu^{2+}. (The IE2 of Cu is 20.3 eV, the highest for any dication stable in aqueous media.) In comparison, microsolvated M^{3+} ions have been reported for just one protic ligand—diacetone alcohol (4-hydroxy-4-methyl-2-pentanone)[30]—and four aprotic ones—dimethyl sulfoxide (DMSO),[13,25] dimethyl formamide (DMF),[13] acetone,[25,28] and acetonitrile.[25,28] For any of those, complexes were observed exclusively for lanthanoids and yttrium (La, Ce, Nd, Sm, and Y for DMSO). Group 3 metals have the lowest IE3 of all elements, varying from 19.2 eV for La to 25.1 eV for Yb. Notably, the values for La and Ce (20.2 eV) are below the IE2 of Cu. The IE3 of other trivalent elements, whether main group or transition metals, are substantially higher, usually above 28 eV (Table 1). Thus solvated gas-phase M^{3+} had been observed only for metals with IE3 < 23 eV. In particular, Co^{3+} could not be coordinated with DMSO.[13,31]

This paper reports the formation of DMSO complexes for a number of triply charged ions of the metals not belonging to group 3, including both transition metals (V, Cr, Fe) and those of the main group (Al, Ga, In, Bi). The IE3 of these elements range through 31 eV, i.e., 8 eV above those of group 3 for which $M^{3+}(DMSO)_n$ had already been encountered. As no complexes of such trications with any other solvent had been reported either, this constitutes the *first observation of microsolvated trications outside of group 3*.

The hallmark feature of ligated metal polycations is charge reduction, which engenders the minimum and critical sizes. As discussed above, the IE3 of a metal always exceeds the first IE of any ligand (L) by a huge margin. For DMSO (IE = 9.1 eV), the gap is over 10 eV even for La with the lowest IE3 of all nonactinoid elements, and reaches 22 eV for Cr. Hence all $M^{3+}L$ are thermodynamically unstable to separation into M^{2+} and L^+. On the other hand, many M^{3+} ions are stable in bulk solutions. Therefore, there may be a minimum size (n_{min}) at which a

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spontaneous charge reduction can still be resisted. This size may be one, as even $M^{3+}L$ may be trapped behind an energy barrier to electron transfer: $M^{3+}(CH_3CN)$ species have recently been found.[32] In the other extreme, macroscopic droplets evidently evaporate neutral ligands only. Thus there must be a critical size (n_{crit}) above which no dissociative electron or proton transfer occurs. In this contribution, the size range for the existence of novel $M^{3+}(DMSO)_n$ species is characterized by collisional fragmentation, with the n_{min} and n_{crit} values determined. Rich fragmentation chemistry of $M^{2+}(DMSO)_n$ has been characterized in detail.[33] Here the dissociation of DMSO-ligated trications, including the seven above and La^{3+}, Yb^{3+}, and Sc^{3+}, is extensively probed.

II. Experimental Protocol

Experiments were performed using a Finnigan TSQ 7000 MS/MS instrument with a heated capillary connecting the API source and vacuum region. The ESI needle voltage was ~4 kV. A moderate nebulizing gas pressure (~20 psi) was used; the auxiliary gas was switched off. $M^{3+}(DMSO)_n$ complexes were produced by spraying millimolar $M(NO_3)_3$ solutions in pure DMSO, at a flow of several microliters per minute. (Since no nitrate was available for V^{3+}, VCl_3 was substituted.) Previously, Blades et al.[13] used $M(NO_3)_3$ dissolved in methanol doped with DMSO. Good yields of $M^{3+}(DMSO)_n$ were obtained here for all metals tried. CID was performed using argon at the laboratory collision energy (E) of 6−360 eV and pressure $P = 1.5$ mTorr. This pressure corresponds to a multicollisional dissociation, necessary to induce a deep fragmentation of large precursor ions at reasonable energies. High energies needed to attain similar fragmentation upon a single collision substantially degrade the mass resolution and accuracy, which is of particular consequence for multiply charged ions. Keeping the heated capillary at 140 °C maximized the trication yield, but varying the temperature from 100 to 200 °C had no qualitative effect on the findings.

Dissociation of metal−DMSO cluster trications turned out to be intricate, yielding diverse triply, doubly, and singly charged fragments. To ensure the integrity of assignments, all MS/MS experiments were repeated with DMSO-d_6 and more than one metal isotope whenever possible. The vast number of observed products prohibit our presenting them all, and only major ones or those of specific significance are labeled in the figures and/or mentioned in the text. Tables 1 and 2S list all fragments identified.

III. Results

1. Source Mass Spectra. As had been noted widely, the total intensity of multiply charged ions maximizes under mild source conditions. This refers to a nominal potential drop (here ~5 V) in the lens region, which minimizes the collisional excitation of ions causing their dissociation accompanied by charge reduction. Under these circumstances, the envelope of trications comprised the species with 8−12 ligands, maximizing at $n = 10-11$ (an example in Figure 2). Unlike $M^{2+}(DMSO)_n$ exhibiting sharp distribution maxima at $n = 5$ or 6 depending on the metal,[33] no pronounced "magic numbers" were found for any $M^{3+}(DMSO)_n$. Similarly, acetonitrile complexes[32] feature extraordinary "magic numbers" at $n = 5$ or 6 for dications, but relatively broad distributions including $n = 7-11$ for trications. In addition to $M^{3+}(DMSO)_n$, the usual $M^{2+}XL_n$, $M^{+}X_2L_n$, and hydrolysis products $M^{2+}OHL_n$ and $M^{+}OHXL_n$ (where X is the monovalent counteranion of the original salt) were observed, depending on the metal.

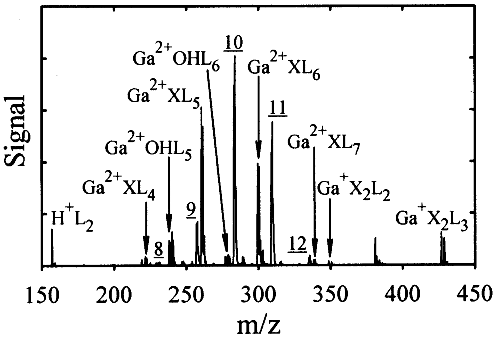

Figure 2. Q1 ESI/MS spectrum of $Ga^{3+}(NO_3)_3$ solution in anhydrous DMSO. Symbols X and L stand for the NO_3^- counteranion and DMSO ligand, respectively. Peaks labeled by underlined numbers $\underline{n}$ are $M^{3+}(DMSO)_n$.

2. Principal Features of $M^{3+}(DMSO)_n$ Fragmentation: The La Complexes Example. The lowest IE3 of all stable elements renders La a starting point for investigations of ligated metal trications. The dissociation of $La^{3+}(DMSO)_n$ (for $n = 6$) was probed,[13] but only the DMSO evaporation down to $n = 3$ was found. This clearly was because of low collision energy that could cause desolvation only to $La^{3+}(DMSO)_3$: this was reproduced here. At higher energies inducing further desolvation, other products appear in large yields as presented in Figure 3A,B.

Perhaps of greatest interest is the homolytic cleavage of C−S bonds in DMSO:

$$M^{3+}(DMSO)_n = M^{3+}[(DMSO)_n - mCH_3] + mCH_3 \quad (1)$$

This process was ubiquitous[33] in the dissociation of DMSO complexes of all common metal dications except Cu^{2+}. There it occurred in precursors with $n = 1-4$, though not each for every metal. The greatest number of sequential CH_3 losses was one for $n = 4$, two for $n = 3$, three for $n = 2$, and one for $n = 1$. Here for $La^{3+}(DMSO)_n$, process (1) is likewise registered for $n \leq 4$ only:[34] one step for $n = 4$, three for $n = 3$, and one for $n = 2$. An abrupt onset and prominence of channel (1) for $n = 4$ (Figure 3A) are of note. In comparison, the intensity of homolytic cleavage for $M^{2+}(DMSO)_n$ was at best minor[33] for $n = 4$, and increased gradually for $n = 3$ and 2. A related process found for $M^{2+}(DMSO)_n$ with $n = 1$ and 2 was the elimination of methane, possibly in sequence with CH_3 losses. This rearrangement is now observed for La^{3+} complexes, here for precursors with up to four ligands:

$$M^{3+}(DMSO)_n = M^{3+}[(DMSO)_n - CH_4] + CH_4 \quad (2)$$

Similarly, this reaction occurs either alone or in conjunction with (1). Products of two sequential rearrangements (2) were also observed (Table 1).

Other dissociation pathways of $M^{3+}(DMSO)_n$ reduce the triple charge. The generic charge-reduction modes in ligated polycations are the electron transfer (3) and, for hydrogen-containing

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[34] Present data do not reveal whether two methyls from the same ligand may be eliminated.

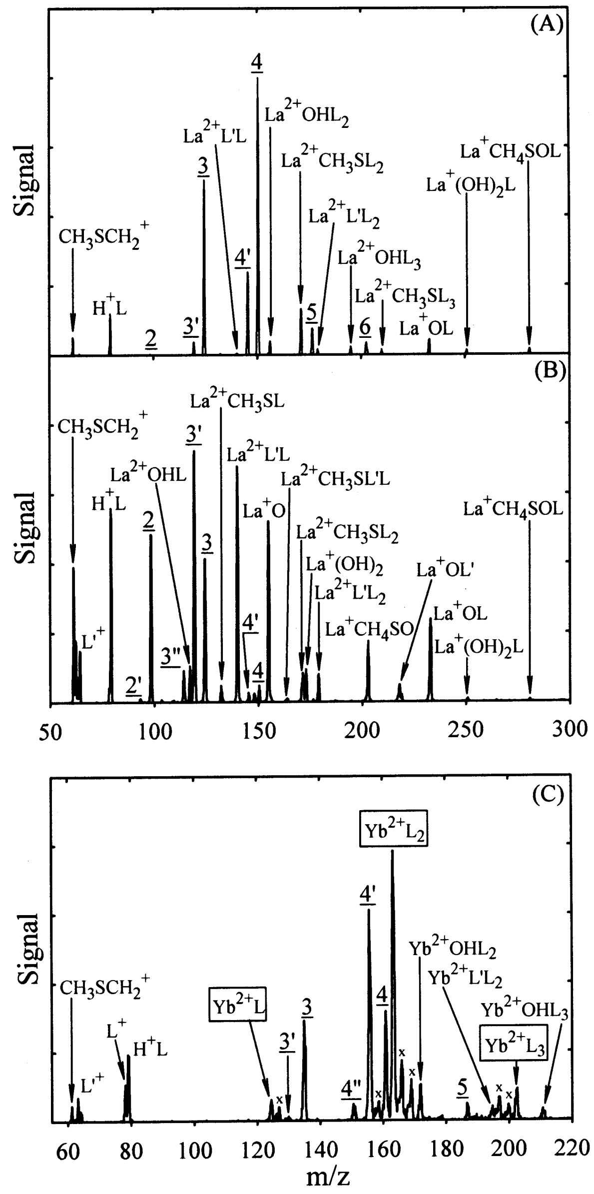

Figure 3. CID spectral windows for $M^{3+}(DMSO)_{10}$: ^{139}La at lower (A, 90 eV) and higher (B, 180 eV) collision energies, and ^{171}Yb (C, $E = 120$ eV). Peaks labeled by numbers $\underline{n}$ are $M^{3+}(DMSO)_n$. Features marked by slanted primes are products of the number of steps of homolytic cleavage (1) given by the number of slanted primes, e.g., $3'' = La^{3+}(DMSO)_3 - 2CH_3 = La^{3+}(CH_3SO)_2(DMSO)$. Tripositive ions are underlined; L stands for the DMSO ligand and L′ stands for for CH_3SO. Products of dissociative electron or proton transfer (both singly and doubly charged) are inside boxes; "x" marks unassigned features for Yb^{3+} complexes deriving from an unknown interference at the precursor mass.

ligands, proton transfer (4):

$$M^{z+}L_n = M^{(z-1)+}L_{n-1} + L^+ \quad (3)$$

$$M^{z+}L_n = M^{(z-1)+}(L-H)L_{n-2} + H^+L \quad (4)$$

Both reactions were common[33] in the breakdown of $M^{2+}(DMSO)_n$ with $n = 1-3$. However, neither (3) nor (4) occurs for La^{3+} complexes of any size. When a ligated polycation fails to exhibit either electron or proton transfer, these processes must be uncompetitive with either desolvation to bare metal ion or intraligand cleavages. The case here is of the second kind: the minimum size observed is $n = 2$.

Dicationic fragments belong to several types. The first encompasses $M^{2+}CH_3SO(DMSO)_n$, $n = 0-4$. Equivalent monocations with $n = 0$, 1 were produced for many $M^{2+}(DMSO)_n$ precursors.[33] Here they appear over a larger range of sizes and in a greater yield, dominating the CID spectrum at some energies. These products might result from a heterolytic C−S cleavage:

$$M^{3+}(DMSO)_n = M^{2+}CH_3SO(DMSO)_{n-1} + CH_3^+ \quad (5)$$

Since, unlike (1), this reaction does not conserve the ionic charge, only one step is possible. However, a minute yield of CH_3^+ at the relevant energies indicates a different major pathway: the electron transfer in products of the cleavage (1).

$$M^{3+}CH_3SO(DMSO)_n = M^{2+}CH_3SO(DMSO)_{n-1} + DMSO^+ \quad (6)$$

This tracks the behavior of dications.[33] Still, reaction 5 must operate, at least to generate $M^{2+}CH_3SO(DMSO)_n$ with $n = 3$ and 4, for which no precursors along scheme (6) are found. No dication analogues of the products of rearrangement (2) were observed.

For several $M^{2+}(DMSO)_n$ species, traces of $M^+CH_3S(DMSO)_n$ and/or $M^+CH_2S(DMSO)_n$ ($n = 0,1$) were identified.[33] Here, $La^{2+}CH_3S(DMSO)_n$ ($n = 1-3$) and, at higher energies, $La^{2+}CH_2S(DMSO)_n$ ($n = 1$, 2) appear in high yield (Figure 3A,B). While these assignments are validated by deuterium labeling, the underlying chemistry remains obscure as the complementary products at $CH_3O^+(DMSO)_n$ masses are missing. There also are fragments, e.g., $La^{2+}CH_3SCH_3SO(DMSO)$, that belong to both types described.

The third cleavage type found for $n \leq 4$ involves a rupture of the S=O bond in DMSO and concomitant proton transfer from a methyl group to oxygen:

$$M^{3+}(DMSO)_n = M^{2+}OH(DMSO)_{n-1} + CH_3SCH_2^+ \quad (7)$$

These products further desolvate to $La^{2+}OH$, an exceptionally stable ion.[35] Process 7 may start from the DMSO "enol" form, $CH_3S(OH)CH_2$, transferring the hydroxyl to metal. An equivalent reaction was observed[33] for some $M^{2+}(DMSO)_n$ ($n = 1-3$). Charge-reduced hydroxides normally arise in the dissociation of ligated metal polycations hydrated in the collision cell by adventitious water. However, this produces complementary $H^+(DMSO)$, not $CH_3SCH_2^+$. Hydroxylated M^{2+} in $M^{2+}OH(DMSO)_n$ can still sever a C−S bond in DMSO, e.g., $La^{2+}OHCH_2SO(DMSO)$ is apparently derived from $La^{2+}OH(DMSO)_2$ via a CH_4 loss analogous to (2).

At higher collision energies, all dications described above charge reduce further. Concisely, several series of products were found. First are $La^+CH_3SO(DMSO)_n$ and $La^+CH_4SO(DMSO)_n$. The former may arise when $La^{2+}CH_3SO(DMSO)_{n+1}$ eliminates[33] $DMSO^+$ or $La^{2+}CH_3S(DMSO)_{n+1}$ loses $(CH_3)_2S^+$. The latter apparently come from $La^{2+}CH_3S(DMSO)_{n+1}$ losing $CH_3SCH_2^+$. The species in the second group (not observed in the dissociation of $M^{2+}(DMSO)_n$) contain two hydroxyls, evidently

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by consecutive operation of reaction 7:

$$M^{2+}OH(DMSO)_n = M^{+}(OH)_2(DMSO)_{n-1} + CH_3SCH_2^{+} \qquad (8)$$

These ions dehydrate to $La^{+}O(DMSO)_{n-1}$, but those must also arise from $La^{2+}OH(DMSO)_n$ directly via the proton transfer, else a strong $H^{+}(DMSO)$ feature is hard to explain. The third group includes ions containing $La^{+}O$ and cleaved DMSO, such as $La^{+}OCH_3SO(DMSO)_n$ and $La^{+}OCH_4SO(DMSO)_n$. The former may originate via homolytic C−S cleavages in $La^{+}O(DMSO)_{n+1}$ or $(CH_3)_2S^{+}$ loss from $La^{2+}CH_3SO(DMSO)_{n+1}$. Losses of CH_3^{+} from $La^{2+}OH(DMSO)_{n+1}$ or of $CH_3SCH_2^{+}$ from $La^{2+}CH_3SO(DMSO)_{n+1}$ are two plausible routes to $La^{+}OCH_4SO(DMSO)_n$. The first is more likely: breakdown of DMSO-coordinated M^{2+} never yielded $M^{+}OCH_4SO(DMSO)_n$, while $M^{2+}CH_3SO(DMSO)_n$ intermediates were abundant.[33]

3. Scandium and Ytterbium: Group 3 Metals with High Third IE. Whereas the IE3 of La (19.2 eV) is about the lowest for group 3 elements, those of Sc (24.8 eV) and Yb (25.1 eV) are nearly the highest. Considering the importance of metal IE to the properties of ligated polycations, it is instructive to look at the complexes of metals with similar valence electrons but different IEs. Dissociation of $Sc^{3+}(DMSO)_n$ (Figure 8S, part A) broadly resembles that of $La^{3+}(DMSO)_n$. One slight difference is n_{min} increasing from 2 to 3; hence the products of cleavage (1) are limited to those derived from $Sc^{3+}(DMSO)_n$ ($n = 3, 4$). The lower limits of triple-charge stability naturally shift up as the IE3 increases. Likewise, the largest precursor in reaction 7 has $n = 5$ for Sc ($n = 4$ for La). A new class of fragments not found in the La case are $M^{2+}OHCH_3SO(DMSO)_n$, $n = 1, 2$. They must result from a homolytic C−S cleavage analogous to (1):

$$M^{2+}OH(DMSO)_{n+1} = M^{2+}OHCH_3SO(DMSO)_n + CH_3 \qquad (9)$$

Singly charged derivatives of $Sc^{3+}(DMSO)_n$ mostly track those of $La^{3+}(DMSO)_n$, though more extensively cleaved products such as $Sc^{+}CH_3SCH_3SO$ and $Sc^{+}OH(CH_3SO)_2$ surface. There also are fragments of $M^{+}(OH)_2CH_2SO$ and $M^{+}(OH)_2CH_3SO$ stoichiometry. While these may derive by CH_4 and CH_3 losses from $Sc^{+}(OH)_2(DMSO)$, their absence for La hints at their origin from an S=O cleavage analogous to (8) in $M^{2+}OHCH_3SO(DMSO)$, an intermediate missing for La.

Despite essentially identical IE3 of Sc and Yb, Sc^{3+} and Yb^{3+} complexes dissociate differently: unlike those of La^{3+} and Sc^{3+}, Yb^{3+} complexes readily reduce via electron transfer (3), Figure 3C. This happens for $n \le 4$ ($n_{min} = 3$ for both Yb and Sc). The increase of IE3 by 6 eV from La to Yb should favor the electron transfer; what is remarkable is that this does not happen for Sc. Physically, Sc^{3+} is much smaller than La^{3+}, which should facilitate ligand cleavages by metal insertion. (DMSO complexes of Be^{2+}, the smallest M^{2+}, exhibit various cleavages but neither electron nor proton transfer.[33]) Then, changing from La to Sc, a larger IE3 promoting electron transfer and smaller radius enhancing cleavages may balance such that the overall fragmentation pattern is affected little. A commensurate increase of IE3 from La to Yb with no reduction of ionic radius would favor electron transfer at the expense of cleavages, as observed. Other fragmentation pathways of Yb^{3+} complexes broadly follow those for Sc^{3+} and La^{3+} ones. Unlike in the Sc case, hydroxide-based dications are encountered only with a whole DMSO. This fits into the picture of large ionic radius discouraging cleavages. Two sequential cleavages (1) in $Yb^{3+}(DMSO)_4$ are notable: only one was previously registered for any tetraligand di- or trication. Though $Yb^{2+}(DMSO)_n$ species are abundant, no $Yb^{+}(DMSO)_n$ species are found for any $n > 0$: charge reduction to (+1) proceeds by cleavages instead. This is caused by a low IE2 of Yb (12.2 eV): $M^{2+}(DMSO)_n$ exhibited neither electron nor proton transfer[33] when the IE2 of M was 12 eV or less.

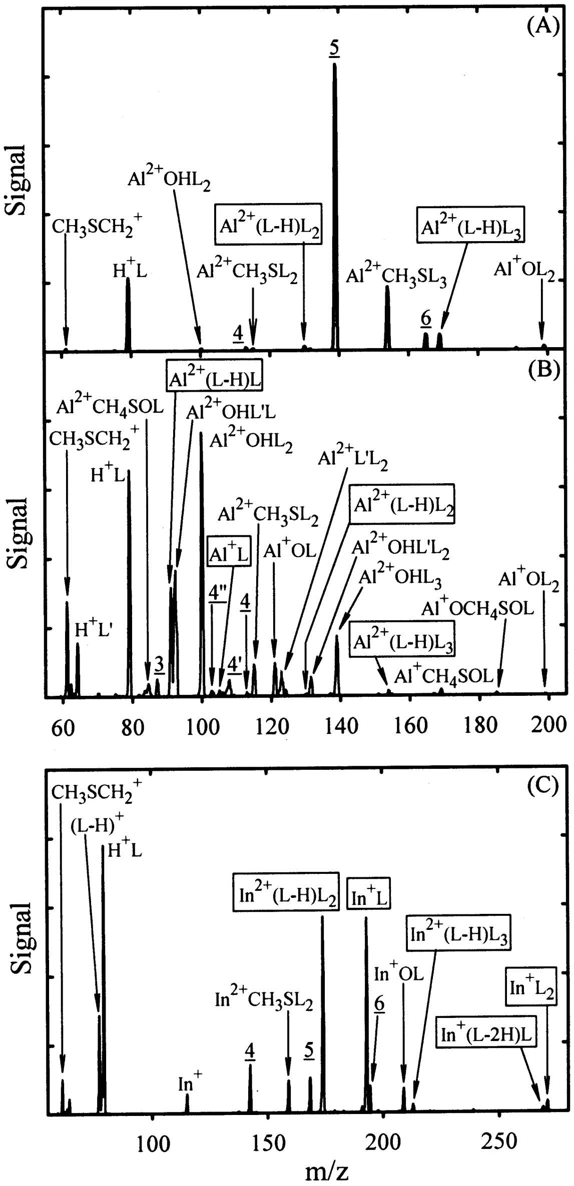

Figure 4. CID spectral windows for $Al^{3+}(DMSO)_{10}$ at $E = 60$ eV (A) and 150 eV (B), and for $^{115}In^{3+}(DMSO)_{10}$ (C, $E = 90$ eV). Notation is as in Figure 3.

4. Group 13 Elements. The IE3 of these metals (Al, Ga, In) exceed even the maximum values for group 3 by 3−5 eV. Accordingly, small trications become less stable. For Al, though $n_{min} = 3$, the extent of cleavage (1) dwindles sharply (Figure 4A,B). This process is now limited to two steps for $n = 4$, and there is no CH_3 loss for $n = 3$. The extent of CH_4 losses (2) decreases proportionately. In a behavior opposite to that of Yb^{3+} complexes, $Al^{3+}(DMSO)_n$ species exhibit proton transfer only rather than electron transfer ($n_{\text{crit}} = 5$). Of all M^{3+} ions investigated here, Al^{3+} has by far the smallest radius. Not surprising, then, Al complexes exhibit an exceptional variety of cleavage products. For dicationic fragments, all the series introduced so far are showing together (Table 1). This includes those based on $M^{2+}OH$, $M^{2+}OHCH_2SO$ and $M^{2+}OHCH_3SO$, $M^{2+}CH_2SO$ and $M^{2+}CH_3SO$, $M^{2+}CH_3S$, and juxtapositions of the last two such as $M^{2+}CH_3SCH_3SO$. There are a few products of more than two cleavages, e.g., $Al^{2+}CH_3S(CH_3SO)_2$. For singly charged products, of novelty is the appearance of Al^+(DMSO), no doubt because of the elemental IE2 increasing to 18.8 eV. No $Al^+(DMSO)_2$ is registered, but this does not signify $n_{\text{crit}} = 2$ for $Al^{2+}(DMSO)_n$: these intermediates were not observed, so Al^+(DMSO) must originate elsewhere. Other monocation fragments are in line with those found for La and Sc cases.

Small trications become yet less stable for In and Ga: $n_{\min}$ increases to 4, while cleavage (1) fades away to one step for $In^{3+}(DMSO)_4$ and none at all for Ga^{3+} complexes (Figures 8S, part B, and 4C). Complexes of Ga^{3+} should be less stable than Al^{3+} ones based on a higher IE3 of Ga; the cause for In^{3+} complexes is unclear as IE3 (In) < IE3 (Al). The number of cleavage products (either di- or monocations) for Ga and In cases is significantly less than that for Al case, and there are essentially no multiple cleavages. In particular, products based on $M^{2+}OH$ and M^+O are associated with DMSO only, not its fragments. There are almost no fragments based on $M^{2+}CH_2SO$ or $M^{2+}CH_3SO$, both common for Al. This likely is due to the low abundance or lack of $M^{3+}CH_3SO(DMSO)_n$ precursors in electron transfer (6), which supports the contention that $M^{2+}CH_3SO(DMSO)_n$ result mostly from this process rather than heterolytic cleavage (5).[36]

For both Ga and In, singly charged fragments include $M^+(DMSO)_2$ absent for Al. A new development is the emergence of $M^+(DMSO-2H)(DMSO)_n$ ($n = 0-2$) ions, likely generated by a second proton transfer in the products of (4):

$$M^{2+}(L-H)L_{n+1} = M^+(L-2H)L_n + H^+L \qquad (10)$$

(Note that $M^{2+}(L-H)L_{n+1}$ precursors were observed for $n \leq 2$.) An analogous sequence was encountered[32] for $M^{3+}(CH_3CN)_n$. However, no $M^+(DMSO-H)(DMSO)_n$ stoichiometry was observed for either Ga or In. This is because no $M^{2+}(DMSO)_n$ fragments are available (the original trications do not dissociate by electron transfer), and $M^{2+}(DMSO-H)(DMSO)_n$ products do not exhibit that either. To yield $M^+(DMSO)_n$, they must lose $(DMSO-H)^+$, which is prominent (Figure 4C,D).

5. Bismuth. Bi belongs to group 15, but its typical oxidation state is (+3). Bi^{3+} complexes fragment differently from the systems reviewed above, offering a few puzzles (Figure 5). First, $n_{\min} = 4$ and $Bi^{3+}(DMSO)_4$ exhibits no cleavage (1). This copies the situation for Ga^{3+} complexes but the IE3 of Bi is ~5 eV lower, so the instability of small ligated Bi^{3+} is abnormal. Second, the intensities of both proton transfer (4) and "enol" cleavage (7) are negligible. Since ligated $Bi^{2+}OH$ species appear but as traces, their $Bi^{2+}OHCH_3SO(DMSO)_{n-1}$ derivatives (9) are missing. There likewise are no fragments with $Bi^{2+}CH_3SO$ nucleus, in view of absent $Bi^{3+}CH_3SO(DMSO)_n$. Instead of all these, $Bi^{2+}CH_3S(DMSO)_n$ ($n = 1-4$) species arise in huge abundance (Figure 5). While the assignment is established by isotopic labeling, the lack of complementary fragments perplexes. At higher energies, these dications further charge reduce by electron transfer yielding $\{Bi^+CH_3S(DMSO)_{n-1}; DMSO^+\}$ pairs ($n = 1, 2$). The $Bi^+(DMSO)_n$ ($n = 1, 2$) fragments might derive from $Bi^{2+}CH_3S(DMSO)_n$ losing CH_3S^+ (this ion is present). Monoxides with one or two DMSO also appear in high yield.

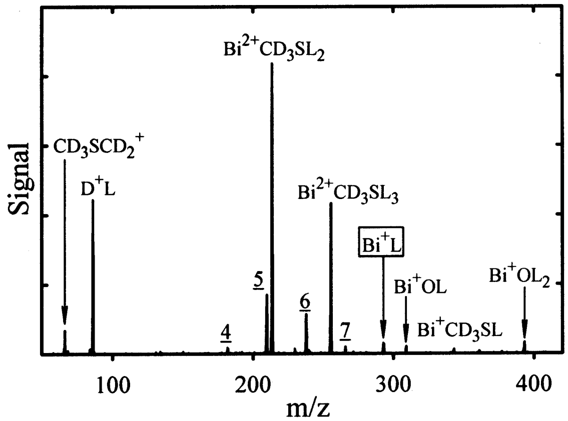

Figure 5. CID spectral window for $Bi^{3+}(DMSO\text{-}d_6)_{10}$, $E = 60$ eV. Notation follows that in Figure 3.

6. First-Row Transition Metals. Of these (except Sc already discussed), the normally trivalent elements are Fe, Cr, and V. Their IE3 are high (29−31 eV), that of Cr being the highest of all metals probed here. The IE3 of Fe (30.7 eV) equals that of Ga, and the dissociation patterns of their complexes are broadly similar. In particular, $n_{\min} = 4$ in both cases. The major distinction is that $Fe^{3+}(DMSO)_n$ species undergo electron transfer only rather than proton transfer (Figure 6A,B). Since no dications containing (DMSO−H) appear, no $M^+(DMSO-2H)$-based species found for Ga result. However, in addition to $Fe^+(DMSO)_n$, $Fe^+(DMSO-H)(DMSO)_{n-1}$ species are observed for $n = 1, 2$. These were not encountered among the dissociation products of $Fe^{2+}(DMSO)_n$ produced by ESI of Fe(II) salt solutions: only electron transfer yielding Fe^+(DMSO) was observed.[33] The structures of $Fe^{2+}(DMSO)_n$ generated by ESI and obtained from $Fe^{3+}(DMSO)_n$ may differ, which could engender divergent dissociation pathways. Alternatively, here $Fe^+(DMSO-H)$-based fragments might originate from other precursors, e.g., $Fe^{2+}CH_3S(DMSO)_n$ losing CH_4S^+ (found among the products). Numerous other monocations (Table 2S) mimic the set observed in the dissociation of Fe^{2+} complexes.

The main novelty for Cr^{3+} complexes is the emergence of $M^{2+}O(DMSO)_n$ ($n = 2-4$) oxide products instead of $M^{2+}OH(DMSO)_n$ hydroxides (Figure 6C). Considering the prominence of $(CH_3)_2S^+$ fragment, this most likely results from a heterolytic S═O cleavage:

$$M^{3+}(DMSO)_n = M^{2+}O(DMSO)_{n-1} + (CH_3)_2S^+ \qquad (11)$$

This reaction resembles the "enol cleavage" (7), except that the S═O bond is severed in the "keto" tautomer of DMSO. No Cr^{2+} complexes have been prepared using ESI. Here, downstream fragmentation of $Cr^{2+}(DMSO)_n$ ($n = 2-5$) resulting from

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[36] However, observation of $Ga^{2+}CH_3SO(DMSO)_n$ ($n = 3, 4$) traces in the absence of tricationic products of homolytic cleavage (1) does not prove that heterolytic cleavage (5) is open even as a minor channel. Products of (1) might simply be unstable enough to immediately dissociate via the electron transfer (6).

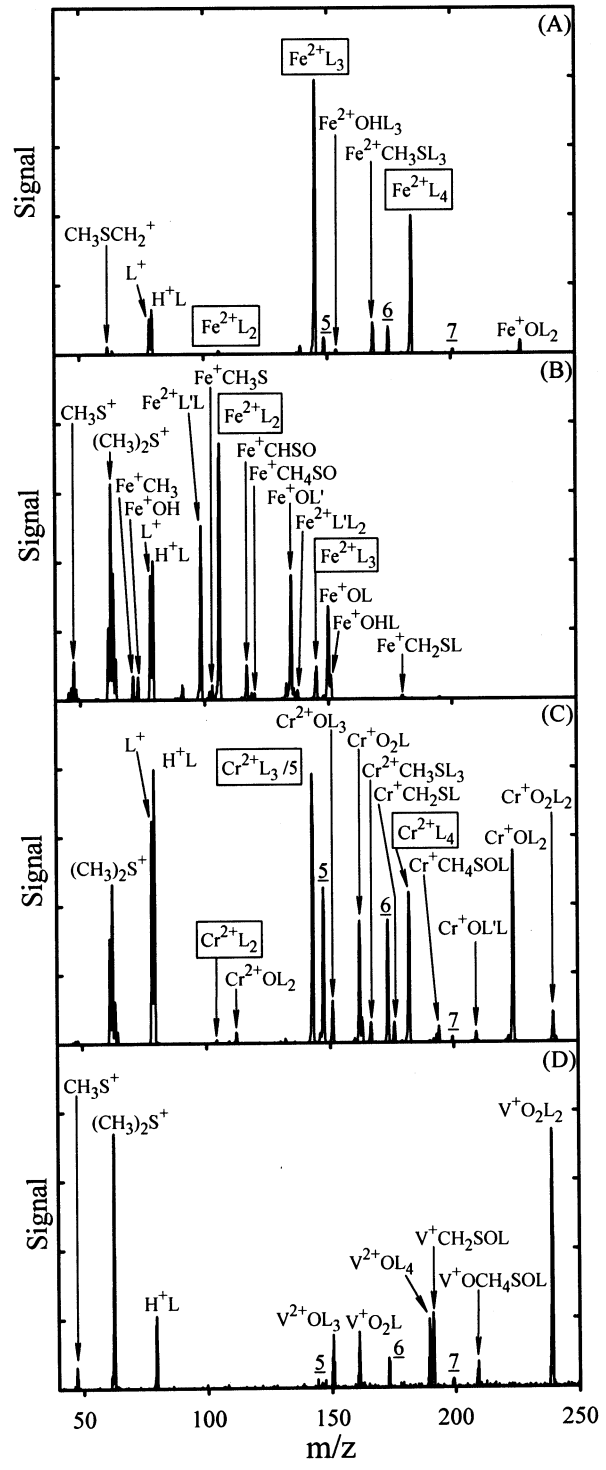

Figure 6. CID spectral windows for $M^{3+}(DMSO)_{11}$: ^{56}Fe at $E = 60$ eV (A) and 180 eV (B), ^{52}Cr (C, $E = 90$ eV), and ^{51}V (D, $E = 90$ eV). The $Cr^{2+}(DMSO)_3$ peak in (C) is scaled by a factor of 1/5. Notation is as in Figure 3.

electron transfer (3) in $Cr^{3+}(DMSO)_{n+1}$ allows a glimpse into the relevant chemistry. The presence of $Cr^+(DMSO)_m$ for $m = 1$ only and the absence of $Cr^+(DMSO{-}H)(DMSO)_m$ at any size indicate that $Cr^{2+}(DMSO)_n$ species charge reduce by electron rather than proton transfer, and the associated $n_{\min}$ and n_{crit} for Cr(II) equal 2. These values are just right[33] for a metal with an IE2 of 16.5 eV (Table 2S). This demonstrates that, for ligated polycations that have not been generated by ESI because the metal assumes a higher oxidation state in solution, characteristic sizes can sometimes still be measured by sequentially reducing a complex of that higher charge state. For monocations, there are the new dioxide fragments $M^+O_2(DMSO)_n$ ($n = 0{-}2$) not found in the Fe case. They emerge together with the oxide dications (11), and probably arise from the recurrence of same process:

$$M^{2+}O(DMSO)_{n-1} = M^+O_2(DMSO)_{n-2} + (CH_3)_2S^+ \quad (12)$$

At higher energies, these become prevailing products.

The tendency for oxide formation in di- and monocations that emerged for Cr reaches a maximum in the V case. In fact, $V^{2+}O(DMSO)_n$ ($n = 3, 4$) species are the only dications found starting from $V^{3+}(DMSO)_n$ (Figure 6D), as neither electron or proton transfer nor other cleavages take place. A huge yield of complementary $(CH_3)_2S^+$ ion fits this picture. For singly charged products, in addition to dioxides (12) with $n = 0{-}2$, usual $V^+O(DMSO)_n$ ($n = 0, 1$) species are observed at high CID energies. However, lack of $DMSO^+$ suggests that these arise not from an electron transfer in $V^{2+}O(DMSO)_n$. Considering the absence of precursors based on $M^{2+}OH$ and $M^+(OH)_2$ and the high appearance energy for (+1) monoxides, they probably derive from (+1) dioxides losing oxygen. Dioxides attached to DMSO fragments, such as $V^+O_2CH_3SO$, appear as well.

IV. Overview of Dissociation Chemistry and Comparison with Dications

1. Electron and Proton Transfer. As had been noted, the relevant IE is the major factor governing the fragmentation of ligated metal polycations. The minimum sizes for $M^{3+}(DMSO)_n$ shift from 2 for La (IE3 ~ 19 eV, about the lowest for any element) to 4 for metals with the highest IE3 in the 29−31 eV range. The critical sizes, i.e., the largest $M^{3+}(DMSO)_n$ species for which a dissociative electron (3) or proton (4) transfer proceeds, also increase from 4 for Yb (IE3 ~ 25 eV) to 5−6 for the elements at the top of IE3 range. Which (if any) of these two processes occurs depends on the metal, not on the precursor size or collision energy. Complexes of transition metals (Yb, Fe, Cr) and main group ones (Al, In, Ga, Bi) exhibit respectively electron and proton transfer. Microsolvated La and Sc undergo neither (3) nor (4): presumably relatively low IE3 of these elements render both processes incompetitive with ligand cleavages. It is instructive to compare the dissociation of ligated polycations across charge states: (+3) here and (+2) studied previously.[33] Similarly to the cases of La(III) and Sc(III), DMSO complexes of the divalent metal with lowest IE2 (Ba) exhibited neither electron nor proton transfer. However, the behavior of dications in terms of preference for either process differed: this was a function of the precursor size, with $M^{2+}(DMSO)_2$ undergoing an electron transfer only and $M^{2+}(DMSO)_3$ experiencing electron and/or proton transfer depending on the metal. The preference for either process was not correlated with the division between main group and transition metals.

Do the stabilities of ligated dications and trications intrinsically differ beyond the factor of metal IP? This question is prompted by the fact that all divalent metals including Cu form dication complexes with water and all alcohols tried, but no trication (except diacetone alcohol, a special case[30]) is known to do that, although the IE3 of some metals (e.g., 19.2 eV for La) are below the IE2 of Cu = 20.3 eV. To begin understanding

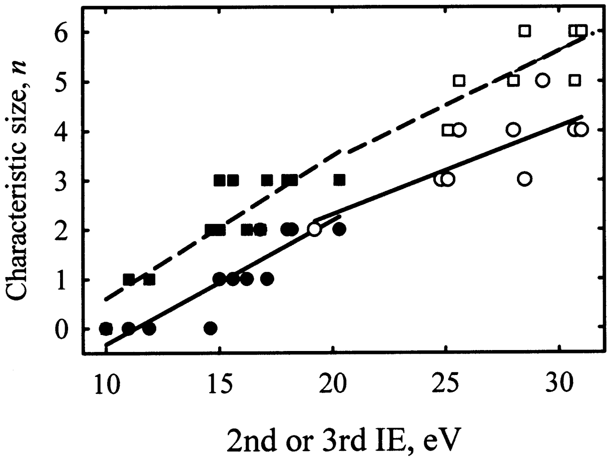

Figure 7. Characteristic sizes for DMSO complexes of metal dications[33] (filled symbols) and trications (empty symbols). Circles and squares stand respectively for minimum and critical sizes. Lines are first-order regressions through the data for each charge state: solid for minimum sizes and dashed for critical sizes.

this, one needs to compare the stabilities of solvated M^{2+} and M^{3+}. Characteristic sizes for $M^{2+}(DMSO)_n$ and $M^{3+}(DMSO)_n$ are plotted in Figure 7. Separate linear regressions through the data for (+2) and (+3) charge states essentially overlap, for both n_{min} and n_{crit}. This shows no gap in the stability of DMSO complexes for M^{2+} and M^{3+}, once the difference in IEs is adjusted for.

This conclusion opens a possibility that even metal tetracations may be microsolvated. None was reported with any ligand besides He;[14] however fourth IE of some commonly tetravalent heavy elements are lower than IE3 of metals presently found to coordinate DMSO. For example, the fourth IE of Th is 28.8 eV, i.e., below the IE3 for V, Fe, Ga, and Cr. If the intrinsic stability of DMSO complexes does not drop between (+3) and (+4) charge states as it does not between (+2) and (+3), some $M^{4+}(DMSO)_n$ species should exist and might be accessible via ESI.

2. Charge-Conserving Cleavages. In addition to electron and proton transfer, DMSO complexes of M^{3+} exhibit cleavages. For metals with IE3 of ~28 eV or less (except Bi), complexes with two to four ligands, depending on the metal, homolytically sever the C−S bonds in DMSO losing up to three CH_3 radicals. This process is shut for the complexes of metals with higher IE (for which $n_{min} = 4$), likely because the ensuing products smaller than $M^{3+}(DMSO)_4$ are unstable to charge reduction. Methyl losses are mirrored by those of methane. This chemistry resembles that of dications,[33] including an increasing yield of rearrangement (2) relative to that of cleavage (1) at each reaction step (an effect of statistical nature) and the absence of these reactions for complexes of metals at the top of IE range. It is remarkable that these cleavages conserve the triple charge of the cation. This means that surmounting an activation barrier to sever a covalent bond can compete with all charge reduction channels, despite enormous disparities between the IE3 of metals involved and the IE of DMSO. The largest size permitting CH_3 or CH_4 elimination for either dications or trications is four. This independence of the charge state and IE suggests the control of this value by common geometry of complexes, possibly involving tetracoordination in the first solvation shell. (Assuming that a cleavage is initiated by proximate activation of ligand bonds by the metal, molecules in outer solvation shells cannot be cleaved, although they may exhibit proton or electron transfer through interactions with inner-shell ligands.) For dications, the products of CH_3 loss only were always more intense than their analogues involving CH_4 loss(es).[33] This is not necessarily the case for M^{3+} complexes.[37]

3. Charge-Reducing Cleavages. There is a much greater diversity of charge-reduced cleavage fragments. The first group comprises dication analogues of the products of CH_3 and CH_4 losses. These ions with a severed C−S bond, consisting of $M^{2+}CH_3SO$ or $M^{2+}CH_2SO$ and zero to four DMSO, are generic to the decay of $M^{3+}(DMSO)_n$: they show up for all cases except Bi and V where another cleavage dominates, but are not selective for any metal. They may arise both from $M^{3+}CH_3SO$ ($M^{3+}CH_2SO$) based species losing $DMSO^+$ or $H^+(DMSO)$ and from homolytic C−S cleavage in $M^{2+}(DMSO)_n$, depending on the availability of these intermediates. Analogous products containing M^+CH_3SO or M^+CH_2SO were ubiquitous for $M^{2+}(DMSO)_n$ precursors.[33]

The second group of $M^{3+}(DMSO)_n$ products encompasses $M^{2+}CH_2S$ and $M^{2+}CH_3S$ solvated by zero to four DMSO; i.e., both C−S and S=O bonds are cut. These are also common for all metals except V, but are extraordinary for Bi with a close to 100% yield. The origin of these species is bewildering, as the complementary ion at CH_3O^+ mass is never observed. Also, if these are produced via a metal-induced cleavage of S=O in DMSO, why should a C−S bond always be cut as well? That is, one would also expect fragments of $M^{2+}(CH_3)_2S$ stoichiometry. The hypothesis of oxygen elimination from $M^{3+}CH_3SO$- or $M^{2+}CH_3SO$-based intermediates would address that difficulty, however, explaining this precursor specificity would be a challenge, and $M^{2+}CH_3S(DMSO)_n$ species appear in huge yields even for the metals where neither was found (e.g., Bi). Like fragments containing M^+CH_2S or M^+CH_3SO have emerged[33] in the dissociation of $M^{2+}(DMSO)_n$, mostly for transition metals. For trications, this channel does not appear more prominent for transition metals in general.

The third group of dipositive fragments are metal hydroxides associated with zero to four DMSO. These are encountered for complexes of all trications except V^{3+}, although for Bi and Cr cases in trace amounts. The underlying chemistry is straightforward, with the complementary $CH_3SCH_2^+$ fragment prominent. For small trications, Sc^{3+} and Al^{3+}, these ligated hydroxides undergo a homolytic C−S cleavage yielding $M^{2+}OHCH_3SO(DMSO)_n$, $n = 1, 2$. Cleavage pathways seem to be favored for cations with smaller radii. Instead of dication hydroxides, Cr^{3+} and V^{3+} complexes yield oxides coordinated with two to four DMSO plus complementary $(CH_3)_2S^+$. In the V case, this is the sole mode of fragmentation. Dwelling on this, one may recall dimethyl sulfoxide reductases, enzymes catalyzing a variety of redox reactions coupled to oxygen transfer.[38,39] These enzymes reduce DMSO to $(CH_3)_2S$ by oxidizing the Mo atom in the active site. While Mo complexes with DMSO were not investigated, Cr and V are the two chemically closest elements to Mo that were. Thus, it is noteworthy that, of all metal trications studied, only these can abstract the DMSO oxygen. Monocation fragments comprised

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(37) For example, $La^{3+}CH_2SOCH_3SO$ peak towers over $La^{3+}(CH_3SO)_2$.
(38) George, G. N.; Hilton, J.; Rajagopalan, K. V. *J. Am. Chem. Soc.* **1996**, *118*, 1113.
(39) George, G. N.; Hilton, J.; Temple, C.; Prince, R. C.; Rajagopalan, K. V. *J. Am. Chem. Soc.* **1999**, *121*, 1256.

of M^+OH and M^+O coordinated with up to two DMSO were observed[33] in the fragmentation of some $M^{2+}(DMSO)_n$ species.

The quantity n_{crit} is attached to dissociation via electron/proton transfer. Analogous "critical sizes" may be defined for cleavages to designate the largest precursor for which a channel is open. By inspection of Table 1, for trications those sizes for any channel do not visibly increase with increasing IP. They are, however, always above the corresponding values for dications. For example, the largest $M^{3+}(DMSO)_n$ species undergoing the "enol cleavage" to produce $M^{2+}OH(DMSO)_{n-1}$ has $n = 6$, while the equivalent reaction for $M^{2+}(DMSO)_n$ proceeds for $n \leq 3$. The corresponding values for oxide formation are 5 for trications but 3 for dications; the largest $M^{2+}CH_3S(DMSO)_n$ and $M^{2+}CH_3SO(DMSO)_n$ generated from trications have $n = 4$, whereas analogous singly charged ions deriving from dications are associated with one DMSO at most.

4. Further Reduction to Monocations. A diversity of dicationic fragments generated by $M^{3+}(DMSO)_n$ provides for a wide range of consecutive singly charged products, most observed in the dissociation[33] of $M^{2+}(DMSO)_n$. The first group includes those containing $M^+(DMSO)$ and $M^+(DMSO-H)$. These products found for Al, In, Ga, Bi, Fe, and Cr generally result from electron and proton transfer in $M^{2+}(DMSO)_n$ or $M^{2+}(DMSO-H)(DMSO)_n$ intermediates.[33] For Ga and In, there also are novel fragments based on $M^+(DMSO-2H)$, arising from the second proton transfer in $M^{2+}(DMSO-H)(DMSO)_n$. However, the same precursors also separate into $M^+(DMSO)_n$ and $(DMSO-H)^+$. The second group of products, encompassing those containing M^+CH_2SO, M^+CH_3SO, or M^+CH_4SO with up to two DMSO was observed for all metals. Their origins have been discussed.[33] The third group, found for all cases except V and Yb, incorporates products with a severed S═O, where a metal is presumably bound to sulfur: M^+CH_2S and M^+CH_3S. These likely derive from $M^{2+}CH_3S(DMSO)_n$ losing $DMSO^+$ or $H^+(DMSO)$, or from $M^{2+}(DMSO)_n$ precursors.[33] The next group, encountered almost universally, includes metal oxides and hydroxides, coordinated by up to three DMSO molecules. These may result from a heterolytic S═O cleavage in $M^{2+}(DMSO)_n$ or elimination of $DMSO^+$ or $H^+(DMSO)$ from dication oxides and hydroxides. There also are novel fragments based on $M^+(OH)_2$ dihydroxides. For most metals, there are oxides ligated by CH_2SO, CH_3SO, or CH_4SO. Finally, V and Cr complexes exhibit dioxides coordinated by up to two DMSO.

Concluding, microsolvated tripositive metal ions outside of group 3 can be readily produced by ESI of the solutions of trivalent metal salts in anhydrous DMSO. This includes both main group elements (Al, Ga, In, Bi) and transition metals (V, Cr, Fe), some with the third ionization energies as high as 31 eV. Complexes with up to six DMSO molecules fragment via channels other than ligand loss. These involve close competition between two different cleavage reactions conserving the triple charge, and charge-reduction processes via dissociative electron transfer, proton transfer, and severance of C−S and/or S═O bonds. The last may proceed with metal binding to either sulfur or oxygen, in both versions with or without proton transfer. All dications thus produced decay to singly charged species at higher energies. Interplay of dependences of these processes on the third and second ionization energies of the metal and its electronic structure creates a fascinating multifaceted fragmentation chemistry.

Acknowledgment. We thank Professor P. Kebarle for his clarifications and Dr. D. R. Doerge, Dr. J. P. Freeman, and Dr. J. G. Wilkes for their help with the experimental work and valuable discussions.

Supporting Information Available: Table 2S listing all singly charged dissociation products observed; Figure 8S presenting CID spectra for Sc^{3+} and Ga^{3+} complexes. This material is available free of charge via the Internet at http://pubs.acs.org.

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