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Fragmentation Chemistry of DMSO Complexes of Metal Dications

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Recent developments in ion sources have enabled generation and mass-spectrometric investigation of multiply charged metal cations coordinated with various ligands. These ions exhibit rich dissociation chemistry, including electron transfer, proton transfer, and ligand cleavage. Dimethyl sulfoxide (DMSO) is the preeminent aprotic solvent. While complexes of two dipositive metal ions with DMSO were observed previously, the fragmentation of these species has remained essentially unknown. Here we present an extensive MS/MS investigation of DMSO complexes of doubly charged divalent metal cations. We determined the minimum sizes at which dications were stable against charge reduction as well as critical sizes above which no electron or proton transfer occurs. For intermediate sizes, low-energy fragmentation pathways were elucidated in detail. Both proton and electron transfers were observed, depending on the metal. We found diverse ligand cleavage channels, the most intense being the sequential scission of one or both carbon−sulfur bonds in one or several DMSO molecules with competitive eliminations of CH_3 and CH_4 neutrals. This behavior is completely different from that exhibited by acetone complexes of metal dications, or from that of acetonitrile complexes, in which ligand cleavage is always accompanied by charge reduction. Scission of a sulfur−oxygen bond in DMSO forming mostly ligated metal oxide cations is less intense; this is always associated with charge reduction.

I. Introduction

Ion solvation has been a cornerstone area of physical chemistry since its origins a century ago.[1] More recently, attention has moved to solvation in finite systems, where the process can be followed experimentally, one solvent molecule at a time, and a close connection to tractable microscopic theory can be made. Solvation of multiply charged ions is especially intriguing because of the possible charge reduction by neutral ligands. Solvation of metal polycations, particularly those of transition metals that have highly directional bonding, is further topical in view of (i) relevance to the self-solvation of metal ion hemes in biological molecules,[2] (ii) connection to stable coordination complexes known in inorganic and solid-state chemistry,[3,4] and (iii) novel strategies in the analytical characterization of organic ions[5−12] (including peptide sequencing[10−12]) that exploit differences in fragmentation between protonated and metalated molecules that can also be metal-specific. Mass-spectrometric methods, in particular collision-induced dissociation (CID), are ideally suited for research on ion solvation in finite systems.

Metal ion−ligand complexes have been of interest for a long time, but most work was limited to singly charged systems because solvated multiply charged metal ions were not accessible experimentally until recently. To produce a ligated ion, bare metal cation would normally be passed through a vapor of the desired ligand where a sequential addition would take place. This procedure is standard for monocations but for polycations is generally disabled by dissociative electron or proton transfer. That is, the second ionization potentials (IPs) of almost all metals are above 12 eV (see Table 1), while the first IPs of organic ligands typically range[13] between 8 and 12 eV. Hence, the charge reduction of a metal polycation by electron transfer from a neutral ligand is normally exothermic and proceeds spontaneously on contact.[14] The dissociation, driven by Coulomb repulsion, ensues immediately.

Routine generation of solvated metal polycations has been made possible by a new paradigm, in which the ions result not from addition of ligands to a bare cation, but by removal of extra ligands starting from larger species. This is realized in the electrospray ionization (ESI) source where ions already present in solution are directly transferred into the gas phase inside solvent shells, which are then partly removed in the desolvation region by thermal or collisional heating. This method, pioneered by Kebarle and co-workers a decade ago,[4,15,16] has successfully produced gas-phase complexes of divalent metal cations with a variety of protic and aprotic ligands,[17−34] including water,[4,15−18,22−28,30,31] alcohols,[18,19,29] acetone,[18,28,33] other ketones,[34] acetonitrile,[18−21,32] pyridine,[16,19] and DMSO.[4,15,16,18] Alternatively, one can first generate a complex of needed size containing a neutral metal center, then raise its charge state, for example by laser or electron-impact ionization.[35] This has been implemented in the pick-up technique of Stace and co-workers.[3,13,36−42] This method has produced complexes of metal dications with water, alcohols, ketones, ethers, ammonia, aromatic hydrocrabons, nitriles, and other ligands. In a variation of this approach known as charge-stripping,[43−46] the original complex to be further ionized is not a neutral but a singly charged cation.

While a bare metal dication (M^{2+}) may spontaneously charge-transfer to a neutral ligand as discussed above, most M^{2+} (when M is a divalent metal) species are stable in bulk solutions in water and other solvents. (The reduction of Ag^{2+} in aqueous media is a rare exception.) Hence, for any metal−ligand combination, there must be a minimum size ($n_{\min}$) at which the complex is still stable against dissociative electron or proton transfer. Further, macroscopic droplets obviously "dissociate" by evaporating neutral ligand molecules only. Thus there must

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TABLE 1: Selected Fragmentation Properties of Doubly charged Metal−DMSO Complexes[a] (The table listing all products observed (including all singly charged cleavage products) is in the Supporting Information.)

metal	IP2, EV	critical sizes for electron or proton transfer		dication cleavage products	
		n_{min}[b]	n_{crit}[c]	products[d] of CH_3 loss (3)	products[e] of rearrangement (5)
Ba	10.0	0	0	1′,2′,3′	?
Sr	11.0	0	1(e)	1′,2″,2′,3′,4′	a
Ca	11.9	0	1(e)	1′,2″,2′,3′,4′	a,c,d
Sn	14.6	0	2(e)	2′	?
Pb	15.0	1	2(e)	?	?
Mg	15.0	1	3(p)	1′,2‴,2″,2′, 3″,3′,4′	a,b,c,d,e
Mn	15.6	1	3(p)	1′,2‴,2″,2′, 3′,4′	a,b,d,e
Fe	16.2	1	2(e)	1′,2‴,2″,2′, 3′,4′	d,e
Cd	16.8	2	2(e)	2′,3′	
Co	17.1	1	3(ep)	2″,2′,3′	
Zn	18.0	2	3(p)	2″,2′,3′,4′	c,d,e
Ni	18.2	2	3(e)	2′,3′	
Be	18.2	2	N/A[f]	2″,2′,3″,3′,4′	c,d,e
Cu	20.3	2	3(e)		

[a] A question mark means the data were insufficient to ascertain the issue (typically because of low signal intensity). [b] Minimum number *n* for which $M^{2+}(DMSO)_n$ was found among the fragmentation products; the entry "0" means bare M^{2+} was observed. [c] Critical number *n* showing the largest $M^{2+}(DMSO)_n$ complex found to dissociate via either electron (e) or interligand proton (p) transfer. The notation (ep) means two processes compete. For $n = 1$, obviously only (e) is feasible. All $M^{2+}(DMSO)_2$ studied exhibited electron transfer (1) only, even when proton transfer (2) only was observed for $n_{crit} = 3$. [d] Products of homolytic cleavage (3). The numeral corresponds to the precursor size *n*, and the number of apostrophes indicates the number of sequential CH_3 losses. For example, 3′ stands for $M^{2+}CH_3SO(DMSO)_2$. No CH_3 loss was encountered for any metal complex with $n > 4$. [e] Products of rearrangement (5) eliminating CH_4: $M^{2+}CH_2SO$ (a), $M^{2+}SOCH_2SO$ (b), $M^{2+}(CH_2SO)_2$ (c), $M^{2+}CH_2SOCH_3SO$ (d), and $M^{2+}CH_2SO(DMSO)$ (e). This process was not observed for any precursor with $n > 2$. [f] No proton or electron transfer was observed for any $Be^{2+}(DMSO)_n$ precursor.

be a critical size (n_{crit}) above which no electron or proton transfer occurs. The coordination of metal dications with water and dissociation of M^{2+} hydrates has been studied extensively, and pertinent n_{min} and n_{crit} values have been measured. At and below n_{crit}, $M^{2+}(H_2O)_n$ species fragment via proton transfer because the activation barrier for electron transfer is significantly higher.[47] Alcohol complexes exhibit analogous behavior.[19] Hence aprotic ligands stabilize multiply charged metal cations substantially better than the protic ones. This makes the coordination of polycations by aprotic ligands of particular chemical interest.

Of the M^{2+} complexes with aprotic ligands, only those with acetonitrile have been studied extensively in MS/MS experiments.[19−21,32] Large $M^{2+}(CH_3CN)_n$, of course, dissociate by losing neutral ligands. Below the critical size (3 or 4 for most metals[32]), there is a close competition between the electron-transfer channel eliminating CH_3CN^+ and proton-transfer yielding HCH_3CN^+. Heterolytic cleavage of a C−C bond yielding M^+CN and $CH_3{}^+$ is also observed as a less intense dissociation channel. Most recently, the CID of acetone complexes of some transition metal dications has been examined.[33]

Dimethyl sulfoxide (DMSO) is arguably the most common aprotic solvent. However, the production of $M^{2+}(DMSO)_n$ ions by ESI was reported for M = Co[4] and Cu[15,16,18] only, and fragmentation of these species has not really been investigated. An attempt to generate $Mg^{2+}(DMSO)_n$ using the pick-up technique failed.[40] Posey and co-workers[48] produced ternary $[Fe(bpy)_3(DMSO)_n]^{2+}$ complexes by passing $Fe^{2+}(bpy)_3$ through DMSO vapor, but opined that "electrospray ionization cannot be carried out of DMSO solutions". In this work, we have successfully generated $M^{2+}(DMSO)_n$ ions by straightforward ESI for every divalent metal ion tried. We have then comprehensively studied the low-energy dissociation pathways of these species, systematically identifying even the minor channels.

II. Experimental Procedures

Experiments were performed using a SCIEX TAGA 6000E triple-quadrupole mass spectrometer (MDS SCIEX, Concord, Ontario) outfitted with a custom-made ESI source.[17,18] As is usual for SCIEX instrumentation, the atmospheric pressure (API) source is interfaced to the vacuum region via two pinholes crossed by an orthogonal flow of curtain gas for desolvation of ions. Most data were reproduced employing a Finnigan TSQ 7000 MS/MS system where the API source and the vacuum region are connected by a heated capillary. Both nebulizing and auxiliary gas were off. The ESI needle voltage was typically 3−4 kV, and the temperature of TSQ heated capillary was in the 100−350 °C range. DMSO complexes of metal dications were produced by spraying 1−10 mM solutions of metal nitrates in pure or aqueous DMSO. Since no nitrates were available for Fe^{2+} and Sn^{2+}, we substituted $FeSO_4$ and $SnCl_2$. Mass-selected ions were fragmented by CID with argon collision gas at a pressure of ∼0.2−1.4 mTorr and laboratory collision energy (*E*) of 40−110 eV. Data sets for different metals were obtained under identical energy and pressure conditions to ensure the clarity of element-specific effects.

The dissociation was mostly by single collisions at the lowest pressures used (0.2−0.3 mTorr), but heavily multicollisional at 1.2−1.4 mTorr. Implementing a multicollisional CID was necessary to induce the desired extent of fragmentation of large precursor ions at comparatively low collision energies. Higher energies needed to effect the same fragmentation in a single-collision regime were substantially degrading the mass resolution of our instruments. We have verified, however, that all findings were effectively identical in low- and high-pressure modes. The MS/MS spectra presented in this work reflect a multicollisional CID.

As widely observed previously, the overall relative yield of multiply charged ions is maximized under mildest source conditions.[31−33] This means a nominal potential drop in the lens region, which minimizes collisional heating of ions that would result in their dissociation accompanied by charge reduction. However, the abundance distribution of ions produced under these conditions peaks sharply at $n = 5$ or 6, depending on the metal. This has already been pointed out[4] for Co^{2+} with $n = 6$, the examples of such "magic numbers" at $n = 5$ for Cu^{2+} and $n = 6$ for Ni^{2+} are presented in Figure 1. Hence, to generate abundant precursor ions with fewer than 4−5 DMSO ligands, one needs to promote desolvation in the source. This is attained at "harsher" conditions, with the voltage drop in the lens region set in the 30−60 V range. This change tends to augment the total ion signal, which often outweighs a relatively lower yield of dications.

Dissociation of metal−DMSO cluster dications turned out to be complex, yielding a variety of singly and doubly charged fragments. To ensure accurate assignments and disentangle mass overlaps, we repeated all experiments with d_6-DMSO (or d_6-DMSO/D_2O). For metals that have more than one abundant stable isotope, CID spectra for all such isotopes were collected. In many cases, the technical complexity of data and a vast

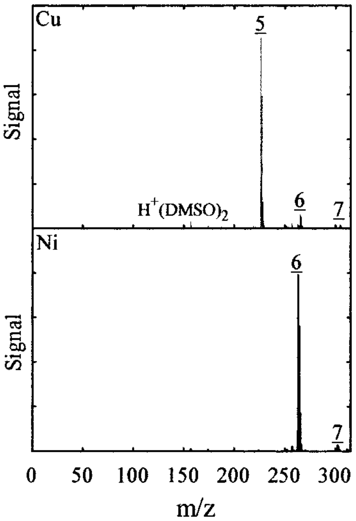

Figure 1. Q1 MS spectra (TSQ) revealing the "magic sizes" in $M^{2+}(DMSO)_n$ cluster sequences: $n = 5$ for copper and $n = 6$ for nickel. Samples were metal nitrates dissolved in anhydrous DMSO. Dications are underlined.

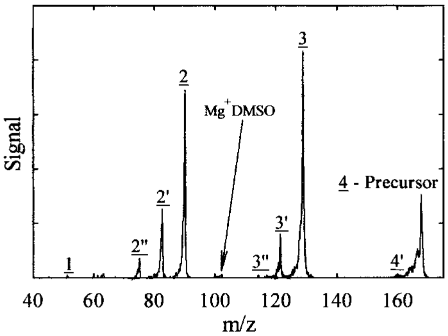

Figure 2. CID spectral windows for $^{24}Mg^{2+}(DMSO)_4$ on TAGA ($E = 110$ eV). Peaks labeled by numbers n are $Mg^{2+}(DMSO)_n$. Features marked by apostrophes are products of the number of steps of homolytic cleavage (eq 3) given by the number of apostrophes. For example, $2'' = Mg^{2+}(DMSO)_2 - 2CH_3 = Mg^{2+}(CH_3SO)_2$. All doubly charged cations are underlined.

number of identified products prohibits our presenting or discussing them all, and only major or particularly significant ones are exhibited in the Figures. More detailed graphs revealing further minor channels and the summary Table 2S listing all products observed are deposited in the Supporting Information.

III. Results

1. Key Features of $M^{2+}(DMSO)_n$ Fragmentation: The Example of Mg. The CID spectra for $Mg^{2+}(DMSO)_4$ and $Mg^{2+}(DMSO)_2$ are presented in Figures 2 and 3, respectively. Clearly, the loss of neutral DMSO is a major channel all the way to $n = 1$. However, bare Mg^{2+} was not observed: apparently Mg^{2+}-DMSO dissociates solely into Mg^+ and $DMSO^+$, and thus the minimum size n_{min} equals 1. This electron-transfer process

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

is also active for $n = 2$, generating $Mg^+(DMSO)$. No $Mg^+(DMSO)_n$ fragments with $n \geq 2$ were found. The dissociative proton transfer

$$M^{2+}(DMSO)_n = M^+(DMSO{-}H)(DMSO)_{n-2} + H^+DMSO \qquad (2)$$

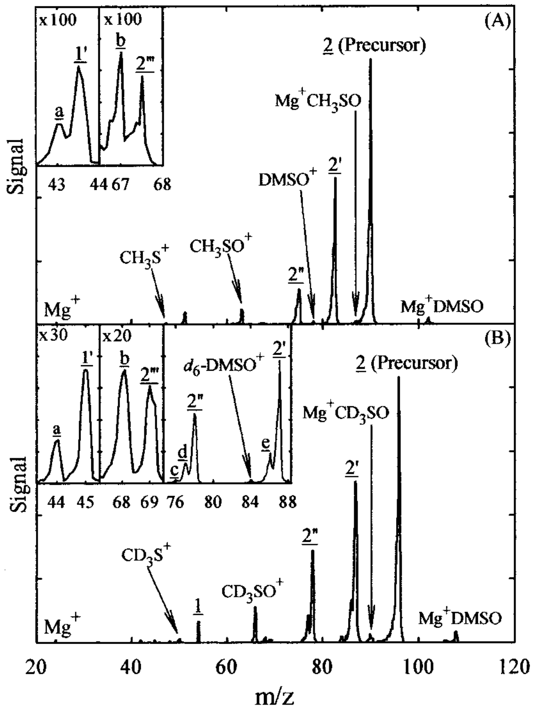

Figure 3. CID spectra for $^{24}Mg^{2+}(DMSO)_2$ (panel A) and $^{24}Mg^{2+}(d_6\text{-}DMSO)_2$ (panel B) measured on TAGA at $E = 40$ eV. Notation follows that in Figure 2. All assignments were confirmed by the data for deuterated and ^{26}Mg analogues. Spectral windows demonstrating the competition between eliminations of CH_3 and CH_4 are presented in the insets. Labels are for the products of CH_4 loss in at least one step: $Mg^{2+}CH_2SO$ (a), $Mg^{2+}SOCH_2SO$ (b), $Mg^{2+}(CH_2SO)_2$ (c), $Mg^{2+}CH_2SOCH_3SO$ (d), and $Mg^{2+}CH_2SO(DMSO)$ (e). An expanded figure showing other minor fragmentation channels and parallel data for the ^{26}Mg complexes is deposited in the Supporting Information.

was not observed for $n = 2$, but encountered as a trace for $n = 3$. Hence the critical size n_{crit} is 3, equal to that for acetonitrile complexes[32] of Mg^{2+}. For comparison, hydrated M^{2+} species reduce their charge via proton-transfer only.[31] This difference may seem trivial considering that water is classified as a protic solvent and DMSO as an aprotic one, except that proton and electron transfers closely compete[32] in the fragmentation of di- and triligand complexes of metal dications (including Mg^{2+}) with acetonitrile, a solvent also deemed aprotic. The proton transfer is, likewise, relatively more favorable[32] for $M^{2+}(CH_3CN)_3$ than for $M^{2+}(CH_3CN)_2$. This might be due to steric crowding in triligand complexes, facilitating an interligand proton transfer.[32]

By inspection of Figures 2 and 3, $Mg^{2+}(DMSO)_n$ with $n \leq 4$ also fragment by homolytic cleavage of C−S bonds in DMSO yielding one or more methyl radicals:

$$M^{2+}(DMSO)_n = M^{2+}[(DMSO)_n - mCH_3] + mCH_3 \qquad (3)$$

This is to be contrasted with heterolytic cleavage of the C−C bond in $M^{2+}(CH_3CN)_n$:[25]

$$M^{2+}(CH_3CN)_n = M^+CN(CH_3CN)_{n-1} + CH_3^+ \qquad (4)$$

Since Mg^+CH_3SO and CH_3^+ fragments were found, $Mg^{2+}(DMSO)$ might also dissociate via heterolytic cleavage of C−S bonds analogous to eq 4. However, a minute yield of CH_3^+ indicates that this reaction is rare, and likely most of the Mg^+CH_3SO immediately results from processes not involving covalent bond cleavage: the loss of relatively abundant CH_3SO^+ or $DMSO^+$ from, resprectively, the $Mg^{2+}(CH_3SO)_2$ or

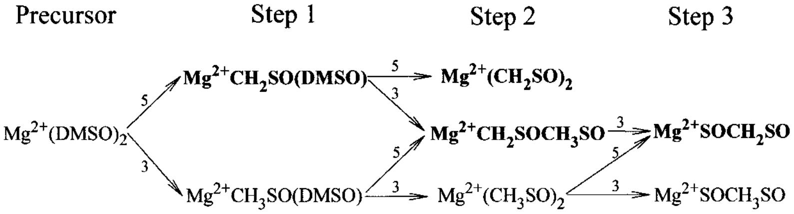

Figure 4. Partition between the losses of CH_3 (channel 3) and CH_4 (channel 5) in the sequential breakdown of $Mg^{2+}(DMSO)_2$. Products containing CH_2SO are in boldface.

$Mg^{2+}CH_3SO(DMSO)$ products of reaction 3. The heterolytic cleavage of C−C in $M^{2+}(CH_3CN)_n$ and homolytic cleavage of C−S dominant for $Mg^{2+}(DMSO)_n$ bring about another distinction between the acetonitrile and DMSO cases. That is, only one methyl group could be excised from an M^{2+} complex with any number of acetonitrile ligands,[32] whereas multiple methyls were sequentially eliminated from $Mg^{2+}(DMSO)_n$. This demethylation appears to be more efficient and deep for smaller precursors: we observed a single CH_3 lost from $n = 4$, two lost from $n = 3$, and three steps of sequential loss from $n = 2$ (Figure 3).[49] For the case of $Mg^{2+}(DMSO)_3$, the information does not suffice to determine whether two methyls were eliminated from different DMSO ligands (in other words, whether the product is $Mg^{2+}SO(DMSO)$ or $Mg^{2+}(CH_3SO)_2$). However, the fact that three CH_3 groups can be excised from $Mg^{2+}(DMSO)_2$ shows that a DMSO ligand can lose both methyls, with only an SO residue remaining in the complex. In the case of acetonitrile,[32] the metalated fragment was always $M^+CN(CH_3CN)_n$ and never $M^+CH_3(CH_3CN)_n$, i.e., the leaving group upon cleavage was methyl. The same is largely true for DMSO.[50]

Yet another major difference from the case of $M^{2+}(CH_3CN)_n$ is that the C−S cleavage in $Mg^{2+}(DMSO)_n$ may involve a proton transfer to the methyl leaving group that converts it into methane:

$$M^{2+}(DMSO)_n = M^{2+}[(DMSO)_n - mCH_4] + mCH_4 \quad (5)$$

This rearrangement competing with eq 3 for $n \leq 2$ is evident in Figure 3 from the products containing $Mg^{2+}CH_2SO$ derived from $Mg^{2+}(DMSO)_2$ and $Mg^{2+}(DMSO)$.[51] The fact that $Mg^{2+}(DMSO)$ undergoes the reaction 5 proves that the proton-transfer here is intraligand, as opposed to the interligand process in eq 2. This is consistent with the absence of a reaction analogous to eq 5 for acetonitrile complexes[32] where each ligand contains one methyl only. While the simple C−S cleavage channel (eq 3) is more intense for both $Mg^{2+}(DMSO)_2$ and $Mg^{2+}(DMSO)$, the relative yield of CH_2SO-containing products tends to increase for smaller precursors: for the first demethylation step, it is zero for $n = 3$, ∼20% for $n = 2$, and ∼40% for $n = 1$ (Figure 3). For a specific precursor, this yield also increases at each successive demethylation step, see the situation for $Mg^{2+}(DMSO)_2$ in Figure 3. This makes sense as CH_4 can be lost at any step, hence the probability of ending up with a CH_2SO ligand accumulates as the dissociation proceeds (Figure 4).

Just as the Mg^+CH_3SO fragment mirrors the $Mg^{2+}CH_3SO$ product of cleavage (eq 3), the observed Mg^+CH_2SO fragment corresponds to the $Mg^{2+}CH_2SO$ product of rearrangement (eq 5). This Mg^+CH_2SO could not come from $Mg^{2+}(DMSO)$ because no CH_4^+ was produced. It could have originated from either $Mg^+(DMSO)$ cleaving neutral methane in a process analogous to eq 5 or $Mg^{2+}(CH_2SO)_2$ or similar species undergoing a charge reduction. In general, $M^{k+}CH_2SO(X)$ could derive from either $M^{k+}CH_3SOCH_2(X)$ or $M^{k+}(X)(DMSO)$ (where X is SO, CH_2SO, or CH_3SO) via a C−S homolytic cleavage or rearrangement severing CH_3 or CH_4, respectively, or from M^{k+1}-$CH_3SOCH_2(X)$ via a C−S heterolytic cleavage eliminating CH_3^+ or charge reduction eliminating CH_3SO^+ or $DMSO^+$, but not from $M^{k+1}(X)(DMSO)$.

Finally, we observed minor charge-reduced products including Mg^+O, e.g., Mg^+OCH_3SO, or Mg^+OH, such as $Mg^+OH(DMSO)$. Traces of hydroxide-based fragments often result from the reduction of metal polycations by water vapor impurity in the collision gas:

$$M^{k+}L_n(H_2O) = M^{(k-1)+}OHL_{n-1} + H^+L \quad (6)$$

where L is a ligand. While this could not be ruled out, we found traces of $CH_3SCH_2^+$, the ion complementary to $Mg^+OH(DMSO)$ in the dissociation of $Mg^{2+}(DMSO)_2$. This ion is not produced when $M^+OH(DMSO)$ results from $M^{2+}(DMSO)_n(H_2O)_m$. Instead H^+DMSO would have been generated via eq 6, but this fragment was absent from our data. Formation of oxide and hydroxide fragments requires an S═O cleavage (with some C−S bonds possibly but not necessarily severed). In acetonitrile complexes of metal dications,[32] the triple C≡N bond was never severed and no nitrides were produced for any metal.

As defined, n_{crit} identifies the largest complex undergoing dissociative electron or proton transfer. This quantity does not relate to ligand cleavages. Hence a complex with $n > n_{crit}$ that cannot dissociate by electron or proton transfer may exhibit a cleavage, possibly associated with charge reduction. This indeed happens for DMSO complexes of many metal dications examined here. For example, $Mg^{2+}(DMSO)_4$ does not break down by electron or proton transfer ($n_{crit} = 3$ for Mg) but yields $Mg^{2+}CH_3SO(DMSO)_3$ via C−S cleavage (eq 3). For other metals, such as Be below, ligand cleavage accompanied by charge reduction may also occur for $n > n_{crit}$. So, unlike the case of hydrates, in which only the neutral ligand loss competes with proton transfer, metal polycations coordinating other ligands with $n > n_{crit}$ should not necessarily dissociate by neutral evaporation only.

2. Other Group 2 Metals. Many key features of the dissociation of $Mg^{2+}(DMSO)_n$ hold for DMSO complexes of other metal dications, but individual elements display specific behaviors. The CID spectra for Be, Ca, and Zn are presented in Figure 5. The second IP (IP2) for Be is some 3 eV above that of Mg (Table 1), so one would expect the dissociative electron (or proton) transfer in Be^{2+} complexes to be more extensive than that in Mg^{2+} ones. This is indeed the case for hydrated ions,[31] in fact the propensity of $Be^{2+}(H_2O)_n$ for proton transfer is abnormally high for a metal with this IP2. For example, no $Be^{2+}H_2O$ could be found while $Ni^{2+}H_2O$ and $Cu^{2+}H_2O$ exist,[31,46,52] despite the fact that the IP2 of Be is equal to that of Ni and 2 eV below that of Cu. The anomalous proton-transfer potency of Be^{2+} is less pronounced in acetonitrile complexes.[32]

Charge reduction is, indeed, easier in $Be^{2+}(DMSO)_n$ (Figure 5A) than in $Mg^{2+}(DMSO)_n$. First, no $Be^{2+}(DMSO)$ could be

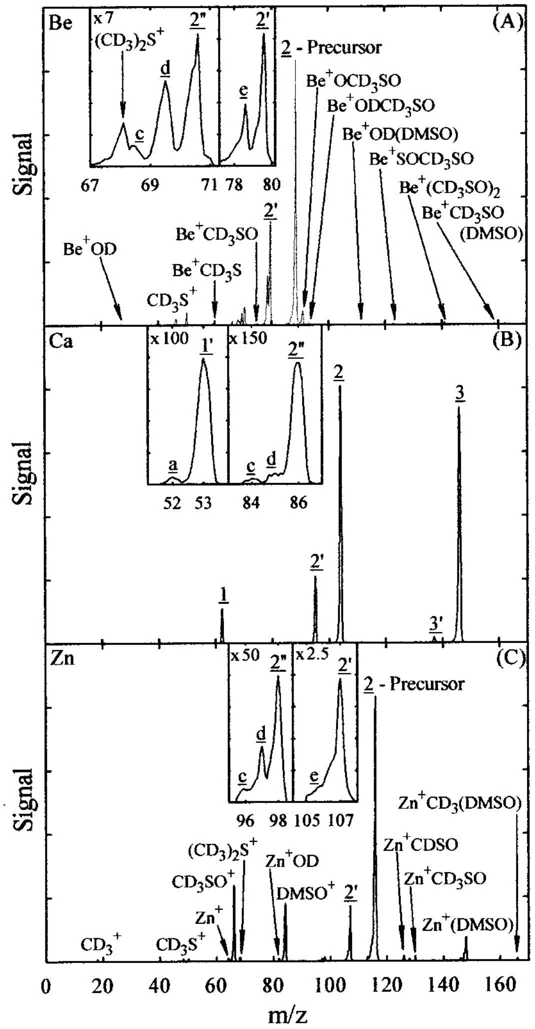

Figure 5. CID spectral windows for DMSO complexes of selected Groups 2 and 12 metal dications: $Be^{2+}(d_6\text{-DMSO})_2$ (panel A), $^{40}Ca^{2+}(d_6\text{-DMSO})_6$ (B), and $^{64}Zn^{2+}(d_6\text{-DMSO})_2$ (C). Data in A and C were measured at $E = 40$ eV using TAGA, B is at $E = 110$ eV on TSQ. Spectral windows exhibiting the competition between eliminations of CH_3 and CH_4 are presented in the insets. Notation is as in Figure 3, all assignments were verified by the data for normal DMSO analogues and, for Zn complexes, using ^{66}Zn and ^{68}Zn isotopes. An expanded figure showing further minor fragmentation channels is deposited in the Supporting Information.

found and the smallest $Be^{2+}(DMSO)_n$ observed had $n_{min} = 2$. Then no $Be^{2+}CH_2SO$ or $Be^{2+}CH_3SO$ originating from $Be^{2+}(DMSO)$ could be produced. Second, no $M^{2+}SOCH_2SO$ or $M^{2+}SOCH_3SO$ fragments observed for Mg were found for Be, presumably because these were unstable to electron transfer. Third, in addition to M^+CH_2SO and M^+CH_3SO (also found for Mg), we observed heavier charge-reduced products mirroring the family of dications produced by C−S cleavage (eq 3) and rearrangement (eq 5), including M^+SOCH_2SO, M^+SOCH_3SO, $M^+CH_2SOCH_3SO$, and $M^+(CH_3SO)_2$. These fragments are unique to Be and were not found for any other metals; their possible origins are outlined in Figure 6. We could not find $Be^+(DMSO)_n$, its $DMSO^+$ complementary, or $Be^+CH_3SOCH_2(DMSO)_n$ for any n. This means that neither electron (eq 1) nor proton (eq 2) transfer operates in any DMSO complexes of Be^{2+}: the barriers to charge reductions via ligand cleavages must be significantly below that for either process. This situation is unprecedented for DMSO complexes of metal dications, and in general for any ligated multiply charged metal ions studied so far.

Another difference between Be and Mg cases is a greater presence of ligated Be^+O fragments. While Mg^+OCH_3SO is a trace product, Be^+OCH_3SO appears in a significant yield (Figure 5A), and $M^+O(DMSO)$ not found for Mg exists for Be. It fits that the $(CH_3)_2S^+$ fragment absent in the case of Mg is present for Be: this ion is complementary to M^+OCH_3SO and $M^+O(DMSO)$ starting from $M^{2+}CH_3SO(DMSO)$ and $M^{2+}(DMSO)_2$ precursors, respectively. We also registered the Be^+CH_3S fragment absent for Mg^+. Its formation requires cutting an S═O bond. Together, these facts indicate a greater potency of Be^{2+} compared to Mg^{2+} in severing S═O bonds. Similarly to the Mg case, we found the series of hydroxide-based fragments. Again, the fact that the $CH_3SCH_2^+$ complementary ion was produced indicates that precursors to those fragments are not water adducts. Beryllium complexes also appear to have the greatest propensity, of all metal dications, for rearrangement (eq 5) relative to cleavage (eq 3).

Ca, Sr, and Ba have the lowest IP2 of all elements (Table 1), so their dications are least likely to abstract an electron from a ligand. For example, $M^{2+}(CH_3CN)_n$ complexes of alkaline earths did not, like other metals, exhibit a dissociative electron or proton transfer at any precursor size.[32] Instead, they evaporated neutral ligands down to bare M^{2+}. The situation for DMSO complexes is largely similar (Figure 5B): among their fragments we observed no ligated Ca^+, Sr^+, or Ba^+. However, bare Ca^+ and Sr^+ traces were found, indicating that dissociative electron transfer (eq 1) is open for $M^{2+}DMSO$ (although Ca^{2+} and Sr^{2+} were also produced). This was not the case[32] for $Ca^{2+}CH_3CN$ and $Sr^{2+}CH_3CN$, but the IP of DMSO is 9.1 eV compared to 12.2 eV for acetonitrile.

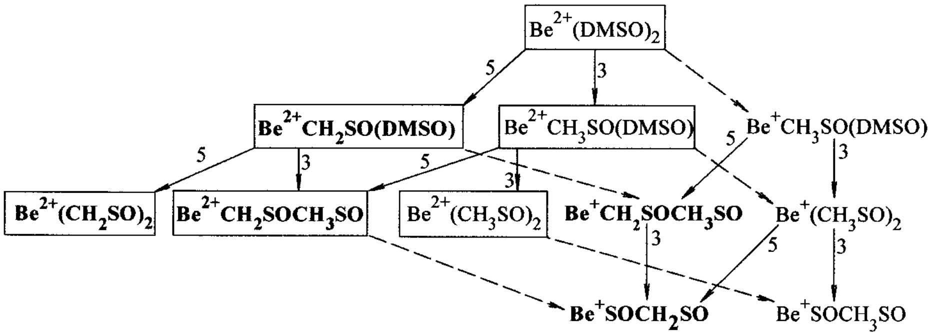

Figure 6. Probable origins of some ligated Be-containing ions in the fragmentation of $Be^{2+}(DMSO)_2$. Solid and dashed arrows code for charge conservation and charge reduction channels, respectively, processes (3) and (5) and their analogues for monocations are marked. Dications are in boxes, and products containing CH_2SO are in boldface. Note that CH_3 can be lost as either neutral or cation, but CH_4 as a neutral only. Hence, charge reduction channels cannot yield species containing CH_2SO unless it has already been present in the precursor.

The heterolytic C−C bond cleavage (eq 4) in $M^{2+}(CH_3CN)_n$ does not clearly correlate with the IP2 of the metal as dissociative electron and proton transfers do.[32] In particular, it is open for acetonitrile complexes of Ca^{2+}, Sr^{2+}, and Ba^{2+}, although it is weaker and may operate for smaller sizes only. Analogously, C−S homolytic cleavage (eq 3) is prominent for DMSO complexes of these elements (see Figure 5B for the case of Ca^{2+}): we observed a single CH_3 loss originating from $n = 4$, 3, or 1; and two sequential losses starting from $n = 2$. The rearrangement (eq 5) was also encountered, albeit with the intensity lower than that for corresponding Mg or Be cases. No oxides were found. Complexes of Sr^{2+} and Ba^{2+} exhibited similar behavior.

3. Zinc and Cadmium. Fragmentation of DMSO complexes with Zn^{2+} (Figure 5C) has parallels to both Mg^{2+} and Be^{2+} cases, but is not identical to either. The IP2 of Zn (18.0 eV) essentially equals that of Be (18.2 eV), which predicates a similarly high extent of charge reduction. As was the case for Be, no $Zn^{2+}(DMSO)$ fragment (and, then, no $Zn^{2+}CH_3SO$ or $Zn^{2+}CH_2SO$) could be obtained. These three species were observed as monocations instead, along with M^+CHSO encountered for neither Be nor Mg. A similarity to the case of Mg (and a difference from that of Be) is a major yield of $Zn^+(DMSO)$ and $DMSO^+$ complementary, and the dissociative proton transfer (eq 2) for $n = 3$. The production of fragments containing metal oxide or hydroxide lies between the small number observed for the case of Mg and the large one for Be. Other heavier singly charged products are completely different from those for either Be or Mg complexes. Neither Zn^+SOCH_2SO nor Zn^+SOCH_3SO were found (though the corresponding dications were missing as well), and $M^+CH_2SOCH_3SO$, $M^+(CH_3SO)_2$, and $M^+CH_3SO(DMSO)$ fragments identified for Be were absent. Instead, we found $Zn^+CH_2SO(DMSO)$, $Zn^+CH_3(DMSO)$, $Zn^+CH_3SCH_3SO$, and $Zn^+CH_3S(DMSO)$. The presence of the last two products is in line with a moderate propensity of Zn^{2+} to induce S=O cleavage.

Another distinction of Zn^{2+} complexes pertains to the competition between reactions 3 and 5. Similarly to the cases of Mg and Be, the largest precursor size for which homolytic C−S cleavage (eq 3) operates is $n = 4$. As for $Be^{2+}(DMSO)_n$, we observed one step of process (eq 3) for $n = 4$ and 3, and two steps for $n = 2$. The lack of $Zn^{2+}SOCH_2SO$ and $Zn^{2+}SOCH_3SO$ fragments can likewise be explained by the high IP2 of Zn. The difference is the absence of $Zn^{2+}CH_2SO(DMSO)$ fragment: the rearrangement (5) opens only at the second step of demethylation of $Zn^{2+}(DMSO)_2$.

Fragmentation of DMSO complexes of Cd^{2+} was less rich than that of Zn^{2+} ones: the cleavage of C−S bond was rare and that of S=O was not encountered. The smallest dication found was $Cd^{2+}(DMSO)_2$, which dissociates almost completely by electron transfer (1). Traces of singly and doubly charged C−S cleavage products such as Cd^+CH_3SO and $Cd^{2+}CH_3SO(DMSO)$ were observed, indicating a single methyl loss (3) possible from $n = 2$ or 3. No evidence for rearrangement (eq 5) was found. This exemplifies that cleavage processes are, unlike dissociative electron or proton transfer, not controlled by the metal IP2: that value for Cd (16.8 eV) is substantially above those for Sr (11.0 eV), Ca (11.9 eV), and Mg (15.0 eV), yet the extent of ligand cleavage in $Cd^{2+}(DMSO)_n$ is way below that for complexes of any of those metals. Likewise, while the IP2 of Zn is some 3 eV above that of Mg, Mg^{2+} complexes have a greater propensity for C−S cleavage.

4. Manganese, Iron, Cobalt, and Nickel. DMSO complexes of these open-shell first-row transition metals exhibit the most diverse decomposition pathways (Figure 7). The IP2 of Mn and Mg are close, and the pattern for Mn^{2+} complexes (Figure 7A) generally resembles that for the Mg^{2+} case. In particular, Mn^{2+}-

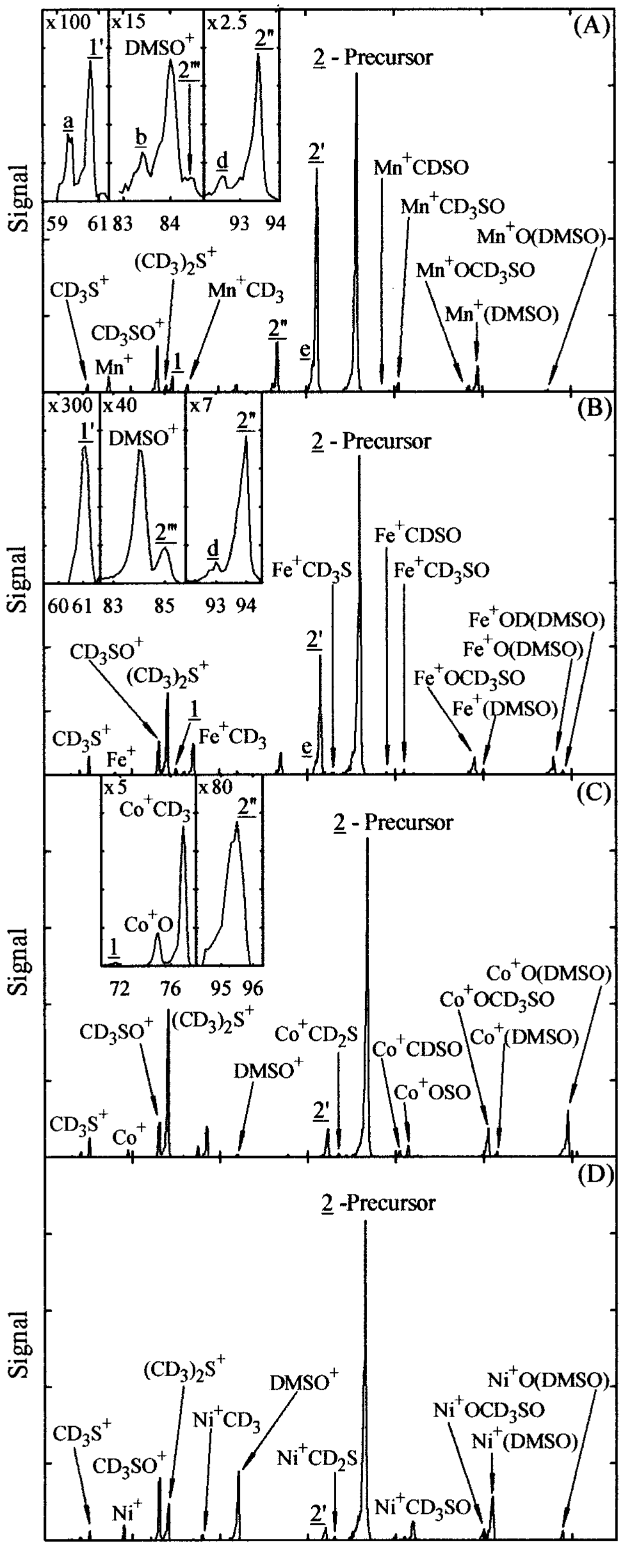

Figure 7. CID spectra for $Mn^{2+}(d_6\text{-DMSO})_2$ (panel A), $^{56}Fe^{2+}(d_6\text{-DMSO})_2$ (B), $Co^{2+}(d_6\text{-DMSO})_2$ (C), and $^{58}Ni^{2+}(d_6\text{-DMSO})_2$ (D); $E = 40$ eV (TAGA). Spectral windows exhibiting the competition between eliminations of CH_3 and CH_4 are presented in the insets. Notation is as in Figure 3, all assignments were verified by the data for normal DMSO equivalents and, for Fe and Ni complexes, using metal isotopes (^{54}Fe, ^{56}Fe and ^{58}Ni, ^{60}Ni). An expanded figure showing further minor fragmentation channels is deposited in the Supporting Information.

(DMSO) was found, but bare Mn^{2+} was not: Mn^+ and $DMSO^+$ appear instead. Mn^+DMSO is prominent, and proton transfer (eq 2) is active for $Mn^{2+}(DMSO)_3$. The relative intensities of (3) and rearrangement (5) operating for $Mn^{2+}(DMSO)$ and in all three steps of methyl loss from $Mn^{2+}(DMSO)_2$ are roughly equal to those for Mg^{2+} analogues. Again, the IP2 value does not govern cleavage as it does electron and proton transfer, and the dissociation of Mn complexes differs from that of Mg ones in a menagerie of singly charged C−S and/or S=O cleavage products beyond the usual M^+CH_2SO and M^+CH_3SO, including Mn^+CHSO, Mn^+CH_3, and Mn^+CH_3S. In this respect, Mn^{2+} complexes bear a greater similarity to Zn^{2+} ones, though certain fragments are unique to the Mn case. The common feature of these species is a severed S=O bond. Such ions were occasionally observed for other elements (e.g., Be^+CH_3S and $Zn^+CH_3SCH_3SO$), but notable only for the open-shell transition metals: Mn, Fe, Co, and Ni. This suggests a significant role of *d*-electrons in cleaving the S=O bonds in DMSO. The regular oxide- and hydroxide-based products were also observed.

As we move to the right through the first transition metal row from Mn to Fe to Co to Ni (Figure 7), the IP2 of elements increases from 15.6 to 18.2 eV (Table 1). This facilitates the dissociative electron transfer: both $M^{2+}CH_3SO$ and $M^{2+}(DMSO)$ exist for Mn and Fe, only $M^{2+}(DMSO)$ was encountered for Co, and neither species could be found for Ni. In an exception to this trend, neither $M^+(DMSO)_2$ nor $M^+CH_3SOCH_2(DMSO)$ observed for Mn were found for Fe, and Fe has an abnormally low $n_{crit} = 2$. Other than that, the electron transfer (eq 1) wins over the proton transfer (eq 2) as we shift from Mn to Co to Ni: $M^{2+}(DMSO)_3$ exhibits (eq 2) only for Mn and (eq 1) only for Ni, while Co^{2+} is the only metal dication we found for which a DMSO complex undergoes both processes.

The propensity for C−S cleavage decreases over the Mn, Fe, Co, Ni sequence. For example, we observed three consecutive steps of homolytic cleavage (eq 3) from $M^{2+}(DMSO)_2$ for Mn and Fe (Figure 7A,B), two such steps for Co (Figure 7C), and only one for Ni (Figure 7D). The intensity of rearrangement (eq 5) falls even faster, as it also decreases relative to that of cleavage (eq 3). In fact, for Co and Ni complexes this process was not observed at all. There are a few differences between the sets of singly charged cleavage products observed. Complexes of Co^{2+} yield an especially large diversity of fragments; strong M^+OSO and M^+OCH_3SO peaks with complementary $(CH_3)_2S^+$ reveal a particular propensity of Co^{2+} for S=O cleavage (Figure 7C). Analogous features in the fragmentation of Fe^{2+} complexes (Figure 7B) indicate a lower but still substantial propensity; this cleavage is least favored in Mn^{2+} and Ni^{2+} complexes (Figure 7 A,D).

5. Copper. The highest IP2 value for metals examined here belongs to copper (20.3 eV). The dissociative electron transfer is, naturally, prominent: no $Cu^{2+}(DMSO)$ and only a trace of $Cu^{2+}(DMSO)_2$ could be found[15] among the fragmentation products of larger complexes (Figure 8). No homolytic C−S cleavage (eq 3) or rearrangement (eq 5) was observed for any precursor, Cu is the only metal studied for which neither was found. Incidentally, Cu^{2+} is the sole dication for which the CID of DMSO complexes had been reported,[15] so the C−S bond cleavage reactions 3 and 5 that typify the fragmentation of $M^{2+}(DMSO)_n$ were missed. Presumably these processes are absent due to the ease of competing charge reduction in small $Cu^{2+}(DMSO)_n$ complexes: indeed singly charged $CuCH_3SO$ and $CuCH_3SO(DMSO)$ (not reported in ref 15) were found (Figure 8A). No S=O cleavage products (including metal oxides or hydroxides) were found either.

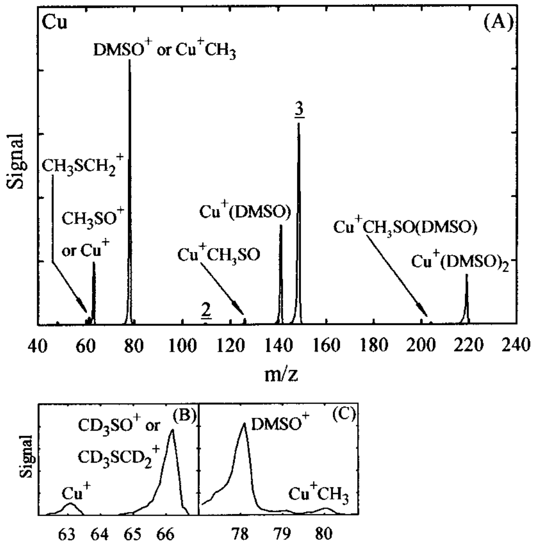

Figure 8. CID of DMSO complexes of Cu^{2+} (TAGA, $E = 40$ eV). Panel A shows the spectrum for $^{63}Cu^{2+}(DMSO)_3$ precursor. All assignments were verified by the data for ^{65}Cu and d_6-DMSO equivalents. In particular, panels B and C exhibit the spectral windows for isotopic substitutions identifying the features hidden in (A) by mass overlaps: $^{63}Cu^+$ and ubiquitous CH_3SO^+ are assigned employing d_6-DMSO (B); Cu^+CH_3 and $DMSO^+$ at $m/z = 78$ are untangled using ^{65}Cu (C). Notation follows that in Figure 3.

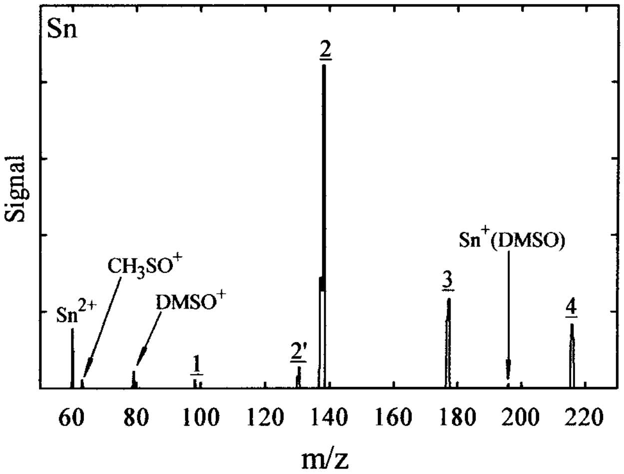

Figure 9. CID spectrum for $^{120}Sn^{2+}(DMSO)_4$ measured at $E = 110$ eV on TAGA. Notation is as in Figure 3, assignments were confirmed by comparison with the data for the ^{118}Sn analogue.

6. Tin and Lead. Salts of Sn^{2+} and Pb^{2+} that we tested were poorly soluble in DMSO. In other such cases, we replaced DMSO by its aqueous solution. However, aqueous Sn^{2+} and Pb^{2+} are strongly hydrolyzed,[31] existing largely as monocations such as $[M_3(OH)_4]^+$ and MOH^+. As ESI does not really generate ions, but merely transfers into the gas phase the species present in solution, no hydrates of these metal dications could be produced and hydroxide monocations were found instead.[17,18,31] This required the use of anhydrous DMSO for sample preparation here, despite poor solubility of the salts. We were able to obtain the DMSO complexes of Sn^{2+} and Pb^{2+} and investigate their fragmentation, but low signal intensity may have obscured minor dissociation pathways. While this prevented our elucidating the CID in detail, the data obtained (Figure 9) contain no surprises. In particular, the extent of dissociative electron-transfer reflected in the values of n_{min} and n_{crit} is consistent with the midrange IP2 values of Sn and Pb (Table 1).

IV. Summary

We have systematically characterized the fragmentation chemistry of gas-phase complexes of dipositive metal ions with DMSO—arguably the most important aprotic solvent. As usual, the extent of dissociative electron/proton transfer is determined by the value of second ionization potential of the metal. In particular, M^{2+}(DMSO) species exist for metals with the second IP below ~17 eV; dications of other metals are stabilized by two DMSO molecules. The largest complex for which an electron or proton-transfer proceeds contains one to three DMSO ligands, depending on the second IP of the metal. Both processes were encountered, but only one or the other was observed for the complexes of any particular metal (except Co). In contrast, the two reactions closely compete for nearly all acetonitrile complexes of metal dications.[32] Aqueous Be^{2+} exhibited an abnormal propensity for charge reduction via proton transfer.[31] In DMSO complexes, Be^{2+} has an unusual potency for charge reduction via C−S bond cleavage. In fact, no proton or electron transfer was observed in any $Be^{2+}(DMSO)_n$: apparently they are not competitive with this cleavage. This is the first example of a ligated metal dication reducing charge exclusively through cleavage, without ever exhibiting either electron or proton transfer for any number of ligands.

The hallmark of $M^{2+}(DMSO)_n$ dissociation chemistry is homolytic ligand cleavage of C−S bonds eliminating CH_3 radicals. This process is prominent for complexes of all M^{2+} (except Cu^{2+}) with three DMSO or less, and was encountered for many tetraligand species. Up to three successive steps of this scission were observed for some $M^{2+}(DMSO)_2$ precursors. For comparison, the cleavage of C−C bonds in $M^{2+}(CH_3CN)_n$ is always a heterolytic one, involving a charge reduction by loss of CH_3^+, and only a single reaction step may occur. Complexes of a few metals (especially Be, Mg, and Mn) with one or two DMSO ligands also readily fragment via a rearrangement eliminating a neutral methane. This rearrangement proceeds via an intraligand proton transfer, as opposed to the interligand one in a dissociative proton-transfer process. This explains why no analogous CH_4 elimination takes place in acetonitrile complexes: each ligand contains one methyl group only. Like the CH_3 loss, this reaction may proceed in consecutive steps. Channels of CH_3 and CH_4 elimination compete, and in the decomposition of a diligand precursor often succeed each other.

We also observed various singly charged cleavage fragments. A subset of them mirrors the dication products of homolytic C−S cleavage. These species (such as M^+SOCH_3SO) are produced from dications by either a heterolytic cleavage of a C−S bond or, more likely, loss of CH_3SO^+ or $DMSO^+$ from cleaved dications. Ions belonging to this group appeared for complexes of all metals with a second IP of 15 eV and higher, but were particularly prominent in the case of Be. Also present was a related group of singly charged fragments corresponding to the dications resulting from the proton rearrangement and CH_4 loss. These ions (such as M^+SOCH_2SO) could arise via homolytic cleavage severing CH_3 or rearrangement eliminating CH_4 from monocation intermediates or charge reduction of the dication products of methane loss. Singly charged products in the third group also result from a cleavage of C−S and not S═O, but have no dication analogues. These species are based on the M^+CH_3 or M^+CHSO nuclei. Some of them were observed for complexes of all metals with the second IP exceeding (again) 15 eV.

All cleavage pathways reviewed above involved C−S bonds only. The other major category includes products with an S═O bond severed. All these are monocations, i.e., the cleavage of S═O is, unlike that of a C−S, always associated with charge reduction. The first group of this category are fragments where a metal is associated with sulfur, such as M^+CH_3S. While complexes of Be^{2+} and Zn^{2+} yield traces of such products, these were significant only for the open-shell transition metals: Mn, Fe, Co, and Ni. The other group of S═O cleavage products is based on the metal oxides and hydroxides, such as M^+OCH_3SO and M^+OH(DMSO). Such fragments were encountered for complexes of all metals with the second IP exceeding the same 15 eV, except Cd and Cu. Oxide-based products are noteworthy for Co^{2+} and Fe^{2+} complexes, in terms of both the number of different species observed and their overall yield. This suggests an important role of *d*-electrons in the S═O cleavage in DMSO.

Concluding, DMSO complexes of metal dications with up to four ligands exhibit rich fragmentation chemistry. It involves a close competition between two different ligand cleavage reactions conserving the (+2) charge state and charge reduction processes via dissociative electron transfer, proton transfer, and cleavage of C−S and/or S═O bonds with metal attaching to either end in both cases. Interplay of subtle dependences of these processes on the second ionization potential of the metal and its valence electron structure creates a complicated, highly element-specific fragmentation behavior.

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Supporting Information Available: Table 2S lists all singly charged dissociation products observed. Figures 3S, 5S, and 7S show minor fragmentation channels. This material is available free of charge via the Internet at http://pubs.acs.org.

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(49) The fact that only one CH_3 could be eliminated from $n = 1$ may be due to the spontaneous dissociative electron transfer in $Mg^{2+}SO$. Mg^+ and SO^+ fragments were indeed observed, though the latter may originate from other parents, such as Mg^+CH_3SO. However, CID of Mg^{2+}(DMSO) proves that $Mg^{2+}CH_3SO$ is derived by homolytic cleavage of that precursor.

(50) A trace of Mg^+CH_3 was encountered. This might have resulted from heterolytic cleavages of C−S bonds in Mg^{2+}(DMSO) or $Mg^{2+}CH_3SO$ with CH_3SO^+ or SO^+ leaving, or could come from homolytic cleavages in Mg^+CH_3SO or Mg^+(DMSO).

(51) In Figure 3, $Mg^{2+}CH_2SO$ may, in part, result from $Mg^{2+}CH_2SO$-(DMSO) losing DMSO. However, that ion is also produced starting from Mg^{2+}(DMSO).

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