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Collisionally Activated Dissociation of Transition Metal Ion/Polyether Complexes in a Quadrupole Ion Trap

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Abstract: For a series of polyether/transition metal ion complexes, collisionally activated dissociation reactions that are mediated by the flexibility of the polyether and the number of coordination sites are reported. The metal ions are generated by a pulsed laser desorption technique, and collision-activated dissociation methods are used to characterize the structures of the resulting metal/polyether complexes. The CAD patterns for the different polyether/metal ion complexes show striking variations depending on the flexibility of the ether, its number of coordination sites, and the type of metal ion. For example, (18-crown-6 + Co^+) dissociates by loss of $CH{=}CH^\bullet$ or $C_2H_3O^\bullet$ radicals, each pathway in conjunction with multiple losses of C_2H_4O, and resulting in products incorporating one covalent or ionic bond between the Co^+ ion and the crown ether. In contrast, (12-crown-4 + Co^+) dissociates by loss of $CH_2{=}CH_2$ or C_2H_4O closed shell neutrals, each pathway in conjunction with additional losses of C_2H_4O and resulting in products that incorporate no covalent bonds to Co^+. The polyether/Ni^+ complexes show dissociation behavior that is similar to that observed for the Co^+ complexes, but the polyether/Cu^+ complexes show uniform dissociation trends that seem to be independent of the flexibility and number of coordination sites of the ether. These differences are rationalized based on the nature of the metal ion, and both the flexibility of the crown ether and its number of coordinating sites, factors which affect the geometry during coordination of the metal ion. This idea is supported by comparative dissociation reactions of metal complexes containing acyclic polyethers (glymes) which have more flexible structures. MS/MS/MS experiments and CAD of complexes formed by model compounds offer support for the dissociation mechanisms.

Introduction

The reactions of metal ions in the gas phase have been extensively studied over the past two decades in part because of the fundamental interest in metal ion chemistry[1−8] and in part because of the potential analytical utility of metal ions as selective reagents that can ionize organic molecules and promote bond cleavages.[8] There have been several excellent reviews of various aspects of metal ion chemistry in the gas phase.[1−8] The transition metal ions have partially filled d orbitals, and are known to promote a rich and diverse reaction chemistry with organic molecules in the gas phase.[1−13]

Molecules that have an array of identical binding sites, such as crown ethers, prove to be intriguing candidates for reactions with metal ions because multisite coordination should be promoted. In fact, this type of process has been extensively studied in terms of molecular recognition.[14−18] Many studies of complexation in solution have involved some of the simplest model guest ions, mainly alkali metal ions, which serve as spherical guests with well-defined sizes and known electronic structures.[14−21] Recently there have been several reports of the examination of aspects of host−guest chemistry in the gas phase, where the intrinsic nature of binding interactions can be evaluated in the absence of solvent effects.[22−29] Although the size of the metal ion and crown ether clearly play an important role in influencing the binding energies and structures of the resulting complexes in the gas phase, the electronic nature of the metal ion is also an important factor.

The main objective of the present work involves the characterization of complexes formed from transition metal ions and polyethers. There have been several previous reports which describe the reactions of transition metal ions with simple

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ethers.[9,10,12] For instance, Fe^+ ions undergo oxidative addition to ethers, including tetrahydrofuran, isopropyl ether, and methyl butyl ether, followed by intramolecular rearrangements primarily through β-hydride shifts.[9] In contrast, Cu^+ ions are generally less reactive toward ethers, and typically abstract CH_3^- or a hydride[9] from the ether molecule, resulting in neutral CuH or $CuCH_3$ species. In the most recent study,[13] the ion chemistry of transition metal ions with dimethyl peroxide was reported. The metal ion inserted into the O−O bond, then promoted a variety of dissociation processes involving radical losses. There have also been numerous studies that have described the reactions of transition metal-containing complexes, such as acetyl acetonate or cyclopentadienyl metal ion species, with polyethers.[30−37] In these reports, the observed products include adducts formed between an intact metal complex and a polyether and adducts generated by substitution of one ligand of a metal complex by a polyether.

There have been fewer studies of the gas-phase reactions of metal ions with larger, more complex organic molecules and the dissociation of the resulting complexes, with little attention yet devoted to the examination of polyethers. One early study of the reactions of Cr^+ and Fe^+ ions with polyethers reported that Fe^+ ions were involved in a richer chemistry with cyclic 12-crown-4 than its acyclic analog, triethylene glycol dimethyl ether.[38,39] The observation that the crown ether was more reactive than its acyclic analog was attributed to the proposal that the cyclic ligand could more fully coordinate the metal ion as compared to the capability of the acyclic ether for multiple attachment, and this phenomenon was termed a "gas-phase macrocylic effect".[39] Several studies have also examined aspects of transition metal complexation by polyethers in solution.[40−43] For example, complexation of the silver ion with crown ethers shows size selectivity in solution. The smaller ring size of the 15-crown-5 makes it more rigid, and thus it undergoes a slower conformational change than 18-crown-6 upon complexation with the silver ion.[40]

In the present study, a systematic examination of the types of complexes formed from reactions of three monopositive transition metal ions with a variety of crown ethers and their acyclic analogs in a quadrupole ion trap mass spectrometer was undertaken. The metal ions (M^+) are generated by laser desorption from a metal foil (copper, cobalt, nickel), and the complexes are formed by subsequent ion−molecule reactions with neutral polyethers (L). Collision-activated dissociation (CAD), including MS/MS/MS, is used to evaluate the structures of the metal/polyether complexes. The primary objective is to examine the fragmentation patterns of the ($L + M^+$) complexes with respect to the identity of the metal ion and the size of the polyether. The most unexpected result stems from the observation that the flexibility and number of coordination sites of the crown ether promote a significant change in the types of fragmentation pathways accessed. In addition, the CAD behavior of the metal complexes containing acyclic polyethers (glymes) was compared to the CAD behavior of the crown ether complexes because the glymes are open chain polyethers that have greater flexibility and should allow less restricted coordination to the metal ions.

Experimental Section

The experiments were performed in a Finnigan MAT quadrupole ion trap mass spectrometer (ITMS)[44] equipped with a probe-mounted fiber optic laser desorption assembly.[45] Metal ions were generated by pulsed laser desorption of a metal foil applied to a Teflon sample support. A Nd:YAG laser operated in the Q-switch mode provided the desorption pulse. Transition metal ions were desorbed with a power density of 2×10^8 W/cm^2. The metal ions are stored in the ion trap and allowed to undergo reactions with neutral polyethers (admitted through a leak valve or on a solids probe) for 20−200 ms. The metal/polyether complexes are mass analyzed by operating the ion trap in the mass selective instability mode in which an rf voltage applied to the ring electrode is used to eject ions onto an externally-located electron multiplier detector. A helium buffer gas pressure of 1−2 mTorr is used to assist in collisional cooling of the complexes. The CAD spectra of the metal complexes were obtained by applying a small AC voltage (500−1000 mV_{p-p}) across the end-cap electrodes at a q value of 0.3 for 5−10 ms.

All polyethers were obtained from Aldrich Chemical Co. (Milwaukee, WI) and used without further purification.

Results and Discussion

In order to characterize the reactions of transition metal ions with polyethers, first the complexes were generated in the gas phase by ion−molecule reactions between laser-desorbed metal ions (M^+) and polyether molecules (L) to form ($L + M^+$) complexes. Because of the energetics of laser desorption, some of the metal ions potentially may exist in excited electronic states due to the high energy deposition of the laser desorption event. To probe the existence of excited states, the helium buffer gas pressure was varied from 0.5 to 2.5 mTorr, the laser power was varied from about 5 to 30 mJ/pulse, and the cooling time prior to the ion−molecule reaction period was varied from 5 to 300 ms. From these systematic studies, there emerges no evidence for the existence of excited states because there are no changes nor irregularities observed in the reactivity patterns of the metal ions as the experimental conditions are varied. Thus, for the remainder of the discussion, the issue of excited states will not be addressed.

Of the three metal ions evaluated, two exist as open-shell species (Ni^+ and Co^+) and one exists as a closed shell species (Cu^+). After desorption and isolation, each metal ion underwent ion−molecule reactions with a selected polyether for 20−200 ms. Upon reaction of the metal ions with each polyether, a variety of products are formed, but the predominant product is the intact polyether/metal ion complex (see Figure 1). The other products are rationalized as fragment ions from spontaneous dissociation of internally excited (polyether + metal ion) adducts. At longer reaction times, the abundances of all product

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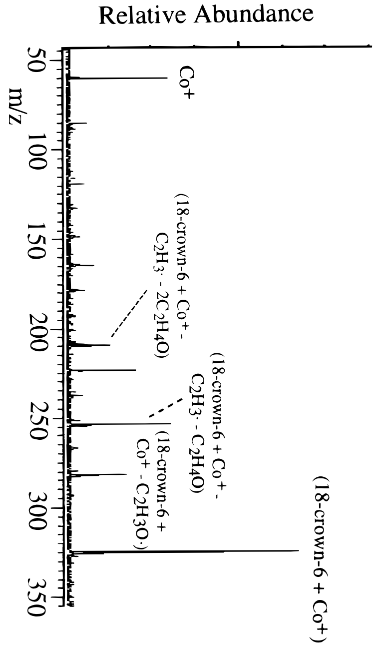


Figure 1. Product spectrum for reactions of Co^+ ions with 18-crown-6 during a 100 ms reaction interval.

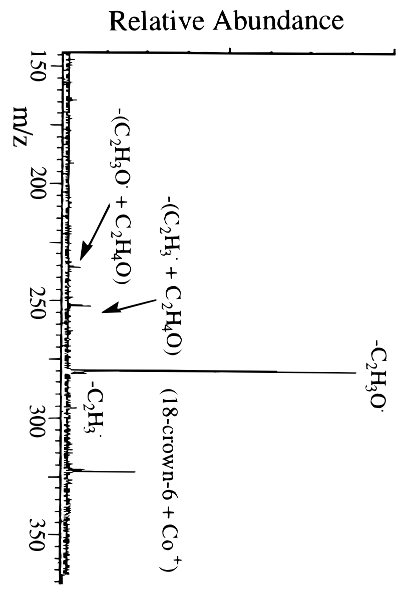


Figure 2. CAD spectrum of (18-crown-6 + Co)$^+$ ions with an activation voltage of 500 mV$_{p-p}$ for 10 ms.

ions increased, but there was no dramatic change in the types or distribution of products formed. Due to the moderately poor shot-to-shot reproducibility of the laser pulse, the product distributions vary by 5−50% for each metal/polyether combination for each laser desorption pulse. Thus, although the same product ions are consistently observed, the relative percentages of each product vary, making extraction of quantitative comparisons of product distributions for different metal/polyether combinations unreliable. Collisionally activated dissociation of specific complexes provides a more confident method of evaluating the products.

Collision-activated dissociation of the intact metal/polyether complexes was used to elucidate the structures of the ions, and mechanisms were proposed to account for the observed dissociation behavior. The fragment ions from the intact (polyether + metal ion) complexes are generally similar to those observed as direct products in the ion−molecule reaction spectra. An example of an ion−molecule reaction product spectrum for the reactions of Co^+ with 18-crown-6 is shown in Figure 1, and an example of a typical CAD spectrum for the (18-crown-6 + Co^+) ions is shown in Figure 2. The main interest in this paper is the formation and dissociation of the intact (polyether + metal ion) adducts, so these adducts were the only products examined in detail. The CAD results are summarized in Tables 1 and 2. The CAD conditions were adjusted for each complex to obtain similar activation conditions. The individual percentage of fragment ion current due to each loss is listed, then the total percentages for related series of neutral losses are summed in Tables 1 and 2. Nearly all the fragment ions in the CAD spectra incorporate the metal ion, so the evidence suggests that it is strongly coordinated to the polyether ligand, regardless of the size of the polyether or the electronic configuration of the metal ion.

Table 1. CAD Spectra of Transition Metal Ion/Crown Ether Complexes: Series of Neutral Losses[a]

complex	12-crown-4	15-crown-5	18-crown-6
(L + Cu^+)	nC_2H_4O, $n = 1, 2, 3$ [53, 3, 2 = 58%]	nC_2H_4O, $n = 1, 2, 3$ [20, 25, 25 = 70%]	nC_2H_4O, $n = 1, 2, 3$ [30, 25, 25 = 80%]
	$C_2H_2 + nC_2H_4O$, $n = 0, 1, 2$ [10, 15, 10 = 35%]	$C_2H_2 + nC_2H_4O$, $n = 0, 1, 2$ [3, 3, 20 = 26%]	$C_2H_2 + nC_2H_4O$, $n = 0, 1, 2$ [3, 5, 7 = 15%]
	$H_2O + nC_2H_4O$, $n = 0, 1$ [2, 5 = 7%]	$H_2O + nC_2H_4O$, $n = 0, 1, 2$ [1, 1, 2 = 4%]	$H_2O + nC_2H_4O$, $n = 0, 1, 2$ [1, 2, 2 = 5%]
(L + Co^+)	nC_2H_4O, $n = 1, 2$ [5, 10 = 15%]	nC_2H_4O, $n = 1, 2, 3$ [2, 15, 6 = 23%]	X
	$C_2H_4 + nC_2H_4O$, $n = 0, 1, 2$ [35, 30, 15 = 80%]	$C_2H_4 + nC_2H_4O$, $n = 0, 1, 2, 3$ [2, 15, 25, 10 = 52%]	X
	C_2H_2 [5%]	X	X
	X	$C_2H_3O^•$ [15%]	$C_2H_3O^• + nC_2H_4O$, $n = 0, 1, 2$ [83, 3, 1 = 87%]
	X	$C_2H_3^• + nC_2H_4O$, $n = 0, 1$ [7, 3 = 10%]	$C_2H_3^• + nC_2H_4O$, $n = 0, 1, 2$ [3, 9, 1 = 13%]
(L + Ni^+)	nC_2H_4O, $n = 1, 2, 3$ [30, 5, 5 = 40%]	nC_2H_4O, $n = 1, 2$ [20, 25 = 45%]	X
	$C_2H_4 + nC_2H_4O$, $n = 0, 1, 2$ [5, 10, 10 = 25%]	X	X
	$C_2H_2 + nC_2H_4O$, $n = 0, 1, 2$ [2, 21, 13 = 35%]	$C_2H_2 + nC_2H_4O$, $n = 1$ [20%]	X
	X	$C_2H_3O^•$ [10%]	$C_2H_3O^• + nC_2H_4O$, $n = 0, 1$ [60, 5 = 65%]
	X	$C_2H_3^• + nC_2H_4O$, $n = 1, 2$ [20, 5 = 25%]	$C_2H_3^• + nC_2H_4O$, $n = 0, 1, 2$ [1, 30, 4 = 35%]

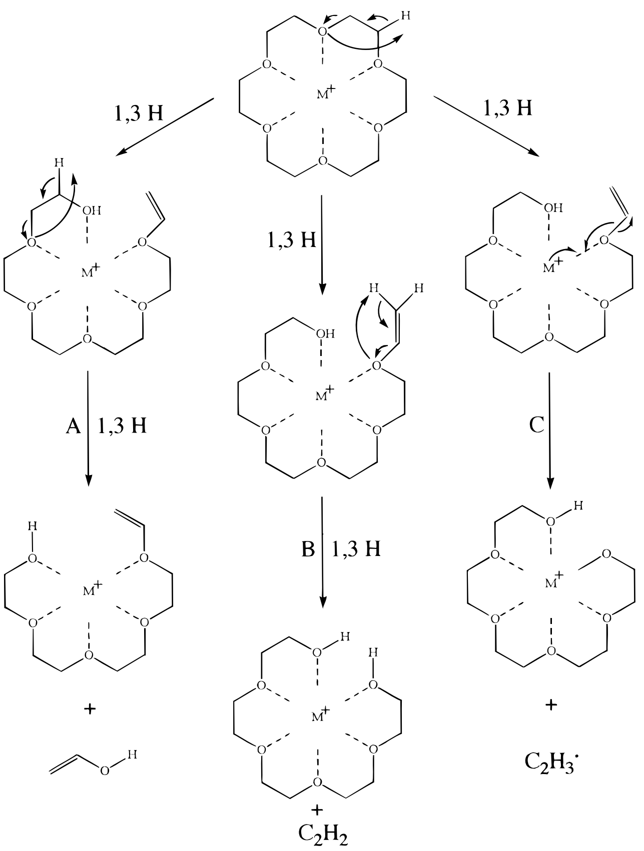
[a] Individual and total percentage of fragment ions in brackets, uncertainty is ±3−5%.

Table 2. CAD Spectra of Transition Metal Ion/Glyme Complexes: Series of Neutral Losses[a,b]

complex	monoglyme	diglyme	triglyme	tetraglyme
$(L + Cu^+)$	CuH [40%]	$CH_3OH + nC_2H_4O$, $n = 0, 1$ [40, 5 = 45%]	$CH_3OH + nC_2H_4O$, $n = 0, 1$ [70, 5 = 75%]	$CH_3OH + nC_2H_4O$, $n = 0, 1$ [30, 30 = 60%]
	CH_2O [20%]	$C_3H_6O + nC_2H_4O$, $n = 0, 1$ [35, 3 = 38%]	$C_3H_6O + nC_2H_4O$, $n = 0, 1$ [20, 5 = 25%]	$C_3H_6O + nC_2H_4O$, $n = 0, 1$ [20, 20 = 40%]
	CH_3OH [20%]	90 [17%]		
	$CuOCH_3$ [20%]			
$(L + Co^+)$	X	$CH_3^\bullet + nC_2H_4O$, $n = 0, 1, 2$ [60, 20, 2 = 82%]	$CH_3^\bullet + nC_2H_4O$, $n = 0, 1, 2$ [25, 20, 10 = 55%]	$CH_3^\bullet + nC_2H_4O$, $n = 0, 1, 2$ [5, 32, 5 = 42%]
	C_3H_6O [40%]	C_3H_6O [6%]	$C_3H_6O + nC_2H_4O$, $n = 0, 1, 2$ [20, 5, 3 = 28%]	$C_3H_6O + nC_2H_4O$, $n = 0, 1$ [10, 30 = 40%]
	CH_4 [26%]	$CH_4 + nC_2H_4O$, $n = 0, 1$ [5, 2 = 7%]	$CH_4 + nC_2H_4O$, $n = 2, 3$ [5, 5 = 10%]	$CH_4 + nC_2H_4O$, $n = 2$ [10%]
	CH_2O [5%]	$CH_2O + nC_2H_4O$, $n = 0$ [5%]	$CH_2O + nC_2H_4O$, $n = 1, 2$ [5, 2 = 7%]	$CH_2O + nC_2H_4O$, $n = 1, 2$ [5, 3 = 8%]
	$C_2H_6O + nC_2H_4O$, $n = 0, 1$ [5, 24 = 29%]			
$(L + Ni^+)$	X	$CH_3^\bullet + nC_2H_4O$, $n = 0, 1, 2$ [7, 3, 1 = 11%]	$CH_3^\bullet + nC_2H_4O$, $n = 0, 1, 2$ [80, 5, 5 = 90%]	$CH_3^\bullet + nC_2H_4O$, $n = 0, 1, 2$ [65, 31, 4 = 100%]
	X	X	$C2H5O^\bullet + nC_2H_4O$, $n = 0, 1$ [3, 2 = 5%]	X
	C_3H_6O [25%]	$C_3H_6O + nC_2H_4O$, $n = 0, 1$ [75, 7 = 82%]	$C_3H_6O + nC_2H_4O$, $n = 0, 1$ [2, 3 = 5%]	X
	CH_3OH [40%]	$CH_3OH + nC_2H_4O$, $n = 0, 1$ [5, 2 = 7%]	X	X
	CH_2O [35%]	X	X	X

[a] Triglyme refers to triethylene glycol dimethyl ether, tetraglyme refers to tetraethylene glycol dimethyl ether. [b] Individual and total percentage of fragment ions in brackets, uncertainty is ±3−5%.

Scheme 1. Proposed Mechanisms for Dissociation of the (Crown Ether + M^+) Complex



There are five types of fragmentation pathways observed for the crown ether complexes, as proposed in Scheme 1 and summarized in Table 1. In fact, all of the mechanisms may proceed through a common type of intermediate, via an opening of the polyether ring and a hydrogen migration. The mechanisms are illustrated to rationalize how a specific neutral loss may occur, but the sequence of steps and final products may vary considerably because the polyethers have multiple identical oxygen coordination sites. The dashed lines in the schemes represent non-specific electrostatic interactions that are possible between any oxygen donor atom of the polyether and the metal center. There are a variety of other reasonable mechanisms and other final products that could be proposed, and we have only chosen to show the ones that best maintain the structural integrity of the polyether skeleton. We would expect that if the polyether skeleton were severely disrupted, then the dissociation behavior observed for the different sizes of polyethers would not differ substantially, a point that is clearly not the case in the present study. Some of the pathways involve formation of products which incorporate no covalent bonds to the metal center, whereas others involve formation of products that incorporate one covalent or ionic bond to the metal ion via loss of radical species and homolytic bond cleavages. As discussed in detail below, the predominant pathways vary for each of the different metal ions, and even more interestingly vary for the different sizes of crown ethers.

Dissociation of (Crown Ether + Cu)$^+$ Complexes. The Cu^+ ion exists in a favorable +1 oxidation state. The (crown ether + Cu^+) complexes dissociate by three pathways, namely elimination of a series of C_2H_4O units (Scheme 1A), elimination of C_2H_2 in conjunction with losses of C_2H_4O units (Scheme 1B), or loss of H_2O in conjunction with C_2H_4O units (a minor set of processes). The mechanisms in Scheme 1 are all initiated with a ring opening and 1,3-hydrogen migration, resulting in an acyclic vinylglycol polyether/metal ion intermediate. For Scheme 1A, a second 1,3-hydrogen migration promotes the loss of $CH_2{=}CHOH$. For Scheme 1B, a different 1,3-hydrogen migration allows the loss of acetylene and results in formation of a glycol/metal ion complex. Each of the (crown ether + Cu^+) complexes dissociate homogeneously, in the sense that the three sizes of crown ethers follow the same three pathways. The first pathway, loss of C_2H_4O units, is increasingly favored as the size of the crown ether increases. It is well-known that protonated crown ethers undergo sequential elimination of C_2H_4O units,[22] so this behavior is not surprising for these closed-shell metal ion complexes. The preference for loss of one, two, or three C_2H_4O units varies with the size of the crown ether, but this variation likely reflects the stabilities of the final product ions and neutrals and does not indicate a noteworthy change in the general mechanism of dissociation. As shown in Schemes 1A and 1B, respectively, the products presumably do not involve formation of covalent bonds to the Cu^+ center, nor does the Cu^+ ion undergo any apparent change in oxidation state.

Dissociation of (Crown Ether + Co^+) and (Crown Ether + Ni^+) Complexes. The monopositive Co^+ and Ni^+ ions are formed in an unfavorable +1 oxidation state. The dissociation behavior of the crown ether complexes involving Co^+ or Ni^+ is quite different from the behavior of the Cu^+ complexes. Not only does each (crown ether + Co^+) and (crown ether + Ni^+) complex dissociate by a unique set of pathways, but many of these pathways are unlike those described above for the (crown ether + Cu^+) complexes. For example, the (12-crown-4 + Co^+) and (12-crown-4 + Ni^+) complexes dissociate by three pathways. One pathway involves simple elimination of multiple units of C_2H_4O, as shown in Scheme 1A. Alternatively, the (12-crown-4 + Co^+) or (12-crown-4 + Ni^+) complexes may eliminate acetylene (Scheme 1B, a minor contribution) or ethylene, which may occur with subsequent or prior losses of C_2H_4O units. The mechanism for the process involving loss of ethylene is proposed to involve formation of the vinyl glycol polyether intermediate shown in Scheme 1 and then another 1,3-hydrogen migration involving transfer of a hydrogen to the terminal vinyl group and elimination of C_2H_4. The product ion would not have any covalent bonds from the polyether to the metal center. These three types of processes involve elimination of closed-shell species (C_2H_4O, C_2H_2, or C_2H_4).

In striking contrast to the CAD behavior of the (12-crown-4 + Co^+) and (12-crown-4 + Ni^+) complexes, the (18-crown-6 + Co^+) and (18-crown-6 + Ni^+) complexes dissociate by none of the three processes described above. Instead, pathways which involve elimination of $C_2H_3O^\bullet$ or $C_2H_3^\bullet$ radicals, in conjunction with losses of C_2H_4O, are predominant. Both of the processes are proposed to start with a 1,3-hydrogen migration and ring opening, resulting in the vinyl glycol/metal ion intermediate shown in Scheme 1. A mechanism for the subsequent loss of $C_2H_3^\bullet$ is proposed in Scheme 1C. A homolytic C−O bond cleavage results in the elimination of a $C_2H_3^\bullet$ neutral. The resulting product incorporates one new covalent bond from a terminal polyether oxygen atom to the metal center. The product can alternatively be considered as one in which the metal ion has attained a favorable +2 oxidation state by donation of an electron to the oxygen atom in order to create an ionic bond between the oxygen atom and metal ion. For the elimination of $C_2H_3O^\bullet$, a different homolytic C−O bond cleavage results in the elimination of a $C_2H_3O^\bullet$ neutral. This product ion has one new covalent (or ionic) bond from a polyether carbon atom to the metal center, and likewise the metal ion may be considered as attaining a +2 oxidation state. The (15-crown-5 + Co^+) and (15-crown-5 + Ni^+) complexes dissociate by *both* series of fragmentation pathways (i.e. similar to the ones proposed for the (18-crown-6 + M^+) and (12-crown-4 + M^+) complexes where M = Ni or Co), and thus generate fragment ions that incorporate zero or one covalent bond to the metal center.

In summary, several clear trends are evident for the crown ether complexes. When a closed-shell metal ion with a favorable oxidation state is involved (i.e. Cu^+), then all of the crown ether complexes follow similar fragmentation pathways which result in closed-shell products that incorporate no covalent bonds to the Cu^+ ion. Only closed-shell neutrals are eliminated. The other two metal ions, Co^+ and Ni^+, are open shell metal ions that promote size-selective dissociation processes of the crown ethers. For the Co^+ and Ni^+ complexes involving the two larger crown ethers (15-crown-5 and 18-crown-6), the products of the dissociation pathways may incorporate one covalent (or ionic type) bond to the metal ion via elimination of neutral radicals, whereas for the 12-crown-4/metal complexes, no covalent bonds are formed and no radical species are lost. The Co^+ and Ni^+ metal ions may undergo a formal change of oxidation state when neutral radicals are lost in the dissociation reaction.

Feasibility of Stepwise Fragmentation. As shown in Table 1, many of the dissociation processes are rationalized as involving sequential units of C_2H_4O. However, it is unclear from the CAD patterns whether the loss of C_2H_4O units occurs separately and stepwise relative to the losses of C_2H_2, C_2H_4, $C_2H_3O^\bullet$, etc., or whether the losses of C_2H_4O are directly incorporated into the neutral losses (i.e. the distinction between the loss of [C_2H_4 + C_2H_4O] vs the loss of $CH_2{=}CHOCH_2CH_3$). In order to probe this point in more detail, MS/MS/MS experiments were performed on several of the polyether/metal complexes. For example, (18-crown-6 + Co^+) was isolated and subjected to a first stage of CAD to promote the loss of $C_2H_3O^\bullet$, then the resulting fragment ion was isolated and subjected to CAD. The (18-crown-6 + Co^+ − $C_2H_3O^\bullet$) ion dissociates by losses of one, two, or three C_2H_4O units (net 40% of the fragment ion current) and by loss of 28 u in conjunction with zero, one, two, or three C_2H_4O units (60% of the fragment ion current). This MS/MS/MS result supports the idea that the losses of C_2H_4O units may occur as independent steps after the losses of the primary organic neutrals. An analogous result is observed for the MS/MS/MS experiment performed for (12-crown-4 + Co^+). This complex fragments by loss of C_2H_4, and then the (12-crown-4 + Co^+ − C_2H_4) ion dissociates by loss of one or two C_2H_4O units. Therefore, the loss of C_2H_4O can be considered as separate steps. These MS/MS/MS experiments support the feasibility of stepwise losses.

MS/MS and MS/MS/MS results also give more insight into the nature of the fragment ions listed in Table 1. For example, the series of losses assigned as (C_2H_4 + nC_2H_4O) from the (18-crown-6 + Co^+ − $C_2H_3O^\bullet$) ion yields fragment ions that have the same mass-to-charge ratios as the series of fragments assigned as losses of nC_2H_4O from the (18-crown-6 + Co^+ − $C_2H_3^\bullet$) ion. This result suggests that the type of product ion identified with the loss of $C_2H_3O^\bullet$ may convert to the type of product ion shown in Scheme 1C by loss of C_2H_4.

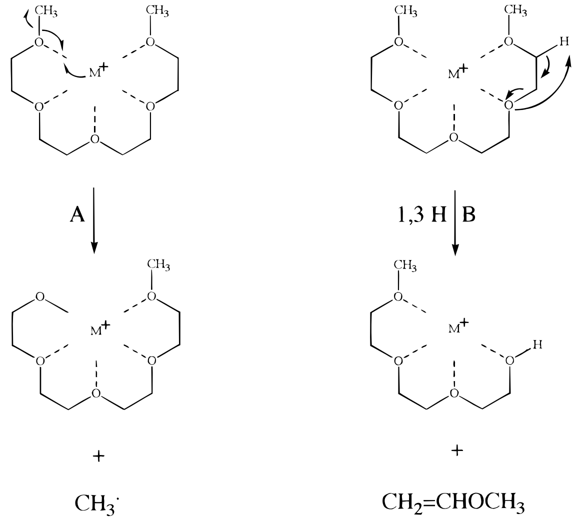
Rationalization of the Size-Dependent Collisionally Activated Dissociation Behavior. There are two concepts which must be examined in order to rationalize the observed “size-dependent” behavior of the crown ether/metal ion complexes. As a starting point, one can assume that the C−C, C−H, and C−O bonds in all of the crown ethers have similar energies, although the C−C−O and C−O−C bond angles in 12-crown-4 are slightly more strained due to the smaller ring size. First, the structures of the initial metal/crown ether complexes formed during the laser desorption/ion−molecule reaction period may be substantially different for 18-crown-6 and 12-crown-4. For instance, during the complexation process the metal ion may insert into the C−C or C−O bonds of 18-crown-6, whereas it may remain coordinated electrostatically to the oxygen atoms in 12-crown-4. These dramatically different precursor structures could thus account for the resulting differences in the CAD patterns. Based on the fact that the bond energies within the various polyethers are similar and the dipole moments of the polyethers are similar, the interaction energies of the metal ion/polyether complexes probably are not sufficiently different to cause C−C or C−O bond activation for one polyether size and not another. Thus, the possibility that the initial polyether/metal ion structures are different for the various sizes of crown ethers does not seem like the strongest rationalization of the observed size-dependent CAD behavior.

Alternatively, the precursor structures may be similar for all of the crown ether/metal complexes (i.e. electrostatically coordinated complexes), but the energetics and thus kinetics of the dissociation pathways may differ greatly for the complexes containing 18-crown-6 vs 15-crown-5 vs 12-crown-4. The factors which underlie the second rationalization include the interaction energy between the metal ion and crown ether, the geometry of the interaction between the metal ion and ether, the conformational flexibility of the complex and likewise the mobility of any parts of the crown ether that are not coordinated to the metal ion, and the number and strength of the binding interactions between the metal ion and crown ether.

The larger crown ethers (18-crown-6 and 15-crown-5) have more flexible skeletons, and therefore may allow more optimal geometries for the type of rearrangement shown in the Scheme 1C and for coordination of the metal ion. In contrast, 12-crown-4 is relatively rigid, with the four oxygen coordination sites situated at corners of the framework. The binding interactions between the 12-crown-4 molecule and the metal ion will therefore be more strained, which presumably could lead to weaker coordinating bonds. The larger crown ethers also have more oxygen binding sites which increase the total interaction energies of the metal/polyether complexes and additionally allow the metal ion to coordinate some of the oxygen atoms while other parts of the crown ether remain free to “swing” in the complex. For example, the critical energies and entropic factors for the fragmentation pathways of the 18-crown-6/metal complexes may be sufficiently lower than those for the corresponding 12-crown-4/metal complexes, such that the radical elimination pathways are kinetically favorable for the activated 18-crown-6/metal complexes but not kinetically competitive for the energized 12-crown-4/metal complexes. To unravel the influence of some of these factors, the dissociation behavior of metal complexes containing glymes (i.e. polyglycol dimethyl ether compounds), open chain analogs of crown ethers, was examined. An acyclic polyether presumably would allow more optimal binding interactions with the metal ions, perhaps also allowing more mobility for some remote skeletal portion of the glymes, and alleviate strain in the complexes and transition states of the activated metal complexes. If the metal complexes containing various sizes of glymes dissociate homogeneously or show size-dependent fragmentation pathways, then the reasons for the unusual behavior of the crown ethers may be more fully elucidated.

Dissociation of Metal Ion/Glyme Complexes. Glymes are the acyclic analogs of crown ethers, and thus they have structural properties that are similar to the crown ethers yet with much greater flexibilities because of the open chain. Metal complexes incorporating ethylene glycol dimethyl ether (monoglyme), diethylene glycol dimethyl ether (diglyme), triethylene glycol dimethyl ether (triglyme), and tetraethylene glycol dimethyl ether (tetraglyme) were generated from ion−molecule reactions between laser-desorbed metal ions and neutral glymes, then these complexes were subjected to collisionally activated dissociation. The results are summarized in Table 2. The Cu^+/glyme complexes dissociate primarily by two pathways: elimination of methanol or elimination of C_3H_6O, both in conjunction with losses of C_2H_4O units. These pathways involve losses of closed-shell neutrals and result in no change in the oxidation state of the Cu^+ ion. A mechanism for the elimination of C_3H_6O is proposed in Scheme 2B. The loss of methanol may be rationalized as involving extraction of a proton from an ethylene unit by one terminal oxygen atom. The product ions incorporate only electrostatic bonds to the Cu^+ ion. The diglyme, triglyme, and tetraglyme complexes behave similarly during dissociation, producing the same types and distribution of fragments. The smallest monoglyme complex dissociates by several other pathways, as shown in Table 2, including elimination of CuH and $CuOCH_3$. In general terms, the characteristics of the glyme dissociation processes are similar to the characteristics of the fragmentation processes noted for the crown ether/Cu^+ complexes.

Scheme 2. Proposed Mechanisms for Dissociation of the (Glyme + M^+) Complex



The Co^+ complexes of diglyme, triglyme, and tetraglyme each dissociate by four types of pathways. The two most predominant routes involve elimination of $CH_3^{\bullet}$ in conjunction with C_2H_4O units (see Scheme 2A), or loss of C_3H_6O in conjunction with C_2H_4O units (as in Scheme 2B). The first series results in formation of a product with one covalent bond between the Co^+ ion and one terminal oxygen atom of the glyme and involves a radical elimination. This type of process could involve a change in the oxidation state of the metal ion if the new bond were an ionic one. The second major process involves elimination of a closed-shell neutral, and presumably involves a product ion that incorporates only electrostatic bonds. Other minor pathways include loss of CH_4 or CH_2O. The interesting point is that the notable methyl radical elimination pathways occur for the diglyme, triglyme, and tetraglyme complexes. Triglyme is the acyclic analog of 12-crown-4, yet the (triglyme + Co^+) complex undergoes the same types of radical elimination pathways that are predominant for the larger (tetraglyme + Co^+) complex. Even the smaller diglyme complex follows the same methyl radical elimination pathways. This result suggests that the increased flexibility of the acyclic

Table 3. CAD Spectra of Model Complexes: Series of Neutral Losses[a]

	$(L + Cu^+)$	$(L + Co^+)$	$(L + Ni^+)$
diethylene glycol vinyl ether	$H_2O + nC_2H_4O$, $n = 0, 1$ [30, 35 = 65%]	X	$H_2O + nC_2H_4O$, $n = 0, 1$ [5, 2 = 7%]
	$C_2H_2 + nC_2H_4O$, $n = 0, 1, 2$ [3, 6, 3 = 12%]	$C_2H_4 + nC_2H_4O$, $n = 0, 1$ [20, 25 = 45%]	$C_2H_4 + nC_2H_4O$, $n = 0, 1$ [15, 25 = 40%]
	X	$C_2H_2 + nC_2H_4O$, $n = 0, 1$ [10, 5 = 15%]	$C_2H_2 + nC_2H_4O$, $n = 0, 1, 2$ [3, 35, 2= 40%]
	nC_2H_4O, $n = 1, 2$ [12, 5 = 17%]	nC_2H_4O, $n = 1, 2$ [3, 5 = 8%]	nC_2H_4O, $n = 1, 2$ [5, 8 = 13%]
	87^+ [6%]	C_3H_6O [32%]	
triethylene glycol	nC_2H_4O, $n = 1, 2$ [60, 10 = 70%]	NA	NA
	$H_2O + nC_2H_4O$, $n = 0, 1$ [25, 5 = 30%]		
tetraethylene glycol	nC_2H_4O, $n = 1, 2$ [50, 20 = 70%]	NA	NA
	$H_2O + nC_2H_4O$, $n = 0, 1$ [20, 10 = 30%]		

[a] Individual and total percentage of fragment ions in brackets, uncertainty is ±3−5%.

polyethers, even for the smaller glymes, enhances their ability to coordinate the metal ion and promote the most favorable fragmentation pathways that result in stable products that have a covalent or ionic bond to the metal ion.

In contrast, the $(\text{monoglyme} + Co^+)$ complex does not eliminate $CH_3^{\bullet}$ radical at all, and a new dissociation pathway is observed: loss of C_2H_6O in conjunction with zero or one unit of C_2H_4O. The other three dissociation pathways, including elimination of CH_2O, CH_4, and C_3H_6O, are all active for the $(\text{monoglyme} + Co^+)$ complex, as already noted for the diglyme, triglyme, and diglyme complexes. Thus, it is not until the complex is composed of the smallest glyme, which has only two oxygen binding sites, that the radical elimination pathways are quenched. This last result supports the idea that the flexibility of the ether and the ability of part of the ether skeleton to swing with some mobility is the factor which determines whether or not the radical elimination pathways are accessible to the activated metal complexes. For monoglyme, it is likely that both oxygen atoms remain coordinated to the metal ion with some ring strain in the complex, so one tail of the ether molecule is not able to rotate close to the metal center for activation of homolytic C−O bond cleavage and subsequent expulsion of $CH_3^{\bullet}$ (as proposed in Scheme 2A). This lack of freedom in the mobility of the monoglyme skeleton and its small number of oxygen coordination sites presumably parallels the same limitations of the 12-crown-4 system, which has more oxygen sites but greater rigidity. Therefore, we speculate that geometric restrictions play an enormous role in influencing the dissociation pathways of the polyether/metal complexes.

The Ni^+ complexes of triglyme and tetraglyme dissociate predominantly (>90% fragment ion intensity) by loss of a $CH_3^{\bullet}$ radical, which may occur to a minor extent in conjunction with elimination of one or two C_2H_4O units (see Scheme 2). For the diglyme/Ni^+ complex, this pathway is less favorable, and the process is not observed at all for the monoglyme/Ni^+ complex. For the two smaller glyme complexes, the loss of methanol is observed as an alternative pathway. The important observation is that the methyl radical dissociation process occurs for the diglyme, triglyme, and tetraglyme complexes, but not for the monoglyme complex. This result reinforces the proposal that only the smallest monoglyme lacks the flexibility to engage in the radical elimination pathways, unlike the CAD behavior of the complexes involving the crown ethers which showed much more substantial size dependences.

Collisionally Activated Dissociation of Model Complexes: Support for CAD Mechanisms. To offer support for some of the mechanisms shown in Schemes 1 and 2, transition metal complexes containing model compounds were generated and subjected to collisionally activated dissociation. The models included diethylene glycol vinyl ether, tetraethylene glycol, and triethylene glycol. The first one was chosen to represent the ring-opened polyether intermediate shown in Scheme 1, whereas the two glycols were chosen to represent the acyclic products shown in Scheme 1B. The CAD results are summarized in Table 3. The $(\text{tetraethylene glycol} + Cu^+)$ and $(\text{triethylene glycol} + Cu^+)$ complexes dissociate in identical ways, by loss of a series of C_2H_4O units and by the loss of water in conjunction with C_2H_4O units. For the relevant comparison, the product ion shown in Scheme 1B consists of a glycol bound to a Cu^+ ion, and thus the CAD pattern of this product ion from the crown ether complexes should presumably match that observed for the model glycol/Cu^+ complexes. The product ion $(\text{15-crown-5} + Cu^+ - C_2H_2 - 2C_2H_4O)$ at m/z 169 was isolated and collisionally activated. The $(\text{15-crown-5} + Cu^+ - C_2H_2 - 2C_2H_4O)$ ion dissociated by loss of one or two C_2H_4O units (50% of fragment ion current) and loss of water with zero, one, or two C_2H_4O units (total of 50% of fragment ion current). Based on this comparison, the fragmentation pattern of the model glycol complexes (Table 3) supports the product sequence shown in Scheme 1B.

The diethylene glycol vinyl ether also proves to be an informative model because this type of structure is shown as an intermediate in Scheme 1. The $(\text{diethylene glycol vinyl ether} + Cu^+)$ complex dissociates predominantly by loss of C_2H_4O units, C_2H_2 in conjunction with C_2H_4O units, and to a lesser extent by loss of H_2O in conjunction with C_2H_4O units (Table 3). These three pathways qualitatively agree with the CAD behavior observed for dissociation of the $(\text{12-crown-4} + Cu^+)$ complex summarized in Table 1.

The $(\text{diethylene glycol vinyl ether} + Co^+)$ complex does not undergo dehydration upon CAD, but instead primarily dissociates by loss of C_2H_4 or C_2H_2 in conjunction with C_2H_4O units. These pathways duplicate the ones observed for dissociation of the $(\text{12-crown-4} + Co^+)$ complex. No radicals are eliminated from the $(\text{diethylene glycol vinyl ether} + Co^+)$ complex, and thus this model complex does not engage in the radical dissociation pathways noted for the metal complexes of the larger crown ethers or glymes. The CAD spectrum of the $(\text{diethylene glycol vinyl ether} + Ni^+)$ complex dissociates by loss of water, C_2H_2, or C_2H_4 in conjunction with C_2H_4O units. Three of these pathways are also dominant for dissociation of the $(\text{12-crown-4} + Ni^+)$ complex. However, the dehydration pathway is not observed for any of the crown ether/metal ion complexes. Since the dehydration pathway only represented 5% of the total fragment ion current for $(\text{diethylene glycol vinyl ether} + Ni^+)$, it is not surprising that this minor dissociation route might not be observed for larger crown ether complexes which have somewhat different dissociation kinetics. No radical losses are observed in the CAD spectrum of $(\text{diethylene glycol vinyl ether} + Ni^+)$, presumably because its low number of oxygen coordination sites does not allow the optimum geometry for the radical losses.

In summary, the models offer support for the viability of the intermediates shown in Scheme 1, in which the crown ethers may undergo ring opening with hydrogen migrations to form glycol or vinyl glycol type structures. Although positive support of the radical elimination mechanism shown in Scheme 1 is not obtained from the diethylene glycol vinyl ether model, it is interesting to note that this small acyclic model does *not* undergo radical eliminations. Thus, this results suggests that even if the (12-crown-4 + Ni^+) or (12-crown-4 + Co^+) complex successfully underwent ring opening to rearrange to a vinyl glycol intermediate, these ions would not necessarily have the appropriate flexibility and number of oxygen atoms to allow part of the polyether to swing freely and thus engage in the radical-type eliminations shown in Scheme 1C.

Conclusions

Our results support an example of "size-dependent" dissociation behavior of polyether/metal ion complexes that depends on the flexibility of the polyether and its number of coordination sites. The open-shell transition metal ions (Co^+, Ni^+) form complexes with 18-crown-6 that dissociate by pathways that involve elimination of radical neutrals. The products are stabilized by the presence of one coordinate covalent bond between the metal ion and the polyether or may be considered as structures in which the metal ion has attained a more favorable +2 oxidation state with an ionic bond from the polyether to the metal ion. In contrast, the (12-crown-4 + Ni^+) and (12-crown-4 + Co^+) complexes dissociate by losses of C_2H_2 or C_2H_4 in conjunction with C_2H_4O units, leading to products that involve no covalent bonds to the metal ion. The complexes involving 15-crown-5 dissociate by an "intermediate" behavior, because a combination of fragmentation pathways that lead to both types of products are accessed. In general, the larger crown ethers (i.e. 18-crown-6 and 15-crown-5) have an enhanced ability to promote dissociation to stable products with formation of covalent bonds between the metal ion and crown oxygen atoms. The basis for the difference in fragmentation behavior may be linked to the greater floppiness of the larger crown ethers, which improves their coordination geometries and allows more flexibility in the rearrangement mechanisms. Moreover, the larger crown ethers have more oxygen atoms which means that some of the oxygen atoms may be coordinated to the metal center, while others are free to participate in remote rearrangement processes. The impact of the skeletal flexibility on the dissociation behavior of the complexes is underscored by comparison of the CAD patterns of the glyme/metal ion complexes. For diglyme, triglyme, and tetraglyme, the metal ion complexes dissociate in similar ways, suggesting that all of these polyethers are sufficiently floppy to accommodate the radical elimination pathways. These pathways lead to stable product ions in which the metal ion is covalently (or ionically) bonded to an oxygen atom of the polyether and may attain a more favorable +2 oxidation state.

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