Gas-Phase Complexation of Monopositive Alkaline Earth Metal Ions with Polyethers: Comparison with Alkali Metal Ion and Aluminum Ion Complexations

Hui-Fen Wu and Jennifer S. Brodbelt*

Contribution from the Department of Chemistry and Biochemistry, University of Texas, Austin, Texas 78712-1167

Received May 13, 1993. Revised Manuscript Received May 3, 1994®

Abstract: The gas-phase reactions of the monopositive alkaline earth metal ions (Ca^+ and Mg^+) with a variety of crown ethers and their acyclic analogues have been studied by laser desorption/quadrupole ion trap mass spectrometry. The initial monopositive Mg^+ and Ca^+ ions were generated directly from laser desorption of a metal foil or salt and then reacted with a variety of neutral polyethers. Collisional activated dissociation (CAD) techniques were employed to evaluate the structures of these metal/polyether adducts. The reactions of these initially monopositive ions (M^+) are of special interest because the reactions with crown ethers or glymes involve incorporation of "OH", corresponding to formation of $(L + (M^{2+}OH^-))^+$ ions, in which the metal ions attain their favored oxidation states. The alkaline earth metal ions apparently react with H_2O, which may be loosely bound to a polyether ligand, by donation of the lone s electron to the oxygen atom in conjunction with elimination of $H^\bullet$. The polyether ligand then solvates the $(M^{2+}OH^-)$ species by formation of multiple electrostatic bonds between the ether oxygen atoms and the metal center. The reactions of the glycols with the metal ions are somewhat different in that the resulting products may be assigned as $(L + (M^{2+}OH^-) - H_2O)^+$, from unstable $(L + (M^{2+}OH^-))^+$ complexes that spontaneously dehydrate, or as $(L + M^{2+} - H^\bullet)^+$, in which the initial Mg^+ ion reacts directly with a hydroxyl terminus of the glycol molecule. Ligand-exchange methods used to measure the relative order of $(Mg^{2+}OH^-)$ binding energies for the polyethers indicate that the relative binding energy increases with the size of the polyether. A comparison of the results with those for reactions of alkali metal ions and aluminum ions with polyethers in the gas phase reveals further insight into the nature of the binding interactions.

Introduction

The binding interactions and reactions of metal atoms with organic ligands have generated increasing interest both in solution and in the gas phase over the past decade.[1-3] Depending on the electronic nature of the metal center, different types of reactions are promoted. For example, it is well-recognized that transition metals may insert into covalent bonds of organic molecules, whereas alkali and alkaline earth metals interact through electrostatic interactions. Of on-going interest is the determination of the structures of the organometallic complexes and the chemical factors which influence their formation, with respect to the nature of the metal center and the reactive sites in the organic ligand. More recently, the alkaline earth metals have been the subject of many studies[4-30] not only due to their importance in biochemical systems[4-7] but also because of the relevant comparison of the behaviors of these metals to those of their d-orbital-rich transition metal neighbors in the periodic table.

Polyethers have the special property of forming stable complexes with alkali and alkaline earth metal ions in solution.[8,9] The bonding of the complexes involves ion–dipole interactions between the cation and the negative dipoles of the oxygen atoms of the polyether backbone.[10] In studies of host–guest complexation involving macrocyclic model hosts,[11-15] there are numerous parameters which define the ion–polyether interactions, such as the relative cation to ligand cavity size ratio, number of ligand binding sites, diameter of the cation, substitution on the macrocyclic ring(s), solvent effects, and macrocyclic effects. For example, it is generally accepted that crown ethers will optimally bind cations of appropriate size to maximize interactions within the cavity, termed the hole–size relationship. Moreover, macrocyclic effects[16-19] are evident when cyclic crown ethers show different complexation parameters compared to those of their acyclic polyether analogues—glymes (polyethylene glycol dimethyl ethers) and glycols. Thus, many factors contribute to the binding properties of the model hosts, stimulating many fundamental studies of complexation.[20-26]

• Abstract published in *Advance ACS Abstracts,* June 15, 1994.

(1) *Organometallic Chemistry*; Abel, E. W., Ed.; Royal Society of Chemistry: Cambridge, 1992; Vol. 21.

(2) *Advances Organometallic Chemistry*; Stone, F. G. A., West, R., Eds.; Academic Press: San Diego, CA, 1992; Vol 34.

(3) Eller, K.; Schwarz, H. *Chem. Rev.* **1991**, *91*, 1121.

(4) Fra'usto da Silva, J. J. R.; Williams, R. J. P. *The Biological Chemistry of the Elements*;Clarendon Press: Oxford, U.K., 1991.

(5) Hughes, M. N. *The Inorganic Chemistry of Biological Processes*, 2nd ed.; John Wiley & Sons: New York, 1972; pp 51–88, 257–295.

(6) Spiro, T. G. In *Inorganic Biochemistry*; Eichhorn, G. L., Ed.; Elsevier Scientific: Amsterdam, 1973; pp 549–881.

(7) O'Sullivan, W. J. In *Inorganic Biochemistry*, Eichhorn, G. L., Ed.; Elsevier Scientific: Amsterdam, 1973; pp 582–607.

(8) Pederson, C. J. *Science* **1988**, *241*, 536.

(9) Christensen, J. J.; Eatough, D. J.; Izatt, R. M. *Chem. Rev.* **1974**, *74*, 351.

(10) Pederson, C. J. *J. Am. Chem. Soc.* **1967**, *89*, 2495.

(11) Pederson, C. J. *J. Am. Chem. Soc.* **1967**, *89*, 7017.

(12) Cram, D. *Science* **1988**, *240*, 760.

(13) Lehn, J. M. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 89.

(14) Sutherland, I. *Chem. Soc. Rev.* **1986**, *15*, 63.

(15) Vogtle, F., Weber, E., Eds. *Host Guest Complex Chemistry: Macrocycles: Synthesis, Structure, Applications*; Springer-Verlag: Berlin, 1985.

(16) Cabbiness, D. K.; Margerum, D. W. *J. Am. Chem. Soc.* **1969**, *91*, 6540.

(17) Hinz, F. P.; Margerum, D. W. *Inorg. Chem.* **1974**, *13*, 2941.

(18) Cram, D. J. In *Applications of Biochemical Systems in Organic Chemistry, Techniques of Chemistry*; Jones, J. B., Sih, C. J., Perlman, D., Eds.; John Wiley & Sons: New York, 1976; Vol. 10, Part II.

(19) Izatt, R. M., Christensen, J. J., Eds. *Synthetic Multidentate Macrocyclic Compounds*; Academic Press: New York, 1978.

(20) Cram, D. *Acc. Chem. Res.* **1978**, *11*, 8.

(21) Haward, R. *Chem. Soc. Rev.* **1983**, *12*, 285.

(22) Graf, E.; Lehn, J. *J. Am. Chem. Soc.* **1976**, *98*, 6403.

(23) Farnham, W.; Roe, D.; Dixon, D.; Calabrese, J.; Harlow, R. *J. Am. Chem. Soc.* **1990**, *112*, 7707.

(24) Dietrich, B.; Hosseini, M.; Lehn, J.; Sessions, R. *J. Am. Chem. Soc.* **1981**, *103*, 1282.

(25) De Boer, J.; Reinhoudt, D.; Harkema, S.; Van Hummel, G.; De Jong, F. *J. Am. Chem. Soc.* **1982**, *104*, 4073.

(26) Popov, A. *Pure Appl. Chem.* **1979**, *51*, 101.

0002-7863/94/1516-6418$04.50/0

Several investigations of the interactions of alkaline earth metal ions and polyethers in solution have been discussed.[27-33] A common feature of the alkaline earth metal ions in aqueous solution is that their hydration directly competes with complexation reactions.[32] With a reduction in the size of the metal cation, the electronic charge density increases and, thus, hydration becomes much more favored than complexation. This factor has been used to explain the low complexing powers of Mg^{2+} and Ca^{2+}, which have the greatest tendencies to hydrate.[33]

There have been several studies of alkaline earth metal binding in the gas phase. Gas-phase reactions of Mg^+ ions with small organic molecules have been studied in a Fourier Transform ion cyclotron resonance mass spectrometer (FTICR) by Freiser et al.[34] Collision-induced dissociation, photodissociation, and equilibrium measurements were done to determine the relative and absolute binding energies of Mg^+ to the organic molecules. The binding energies ranged from 61 to 67 kcal/mol for small alcohols and ketones.[34a] The binding energy of Mg^+–OH was determined to be 75 ± 4 kcal/mol from photodissociation experiments.[34b] The results were also compared with some other acidic cations such as H^+, Cu^+, Mn^+, and Al^+. It was determined that Mg^+ ions act as softer acids than H^+ and Al^+ ions but are comparable to Mn^+ and Cu^+ ions. In a more recent study, Duncan et al. estimated the dissociation energy of $Mg^+–H_2O$ as 24.3 kcal/mol from photodissociation spectroscopic measurements in a time of flight instrument.[35] The reactions of Mg^+ with alcohols and organic halides have also been studied by Staley et al.,[36] by using ICR mass spectrometry. Mg^+ ions reacted with alkyl chlorides to produce Mg^+–alkene and $Mg(RCl)_2^+$ products. Mg^+ ions also induced the dehydration of alcohols (ROH) to form intermediate $Mg(H_2O)^+$ ions, which then underwent secondary reactions with ROH to produce $Mg(ROH)^+$ and $Mg(ROH)_2^+$ products. The relative order of Mg^+ binding energies for a series of alcohols was also determined, and as expected, the metal binding energy generally increased with the size of the alcohol. Most recently, the kinetic energy dependences of reactions of monopositive alkaline earth ions with H_2 have been reported,[37] in which differences in reactivity were attributed to variations in the empty orbitals of the metal ions. For example, the 3*p* orbitals of Mg^+ ions were found to be too high in energy to participate in bonding, unlike the 3d orbitals of Ca^+. Reactions of monopositive rare earth metals ions, Sc^+, Y^+, and Lu^+, with methanol resulted in formation of dimethoxide metal ions and metal hydroxide ions.[38] A variety of other products were proposed to result from metal ion insertion into C–O or O–H bonds.

Several reports have specifically described gas-phase analytical applications involving the use of alkaline earth metal ions, such as studies of their interactions with fatty acids,[39] peptides,[40-43] and prostaglandins,[44] by mass spectrometry. For example, the collision-activated dissociation (CAD) spectra acquired for the (L − H + metal)$^+$ ions of peptide/alkaline earth metal ion complexes with a tandem mass spectrometer proved useful for providing peptide sequence information.[40-43] Depending on the size of the alkaline earth metal ion, the favored coordination geometry of the cation changes and thus the nature of the fragmentation patterns of the peptide complexes vary. Similarly, the structural analysis of fatty acids was performed by collisional activation of (L − H + metal)$^+$ ions,[39] and fast atom bombardment MS/MS was used to reveal the structures of prostaglandins.[44] These gas-phase mass spectrometric studies have demonstrated the potential of alkaline earth metals for assisting in the characterization of molecules of analytical relevance.

The gas-phase study presented herein describes the investigation of the types of complexes formed from reactions of monopositive alkaline earth metal ions (Ca^+ and Mg^+) with a variety of crown ethers and acyclic analogues. The electronic properties of Mg^+ and Ca^+ cations differ from those of their alkali metal ion counterparts because they have ns^1 instead of np^6 configurations, so different types of complexation behaviors are expected. For example, some covalent-type binding between Mg^+ and n-donor bases may occur due to the delocalization of electrons from the organic ligand to the half-filled 3s orbital of Mg^+. The nature of alkali metal ion complexation with polyethers has already been extensively studied in the gas phase,[45-48] and it was shown that those complexes are loosely bound and dissociate readily by simple decomplexation, rather than by induction of any polyether skeletal cleavages.

In this study, laser desorption (LD) was employed to generate monopositive Mg^+ and Ca^+ ions in a quadrupole ion trap mass spectrometer, and these metal ions were allowed to interact with neutral polyethers. The polyethers consisted of an array of crown ethers and their acyclic analogues: polyethylene glycols (glycols) and polyethylene glycol dimethyl ethers (glymes). Collisionally activated dissociation (CAD) techniques were used to investigate the structures of the metal/polyether complexes. In addition, ligand-exchange methods were performed to establish the relative order of ligand binding energies for the polyethers. A comparison of the gas-phase complexation reactions is made to prior results obtained for alkali metal ion/polyether complexes in the gas phase.[45-48] Due to the unexpected finding that Ca^+ and Mg^+ ions promote complexation with the polyethers in conjunction with "OH" attachment in order to attain their favored oxidation states, the reactions of monopositive Al^+ ions, another metal with empty p orbitals, filled s orbitals, and an unnatural valence state, were examined.

Experimental Section

All experiments were carried out in a Finnigan quadrupole ion trap mass spectrometer (ITMS).[49] It was equipped with a probe-mounted fiber optic laser desorption assembly.[50] The output of a Nd:YAG laser which was operated in the Q-switch mode at 1064 nm (a power density of about 2×10^7 W/cm^2) was focused into a fiber optic that was directed at a piece of magnesium ribbon, aluminum foil, or a film of calcium bromide. The metal target and fiber optic were positioned inside the ion trap electrode volume through a hole in the center of the ring electrode.

The monopositive magnesium, aluminum, or calcium ions were formed in the ion trap, isolated by application of a combination of DC and RF

---

(27) Gokel, G. W.; Goli, D. M.; Minganti, C.; Echegoyen, L. *J. Am. Chem. Soc.* **1983**, *105*, 6786.

(28) Lamb, J. D.; Izatt, R. M.; Swain, C. S.; Christensen, J. J. *J. Am. Chem. Soc.* **1980**, *102*, 476.

(29) Izatt, R. M.; Bradshaw, J. S.; Steven, A. N.; Lamb, J. D.; Christensen, J. J. *Chem. Rev.* **1985**, *85*, 271.

(30) Frensdorf, H. K. *J. Am. Chem. Soc.* **1971**, *93*, 600.

(31) Haymore, B. L.; Lamb, J. D.; Izatt, R. M.; Christensen, J. J. *Inorg. Chem.* **1982**, *21*, 1598.

(32) Pedersen, C. J.; Frensdorff, H. K. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 16.

(33) Pedersen, C. J. *J. Am. Chem. Soc.* **1967**, *89*, 7017.

(34) (a) Operti, L.; Tews, E. C.; Freiser, B. S. *J. Am. Chem. Soc* **1988**, *110*, 384. (b) Operti, L.; Tews, E. C.; MacMahon, T. J.; Freiser, B. S. *J. Am. Chem. Soc.* **1989**, *111*, 9152.

(35) Willey, K. F.; Yeh, C. S.; Robbins, D. L.; Pilgrim, J. S.; Duncan, M. A. *J. Chem. Phys.* **1992**, *97*, 886.

(36) Uppal, J. S.; Staley, R. H. *J. Am. Chem. Soc.* **1982**, *104*, 1229.

(37) Dalleska, N. F.; Crellin, K. C.; Armentrout, P. B.; *J. Phys. Chem.* **1993**, *97*, 3123.

(38) Azzaro, M.; Breton, S.; Decouzon, M.; Geribaldi, S. *Int. J. Mass Spectrom. Ion Processes* **1993**, *128*, 1.

(39) Davoli, E.; Gross, M. L. *J. Am. Soc. Mass Spectrom* **1990**, *1*, 320.

(40) Teesch, L. M.; Adams, J. *J. Am. Chem. Soc.* **1990**, *112*, 4110.

(41) Zhao, H.; Reiter, A.; Teesch, L. M.; Adams, J. *J. Am. Chem. Soc.* **1993**, *115*, 2865.

(42) Hu, P.; Gross, M. L. *J. Am. Chem. Soc.* **1992**, *114*, 9153.

(43) Hu, P.; Gross, M. L. *J. Am. Chem. Soc.* **1992**, *114*, 9161.

(44) Zirrolli, J. A.; Davoli, E.; Bettazzoli, L.; Gross, M. L.; Murphy, R. C. *J. Am. Soc. Mass Spectrom.* **1990**, *1*, 325.

(45) Zhang, H.; Chu, I.-H.; Leming, S.; Dearden, D. *J. Am. Chem. Soc.* **1991**, *113*, 7415.

(46) Maleknia, S.; Brodbelt, J. *J. Am. Chem. Soc.* **1992**, *114*, 4295.

(47) Liou, C.-C.; Brodbelt, J. *J. Am. Soc. Mass Spectrom.* **1992**, *3*, 543.

(48) Chu, I. H.; Zhang, H.; Dearden, D. V. *J. Am. Chem. Soc.* **1993**, *115*, 5736.

(49) March, R. E.; Hughes, R. J.; Todd, J. F. J. *Quadrupole Ion Storage Mass Spectrometry*; Wiley: New York, 1989.

(50) McIntosh, A.; Donovan, T.; Brodbelt, J. *Anal. Chem.* **1992**, *64*, 2079.

voltages to the ring electrode,[51] and then reacted with neutral polyethers for a period of 0–100 ms. All compounds were admitted through a leak valve or by a heated solids probe. Typical sample pressure was nominally (3–5) × 10^{-6} Torr. Pressures of the less volatile polyethers were estimated from comparisons of total electron ionization signal intensity vs nominal ionization gauge pressure reading and from examination of proton transfer rates at different nominal ionization gauge pressures. These methods are described in detail in Dearden's recent work.[48] The helium buffer gas pressure was maintain at 1 mTorr. In one series of experiments, water vapor was added to 1 × 10^{-6} Torr as a controlled source of H_2O.

In some cases, broad-band dc isolation procedures were used to enhance the resolution of mass spectral regions marred by space–charge effects. Slight space–charge distortion of peak shapes is common in laser desorption experiments because it is difficult to control the laser power density on a shot-to-shot basis. Relative percentages of product ions are reported with moderately large standard deviations due to the inadequate shot-to-shot reproducibility of the laser pulse which altered the number of metal ions and other species formed and the transient pressure in the trap and, thus, limited the reproducibility of the product spectra. For this same reason, reactions could not be precisely monitored as a function of time. The values reported in Tables 1, 2, and 6 represent the products formed during a 150-ms trapping time.

The CAD spectra of each metal complex was obtained by dc isolation of the ion of interest followed by application of an ac voltage (500–1000 mV_{p-p}) across the end-cap electrodes at a q_z value of 0.35 for 5–10 ms. The frequency of the supplementary voltage was typically about 139 000 Hz.

Ligand-exchange techniques[36] were used to measure the relative metal ion affinities of the polyethers. Ligand-exchange reactions have been used previously to bracket relative gas-phase basicities of polyethers in a quadrupole ion trap[52] and thus far have proven reliable for distinguishing differences in thermochemical values. Thus, despite the large rf field applied to the ion trap which continuously accelerates ions into low-energy collisions with helium, relative differences in ion affinities apparently can be extracted if the ion transfer reactions are monitored in both directions. Moreover, since all the ligands and metal ions are studied under similar conditions in the ion trap, it is expected that the slightly hot trapping environment will tend to affect all complexes similarly.

All polyethers were purchased from Aldrich Chemical Co. (Milwaukee, MN) except 21-crown-7, which was obtained from Parish Chemicals (Orem, UT). The magnesium ribbon was obtained from Spectrum Chemical Co. (Gardena, CA).

Results and Discussion

I. Formation of Mg^+ and Ca^+/Polyether Complexes. In order to compare the reactions of Mg^+ and Ca^+ ions with polyethers, each polyether (L) was admitted into the ion trap, and ion–molecule reactions between selectively-isolated monopositive Mg^+ or Ca^+ ions and the polyethers were examined. Typical product spectra are shown in Figures 1 and 2 for 12-crown-4 and tetraethylene glycol with Mg^+ and in Figures 3 and 4 for reactions of Ca^+ ions with 12-crown-4 and triethylene glycol, respectively. Results of the reactions of Mg^+ and Ca^+ with other polyethers are summarized in Tables 1 and 2, respectively. The variation of relative product abundances as a function of storage time is an inherent condition in all ion-trapping devices, and thus, the reaction time chosen to represent the average product ion population is 150 ms. The product ions that are consistently observed are the ones listed; however, at very high pressures of the polyether, with extremely long reaction times, or at very high laser power densities, some other product ions of lower abundance are formed. Typically, these products arise at mass-to-charge ratios that suggest they consist of various multiple fragmented portions of the polyether bound to a single metal ion. For example, two or three additional C_2H_4O units and one whole polyether molecule may be attached to a single metal ion. The exact formation process for these ions is unclear, but it seems reasonable that they result from spontaneous fragmentation of metal-cationized polyether dimer species.

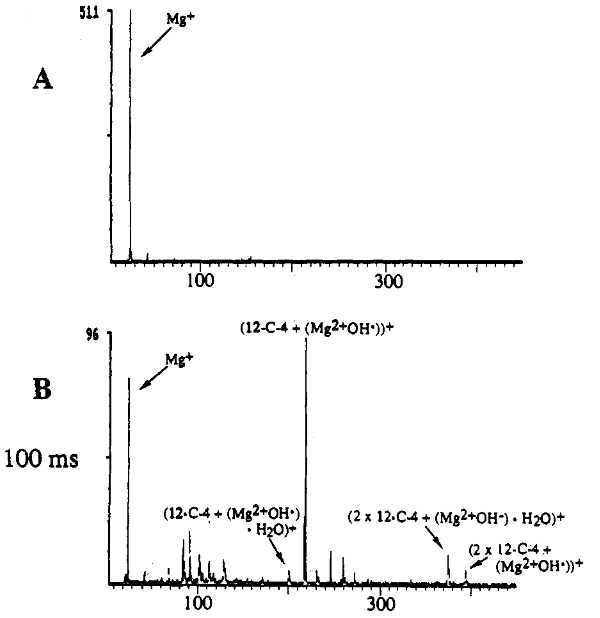


Figure 1. Product spectrum for reactions of Mg^+ ions (A) with 12-crown-4 (B) for a 100-ms reaction time.

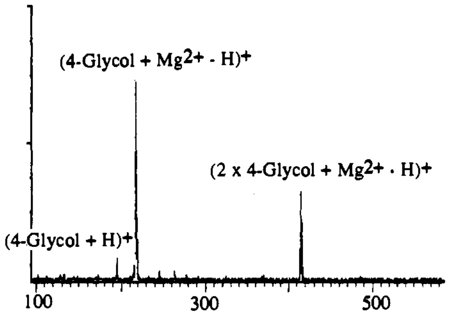


Figure 2. Product spectrum for reactions of Mg^+ ions with tetraethylene glycol (4-glycol).

All of the reactions between Mg^+ or Ca^+ ions and the crown ethers or glymes result in incorporation of "OH". For example, the following products are consistently observed (with the metal ions shown in their intrinsically favored oxidation states): $(L + (Mg^{2+}OH^-))^+$, $(L + (Mg^{2+}OH^-) - H_2O)^+$, $(2L + (Mg^{2+}OH^-) - H_2O)^+$, and $(2L + (Mg^{2+}OH^-))^+$, with relative abundances that vary depending on the reaction time and polyether pressure. As the nominal structural formulas are indicated, the original monopositive Mg^+ ions attain the +2 oxidation state, the incorporated "OH" unit is actually *hydroxide*, and the net charge on the ion is +1. The similarities in the product spectra generated for the crown ethers and acyclic glymes suggest that the binding interactions are similar for these two different structural types of polyethers.

The source of "OH" is speculated to arise from two possible sources: via the breakdown of water molecules embedded and adsorbed on the magnesium foil or calcium salt which are released during the laser desorption event *or* from water molecules hydrogen-bonded to the polyethers during their diffusion into the ion trap chamber. These latter species, (L + nH_2O), exist in solution due to the hydrophilic nature of the polyethers. They are not observed in the gas phase under conventional EI/CI ionization conditions because these ionization techniques impart too much energy to permit the loosely-bound solvated species to remain intact.

A reasonable explanation of the formation pathway is outlined as follows: a monopositive Mg^+ ion reacts with H_2O, donating its lone 3s electron and causing homolytic bond cleavage of an O–H bond (see step 1 below). Thus, a hydrogen atom (not a proton) is released in the process, and the net product is $(Mg^{2+}\text{---}OH^-)^+$, bound by a strong ionic bond. The H_2O molecule

---

(51) Weber-Grabau, M.; Kelley, P. E.; Syka, J. E. P.; Bradshaw, S.C.; Brodbelt, J. S. Proceedings of the 35th Annual Conference of the ASMS, Denver, CO, 1987; p 1114.

(52) Wu, H.-F.; Liou, C.-C.; Brodbelt, J. S. *J. Am. Soc. Mass Spectrom.* **1993**, *4*, 718.

Table 1. Relative Percentage of Products from Ion–Molecule Reactions of Magnesium Ions with Polyethers

polyether	$(L + Mg)^+$	$(L + (Mg^{2+}OH^-) - H_2O)^+$	$(L + (Mg^{2+}OH^-))$	$(L + (Mg^{2+}OH^-) + 28)^+$	$(2L + (Mg^{2+}OH^-) - H_2O)^+$	$(2L + (Mg^{2+}OH^-))^+$
12-C-4[a]	3 ± 2	5 ± 3	65 ± 10	10 ± 5	10 ± 5	5 ± 3
15-C-5	5 ± 3	5 ± 3	80 ± 10	7 ± 3	5 ± 3	0
18-C-6	3 ± 2	3 ± 2	75 ± 10	10 ± 5	7 ± 3	0
3-glycol	0	75 ± 10	0	0	25 ± 5	0
4-glycol	0	70 ± 10	0	0	30 ± 5	0
3-glyme	5 ± 3	5 ± 3	55 ± 10	20 ± 5	10 ± 5	5 ± 3
4-glyme	3 ± 2	5 ± 3	80 ± 10	10 ± 5	2 ± 1	0

[a] The abbreviation for a crown ether is "*n*-C-*m*". "*A*-Glyme" is the abbreviation for polyethylene glycol dimethyl ether with *A* ethylene units. Percentages are estimated from peak areas, and values greater than 10% are rounded to the nearest 5%. Standard deviations are based on estimations of fluctuations in peak areas among two or three measurements.

Table 2. Relative Percentage of Products from Ion–Molecule Reactions of Calcium Ions with Polyethers

polyether	$(L + Ca)^+$	$(L + (Ca^{2+}OH^-) - H_2O)^+$	$(L + (Ca^{2+}OH^-)^+$	$(L + (Ca^{2+}OH^-) + 28)^+$	$(2L + (Ca^{2+}OH^-) - H_2O)^+$	$(2L + (Ca^{2+}OH))^+$
12-C-4[a]	3 ± 2	60 ± 15	3 ± 2	10 ± 5	15 ± 5	5 ± 3
15-C-5	2 ± 1	80 ± 10	10 ± 3	5 ± 3	0	0
18-C-6	2 ± 1	85 ± 10	10 ± 5	3 ± 2	0	0
3-glycol	0	80 ± 10	0	0	20 ± 10	0
4-glycol	0	65 ± 10	0	0	35 ± 10	0
3-glyme	3 ± 2	85 ± 10	3 ± 2	3 ± 2	2 ± 1	3 ± 2
4-glyme	3 ± 2	85 ± 10	5 ± 3	3 ± 2	3 ± 2	0

[a] The abbreviation for a crown ether is "*n*-C-*m*". "*A*-Glyme" is the abbreviation for polyethylene glycol dimethyl ether with *A* ethylene units. Percentages are estimated from peak areas, and values greater than 10% are rounded to the nearest 5%. Standard deviations are based on estimations of fluctuations in peak areas among two or three measurements.

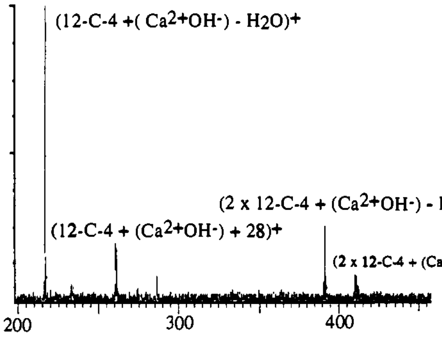


Figure 3. Product spectrum for reactions of Ca^+ ions with 12-crown-4.

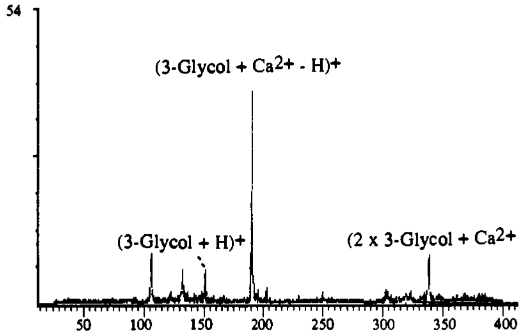


Figure 4. Product spectrum for reactions of Ca^+ ions with triethylene glycol (3-glycol).

may be a free molecule or may be loosely bound to a polyether ligand during this reaction. The reaction product is then effectively "solvated" by a polyether molecule (step 2), resulting

$$Mg^+ + H_2O \rightarrow [Mg^+\text{- -}H_2O] \rightarrow (Mg^{2+}\text{–}OH^-)^+ + H^\bullet \quad (1)$$

$$(Mg^{2+}\text{–}OH^-) + L \rightarrow [L\text{- - -}(Mg^{2+}\text{–}OH^-)]^+ \quad (2)$$

in $(L + (Mg^{2+}OH^-))^+$ with numerous electrostatic bonds between the polyether oxygen atoms and the metal center. From this sequence of events, it therefore appears that an initially monopositive alkaline earth metal ion achieves its favored oxidation state in the gas phase.

The total amount of free water vapor is extremely low as estimated from examination of the electron ionization mass spectrum of background vapor in the ion trap chamber, but there can conceivably be a transient high density of water molecules during the laser desorption event and also many of the polyether ligands can exist as solvated neutrals. Regardless of the source of water, the incorporation of "OH" is especially unusual because it is *not* observed upon reaction of other metal ions with polyethers.[48,53] For example, the hydroxide attachment process does not occur for alkali or transition metal ion reactions with polyethers, even when a high pressure of water is admitted into the ion trap. This result suggests that there is some special characteristic of alkaline earth metal ions that promotes the hydroxide attachment.

To further examine the hydroxide attachment process, the apex-isolation mode[51] was used to selectively store only Mg^+ ions prior to reaction with the polyethers. Most importantly, a clean supply of bare Mg^+ ions was generated, thus assuring that these nonsolvated monopositive Mg^+ ions are ultimately responsible for formation of the resulting polyether complexes. During the subsequent reaction period of 50–200 ms, minor $Mg^+(H_2O)$ (m/z 42) and $(Mg^{2+}OH^-)^+$ (m/z 41) ions are observed (less than 5% ion current relative to all other products observed); however, abundant $(L + (Mg^{2+}OH^-))^+$ complexes and other polyether adducts as listed in Table 1 are produced. Even continuous ejection of all ions at m/z 41 and 42 during the reaction period causes no perceptible change in the formation of $(L + (Mg^{2+}OH^-))^+$ complexes. This latter result suggests two possibilities: the $Mg^+(H_2O)$ or $(Mg^{2+}OH^-)^+$ ions are *not* important precursors to the final $(L + (Mg^{2+}OH^-))^+$ polyether complexes *or* the reaction leading to final formation of the $(L + (Mg^{2+}OH^-))^+$ complexes is extremely fast relative to the initial formation of $Mg^+(H_2O)$ or $(Mg^{2+}OH^-)^+$ ions. In either case, neither $(Mg^{2+}OH^-)^+$ nor $Mg^+(H_2O)$ ions are experimentally observed as abundant precursors in the reaction scheme.

Moreover, ion–molecule reactions of the non-hydroxylated $(L + Mg)^+$ ions with water vapor do not result in formation of $(L + (Mg^{2+}OH^-))^+$ complexes. This result demonstrates that these bare $(L + Mg)^+$ ions are not the appropriate precursors to the final $(L + (Mg^{2+}OH^-))^+$ products observed after the laser desorption sequence. For example, the $(L + Mg)^+$ ions isolated in this manner may be too internally or translationally "cool" to

---

(53) Brodbelt, J. S.; Liou, C.-C.; Wu, H.-F. Manuscript in preparation. Preliminary results are presented in the Proceedings of the 41st ASMS Conference on Mass Spectrometry and Allied Topics, San Francisco, CA, May 31-June 4, 1993; p 162a.

promote the subsequent hydroxylation reaction. Alternatively, isolated (L + Mg)$^+$ ions may possess a different stable structure than transient "reactive" (L + Mg)$^+$ ions. Another possibility is that the (L + (Mg^{2+}OH$^-$))$^+$ complexes are only formed when a monopositive Mg$^+$ ion interacts with a presolvated polyether, such as (L$\cdots n$H$_2$O). A final possibility that cannot be overlooked is the possible existence of electronically excited monopositive Mg$^+$ ions that are the special reactive precursors to the (L + (Mg^{2+}OH$^-$))$^+$ complexes. Excited state Mg$^+$ has a 3p^1 configuration and is 4.42 eV above the ground state.[37] Since the Mg$^+$ ions are generated from laser desorption, it is possible that excited-state ions are produced, even ones that do not collisionally cool rapidly in the 1-mTorr helium buffer gas. Such excited-state ions may have sufficient energy to uniquely promote the reaction with H$_2$O.

Introduction of D$_2$O directly into the vacuum chamber results in formation of (L + (Mg^{2+}OD$^-$))$^+$ complexes. Since the D$_2$O may adsorb onto the alkaline earth metal surface prior to laser desorption, solvate the polyether molecules, or exist freely in the vacuum chamber, the admission of this new source of water does not uniquely specify the mechanism of the hydroxide attachment. However, admission of additional H$_2$O vapor to 1.0×10^{-6} Torr causes no perceptible change in the types or relative abundances of products formed, a result which suggests that the hydroxylation process is not water-limited under standard laser desorption conditions.

The results for the reactions of Ca$^+$ demonstrate that stable hydroxide attachment products are typically not observed for any of the polyethers; however, abundant products corresponding to (L + (Ca^{2+}OH$^-$) − H$_2$O)$^+$ are formed (Table 2). The predominance of this dehydration process may indicate that the reactions with monopositive Ca$^+$ ions are somewhat more exothermic than the reactions with Mg$^+$ ions. The larger size of the Ca$^+$ ion may also improve its capability to coordinate to more oxygen donors, thus assisting in the displacement of water. Additionally, it has been noted that Ca$^+$ ions may react differently from Mg$^+$ ions because Ca$^+$ has low-energy empty p and d orbitals which may participate in bonding, whereas the empty 3p orbitals of Mg$^+$ are of much higher energy.[37]

Interestingly, reactions of Mg$^+$ or Ca$^+$ ions with the glycols do *not* result in stable hydroxide attachment complexes (see Table 1 and Figure 2). As illustrated, the identities of the products may be assigned as (L + (M^{2+}OH$^-$) − H$_2$O)$^+$, from unstable (L + (M^{2+}OH$^-$))$^+$ complexes that spontaneously dehydrate (pathway 1 as shown in the first part of Scheme 3), or as (L + M^{2+} − H$^\bullet$)$^+$, in which the initial M$^+$ ion reacts directly with a hydroxyl terminus of the glycol molecule (pathway 2). The first route is analogous to the proposed reaction pathway of the crown ethers and glymes, with the exception that dehydration occurs spontaneously, as is known to be favored for molecules with terminal hydroxyl groups.[54] In this case, the attachment of the Mg$^+$ or Ca$^+$ ion therefore must be a sufficiently exothermic process to promote the dissociation reaction. The second pathway requires that the initial monopositive M$^+$ ion reacts with one of the terminal hydroxyl groups of the glycol, rather than with a water molecule. A hydrogen atom would be eliminated upon formation of a strong ionic bond between the terminal oxygen and the magnesium ion (refer to the first structure shown in Scheme 4). Both pathways appear to be reasonable given the nature of the products; however, collisionally activated dissociation experiments offer some additional support for pathway 1. Because of the ambiguity, these complexes will simply be referred to as net (L + M^{2+} − H$^\bullet$)$^+$ complexes for the remainder of the report.

Isolation of the glycol/magnesium ion complexes, followed by a short reaction period, indicates that these ions may rapidly attach a second glycol ligand (see Figure 5). This dimerization suggests that further solvation of the Mg^{2+} ion is a favorable process in the gas phase. Other competing reactions of the glycol complexes or further fragmentation of the dimers does not occur.

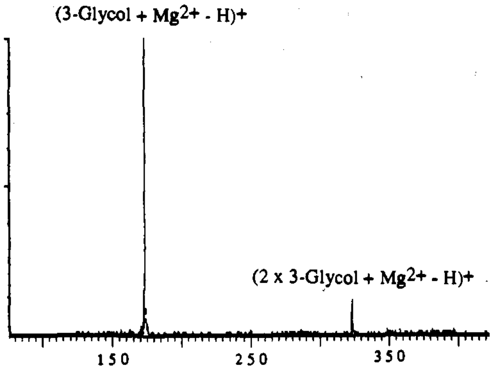


Figure 5. Reaction products from a 100-ms reaction of (triethylene glycol + Mg^{2+} − H)$^+$ ions with neutral triethylene glycol.

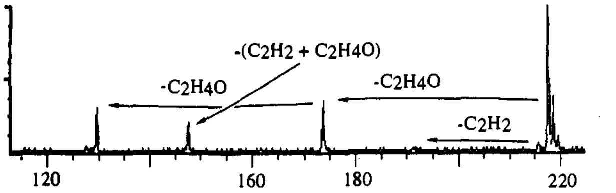


Figure 6. CAD spectrum of (tetraethylene glycol + Mg^{2+} − H)$^+$ ions.

Since the amount of residual water is typically very low and because the hydroxide attachment reactions have not been observed for reactions of other types of metal ions with the polyethers,[53] it is speculated that the monopositive Ca$^+$ and Mg$^+$ ions have a special affinity for promoting such reactions. The notable distinction of these alkaline earth metal ions relative to all the other metal ions in the periodic table is their electronic configuration and thus most favorable valence state. These metal ions are naturally divalent and apparently promote interesting reactions with water in order to attain their preferred oxidation states in the gas phase. The paucity of previous fundamental gas-phase studies of these monopositive metal ions provides little historical insight into their unusual reactivities. However, an array of relevant comparisons is obtained from the previous analytical studies on peptide/alkaline earth metal ion complexes.[40-43] In those prior studies, (L − H$^+$ + Mg^{+2})$^+$ were produced by some combination of solution and gas-phase reactions during fast atom bombardment ionization in which an alkaline earth metal salt is mixed with the analyte in a suitable matrix. As shown in one very enlightening and systematic study,[40] the alkaline earth metal ion promotes deprotonation of the peptide, resulting in formation of one strong ionic bond between the metal ion and an amide nitrogen, plus other stabilizing electrostatic interactions between the metal ion and nitrogen or oxygen atoms. The present study differs from the earlier one in that clearly it is a *monopositive* alkaline earth metal ion which initiates the chemistry in a purely gas-phase reaction in the ion trap, whereas in the prior studies, the divalent metal ions may be preformed and thus react with the peptides in solution or in the gas phase during the fast atom bombardment process.

II. CAD Spectra of Alkaline Earth Metal/Polyether Ion Complexes. Each alkaline earth metal/polyether complex was subjected to collisional activation in order to evaluate the types of dissociation reactions that the complexes undergo. The CAD spectra of the (tetraglycol + Mg^2 − H)$^+$, (tetraglyme + (Mg^{2+}OH$^-$))$^+$, and (18-crown-6 + (Mg^{2+}OH$^-$))$^+$ complexes are shown in Figures 6–8 as examples, and the results for CAD of other representative Mg$^+$ and Ca$^+$/polyether reaction products are summarized in Tables 3 and 4 , respectively. The CAD experiment for each polyether/metal ion complex confirmed that the metal ion is always retained by the polyether fragment,

---

(54) Maleknia, S.; Liou, C.-C.; Brodbelt, J. S. *Org. Mass Spectrom.* **1991**, *26*, 997.

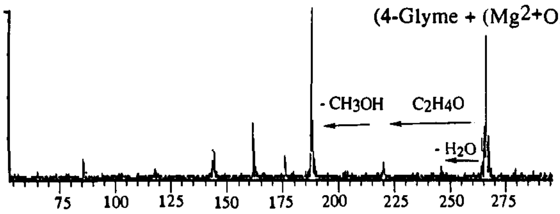


Figure 7. CAD spectrum of (tetraglyme + ($Mg^{2+}OH^-$))$^+$ ions.

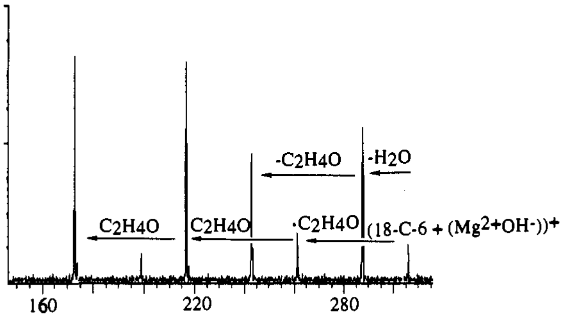


Figure 8. CAD spectrum of (18-crown-6 + ($Mg^{2+}OH^-$))$^+$ ions.

confirming that it is quite tightly bound in these complexes. In general, the Ca^{2+}/polyether complexes dissociate in patterns that are analogous to the corresponding Mg^{2+} complexes.

Common losses from the (L + ($Mg^{2+}OH^-$))$^+$ complexes of the crown ethers and glymes include losses of several C_2H_4O units, which may also occur in conjunction with dehydration. These types of fragmentation processes (i.e., multiple losses of C_2H_4O units) are similar to ones noted in the CAD spectra of protonated polyethers.[54] A mechanism depicting the elimination of H_2O and one C_2H_4O unit is shown in Scheme 1 for the 12-crown-4 complex. As shown, the new ionic bond formation between one oxygen atom of the polyether and the Mg^+ ion initiates the sequence. The glyme complexes may also undergo elimination of methanol, which may occur in conjunction with additional C_2H_4O losses. A proposed mechanism is shown in Scheme 2.

The (L + Mg^{2+} − H)$^+$ glycol complexes dissociate by elimination of a series of C_2H_4O units or elimination of C_2H_2 in conjunction with C_2H_4O units. Direct dehydration of these glycol ions is not observed, presumably because the original hydroxyl groups have been substantially altered (such as shown in the structures illustrated in Schemes 3 and 4). The loss of C_2H_2 is consistent with the structure and mechanism shown in Scheme 3, in which the net (L + Mg^{2+} − H$^\bullet$)$^+$ ions are actually the (L + ($Mg^{2+}OH$) − H_2O)$^+$ type ions. The preliminary dehydration reaction involves one hydroxyl terminal group from the glycol but does not involve the hydroxide unit attached to the Mg^{2+} ion. Alternatively, the mechanism shown in Scheme 4 represents the (L + M^{2+} − H$^\bullet$)$^+$ type structure with elimination of a C_2H_4O unit occurring by an intramolecular rearrangement similar to that proposed for the crown ether and glyme complexes.

The common theme in the mechanisms involves the proposal that one of the oxygen donor atoms promotes true ionic bond formation, in addition to the weak electrostatic interactions between other oxygen atoms and the metal center which mimic solvating forces. These features would explain the special stabilities of the resulting complexes, in particular the fact that the metal ion always remains attached to the polyether, even during quite complicated dissociation processes.

When D_2O was added to promote formation of (L + ($Mg^{2+}OD^-$))$^+$ complexes, the CAD spectra also provided some relevant information. The crown ether and glyme/($Mg^{2+}OD^-$)$^+$ complexes consistently eliminate HDO exclusively, suggesting that the loss of water directly involves the hydroxide unit attached to the Mg^{2+} ion. Likewise, the losses of C_2H_4O units never incorporate a deuterium atom, proving that extensive atom scrambling does not occur. The D_2O experiments proved less conclusive for the glycol complexes because the protons situated at the hydroxyl termini of glycols readily exchange with the protons in free D_2O. Thus, glycol/Mg^{2+} complexes may incorporate more than one deuterium atom, and the specific identity and location of the protons and deuterons is lost.

The dimer complexes were also examined by application of collisionally activated dissociation. As a representative example, the dimer of triethylene glycol dimethyl ether, (2L + ($Mg^{2+}OH^-$))$^+$, dissociates exclusively by eliminating one of the triglyme ligands, resulting in (L + ($Mg^{2+}OH^-$))$^+$. This behavior indicates that the dimer may exist as a weakly-bound sandwich structure in which the ($Mg^{2+}OH^-$)$^+$ moiety is positioned *between* the two polyether molecules, and thus is fully "solvated" by two ether ligands.

III. **Comparison of CAD Spectra of Alkaline Earth Metal/Polyether Complexes to Alkali Metal/Polyether Complexes.** As a comparison to the alkaline earth metal/polyether complexes, collisionally activated dissociation spectra of the (L + metal)$^+$ ion complexes involving alkali metal ions were examined.[42] Dissociation of the (L + metal)$^+$ complexes results exclusively in formation of bare alkali metal ions. Apparently the alkali metal/polyether complexes simply disassemble upon activation, and there is no evidence for any polyether skeletal fragmentation. Due to the low ionization energies of alkali metals, they retain the charge more effectively than the polyethers during the decomplexation process. According to the results of CAD of the ($Mg^{2+}OH^-$)$^+$ and ($Ca^{2+}OH^-$)$^+$/polyether complexes, it is clear

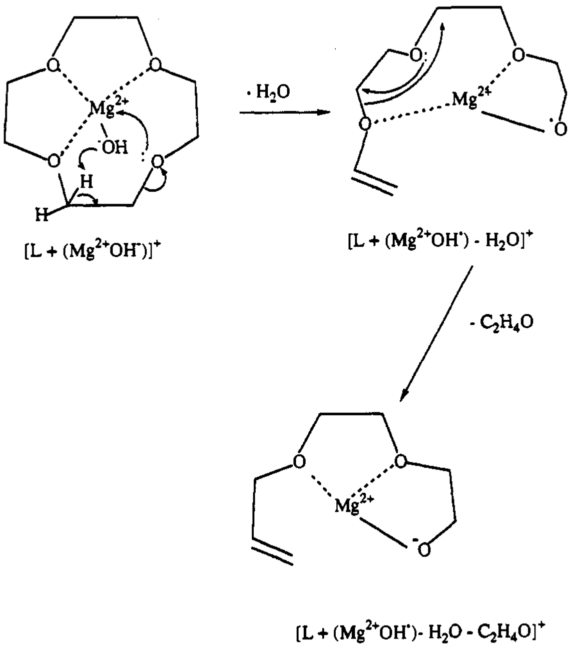
Table 3. CAD of Mg^{2+}/Polyether Ions

polyether	*m/z* of selected ion	*m/z* of fragment ions	neutrals lost
12-C-4	217 (L + ($Mg^{2+}OH^-$))$^+$	199	H_2O
		173, 129	nC_2H_4O, $n = 1, 2$
15-C-5	261 (L + ($Mg^{2+}OH^-$))$^+$	243	H_2O
		217, 173	nC_2H_4O, $n = 1, 2$
18-C-6	305 (L + ($Mg^{2+}OH^-$))$^+$	261, 217, 173	nC_2H_4O, $n = 1, 2, 3$
		287, 243, 199	$H_2O + nC_2H_4O$, $n = 0, 1, 2$
3-glycol	173 (L + Mg^{2+} − H)$^+$	129, 85	nC_2H_4O, $n = 1, 2$
		147	C_2H_2
	323 (2L + Mg^{2+} − H)$^+$	173	L
		129	L + C_2H_4O
4-glycol	217 (L + Mg^{2+} − H)$^+$	173, 129	nC_2H_4O, $n = 1, 2$
		191, 147	$C_2H_2 + nC_2H_4O$, $n = 0, 1$
3-glyme	219 (L + ($Mg^{2+}OH^-$))$^+$	187, 143	$CH_3OH + nC_2H_4O$, $n = 0, 1$
		175	nC_2H_4O, $n = 1$
		219	H_2O
		161	58
	397 (2L + ($Mg^{2+}OH^-$))$^+$	219	L
4-glyme	263 (L + ($Mg^{2+}OH^-$))$^+$	187, 143	$CH_3OH + nC_2H_4O$, $n = 1, 2$
		245	H_2O
		219, 175	nC_2H_4O, $n = 1, 2$
		205, 161	58 + nC_2H_4O, $n = 0, 1$

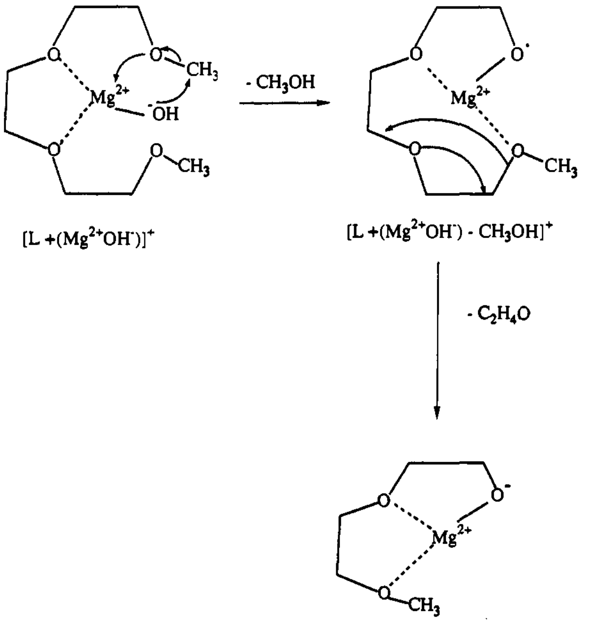
Table 4. CAD of Ca^+/Polyether Ions

polyether	*m/z* of selected ion	*m/z* of fragment ions	neutrals lost
12-C-4	215 $(L + (Ca^{2+}OH^-) - H_2O)^+$	171, 127	nC_2H_4O, $n = 1, 2$
	391 $(2L + (Ca^{2+}OH^-) - H_2O)^+$	215	L
15-C-5	259 $(L + (Ca^{2+}OH^-) - H_2O)^+$	171, 215	nC_2H_4O, $n = 1, 2$
18-C-6	303 $(L + (Ca^{2+}OH^-) - H_2O)^+$	259, 215, 171	nC_2H_4O, $n = 1–3$
3-glycol	339 $(2L + Ca^{2+} - H)^+$	189	L
3-glyme	217 $(L + Ca^{2+}OH^-) - H_2O)^+$	141, 173	$C_2H_4O + CH_3OH$, $n = 1, 2$
4-glycol	233 $(L + Ca^{2+} - H)^+$	189, 145	nC_2H_4O, $n = 1, 2$
	427 $(2L + Ca^{2+} - H)^+$	233, 189	L, C_2H_4O
4-glyme	261 $(L + (Ca^{2+}OH^-) - H_2O)^+$	217, 185	C_2H_4O, CH_3OH

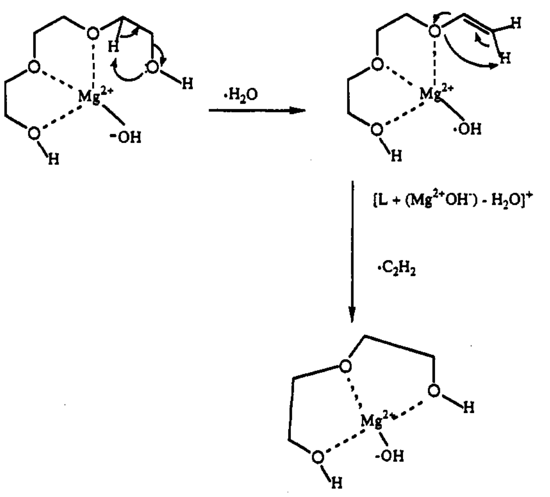
Scheme 1. Mechanism for Elimination of H_2O and C_2H_4O from the $(L + (Mg^{2+}OH^-))^+$ Complex of 12-Crown-4



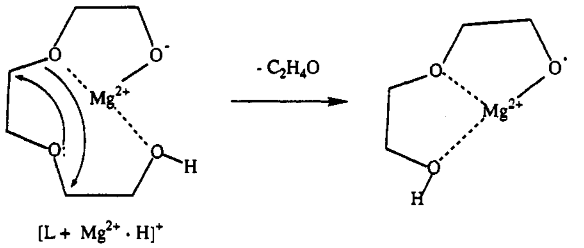
Scheme 2. Mechanism for Elimination of CH_3OH and C_2H_4O from the $(L + (Mg^{2+}OH^-))^+$ Complex of Triglyme



Scheme 3. Mechanism for Elimination of H_2O and C_2H_2 from the $(L + (Mg^{2+}OH^-))^+$ Complex of Triglycol



Scheme 4. Mechanism for Elimination of C_2H_4O from the $(L + Mg^{2+} - H)^+$ Complex of Triglycol



that each alkaline earth metal/polyether complex is bound by a very strong ionic bond and many electrostatic interactions, whereas the alkali metal complexes are bound only through weak electrostatic forces. The obvious reason for this difference is that the alkali metal ions have inert np^6 electronic configurations. For the alkaline earth metal ions, their electronic configurations promote stronger ion–dipole electrostatic forces and allow the critical ionic bond development via donation of the lone s electron to an oxygen atom.

IV. Ligand-Exchange Experiments. To compare the binding strengths of the polyethers, ligand exchange experiments were performed.[55] For this method, a selected $(L_1 + \text{metal})^+$ ion is isolated and allowed to react with another neutral polyether (L_2) for a period of 0–100 ms. Both polyethers are admitted to similar pressures in the ion trap chamber to ensure nearly equal collision probabilities. If the metal cation transfers from L_1 to L_2, then the metal ion affinity of L_2 must be larger than L_1. This experiment is repeated for many different pairs of polyethers, in order to establish a relative order of metal binding affinities. Most of the polyethers prefer to form $(L + (Mg^{2+}OH^-))^+$ ions, so the $(L + (Mg^{2+}OH^-))^+$ ions incorporating 12-crown-4, 15-crown-5, 18-crown-6, and several glymes were isolated to evaluate whether those complexes transfer $(Mg^{2+}OH^-)^+$ or just Mg^+ or Mg^{2+} to the second ether.

The results of this type of exchange are summarized in Table 5. Interestingly, the Mg^{2+} is always transferred *with* the hydroxide unit [net $(Mg^{2+}OH^-)^+$], and no other competing product pathways are observed. It may also be possible that only the Mg^{2+} ion is transferred, then a fast secondary reaction occurs that replaces the ^-OH group. However, this latter pathway seems unlikely in

---

[55] Uppal, J. S.; Staley, R. H. *J. Am. Chem. Soc.* **1982**, *104*, 1235.

Table 5. Ligand Exchange of $(L_1 + (Mg^{2+}OH^-))^+$ Ions

L_1	L_2	order
12-C-4	15-C-5	15-C-5 > 12-C-4
15-C-5	12-C-4	15-C-5 < 12-C-4
15-C-5	18-C-6	18-C-6 > 15-C-5
18-C-6	15-C-5	15-C-5 < 18-C-6
3-glyme	15-C-5	15-C-5 > 3-glyme
15-C-5	3-glyme	3-glyme < 15-C-5
3-glyme	4-glyme	3-glyme < 4-glyme
4-glyme	3-glyme	4-glyme > 3-glyme

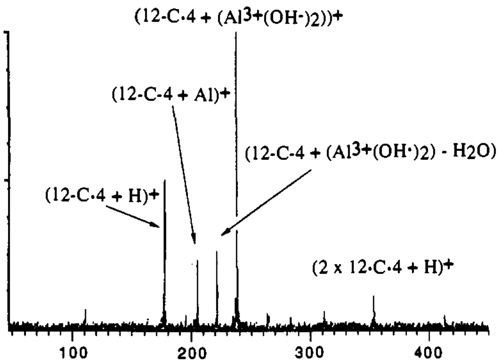


Figure 9. Product spectrum for reactions of Al^+ ions with 12-crown-4.

light of the large binding energy of an Mg–O ionic bond. As shown in Table 5, 18-crown-6 has the largest affinity for $(Mg^{2+}OH^-)^+$. This result is expected due to the larger polarizability of the 18-crown-6 relative to the other smaller polyethers, which enhances the ability to stabilize positive charge buildup in the complex. In general, the relative orders agree with those established for the binding of alkali metal ions by polyethers,[48] a comparison which suggests that the overall polarizability of the ligand plays the most important role in terms of stabilizing the cationic center.

V. **Reactions of Aluminum Ions.** Because both monopositive Mg^+ and its neighbor in the periodic table, Al^+, lack p and d electrons and are formed in intrinsically unnatural oxidation states, their reactions with the polyethers were compared in order to further evaluate the hydroxide attachment phenomena. The gas-phase reactions of Al^+ ions with simple alcohols, ethers, and ketones have been examined previously in an FTICR spectrometer,[34-35,50] and it was found that the energies for binding of Al^+ and Mg^+ to organic ligands are similar. In these earlier studies, hydroxide attachment in conjunction with complexation was not observed. In the present studies undertaken in a quadrupole ion trap, reactions of the Al^+ ions with the crown ethers or glymes result in formation of three predominant products: $(L + Al)^+$, $(L + Al + 16)^+$, and most surprisingly $(L + Al + 34)^+$ (see Table 6 and Figure 9). On the basis of CAD experiments, the latter two products are assigned as $(L + (Al^{3+}(OH^-)_2) - H_2O)^+$ and $(L + (Al^{3+}(OH^-)_2)^+$. The tendency for hydroxide addition parallels that observed for the alkaline earth metal ion reactions; however, the fact that *two* molecules of ^-OH are added is striking. This difference supports the idea that the hydroxide attachment is directly related to the favored valence state of the metal ion. Aluminum, which is trivalent, apparently promotes reaction with two units of water. As mentioned earlier, the reactions with water may occur between the aluminum ions and free water or between aluminum ions and $(L + nH_2O)$ solvated polyether ligands.

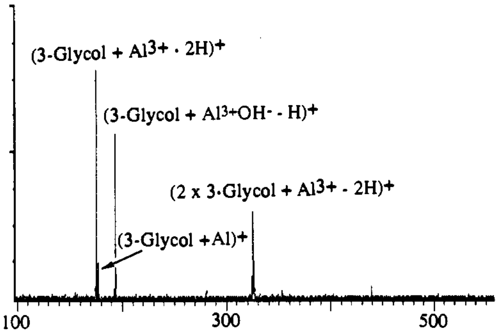


Figure 10. Product spectrum for reactions of Al^+ ions with triglycol.

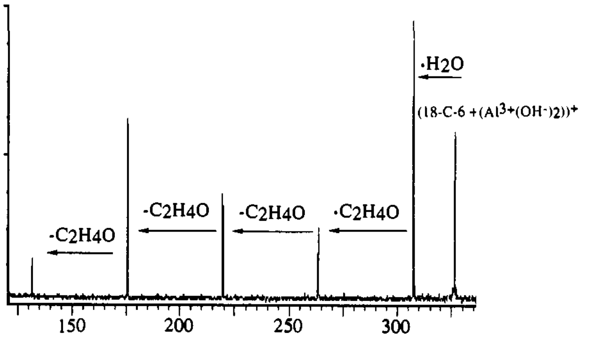


Figure 11. CAD spectrum of $(18\text{-crown-}6 + (Al^{3+}(OH^-)_2))^+$ ions.

A second similarity within the reactive behaviors of the Al^+ ions and alkaline earth metal ions lies with the glycol complexation: the complexes tend to favor spontaneous dehydration (see Figure 10). Thus, for the glycols, the common products observed are nominally $(L + Al - 2)^+$ and $(L + Al + 16)^+$. These products may be assigned as $(L + (Al^{3+}(OH^-)_2) - 2H_2O)^+$ [or net $(L + Al^{3+} - 2H)^+$] and $(L + (Al^{3+}(OH^-)_2) - H_2O)^+$ [or net $(L + Al^{3+}OH^- - H)^+$], respectively. For the aluminum ion/glycol complexes, two stages of dehydration (or hydrogen elimination) may occur spontaneously, which is directly analogous to the single stage promoted by the alkaline earth metal ions.

Collisional activated dissociation was used to characterize the various aluminum/polyether complexes (Table 7). For the crown ethers and glymes, the $(L + (Al^{3+}(OH^-)_2) - H_2O)^+$ and $(L + (Al^{3+}(OH^-)_2)^+$ ions were examined. The $(L + (Al^{3+}(OH^-)_2 - H_2O)^+$ ions dissociate by elimination of C_2H_4O units, but dehydration is not observed despite the availability of the remaining hydroxyl group attached to the Al^{3+} ion. This latter result is consistent with the mechanism shown in Scheme 1 in which an unsaturated product ion results from the first dehydration. Thus, there is no obvious driving force for a second dehydration. In contrast, the $(L + (Al^{3+}(OH^-)_2)^+$ ions dissociate by elimination of water in conjunction with C_2H_4O (see Figure 10). The glymes can alternatively eliminate water or methanol

Table 6. Relative Percentage of Products from Ion–Molecule Reactions of Aluminum Ions with Polyethers

polyether	$(L + Al)^+$	$(L + (Al^{3+}(OH^-)_2) - 2H_2O)^+$	$(L + (Al^{3+}(OH^-)_2) - H_2O)^+$	$(L + (Al^{3+}(OH^-)_2)^+$	$(2L + (Al^{3+}(OH^-)_2) - 2H_2O)^+$
12-C-4[a]	15 ± 5	0	15 ± 5	70 ± 10	0
15-C-5	10 ± 5	0	20 ± 10	70 ± 15	0
18-C-6	25 ± 3	0	10 ± 5	65 ± 15	0
3-glycol	5 ± 3	50 ± 10	30 ± 10	0	15 ± 5
4-glycol	3 ± 2	55 ± 10	15 ± 5	0	25 ± 10
3-glyme	10 ± 5	0	15 ± 5	75 ± 10	0
4-glyme	2 ± 1	0	20 ± 5	80 ± 10	0

[a] The abbreviation for a crown ether is "*n*-C-*m*". "*A*-Glyme" is the abbreviation for polyethylene glycol dimethyl ether with *A* ethylene units. Percentages are estimated from peak areas, and values greater than 10% are rounded to the nearest 5%. Standard deviations are based on estimations of fluctuations in peak areas among two or three measurements.

Table 7. CAD of Al^+/Polyether Ions

polyether	*m/z* of selected ion	*m/z* of fragment ions	neutrals lost
12-C-4	203 $(L + Al^+)$	175, 131	$C_2H_4 + nC_2H_4O$, $n = 0, 1$
		159	C_2H_4O
	219 $(L + (Al^{3+}(OH^-)_2) - H_2O)^+$	191	C_2H_4
		175, 131	nC_2H_4O, $n = 1, 2$
	237 $(L + (Al^{3+}(OH^-)_2))^+$	219, 175, 131	$H_2O + nC_2H_O$, $n = 0, 1, 2$
		193	C_2H_4O
15-C-5	247 $(L + Al^+)$	175, 131	$C_2H_4 + nC_2H_4O$, $n = 1, 2$
	263 $(L + (Al^{3+}(OH^-)_2) - H_2O)^+$	219, 175, 131	nC_2H_4O, $n = 1, 2, 3$
	281 $(L + (Al^{3+}(OH^-)_2))^+$	263, 219, 175, 131	$H_2O + nC_2H_4O$, $n = 0, 1, 2, 3$
		193	$2C_2H_4O$
18-C-6	291 $(L + Al^+)$	263, 219, 175, 131	$C_2H_4 + nC_2H_4O$, $n = 0–3$
	307 $(L + (Al^{3+}(OH^-)_2) - H_2O)^+$	263, 219, 175, 131	nC_2H_4O, $n = 1, 2, 3, 4$
	325 $(L + (Al^{3+}(OH^-)_2))^+$	307, 263, 219	$H_2O + nC_2H_4O$, $n = 0–4$
		175, 131	
3-glycol	175 $(L + Al^{3+} - 2H)^+$	147, 103	$C_2H_4 + nC_2H_4O$, $n = 0, 1$
		131	C_2H_4O
		157, 113	$H_2O + nC_2H_4O$, $n = 0, 1$
		149, 105	$C_2H_2 + nC_2H_4O$, $n = 0, 1$
	193 $(L + (Al^{3+}OH^-) - H)^+$	175	H_2O
	325 $(2L + Al^{3+} - 2H)^+$	175	L
4-glycol	219 $(L + Al^{3+} - 2H)^+$	175	C_2H_4O
		193, 149, 105	C_2H_2 $n = 0, 1, 2$
		147	$C_2H_4 + C_2H_4O$
3-glyme	205 $(L + Al^+)$	161, 117	nC_2H_4O, $n = 1, 2$
		177, 133	$C_2H_4 + nC_2H_4O$, $n = 0, 1$
	221 $(L + (Al^{3+}(OH^-)_2) - H_2O)^+$	145, 101	$CH_3OH + nC_2H_4O$, $n = 1, 2$
		177	C_2H_4O
		163, 119	$58 + nC_2H_4O$, $n = 0, 1$
	239 $(L + (Al^{3+}(OH^-)_2))^+$	221, 177, 133	$H_2O + nC_2H_4O$, $n = 0, 1, 2$
		163, 119	$CH_3OH + nC_2H_4O$, $n = 0, 1$
		151	C_2H_4O
		181, 137	$58 + nC_2H_4O$, $n = 0, 1$
4-glyme	249 $(L + Al^+)$	177, 133	$C_2H_4 + nC_2H_4O$, $n = 1, 2$
		205, 161	nC_2H_4O, $n = 1, 2$
	265 $(L + (Al^{3+}(OH^-)_2) - H_2O)^+$	221, 177	nC_2H_4O, $n = 1, 2$
		207, 163, 119	$58 + nC_2H_4O$, $n = 0, 1, 2$
	283 $(L + (Al^{3+}(OH^-)_2))^+$	265, 221	$H_2O + nC_2H_4O$, $n = 0, 1$
		207, 163	$CH_3OH + nC_2H_4O$, $n = 1, 2$

in conjunction with C_2H_4O. The CAD patterns of the $(L + (Al^{3+}(OH^-)_2)^+$ ions are directly analogous to those obtained for the $(L + (Mg^{2+}OH^-))^+$ ions.

For the glycols, the two major products that were characterized by CAD included the $(L + (Al^{3+}(OH^-)_2 - H_2O)^+$ and $(L + (Al^{3+}(OH^-)_2 - 2H_2O)^+$ ions. The $(L + (Al^{3+}(OH^-)_2 - H_2O)^+$ ions dissociate exclusively by elimination of water, and no other competing or sequential fragmentation occurs. The $(L + (Al^{3+}(OH^-)_2 -2\,H_2O)^+$ ions eliminate C_2H_2 in conjunction with C_2H_4O units, a pattern analogous to that observed for the $(L + (Mg^{2+}OH^-) - H_2O)^+$ glycol complexes.

In summary, the reactions and product formation of the aluminum ions apparently resemble those noted for the alkaline earth metal ions, with the noteworthy difference that the aluminum ion reactions incorporate a second hydroxide unit. The resemblances are attributed to the obvious valence state irregularities of the initially monopositive metal ions. Aluminum ion is naturally trivalent which means that each s electron of the monopositive cation may activate bond formation to a water molecule, resulting in net attachment of two hydroxide units.

Conclusions

A variety of products were formed from ion–molecule reactions between laser-desorbed monopositive Ca^+ or Mg^+ ions and polyethers in a quadrupole ion trap mass spectrometer. A hydroxide unit is often incorporated into the alkaline earth metal ion/crown ether or glyme products; and the calcium ion/polyether complexes have a greater tendency to dehydrate spontaneously after formation. Stable complexes incorporating the hydroxide unit are not observed for the glycols; instead, dehydration always occurs or the metal ion directly reacts with a hydroxyl terminus with concomitant elimination of hydrogen. Collisional activated dissociation (CAD) techniques reveal that the metal ion remains attached to the polyether structure throughout the energization process, and in many cases, the hydroxide unit associated with the Mg^{2+} ions also remains bound to the metal ion. Partial covalent-type binding or strong ionic bonds may exist between Mg^{2+} or Ca^{2+} ions and polyethers, caused by the delocalization of electrons from the oxygen atoms of the polyethers to the s orbitals of the metal ions. One net conceptual view of the formation of these alkaline earth metal/polyether complexes involves solvation of a $(Mg^{2+}OH^-)$ or $(Ca^{2+}OH^-)$ unit by a polyether in the gas phase, in some cases followed by spontaneous dehydration. Currently, we are also undertaking the same kind of study for an array of transition metals with a variety of electronic configurations and sizes.[53] These results will be compared to the present ones in the future.

Acknowledgment. This research was supported by grants from the NSF (CHE-9122699), Welch Foundation (F1155), NIH (R01-GM46723-01), and ACS-PRF (25485-AC5). J.S.B. acknowledges The Camille and Henry Dreyfus Teacher-Scholar Awards Program, the Alfred P. Sloan Research Fellow Program, and the NSF-NYI program (CHE-9357422).