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Relative Binding Energies of Gas-Phase Pyridyl Ligand/Metal Complexes by Energy-Variable Collisionally Activated Dissociation in a Quadrupole Ion Trap

Mary Satterfield and Jennifer S. Brodbelt*

Department of Chemistry and Biochemistry, University of Texas at Austin, Austin, Texas 78712

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The relative binding energies of a series of pyridyl ligand/metal complexes of the type $[M^IL_2]^+$ and $[M^{II}L_3]^{2+}$ are investigated by using energy-variable collisionally activated dissociation in a quadrupole ion trap mass spectrometer. The pyridyl ligands include 1,10-phenanthroline and various alkylated analogues, 2,2′-bipyridine, 4,4′-dimethyl-2,2′-bipyridine, and 2,2′:6′,2″-terpyridine, and the metal ions include cobalt, nickel, copper, zinc, cadmium, calcium, magnesium, lithium, sodium, potassium, rubidium, and cesium. The effect of the ionic size and electronic nature of the metal ion and the polarizability and degree of preorganization of the pyridyl ligands on the threshold activation voltages, and thus the relative binding energies of the complexes, are evaluated. Correlations are found between the binding constants of $[M^{II}L_3]^{2+}$ complexes in aqueous solution and the threshold activation voltages of the analogous gas-phase complexes determined by collisionally activated dissociation.

Introduction

Pyridyl ligands, including the well-known phenanthroline compounds, are among the most extensively studied chelating agents in coordination chemistry.[1−13] They strongly bind transition metals possessing both low and high oxidation states, often forming bis- and tris-ligand complexes. The bidentate 1,10-phenanthroline and 2,2′-bipyridine ligands are thought to participate in strong chelating interactions in part due to the possibility of $d_\pi-p_\pi$ bonding from the metal to the ligand, giving some aromatic character to the resulting chelate ring.[3,4] The binding constants of many pyridyl ligands in aqueous solution have been thoroughly investigated using traditional methods such as potentiometry or spectrophotometry.[1−13] To date, most studies of the chelation of metal ions by phenanthroline ligands or other pyridyl ligands have involved solution environments, but mass spectrometry offers the ability to examine aspects of metal coordination in the gas phase. Intrinsic aspects of binding selectivity, binding energies, and coordination sites can be studied in a solvent-free environment. Several recent gas-phase studies[14−19] have reported trends in metal complexation of phenanthrolines by using such well-established methods as laser desorption and electrospray ionization (ESI)[20,21] to create the complexes and ligand exchange or collisionally activated dissociation methods to evaluate the binding interactions. In fact, several groups have begun to use ESI-MS to determine binding constants and selectivities, especially in the field of host−guest chemistry.[22−30] Direct correlations between mass spectral ion intensities and calculated solution equilibrium distributions have been found, thus opening a novel avenue for further exploration of complexation phenomena.

Absolute and relative binding energies of metal-containing complexes can be estimated on the basis of energy-variable collisionally activated dissociation measurements (CAD).[31−34] Armentrout and co-workers have pioneered a method for the

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* Corresponding author. Phone: 512-471-0028. Fax: 512-471-8696. E-mail: jbrodbelt@mail.utexas.edu.

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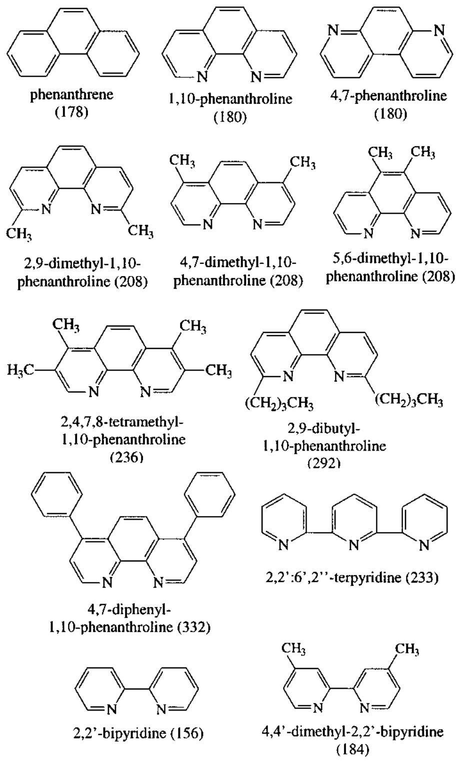

Figure 1. Pyridyl ligands used in this study (molecular weight).

determination of absolute binding energies by using a guided ion beam instrument in which the kinetic energy of selected ions is varied, thus altering the resulting energy deposition upon collision with a target gas.[34] The binding energies of a variety of alkali metal complexes and transition metal complexes have been determined in this way. A simplified method was developed to estimate critical energies for dissociation in a quadrupole ion trap mass spectrometer[33] in which the activation voltage used to resonantly excite selected ions was varied to identify the threshold for dissociation. This method was used to estimate the critical energies for a variety of proton-bound dimers.

In the present study, energy-variable collisional activation is used to promote the dissociation of pyridyl ligand/metal complexes produced by electrospray ionization in a quadrupole ion trap mass spectrometer in order to estimate the relative metal−ligand binding energies and determine how the relative binding energies are affected by factors such as the size of the metal ion, coordination number, and electronic state. The transition metals cobalt, nickel, and copper, group IIB metals zinc and cadmium, alkaline earth metals calcium and magnesium, and the entire group of alkali metal ions were used. The pyridyl ligands employed in this study include 1,10-phenanthroline, 2,9-dimethyl-1,10-phenanthroline (neocuproine), 4,7-dimethyl-1,10-phenanthroline, 5,6-dimethyl-1,10-phenanthroline, 2,9-dibutyl-1,10-phenanthroline, 3,4,7,8-tetramethyl-1,10-phenanthroline, 4,7-diphenyl-1,10-phenanthroline (bathophenanthroline), 4,7-phenanthroline, phenanthrene, 2,2′-bipyridine, 4,4′-dimethyl-2,2′-bipyridine, and 2,2′:6′,2″-terpyridine (see Figure 1). The methyl-substituted phenanthrolines were chosen to investigate the effect of both the placement of the methyl substituents and the changes in relative binding strengths due to the added electron-releasing groups. The electron-releasing effect of the methyl groups is known to be the greatest in solution when they are placed *ortho* or *para* to the coordinating nitrogens.[35] However, groups at *ortho* positions often cause significant steric hindrance. The relative roles of steric hindrance are investigated in the present gas-phase study by comparison of 2,9-dimethyl-1,10-phenanthroline and 2,9-dibutyl-1,10-phenanthroline. The solution binding constants of the phenanthroline ligands are typically larger than those of 2,2′-bipyridine and its analogues[36] because the rigidity of the phenanthroline structure gives it a greater degree of preorganization. To explore the role of this factor in the gas phase, complexes of several bipyridine ligands were also studied.

We also report correlations between binding constants of a series of pyridyl ligands determined in aqueous solution and the threshold activation voltages determined by collisionally activated dissociation in a quadrupole ion trap mass spectrometer. In this study, the threshold activation voltage is defined as the voltage sufficient to produce fragments that constitute 2% of the total ion intensity.

Experimental Section

A ThermoFinnigan LCQ Duo quadrupole ion trap mass spectrometer equipped with an electrospray interface was used in the majority of experiments. An ESI flow rate of 5 μL/min was used with optimization of the lens and octapole voltages, sheath gas flow rate, needle voltage, and capillary voltage to maximize the ions of interest. The capillary temperature was kept at 200 °C, except where noted. The temperature of the unheated ion trap was nominally 25 °C. The uncorrected base pressure in the ion trap with helium added was nominally 1.0×10^{-5} Torr, as measured with the ionization gauge. Full scan spectra represent ion injection times of 1−100 ms and an average of 20 microscans. CAD spectra required ion injection times of between 1 and 1000 ms and an average of 20 microscans. For CAD experiments, an auxiliary ac voltage of up to 5.0 V_{p-p} was applied across the endcaps.

The effects of the capillary temperature and ESI gate time on the threshold activation voltage were investigated. A capillary temperature in the range of 50−200 °C did not affect the threshold activation voltages, although the intensity of the observed complexes was affected. Likewise, gate time did not have an observable effect on threshold activation voltages.

Stock solutions of the pyridyl ligands in methanol were 10^{-3} M, and stock metal solutions in methanol were 10^{-3} or 10^{-2} M. Solutions for investigation were made to be 10^{-5} M with 1:5 ligand:metal salt ratios.

The pyridyl ligands 1,10-phenanthroline, 2,9-dimethyl-1,10-phenanthroline (neocuproine), 4,7-dimethyl-1,10-phenanthroline, 5,6-dimethyl-1,10-phenanthroline, 3,4,7,8-tetramethyl-1,10-phenanthroline, 4,7-diphenyl-1,10-phenanthroline (bathophenanthroline), 4,7-phenanthroline, phenanthrene, 2,2′-bipyridine, 4,4′-dimethyl-2,2′-bipyridine, and 2,2′:6′,2″-terpyridine were purchased from Aldrich Chemical Co. (Milwaukee, WI). 2,9-Dibutyl-1,10-phenanthroline was purchased from TCI America (Portland, OR). Bromides of cobalt(II), nickel(II), copper(II), zinc(II), and cadmium(II) were purchased from Aldrich Chemical Co., as were chloride salts of calcium, magnesium, lithium, sodium, potassium, rubidium, and cesium. The HPLC-grade methanol came from EM Science (Gibbstown, NJ). All materials were used without further purification.

Results and Discussion

Formation of Complexes by ESI-MS. The correlations reported in this study involve a series of energy-variable CAD

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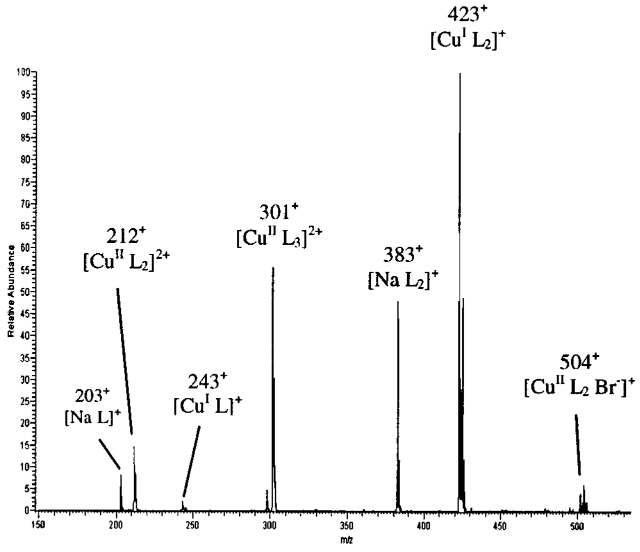

Figure 2. ESI-MS of 1,10-phenanthroline and $CuBr_2$.

experiments in which the dissociation of the pyridyl ligand/metal complex, either $[M^IL_2]^+$ or $[M^{II}L_3]^{2+}$ where is M is a metal and L is the ligand, is monitored for the loss of one ligand. A typical ESI-mass spectrum for a solution containing a pyridyl ligand (i.e., 1,10-phenanthroline) and a metal salt (i.e., $CuBr_2$) is shown in Figure 2. Both $[M^IL_2]^+$ and $[M^{II}L_3]^{2+}$ complexes are observed in addition to those that contain one counterion and sodium/1,10-phenanthroline complexes. (Sodium complexes are commonly observed due to widespread sodium contamination of the instrument and glassware.) For solutions containing transition metals, $[M^IL_2]^+$ complexes presumably result from metal ion reduction during the electrospray process. While $[Cu^IL_2]^{2+}$ complexes were seen directly in the ESI mass spectra, as shown in Figure 2, monovalent complexes of the other transition metals were not evident except upon isolation and with increased gate time. (The gate time defines the amount of time that ions are admitted into the trap and thus defines the total number of ions.) Complexes containing counterions, although interesting, were not a focus of the present study. $[M^{II}L_2]^{2+}$ complexes were commonly observed, but these dissociated nearly spontaneously by loss of $L^{+\bullet}$ upon isolation, preventing further evaluation of their binding energies by energy-variable CAD. Each of the two complexes of interest, $[M^IL_2]^+$ and $[M^{II}L_3]^{2+}$, was isolated and subjected to CAD, as shown in Figure 3. The loss of a single ligand, which may occur with spontaneous solvent adduction, was the process monitored for the determination of the threshold activation voltage.

Evident in Figure 3A is the addition of water after the loss of one ligand upon dissociation of the bis-ligand complex, $[Cu^I(1,10\text{-phenanthroline})_2]^+$, but not upon dissociation of the tris-ligand complex, $[Cu^{II}(1,10\text{-phenanthroline})_3]^{2+}$ (Figure 3B). This behavior was typical of the transition metal complexes in which the monopositive bis-ligand complexes generally exhibited the addition of water or methanol upon dissociation, whereas the doubly charged tris-ligand complexes did not. Solvent addition to metal complexes in a quadrupole ion trap has been observed previously.[37−39] It has been documented that complexes containing coordinately unsaturated metals may react by solvent adduction,[37−39] and in fact, Vachet et al. related the occurrence of solvent adduction to the coordination state of the metal ion in a variety of metal complexes.[38,39]

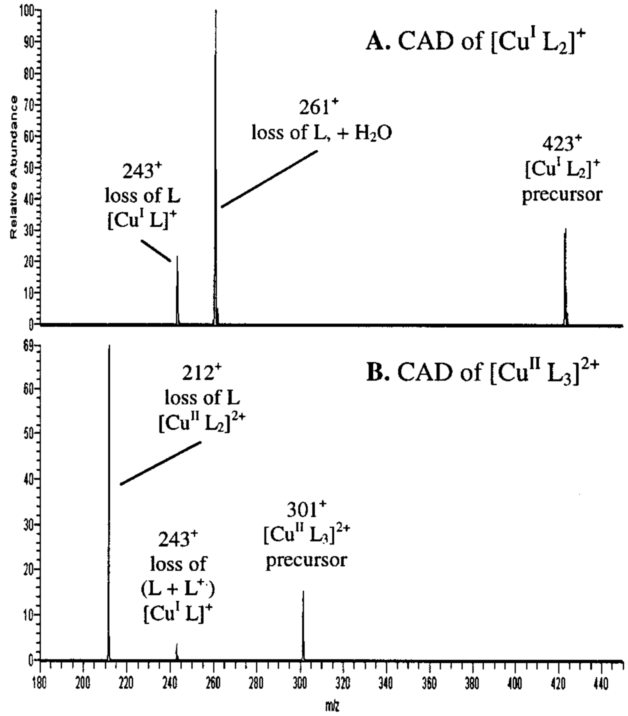

Figure 3. Dissociation of 1,10-phenanthroline/copper complexes, with evident loss of L.

Solvent adduction to the $[M^IL]^+$ products stems from the preference of the metal ion to remain more fully coordinated, thus favoring the attachment of one molecule of water or methanol to stabilize the complex. Little solvent addition was seen after CAD of the $[Cd^IL_2]^+$ complexes, perhaps as a result of the lower charge density of Cd^+ relative to the other transition metal ions, leading to a lower electrostatic attraction. The only case in which a dissociation of the bis-ligand complexes occurred without the subsequent addition of water involved 2,9-dibutyl-1,10-phenanthroline, possibly because the steric hindrance of the ligand prevented the approach of the solvent molecule to the $[M^IL]^+$ ion.

The lack of solvent adduction to the $[M^{II}L_2]^{2+}$ products formed upon CAD of the $[M^{II}L_3]^{2+}$ complexes suggests two possibilities: (1) the $[M^{II}L_2]^{2+}$ products have an activation barrier for solvent attachment, or (2) the coordination geometry of the metal changes from octahedral in the $[M^{II}L_3]^{2+}$ complex to tetrahedral in the resulting $[M^{II}L_2]^{2+}$ product, thus giving complete coordination by two bidentate ligands.

Adduction of water was also observed upon dissociation of tris-ligand complexes containing an alkaline earth metal (Mg^{2+} or Ca^{2+}). The solvent adduction to the $[Mg^{II}L_2]^{2+}$ and $[Ca^{II}L_2]^{2+}$ products is likely caused by the high charge density of the metal ions and their lack of a specific coordination geometry, thus allowing the nonspecific attachment of a solvent molecule. Water addition was also noted upon CAD of the bis-ligand complexes containing lithium (with the exception of the 2,9-dibutyl-1,10-phenanthroline complexes), but not the other alkali metals. For the $[LiL]^+$ products formed upon CAD of $[LiL_2]^+$, the attachment of water occurs because of the high charge density of Li^+ relative to that of Na^+, K^+, Rb^+, or Cs^+. Adducts were not observed upon dissociation of $[Li(2,9\text{-dibutyl-1,10-phenanthroline})_2]^+$ complexes due to the steric hindrance of the ligand and the small radius of the lithium ion.

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Table 1. Threshold Activation Voltage (V_{p-p}) for Pyridyl Ligand/Alkali Metal Complexes

	polarizability[a]	$[LiL_2]^+$	$[NaL_2]^+$	$[KL_2]^+$	$[RbL_2]^+$	$[CsL_2]^+$
1,10-phenanthroline	23.6	1.01[b]	0.84	0.68	0.56	0.47
4,7-phenanthroline	23.6	0.88	–[c]	–	–	–
2,9-dimethyl-1,10-phenanthroline	27.3	1.09	0.88	0.68	0.57	0.47
4,7-dimethyl-1,10-phenanthroline	27.3	1.14	1.04	0.75	0.65	0.51
5,6-dimethyl-1,10-phenanthroline	27.3	1.14	0.91	0.74	0.64	0.52
2,4,7,8-tetramethyl-1,10-phenanthroline	32.4	1.26	1.09	0.80	0.70	0.59
2,9-dibutyl-1,10-phenanthroline	38.2	1.07	1.00	0.76	0.65	0.53
4,7-diphenyl-1,10-phenanthroline	42.9	1.29	1.07	0.80	0.70	0.63
2,2′-bipyridine	18.7	0.88	0.71	–	–	–
4,4′-dimethyl-2,2′-bipyridine	22.3	1.00	0.86	0.51	–	–
2,2′:6′,2″-terpyridine	27.6	0.71	0.73	–	–	–

[a] In units of Å^3. [b] Maximum standard deviation of ±0.04 V. [c] Dashes indicate a lack of complex formation.

Energy-Variable CAD: Threshold Activation Voltages. In an ion trap, the collision energies of ions in CAD experiments are strongly influenced by the activation voltage, an auxiliary ac voltage applied across the endcap electrodes to resonantly excite ions. Due to the dynamic nature of the collisional activation process (i.e., multiple collisions with helium, variable kinetic energy of ions in an ion trap), it is not possible to calculate a collision energy, so raw activation voltages are reported. As reported in Tables 1–3, the threshold activation voltages of a series of bis- and tris-pyridyl ligand complexes were determined using energy-variable CAD in which the activation voltage was varied in a stepwise fashion and the signal intensities of the fragments and precursor were monitored. To assess the reproducibility of this method and to determine the best point for comparing the dissociation behavior of different ions, three trials of the CAD method were undertaken for $[Na(1,10\text{-phenanthroline})_2]^+$. The greatest precision (±5% standard deviation, typically ±0.04 V) was at the point at which the complex began to dissociate, prompting the choice of the "threshold activation voltage level" as the voltage sufficient to produce fragments that constitute 2% of the total ion intensity. In general, sequential experiments on a single day resulted in a variation of ±5% in the measured threshold activation voltage, but the standard deviations for experiments undertaken on different days varied between 5 and 20%, a level of variation likely related to the cleanliness of the instrument and the nature of the background molecules in the trap. Thus, for the data reported in the tables, all results within any single column or row were acquired in a continuous back-to-back data collection process.

In Figure 4, the energy-variable CAD curves for a whole series of $[LiL_2]^+$ complexes are shown; the differences in the amount of activation voltage required to fragment the complexes are clearly visible. As discussed below, the threshold activation voltages correlate with the relative gas-phase binding energies of the complexes, the binding constants determined in aqueous solution (i.e., log K values for ML_3 complexes) for some of the common transition metals, and the polarizability of the ligands. It should also be noted that a simple account of the degrees of freedom of the ligands does not correlate with the trend in threshold activation voltages for all of the ligands, as would be expected if the larger ligands uniformly required greater activation voltages due to their greater number of vibrational modes. In fact, the $[Li(2,2'\text{:}6',2''\text{-terpyridine})_2]^+$ complex required the lowest threshold activation voltage despite its large number of degrees of freedom; likewise, $[Li(2,9\text{-dibutyl-10-phenanthroline})_2]^+$ had an unusually low threshold activation voltage relative to its size. The results for the complexes containing these two ligands suggest that other factors play a more important role in influencing the observed threshold activation voltages than just the total degrees of freedom.

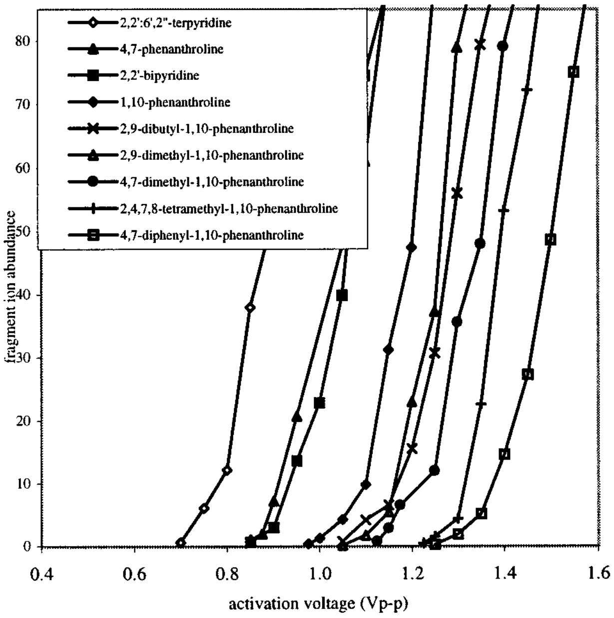

Figure 4. Energy-variable CAD curves of $[LiL_2]^+$.

Trends in Threshold Activation Voltages. A. Ligand-Dependent Trends. i. Alkali Metal Complexes: CAD of $[M^IL_2]^+ \rightarrow [M^IL]^+$. Typical CAD curves for alkali metal complexes of the type $[M^IL_2]^+$ are shown in Figure 4, and the threshold activation voltages obtained by energy-variable measurements are summarized in Table 1. The progression in the threshold activation voltages in going from the $[Li(2,2'\text{:}6',2''\text{-terpyridine})_2]^+$ complexes to the $[Li(4,7\text{-diphenyl-1,10-phenanthroline})_2]^+$ complexes is evident in Figure 4. The ionic radius of the alkali metal ion[40] is plotted vs the threshold activation voltage in Figure 5; there is a clear inverse relationship between ionic size and threshold activation voltage. This trend reflects the decreasing charge density of the metal ion as the size of the metal ion increases, reducing the strength of the electrostatic interactions between the metal ion and pyridyl ligands. This correlation supports the feasibility of comparing the relative binding energies of the chelation complexes on the basis of the threshold activation voltages.

In general, the alkali metal complexation of phenanthroline and other pyridyl ligands has not been comprehensively studied in solution,[42] in part because the formation of coordination compounds involving the alkali metals is relatively uncommon. It has been recognized that some 1,10-phenanthroline derivatives

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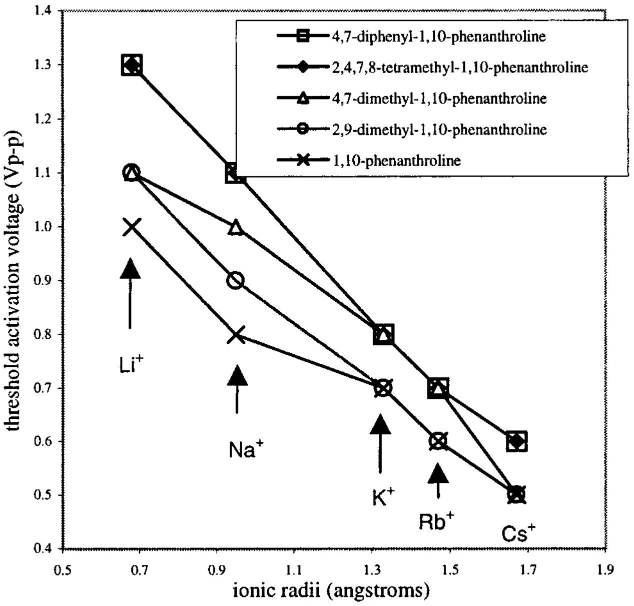

Figure 5. Effect of ionic radii of alkali metals on threshold activation voltage.

are effective ionophores for Li^+.[42] 2,9-Dimethyl-1,10-phenanthroline and 2,9-di-*n*-butylphenanthroline have demonstrated exceptionally high Li^+ selectivity relative to their affinities for Na^+, K^+, Mg^{2+}, or Ca^{2+} in solution on the basis of incorporation of the ionophores in ion-selective electrodes.[42] The complexes formed with Li^+ are 2:1 ligand:metal complexes with tetrahedral coordination geometries.[42] The unsubstituted 1,10-phenanthroline ligand also forms 2:1 ligand:metal complexes with Li^+, Na^+, K^+, Mg^{2+}, and Ca^{2+}, but with much less selectivity. These previous studies have shown that the binding constants for the alkaline earth metal complexes are slightly higher than the binding constant for the Li^+ complex for 1,10-phenanthroline in solution,[42] a reasonable outcome considering the higher charge density of the divalent metals.

The polarizability of the ligand clearly influences the binding energies of the pyridyl ligand/metal complexes in the present ESI-MS studies. Polarizability, the ability to deform the electron cloud for enhanced coordination, is based on ligand size and bond type. The polarizabilities of the pyridyl ligands used in this study were calculated using the Miller additivity method[41] and are listed in Table 1. The effect of polarizability on the relative binding energies is seen upon comparison of the complexes containing 1,10-phenanthroline and its alkylated analogues. The polarizability of 4,7-diphenyl-1,10-phenanthroline is the greatest of the alkyl-substituted 1,10-phenanthrolines, and the resulting alkali metal complexes have the greatest threshold activation voltages and therefore the greatest binding energies. The threshold activation voltages of the complexes decrease from 4,7-diphenyl-1,10-phenanthroline to 3,4,7,8-tetramethyl-1,10-phenanthroline to the three dimethyl-1,10-phenanthroline isomers to 1,10-phenanthroline, in agreement with the reduction in polarizabilities of the ligand and their lower interaction energies with the metal ions.

The threshold activation voltages for the complexes containing the 4,7-dimethyl- and 5,6-dimethyl-1,10-phenanthroline isomers were not clearly differentiated, but they were generally larger than those of the 2,9-dimethyl-1,10-phenanthroline complexes, indicating the negative impact of the sterically hindering methyl groups in the 2,9-positions. Prior studies involving the methyl-substituted 1,10-phenanthrolines in which the methyl groups are alpha to the nitrogens have shown that steric effects are significant for these ligands.[4] Likewise, the threshold activation voltages of the complexes containing 2,9-dibutyl-1,10-phenanthroline were consistently lower than those of the 2,4,7,8-tetramethyl-1,10-phenanthroline complexes, despite the greater polarizability of the dibutyl ligand. This result confirms the significant steric influence of the butyl substituents adjacent to the nitrogen donor atoms, as expected on the basis of the known steric effects from prior metal complexation studies in solution.[42]

Another interesting trend is revealed upon comparison of the threshold activation voltages for the various alkali metal complexes containing 2,9-dimethyl-1,10-phenanthroline vs 2,9-dibutyl-1,10-phenanthroline. Both ligands are sterically hindered near the nitrogen donor atoms, but the dibutyl ligand is substantially more polarizable and thus might be predicted to bind the ions more strongly. The threshold activation voltage of the $[Li(2,9\text{-dibutyl-1,10-phenanthroline})_2]^+$ complex is slightly lower than that of the $[Li(2,9\text{-dimethyl-1,10-phenanthroline})_2]^+$ complex, whereas the order of threshold activation voltages reverses for the analogous complexes containing Na^+, K^+, Rb^+, and Cs^+. This reversal likely stems from the alleviation of steric effects in the 2,9-dibutyl-1,10-phenanthroline complexes as the size of the metal ion increases, as well as the reduced electrostatic attraction caused by lower charge density at the metal center.

The difference in the preorganization of the pyridyl ligands is also an important factor in complex formation and the resulting binding energies of the complexes. 1,10-Phenanthrolines possess two nitrogen donors that are permanently aligned and thus are more preorganized chelators than the 2,2′-bipyridine ligands, where the two pyridine rings are free to rotate. Although free 2,2′-bipyridine is known to exist in a *trans*-planar conformation in solution, it converts to a fixed *cis*-planar conformation upon metal complexation.[4] 1,10-Phenanthroline, which is fixed in a planar *cis* conformation, therefore is known to have a much greater dipole moment (3.64 D) than 2,2′-bipyridine (0.69 D) in benzene.[4] This difference is likewise reflected in the greater threshold activation voltages of the phenanthroline complexes relative to those of the analogous bipyridine complexes in the mass spectrometric measurements.

Phenanthrene, lacking the nitrogen donors of 1,10-phenanthroline, was not observed to form complexes with any of the metals and thus could not be studied further. 4,7-Phenanthroline, with its nitrogen donors in positions that prohibit simultaneous coordination of the metal, formed substantial complexes only with lithium. It is possible that other metal complexes were formed in solution but were so fragile that they dissociated in the ESI process. The $[Li(4,7\text{-phenanthroline})_2]^+$ complexes were surprisingly stable, with threshold activation voltages similar to that of the 2,2′-bipyridine complexes. Although bidentate complexation of each 4,7-phenanthroline ligand with the alkali metal is not possible, the possible participation of $\pi{-}Li^+$ interactions may assist in the stabilization of the complexes. However, the lack of metal complexes for phenanthrene implies that cation$-\pi$ binding interactions are far less important than the interactions involving the nitrogen lone pairs.

Although 2,2′:6′,2″-terpyridine lacks the rigid preorganization of the phenanthrolines, it may engage in tridentate coordination of the alkali metals. In fact, the threshold activation voltages of the $[M^I(2,2'{:}6',2''\text{-terpyridine})_2]^+$ complexes were among the lowest of the ligands investigated, and the K^+, Rb^+, and Cs^+/bis-terpyridine complexes were never observed. A single 2,2′:6′,2″-terpyridine molecule is likely to strongly coordinate the metal ion, effectively delocalizing its charge and preventing the

Table 2. Threshold Activation Voltage (V_{p-p}) for Reduced Bis-Pyridyl Ligand/Metal Complexes

	$[Co^{I}L_2]^+$	$[Ni^{I}L_2]^+$	$[Cu^{I}L_2]^+$	$[Zn^{I}L_2]^+$	$[Cd^{I}L_2]^+$
1,10-phenantholine	1.37[a]	1.37	1.17	1.30	0.93
4,7-phenanthroline	–[b]	–	1.21	–	–
2,9-dimethyl-1,10-phenanthroline	–	–	1.24	1.23	1.31
4,7-dimethyl-1,10-phenanthroline	1.55	1.52	1.33	1.45	1.15
5,6-dimethyl-1,10-phenanthroline	1.57	1.44	1.35	1.40	1.07
2,4,7,8-tetramethyl-1,10-phenanthroline	1.72	1.48	1.39	1.51	1.12
2,9-dibutyl-1,10-phenanthroline	–	1.12	1.26	1.27	–
4,7-diphenyl-1,10-phenanthroline	2.03	1.73	1.61	1.60	1.26
2,2′-bipyridine	1.34	1.30	1.06	1.16	1.06
4,4′-dimethyl-2,2′-bipyridine	1.41	1.37	1.26	1.22	0.93
2,2′:6′,2″-terpyridine	1.22	0.89	0.76	–	–

[a] Maximum standard deviation of ±0.04 V. [b] Dashes indicate a lack of complex formation.

attachment of a second bulky 2,2′:6′,2″-terpyridine or only allowing a weak coordination of the second ligand, thus rendering low threshold activation voltages for dissociation of the bis complexes. Moreover, terpyridine distorts via a pinching inward of the outer pyridine rings to form obligate planar complexes. This distortion causes strain in the resulting complexes and may not allow an optimal orbital overlap of the second ligand with the metal ion. In solution, 1:1 complexes of both lithium and sodium/2,2′:6′,2″-terpyridine have been reported in solution, whereas 2:1 complexes have not.[1] In addition, it was determined by ^{23}Na NMR experiments that 2,2′:6′-2″-terpyridine binds sodium more strongly than 2,2′-bipyridine but less strongly than 1,10-phenanthroline in the 1:1 complexes. The relative binding energies of these types of 1:1 complexes, although observed in the present ESI-mass spectra, could not be determined because the sole expected product is either Na^+ or Li^+, neither of which is effectively trapped during activation of the higher-molecular-weight complexes.

ii. Transition Metal and Group IIB Complexes: CAD of $[M^{I} L_2]^+ \rightarrow [M^{I} L]^+$. The threshold activation voltages for the dissociation of the $[M^{I}L_2]^+$ complexes where $M^{I} = Co^+$, Ni, Cu^+, Zn^+, or Cd^+, resulting in $[M^{I}L]^+$ products, are summarized in Table 2. The general trend for the influence of the ligand on the relative binding energies is 4,7-diphenyl-1,10-phenanthroline > 3,4,7,8-tetramethyl-1,10-phenanthroline > 4,7-dimethyl-1,10-phenanthroline ≥ 5,6-dimethyl-1,10-phenanthroline > 1,10-phenanthroline > 2,9-dimethyl-1,10-phenanthroline > 2,9-dibutyl-1,10-phenanthroline. This trend correlates with the polarizability of the ligands (Table 1) and the negative impact of steric effects for those ligands with alkyl substituents in the 2,9-positions. In fact, stable complexes were not observed for some of the metals with the 2,9-substituted ligands, indicating that the complexes failed to form in solution or did not survive the ESI process. The low binding energies of the $[M^{I}(2,2':6',2''\text{-terpyridine})_2]^+$ complexes likely indicate that the second tridentate ligand is weakly coordinated due to the strong coordination and charge delocalization from the first tridentate ligand, with concomitant strain due to the reduction of the interannular angle of the pyridine rings in the bis complexes. 2,2′:6′,2″-Terpyridine, although possessing a *trans*, *trans* conformation in its free form in solution, converts to a *cis*, *cis* conformation upon metal complexation.[2] The ligand must distort by reducing the angle between the three pyridine rings in order to effectively engage in tridentate coordination. Apparently, the carbon−nitrogen angles decrease from 116 to 114°, and the dihedral angle between the pyridyl rings increases from 5.7 to 7.1° in the metal complexes, creating more strain in the chelate complexes.[2]

The threshold activation voltages of these transition metal bis-ligand complexes are consistently higher than those of the alkali metal complexes, despite the similar charge densities of some of the metal ions (i.e., Cu^+ and Na^+). This result, discussed later, confirms that the electronic nature of the metal has a significant influence in the formation of stable complexes in the gas phase.

Complexes involving +1 transition metal ions have not been extensively studied in solution, partly because this oxidation state is uncommon.[1−3] The formation and binding constants of complexes containing Cu(I) have been reported only for 1,10-phenanthroline and 2,2′-bipyridine.[36] The ability of 1,10-phenanthroline and related pyridyl ligands to form complexes with the +1 transition metals is believed to result from transfer of electron density from the metal to the ligand,[1] and this likely contributes to the formation of the stable +1 complexes observed for many of the transition metals and ligands in the ESI-MS experiments.

iii. Transition Metal and Group IIB Complexes: CAD of $[M^{II} L_3]^{2+} \rightarrow [M^{II} L_2]^{2+}$. The threshold activation voltages for the dissociation of the $[M^{II}L_3]^{2+}$ complexes where $M = Co^{2+}$, Ni^{2+}, Cu^{2+}, Zn^{2+}, and Cd^{2+}, giving $[M^{II}L_2]^{2+}$ complexes, are shown in Table 3. Tris-ligand complexes were not observed for 4,7-phenanthroline, the 2,9-alkyl-substituted ligands, and 2,2′:2′,6″-terpyridine, and thus their relative binding energies could not be evaluated. These latter 3:1 ligand:metal complexes have not been reported in conventional solution studies either. Previous studies have found that the dimensions of the 1,10-phenanthroline and 2,2-bipyridine/metal complexes vary little with the coordination number or type of first-row transition metal,[4] and thus it was expected that these complexes could be successfully evaluated in the gas phase, too. In general, the relative gas-phase binding energies follow the trend 4,7-diphenyl-1,10-phenanthroline > 2,4,7,8-tetramethyl-1,10-phenanthroline > 4,7-dimethyl-1,10-phenanthroline ≥ 5,6-dimethyl-1,10-phenanthroline > 1,10-phenanthroline > 4,4′-dimethyl-2,2′-bipyridine > 2,2′-bipyridine, once again implicating the roles of sterics and polarizability in the formation of these tris-ligand complexes.

It was of interest to determine if there existed a correlation between the relative binding energies of the $[M^{II}L_3]^{2+}$ complexes in the gas phase and the binding constants reported for the $[M^{II}L_3]^{2+}$ complexes in aqueous solution. The binding constants, reported as log K values for the formation of ML_3 complexes[31] in Table 5, can be converted to binding free energies, so some correlation with the relative gas-phase binding energies was reasonably expected. The correlations are mapped in Figure 6 for the metals Co(II), Ni(II), Cu(II), and Zn(II) and the ligands 1,10-phenanthroline, 4,7-dimethyl-1,10-phenanthroline, 5,6-dimethyl-1,10-phenathroline, 4,4′-dimethyl-2,2′-bipyridine, and 2,2′-bipyridine. For each of the four metals, there is a positive correlation in Figure 6, suggesting that solvation-mediated effects are secondary to the intrinsic nature of the binding interactions of the $[M^{II}L_3]^{2+}$ complexes, which are dominated by strong covalent bonds that differ in net strength based on the coordination geometries and available d orbitals of the metals.

iv. Alkaline Earth Metal Complexes: CAD of $[M^{II} L_3]^{2+} \rightarrow [M^{II} L_2]^{2+}$. The threshold activation voltages for $[M^{II}L_3]^{2+}$ complexes where $M^{II} = Mg^{2+}$ or Ca^{2+} are shown in Table 3.

Table 3. Threshold Activation Voltage (V_{p-p}) for Tris-Pyridyl Ligand/Metal Complexes

	$[Co^{II}L_3]^{2+}$	$[Ni^{II}L_3]^{2+}$	$[Cu^{II}L_3]^{2+}$	$[Zn^{II}L_3]^{2+}$	$[Cd^{II}L_3]^{2+}$	$[Mg^{II}L_3]^{2+}$	$[Ca^{II}L_3]^{2+}$
1,10-phenantholine	0.91[a]	1.01	0.74	0.84	0.86	1.05	1.12
4,7-phenanthroline	–[b]	–	–	–	–	–	–
2,9-dimethyl-1,10-phenanthroline	–	–	–	–	–	–	0.88
4,7-dimethyl-1,10-phenanthroline	1.01	1.10	0.82	0.95	0.97	1.14	1.18
5,6-dimethyl-1,10-phenanthroline	1.00	1.11	0.85	0.93	0.96	1.16	1.18
2,4,7,8-tetramethyl-1,10-phenanthroline	1.00	1.09	0.86	0.92	1.0	1.24	1.30
2,9-dibutyl-1,10-phenanthroline	–	–	–	–	–	–	0.76
4,7-diphenyl-1,10-phenanthroline	1.22	1.30	0.98	1.03	1.15	1.35	1.40
2,2′-bipyridine	0.87	0.93	0.61	0.75	0.75	0.95	0.96
4,4′-dimethyl-2,2′-bipyridine	0.90	1.01	0.68	0.80	0.86	1.06	1.11
2,2′:6′,2″-terpyridine	–	–	–	–	–	–	0.63

[a] Maximum standard deviation of ±0.04 V. [b] Dashes indicate a lack of complex formation.

Table 4. Ionic Radii of Metal Ions Used in this Study[a]

metal ion	ionic radius (Å) M^{2+}	ionic radius (Å) M^+
Co	0.72	>0.72
Ni	0.69	>0.69
Cu	0.72	0.96
Zn	0.74	0.89
Cd	0.97	1.14
Mg	0.66	–
Ca	0.99	–
Li	–	0.68
Na	–	0.95
K	–	1.33
Rb	–	1.47
Cs	–	1.67

[a] From ref 40.

Table 5. Log *K* Values of $ML_3/M.L^3$ for Selected Pyridyl Ligands[36]

	Co(II)	Ni(II)	Cu(II)	Zn(II)
1,10-phenanthroline	19.8	24.3	21.0	17.1
4,7-dimethyl-1,10-phenanthroline	24.5	25.0	22.0	19.1
5,6-dimethyl-1,10-phenanthroline	23.6	24.8	21.1	18.6
2,2′-bipyridine	16.0	20.2	16.9	13.2
4,4′-dimethyl-2,2′-bipyridine	16.6	–	–	–

These values are generally somewhat greater than those of the analogous transition metal complexes, a result attributed to the lack of valence electrons of the divalent alkaline earth metal ions, which leads to higher nuclear charges than those of the divalent transition metals.[43] Complex formation with Mg^{2+} and/or Ca^{2+} was observed with all the pyridyl ligands except the nonchelators, 4,7-phenanthroline and phenanthrene. A ranking of the relative threshold activation voltages for the pyridyl ligand complexes revealed the following trend: 4,7-diphenyl-1,10-phenanthroline > 2,4,7,8-tetramethyl-1,10-phenanthroline > 5,6-dimethyl-1,10-phenanthroline ≥ 4,7-dimethyl-1,10-phenathroline > 1,10-phenanthroline ~ 4,4′-dimethyl-1,10-bipyridine > 2,2′-bipyridine > 2,9-dimethyl-1,10-phenanthroline > 2,9-dibutyl-1,10-phenanthroline > 2,2′:6′,2″-terpyridine, again correlating with the polarizability of the ligand and steric effects. The threshold activation voltages were similar for complexes with Ca^{2+} and Mg^{2+}, despite the greater size and lower charge density of Ca^{2+}. This result likely reflects the alleviation of ligand–ligand repulsions in the Ca^{2+} complexes, a factor that compensates for the reduction in binding energies that would otherwise be expected due to the lower charge density relative to that of Mg^{2+}.[43] Complexes of $[CaL_3]^{2+}$, but not $[MgL_3]^{+2}$, were also observed for the sterically hindered ligands 2,9-dimethyl-1,10-phenanthroline and 2,9-dibutyl-1,10-phenanthroline and the tridentate ligand 2,2′:6′,2″-terpyridine. The greater size of the Ca^{2+} ion relative to that of the Mg^{2+} ion permits coordination of even sterically hindered pyridyl ligands.

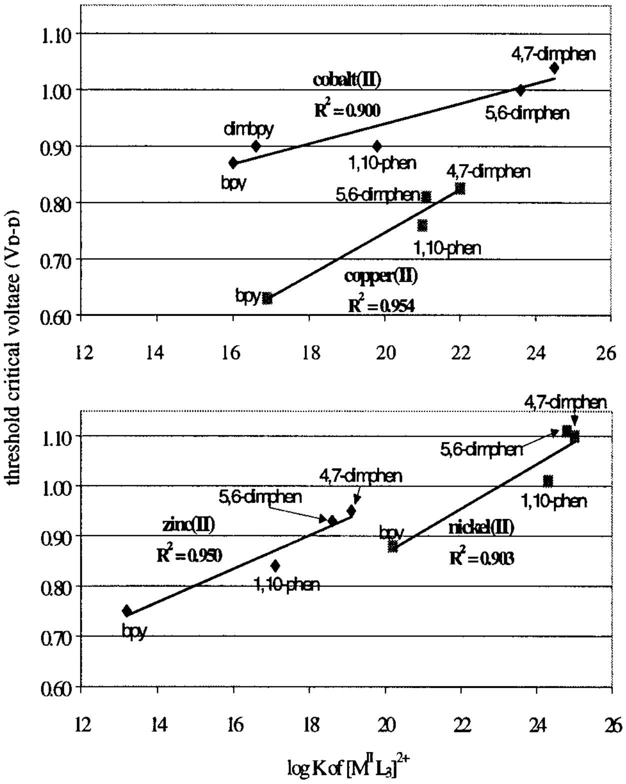

Figure 6. Correlations between solution log *K* values and threshold activation voltage of $[M^{II}L_3]^+$ determined in the gas phase.

B. Metal-Dependent Trends. i. Pyridyl Ligand/Metal Complexes: CAD of $[M^I L_2]^+ \rightarrow [M^I L]^+$. For the series of bis-ligand complexes, the binding energies of the Co^+ complexes were consistently greater than those of the other transition metal complexes (Table 2), as indicated by the higher threshold activation voltages needed to cleave one ligand from the complexes. The general order of binding energies, based on the identity of the metal, is $Co^+ > Ni^+ > Zn^+ > Cu^+ > Cd^+ \sim Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$. For ions of similar ionic radii (Cu^+ and Na^+, for example), the binding energies of the alkali metal complexes $[M^IL_2]^+$ are less than those of the transition metal complexes due to the types of bonds involved (degree of semicovalent character, possibility of π bonding and sd-σ hybridization in the transition metal complexes);[44] this illustrates the influence of the electronic nature of the metal ion beyond that of simple charge density effects. The alkali metals act as

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(43) Bauschlicher, C. W.; Sodupe, M.; Partridge, H. *J. Chem. Phys.* **1992**, *96*, 4453–4463.

spheres of charge. On the other hand, the transition metals may have particular coordination geometries and the ligand binding may involve the d orbitals on the electron-deficient metal ion.

ii. Pyridyl Ligand/Metal Complexes: CAD of $[M^{II} L_3]^{+2} \rightarrow [M^{II} L_2]^{+2}$. Examination of the threshold activation voltages obtained from the energy-variable CAD curves of $[M^{II}(1,10\text{-phenanthroline})_3]^+$ complexes containing the divalent transition metals and alkaline earth metals (Table 2) reveals trends based on the size and electronic nature of the metal ion. For the transition metals, the trend in threshold activation voltages is Ni^{2+} (0.69 Å) > Co^{2+} (0.72 Å) > Cu^{2+} (0.72 Å), in accordance with the size of the metal and coordination geometry. Complexes of transition metal ions with six coordination sites, as in $[M^{II}L_3]^{+2}$, are typically octahedral. Copper(II), a d^9 metal ion, also forms octahedral complexes (albeit distorted) but with greater strain than the other metal ions due to repulsion along two axes (the Jahn–Teller distortion); thus, the threshold activation voltages of the tris-copper(II) complexes are lower than expected on the basis of only charge density. The complexes of the group IIB metals, Zn^{2+} and Cd^{2+}, also have generally lower threshold activation voltages than the transition metal complexes, likely reflecting the decreased participation of d–π bonding for these metals.

Differences between the threshold activation voltages for the $[M^{II}L_3]^{2+}$ complexes of the alkaline earth metals and those of the transition metals are also apparent in Table 3. These are not due to ionic size since the ionic radii are similar (Ca^{2+} and Cd^{2+}, Mg^{2+} and Ni^{2+}) but are due to a combination of other factors, including the nature of the binding forces and geometric restrictions. The less-specific coordination geometries of the alkaline earth metal ions, along with their lack of valence electrons and consequent reduction of ligand–metal repulsions, result in stronger binding interactions than those for the transition metal complexes with bonds at specific coordination sites and d valence electrons.

Correlation of Threshold Activation Voltages with Critical Energy Values. As an initial assessment of the validity of the energy-variable CAD method for quantitative measurements, the threshold activation voltages of four crown ether/alkali metal complexes were measured for comparison with critical energy values determined by Rodgers and Armentrout[34] using a guided ion beam mass spectrometer. As seen in Figure 7, a direct correlation between the critical energies determined by Armentrout and the threshold activation voltages was found. This suggests that it may be possible to calibrate the energy scale in the ion trap and determine absolute values of binding energies instead of relative values. Such a calibration would require the analysis of complexes possessing higher binding energies since the crown ether complexes[34] have threshold activation voltages in the lower range of those observed for the pyridyl ligand/metal complexes. This issue will be further investigated in a future study.

In addition, one could imagine that the correlation between the measured threshold activation voltages of the crown ether complexes, or other types of metal/ligand complexes, and known binding constants in solution could be examined, as shown in Figure 6 for the pyridyl ligand/transition metal complexes. However, these types of correlations may be somewhat limited because the CAD method in the ion trap becomes ineffective for cases in which the masses of the fragment ions of interest differ greatly from the masses of the precursor complexes, which is the case for complexes such as (18-crown-6 + Li^+), which dissociates to Li^+. The inability to trap the Li^+ product while activating the (18-crown-6 + Li^+) complex prevents the assessment of the threshold activation voltage, and this type of limitation thus restricts the general applicability of the method and the ability to construct correlations with binding constants in solution.

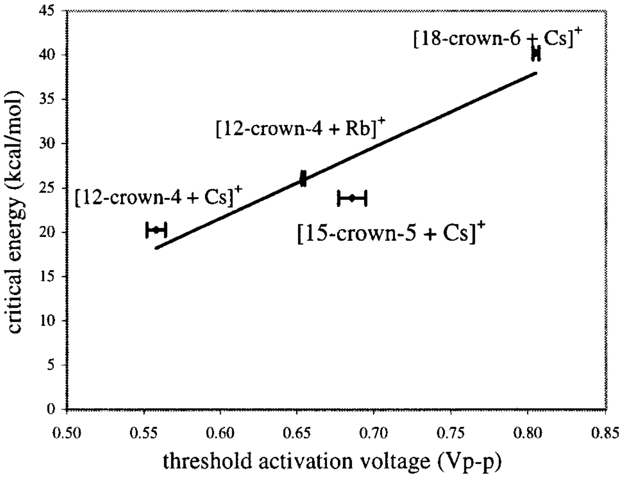

Figure 7. Correlation between critical energies determined by Rodgers and Armentrout[34] and threshold activation voltages of crown ether/alkali metal complexes. Error bars represent one standard deviation.

Conclusion

Complexes consisting of a series of pyridyl ligands with alkali, alkaline earth, and transition metals of the types $[M^{II}L_3]^{2+}$ and $[M^{I}L_2]^+$ have been investigated, and energy-variable collisionally activated dissociation has been used to probe their relative binding energies in a quadrupole ion trap. The type of metal ion, its electronic nature, and structural features of the pyridyl ligands influence the threshold activation voltages of the pyridyl ligand/metal complexes. For example, the threshold activation voltages were greater for the monopositive bis-pyridyl ligand/transition metal complexes than for the corresponding alkali metal complexes, confirming that the electronic nature of the metal ion, including the possibility of sd-σ hybridization and participation of d orbitals in binding, mediates the strength of the interactions in the gas phase. Polarizability, preorganization, chelating effects, and steric hindrance of the pyridyl ligands were important factors in the formation of complexes and in the observed threshold activation voltages. Of the pyridyl ligands investigated, complexes containing 4,7-diphenyl-1,10-phenanthroline and 2,4,7,8-tetramethyl-1,10-phenanthroline generally had the greatest threshold activation voltages, followed by the various methyl-substituted phenanthrolines, and then the nonsubstituted 1,10-phenanthroline, thus correlating with ligand polarizability. A direct correlation between log K values for the formation of ML_3 pyridyl ligand/transition metal complexes in aqueous solution and the threshold activation voltages of the $[M^{II}L_3]^{2+}$ complexes in the gas phase was found, reflecting the dominance of the intrinsic strength of the binding interactions over solvent-mediated effects.

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Supporting Information Available: Graphs of ligand- and metal-dependent trends. This material is available free of charge via the Internet at http://pubs.acs.org.

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