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# Gas-Phase Chelation Reactions of Monopositive Cations with Heteroaromatic Ligands

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Understanding fundamental aspects of coordination chemistry is important in the study of catalysis, many enzymatic systems, and even biomedical processes. In the present investigation, gas-phase ion−molecule reactions between an array of heteroaromatic ligands and a series of monopositive metal ions are examined. Production formation, with respect to dimerization or trimerization, is correlated with the electronic configuration of the metal ion and the polydentate properties of the ligand. The orders of relative metal ion binding affinities of the heteroaromatic ligands are determined from ligand exchange techniques in order to establish the influence of the size and electronic configuration of the metal ion and size and flexibility of the aromatic ligand. Typically terpyridine demonstrates the greatest metal ion binding strength, followed by phenanthroline, 2,2′-bipyridine, then pyridine. For many of the monomer metal complexes, a molecule of water may be incorporated at longer reaction times, but this hydration process is not observed for the dimer or trimer complexes.

## Introduction

Traditionally, coordination chemistry has been concerned with the evaluation of chemical and physical changes observed upon complexation of metal ions with organic ligands. Heteroaromatic compounds such as pyridine, 2,2′-bipyridine, 1,10-phenanthroline, and their many derivatives have played a formative role in the fundamental understanding of coordination chemistry in solution.[1−3] For example, coordination of these heterocyclic ligands to metal ions may open up reaction pathways involving electrophilic or nucleophilic attack which are not accessible for the free ligand.[4−15] There have been numerous other fundamental studies of metal−ligand complexation,[16−19] some which have evaluated the structures of the complexes, determined equilibrium constants, and examined the kinetics of the processes. The metal complexes may also function as catalysts, and there are many metal-directed reactions known in enzymatic systems. Thus, the importance of the series of heterocyclic compounds is well-known not only in coordination chemistry but also in their biological and medicine applications.

Many reports have shown that fully coordinated 1,10-phenanthroline and 2,2′-bipyridine transition metal chelates have widespread activities in biological and clinical systems.[20−33] Metal chelates have antibacterial, antifungal, antiviral, and antimicrobial activities which are dependent on the nature of the organic ligand and the type of metal ion. For instance, Ru(II) chelates of substituted 1,10-phenanthroline and 2,2′-bipyridine bases can inhibit the growth of Landschutz ascites tumor cells both in vitro and in the mouse.[28,29] It is also believed that the organic ligand assists in the selective transport of metal cations which might otherwise be sequestered and deactivated by other compounds in the bacterial cells.

In solution, divalent metal ions typically may attach up to two terpyridine ligands, three 2,2′-bipyridine or 1,10-phenanthroline ligands, or four pyridine molecules. The resulting structures are dependent on the electronic configuration of the metal, the strain and steric hindrance of the ligand, and charge density of the metal ion. Monovalent metal ions, such as $Ag^+$ and $Cu^+$, typically result in formation of bis complexes in solution, with the exception of terpyridine which fully coordinates a single metal ion and pyridine which may form tetramers.

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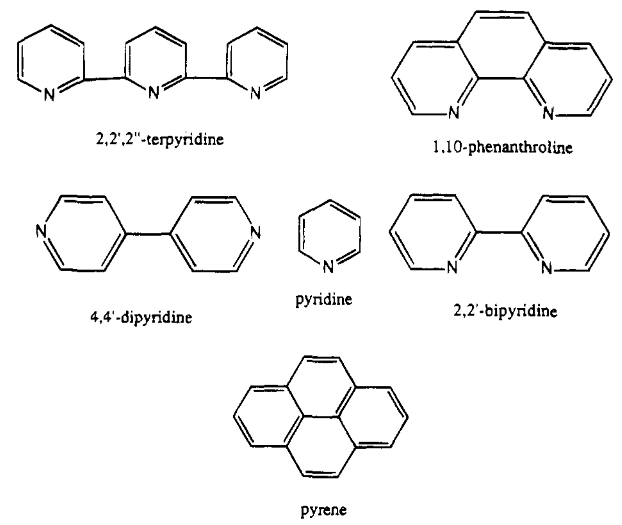

**Figure 1.** Structures of ligands.

With regards to some of the more unusual structures of the complexes, sometimes "double-bonded" structures have been proposed for metal complexes containing pyridine.[32] In these structures, it is predicted that the metal ion can alternately donate or accept electrons to or from the pyridine ligand. The high stability of iron triad chelates of 2,2′-bipyridine and 1,10-phenanthroline are believed to correlate with analogous double-bonded structures.[33]

Reactions undertaken in the solvent-free environment of a mass spectrometer provide a new perspective for understanding the intrinsic binding properties of these interesting chelators. In fact, advanced mass spectrometric techniques allow the generation of selectively-solvated cluster ions,[34–36] whose reactions can be studied as the degree of solvation is varied. These latter developments provide a promising means for truly understanding the role that solvent plays in chemical processes in solution. In order to understand some of the factors which mediate complexation in the gas phase, we have undertaken several systematic studies of host–guest chemistry in the gas phase involving an array of crown ethers and their acyclic analogs as model hosts.[37–39] The interactions of these hosts with a variety of model guests, such as alkali metal ions or ammonium ions, involve predominantly electrostatic and hydrogen-bonding forces. Because of the success of these prior studies involving host–guest complexation, the evaluation of chelation in the gas phase was targeted in the present report.

The study described herein involves the examination of complexes formed from reactions of a variety of monopositive cations with pyridine, 2,2′-bipyridine, 4,4′-bipyridine, 1,10-phenanthroline, 2,2′,2″-terpyridine, and pyrene (Figure 1). A variety of metal ions with a diverse array of electronic configurations were studied in order to determine the importance of this factor in influencing the relative binding affinities and extent of complex formation with the different aromatic ligands. The metal ions are produced by laser desorption (LD) in a quadrupole ion trap mass spectrometer, and the complexes are formed from subsequent ion–molecule reactions with these ligands. A summary of the electronic configurations of the metal ions is given in Table 1. Complexation with the ammonium ion was also investigated due to the large size and polyatomic nature of this cation, relative to the atomic metal ions. The ligand exchange technique was used to determine the relative orders of metal ion affinities[40] and also gas-phase basicities as a comparison. Many different types of binding interactions would be expected including electrostatic interactions, hydrogen-bonding, and covalent bonds, due to the different electronic nature of the cations. Despite the fact that many of the chelation studies performed in solution have involved the examination of divalent metal ions, we believed that the reactions of monopositive metal ions in the gas phase would allow the informative determination of complexation trends based on the *n*-dentate nature of the ligands, regardless of the formal valence state of the metal ion.

**Table 1.** Ground State Electronic Configurations of Metal Ions

| metal ion | configuration | metal ion | configuration |
|---|---|---|---|
| $Mg^+$ | (Ne) $3s^1$ | $Ni^+$ | (Ar) $3d^9$ |
| $Al^+$ | (Ne) $3s^2$ | $Cu^+$ | (Ar) $3d^{10}$ |
| $Fe^+$ | (Ar) $3d^8$ | $Ag^+$ | (Kr) $4d^{10}$ |
| $Co^+$ | (Ar) $3d^9$ | | |

With respect to the heteroaromatic ligands examined herein, the effects of the rigidity of the ligand were evaluated by comparing 1,10-phenanthroline with 2,2′-bipyridine, since 2,2′-bipyridine possesses a *trans* configuration both in solution[41] and in the solid state.[42] However, it can rotate and stabilize in the *cis* configuration after overcoming a low energy barrier upon complexation with a cation. Comparing pyridine with 2,2′-bipyridine and 2,2′,2″-terpyridine complexes also allows the evaluation of the importance of the number of chelating sites of each ligand. Pyrene is the only ligand which is not a heterocyclic compound, and thus it is used to compare the importance of the heteroatom on the binding properties of the aromatic ligand.

## Experimental Section

The experiments were performed in a Finnigan quadrupole ion trap mass spectrometer (ITMS)[43] equipped with a fiber optic laser desorption interface.[44] The Nd:YAG laser used for all infrared desorption studies was operated in the Q-switch mode, and the beam was focused into a probe-mounted fiber optic. The power density was maintained from 2 x $10^7$ to 2 x $10^8$ W/cm$^2$, depending on the metal source (salts or foils).

The metal ions including $Al^+$, $Mg^+$, $Fe^+$, $Co^+$, $Ni^+$, $Zn^+$, $Cu^+$, and $Ag^+$ were generated, stored in the ion trap, and allowed to react with the aromatic ligands. Because of the high energy deposition of the laser desorption event, some of the ablated metal ions may exist in excited states. There is no efficient way to ensure complete cooling of all excited state ions to their ground states, so the reported results reflect the possible mixture of reactions of metals ion in ground and excited electronic states. The products are reproducible from day to day, and at various pressures and laser power densities, so we have no evidence that the metal ions behave differently in the possible states or even exist in different electronic states. Therefore, because of the absence of any irregularities in the results, the presence of excited states is not addressed further in this study.

All compounds were admitted through a solids probe with the temperature controlled at 100–180 °C, except pyridine which was introduced through a leak valve to $10^{-6}$ Torr. The metal/aromatic complexes were mass-analyzed by operating the ion trap in the mass selective instability mode. The helium buffer gas pressure was maintained at 1.5 mTorr to assist in collisional cooling of the complexes.

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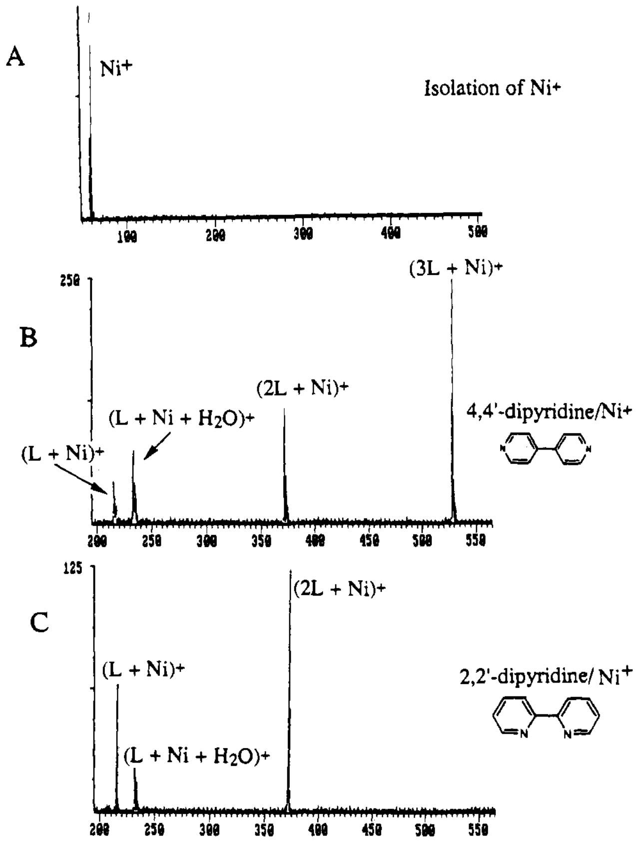

**Figure 2.** (A) Isolation of $Ni^+$ ions, followed by reactions with (B) 4,4′-bipyridine and (C) 2,2′-bipyridine.

For some experiments, $H_2O$, $D_2O$, or methanol was admitted to $2.0 \times 10^{-6}$ Torr in order to study solvation of the metal complexes.

For the ligand exchange experiments,[40] each pair of ligands was admitted inside the chamber at about the same pressures. A selected $(L_1 + \text{metal})^+$ ion was isolated and then allowed to react with another ligand ($L_2$) for a period of 0–100 ms. Exchange reactions were evaluated in both the forward and reverse directions.

All compounds were purchased from Aldrich Chemical Co. (Milwaukee, WI) except pyridine which was obtained from EM Science (Gibbstown, NJ).

## Results and Discussion

**I. Formation of Metal/Aromatic Ligand Complexes.** One primary objective was to determine the extent of reactivity of each monopositive metal ion in order to determine whether there were specific trends characteristic of each different electronic configuration or whether the net charge density of the metal ions mediated the extent of their reactivity, in which case few distinctions would be noted among the types of reaction products generated for each ligand. In order to obtain an overview of the reactions of metal ions with aromatic ligands, each aromatic ligand (L) was allowed to react with a selected metal ion ($M^+$), and the distribution of simple ion–molecule complexes was systematically examined. The products of special interest included $(L + M)^+$, $(2L + M)^+$, $(3L + M)^+$, and $(L + M + H_2O)^+$, where L represents the aromatic ligand and M represents the metal cation. Typical product spectra are shown in Figures 2 and 3, and a summary of the complete list of the products of ion–molecule reactions between metal ions and each of the various aromatic ligands is given in Table 2. For each metal ion examined, the monomer and dimer complexes are formed for each heteroaromatic ligand. The only differences in the reactivities are noted in the absence or presence of the trimer complexes, which vary for each combination of metal ion and heteroaromatic ligand.

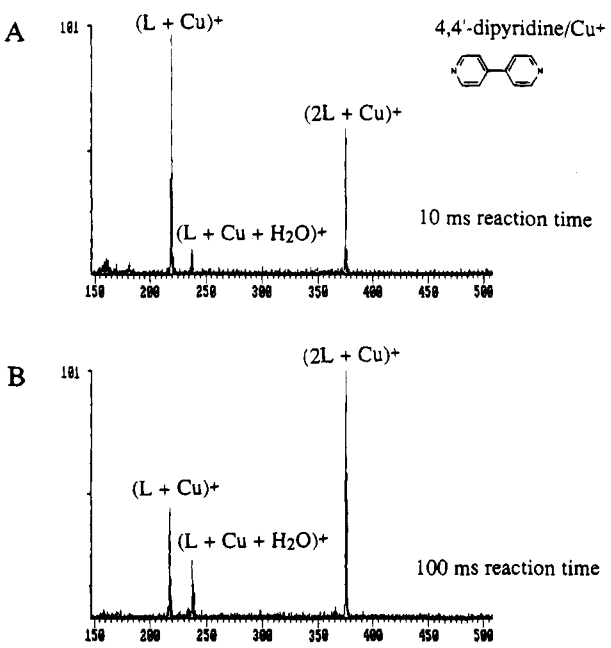

**Figure 3.** Reactions of $Cu^+$ ions with 4,4′-bipyridine for (A) 10 ms and (B) 100 ms.

**Table 2.** Products of Reactions of Cations with Aromatic Ligands[a]

| cation | 1,10-phenanthroline | 2,2′-bipyridine | 4,4′-bipyridine | 2,2′,2″-terpyridine | pyridine | pyrene |
|---|---|---|---|---|---|---|
| $Mg^+$ | | | | | | |
| $(L + M)^+$ | + | + | + | + | + | + |
| $(2L + M)^+$ | + | + | + | + | + | 0 |
| $(3L + M)^+$ | + | + | 0 | 0 | 0 | 0 |
| $Al^+$ | | | | | | |
| $(L + M)^{2+}$ | + | + | + | + | + | + |
| $(2L + M)$ | + | + | + | + | + | 0 |
| $(3L + M)^+$ | + | + | 0 | 0 | 0 | 0 |
| $Fe^+$ | | | | | | |
| $(L + M)^+$ | + | + | + | + | + | + |
| $(2L + M)^+$ | + | + | + | + | + | + |
| $(3L + M)^+$ | + | + | 0 | 0 | 0 | 0 |
| $Co^+$ | | | | | | |
| $(L + M)^+$ | + | + | + | + | + | + |
| $(2L + M)^+$ | + | + | + | + | + | + |
| $(3L + M)^+$ | + | + | 0 | 0 | 0 | 0 |
| $Ni^+$ | | | | | | |
| $(L + M)^+$ | + | + | + | + | + | + |
| $(2L + M)^+$ | + | + | + | + | + | + |
| $(3L + M)^+$ | 0 | 0 | + | 0 | + | 0 |
| $Cu^+$ | | | | | | |
| $(L + M)^+$ | + | + | + | + | + | + |
| $(2L + M)^+$ | + | + | + | + | + | + |
| $(3L + M)^+$ | 0 | 0 | 0 | 0 | 0 | 0 |
| $Ag^+$ | | | | | | |
| $(L + M)^+$ | + | + | + | + | + | + |
| $(2L + M)^+$ | + | + | + | + | + | + |
| $(3L + M)^+$ | 0 | 0 | 0 | 0 | 0 | 0 |
| $Zn^+$ | | | | | | |
| $(L + M)^+$ | + | + | + | + | + | + |
| $(2L + M)^+$ | + | + | + | + | + | + |
| $(3L + M)^+$ | + | + | 0 | 0 | 0 | 0 |
| $NH_4^+$ | | | | | | |
| $(L + H)^+$ | + | + | + | + | + | + |
| $(2L + H)^+$ | + | + | 0 | 0 | + | 0 |
| $(L + NH_4)^+$ | 0 | 0 | 0 | 0 | 0 | + |

[a] Depending on the reaction time, $(L + M + H_2O)^+$ is also observed.

The electronic configuration of the metal ion and the number of coordination sites of the aromatic ligand are the factors which dominate the types of products formed. Reactions of $Al^+$, $Fe^+$, $Co^+$, $Zn^+$, or $Mg^+$ ions result in formation of dimer and trimer

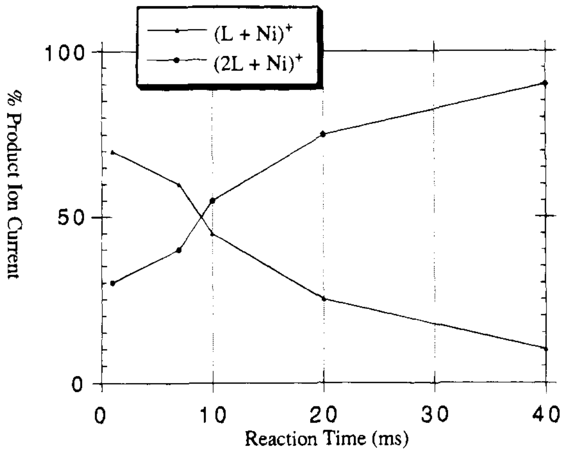

**Figure 4.** Reaction of $Ni^+$ ions with 2,2′-bipyridine as a function of time.

complexes with 1,10-phenanthroline and 2,2′-bipyridine, but only up to dimers with 4,4′-bipyridine, pyridine, and 2,2′,2″-terpyridine. The observation that 2,2′,2″-terpyridine does not from trimers may be rationalized in two ways. Since terpyridine has three chelation sites, it may fully coordinate the metal cation in the gas phase and thus chemically prevent the addition of a third ligand. In addition, the terpyridine molecule may be sufficiently bulky that coordination of two ligands, regardless if each is bi- or tricoordinate, physically blocks the approach of a third ligand. Because they are not bidentate ligands, 4,4′-bipyridine and pyridine do not favor formation of tris complexes with these metal ions in the gas phase.

The reactions with $Ni^+$ are somewhat unusual in that 1,10-phenanthroline, 2,2′,2″-terpyridine, and 2,2′-bipyridine form only the dimer product, whereas 4,4′-bipyridine and pyridine surprisingly form the trimer species (see Figure 2). This is the only case in which the monodentate ligands form complexes containing more ligands than the bidentate ligands. At increasing reaction times, the dimer complexes predominate for the bidentate ligands (see Figure 4), but trimers are never observed. These patterns presumably are due to the ability of 2,2′-bipyridine and 1,10-phenanthroline to function as bidentate ligands and fully coordinate the metal ion, as opposed to pyridine and 4,4′-bipyridine which serve only as monodentate ligands. Clearly in this case, the number of electrons of the $Ni^+$ ion ($d^9$) plays an important role in differentiating its behavior from $Co^+$ and $Fe^+$ ions, ($d^8$ and $d^7$, respectively).

Both $Ag^+$ and $Cu^+$ ions possess similar valence electronic configurations ($d^{10}$), and they form exactly the same types and extent of complexes for all of the aromatic ligands. Abundant $(L + M)^+$ and $(2L + M)^+$ but no $(3L + M)^+$ product ions are observed upon reaction of any of the ligands with $Ag^+$ or $Cu^+$ ions. At longer reaction times, the dimer complex is increasingly produced (Figure 3). This result is analogous to that observed in solution, in which dimer complexes are observed and is related to the well-known sp hybridization of these $d^{10}$ type metal ions.[45]

Pyrene forms some multiply coordinated bis complexes, including $(2L + Fe)^+$ and $(2L + Co)^+$, $(2L + Ni)^+$, and $(2L + Cu)^+$, but trimers are never observed. The structures of the dimers should be sandwich-type via π-bonding, making it sterically impossible for a third molecule of pyrene to add to the dimer to form the tris product $(3L + M)^+$.

With the exception of pyrene, the ammonium ion did not form stable adducts with any of the heteroaromatic ligands. Instead, a proton transfer reaction occurred as shown below:

$$NH_4^+ + L \rightarrow [NH_3\cdots H^+\cdots L]^* \rightarrow NH_3 + (L + H)^+$$

The nitrogen-containing aromatic ligands are substantially more basic (by 15–20 kcal/mol) than ammonia (~196 kcal/mol);[46] therefore, the intermediate proton-bound complex, $(L + H + NH_3)^+$, is too internally excited to remain as a stable intact ion. The complex dissociates more rapidly than collisional deactivation occurs, and thus only protonated ligands are observed. Pyrene, in contrast, has a lower relative gas-phase basicity (~200 kcal/mol), and thus a stable $[NH_3\cdots H^+\cdots L]$ complex is observed. The lack of stability of most of these aromatic complexes contrasts with the numerous types of stable complexes observed for the reactions of metal ions with the aromatic ligands. This contrast reflects the different types of bonding interactions that are operative in each situation. For the ammonium ion reactions, complexes are produced via formation of one or more hydrogen bonds, interactions which are known to be relatively weak. The reactions of the metal ions may clearly promote covalent and ionic-type bonding.

**II. Hydration Phenomena.** As noted in the earlier spectral figures, some of the coordination complexes observed incorporate one molecule of water, identified as the $(L + M^+ + H_2O)$ ions. In fact, the 4,4′-bipyridine ligand is the heteroaromatic compound that most favors hydration, whereas in contrast the analogous hydration reaction does not always occur for terpyridine, such as for the reactions of $Cu^+$ ions with terpyridine. All of the other heteroaromatic ligands promote water addition to some extent if auxiliary water vapor is added to the vacuum chamber. The observation that the 4,4′-bipyridine/metal complexes demonstrate the highest propensity to add water may be related to the large polarizability of 4,4′-bipyridine yet its inability to coordinate a metal ion through two sites, thus leaving the metal ion highly exposed for water attachment. 4,4′-Bipyridine is a bulky ligand with the coordination sites at opposite ends, making the monomer complex not fully coordinated because both binding sites cannot interact with the metal ion. Thus, water addition may compete kinetically with dimerization, without in any way destabilizing the monomer complex. Because of its size, 4,4′-bipyridine is quite polarizable, a factor which may further assist in stabilizing the hydrated complex. By contrast, terpyridine clearly disfavors hydration, suggesting that its ability to bind the metal ion through multiple interactions fills up the metal's acceptor orbitals and may also provide steric shielding.

Water addition is only observed for the monomer $(L + M)^+$ metal complexes, not for the dimers $(2L + M)^+$ or trimers $(3L + M)^+$, even at long reaction times and at high pressures of water vapor. This absence of hydration for the dimer and trimer complexes appears reasonable because the dimers and trimers are sufficiently blocked and fully coordinated, thus disfavoring the attachment of a water molecule to the metal ion. Furthermore, the ligand–metal bond energies are expected to be larger than the water–metal bond energy; therefore, the water molecule may be preferentially displaced by attachment of a second aromatic ligand. A second reason for the lack of hydration of the dimer complexes relates to charge density: the less highly charged the central metal ion, the lower its polarizing power on the C–N bonds.[47] For the gas-phase reactions described herein in which only monovalent cations were involved, the weak polarizing forces on all of the C–N bonds in the dimer complexes may prohibit water attachment.

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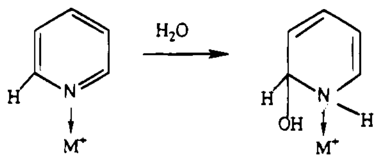
When methanol vapor is added to the vacuum chamber, methanol-solvated complexes are observed at somewhat overall lower relative abundances than observed for the hydrated complexes. Again, the methanol adds only to the monomer ligand complex, not to the dimer or trimer complexes.

In solution, it has been reported that nucleophilic reactions of coordinated pyridines are accessible due to the buildup of positive charge on the ring.[48] For example, the hydration of coordinated pyridines in solution may involve the contributions of free energy changes from the formation of C−OH and N−H bonds and from loss of aromatic character:[49]



In the gas phase, collisionally activation of the (L + Cu + $H_2O$)$^+$ product of 4,4′-bipyridine causes facile elimination of water, supporting the proposal that the water is weakly bound to the metal ion, such as electrostatically attached to the metal center. There is no evidence for any covalent interactions of the water molecule with the complex.

**III. Comparison of the Orders of Relative Metal Ion Binding Affinities.** The ligand exchange technique[40] was used to compare the relative binding strengths of the aromatic ligands for different metal ions. This technique has proven useful for measuring binding energies for a variety of ligands in the past and comparing the relative binding energies for different metal ions. The objective was to evaluate the structural factors that influence the nature of metal ion binding for the various ligands, with respect to such features as the number and location of the heteroatom binding sites and the rigidity of the ligand. A typical example is shown in Figure 5 for determination of the relative order of $Cu^+$ binding energies of 1,10-phenanthroline and 2,2′-bipyridine, and other results of this type of exchange are summarized in Table 3. For the ligand exchange experiments, both of the aromatic ligands are admitted to nearly the same pressures (i.e. concentrations) in the ion trap chamber to ensure almost the same collision probabilities. As shown in Figure 5, $Cu^+$ ions are isolated (A) and allowed to react with two neutral ligands (B). In Figure 5C, the (2,2′-bipyridine + $Cu^+$) complex is isolated, then allowed to react with 1,10-phenanthroline for 200 ms to produce the spectrum shown in Figure 5D. The 1,10-phenanthroline ligand efficiently captures the $Cu^+$ ion. The procedure is reversed in Figure 5E, in which the (1,10-phenanthroline + $Cu^+$) complex is isolated and allowed to react with neutral 2,2′-bipyridine. Since the $Cu^+$ affinity of 1,10-phenanthroline is larger than that of 2,2′-bipyridine, the transfer of the $Cu^+$ ion is not observed in Figure 5F. This type of experiment was repeated for each pair of aromatic ligands and each metal ion in order to derive the orders shown in Table 3.

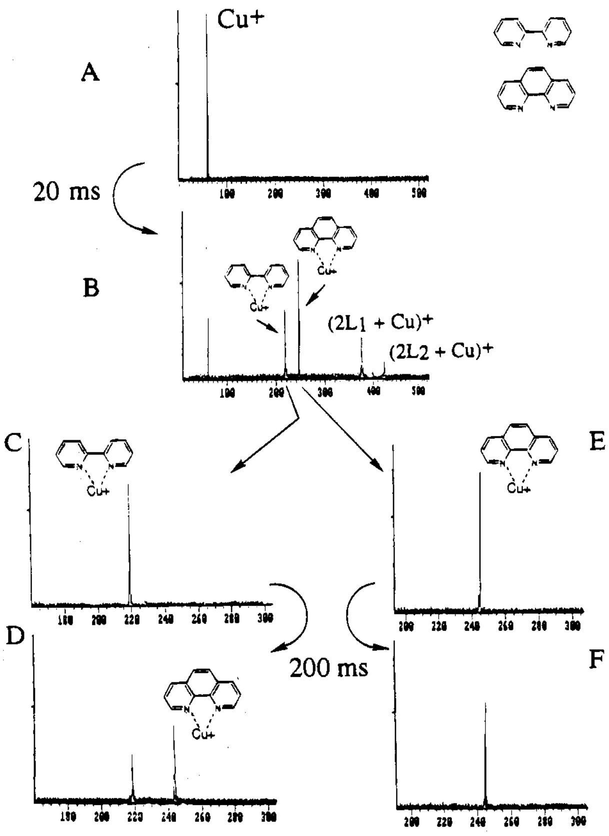


**Figure 5.** Ligand exchange experiment between 2,2′-bipyridine and 1,10-phenanthroline and $Cu^+$ ions: (A) isolation of $Cu^+$ ions; (B) reaction with the two ligands; (C) isolation of (2,2′-bipyridine + $Cu^+$) or (E) (1,10-phenanthroline + $Cu^+$); (D, F) subsequent 200 ms reaction with the other neutral ligand. The 1,10-phenanthroline ligand has a higher $Cu^+$ affinity.

In general, the number of heteroatom binding sites of the aromatic ligands play the most important role in influencing the relative binding energies in this gas-phase study. For all of the cations, terpyridine has the greatest binding affinity, 1,10-phenanthroline has a larger ion affinity than 2,2′-bipyridine, and pyridine demonstrates the lowest binding affinity of all the heteroaromatic ligands. This trend may be attributed to several factors. First, terpyridine has three donor sites (the nitrogen atoms) and is flexible enough to adopt the optimum configuration for fully coordinating the metal cation. Second, 1,10-phenanthroline possesses a larger polarizability and is more rigid than 2,2′-bipyridine, thus the higher degree of preorganization favors the formation of more stable metal ion complexes. 2,2′-Bipyridine undergoes a large conformational change due to the adoption of the *cis*-coplanar structure upon complexation with a metal ion, and this process does not result in the equivalent rigidly-fixed structure as 1,10-phenanthroline. Furthermore, the multidentate ligands (terpyridine, phenanthroline, 2,2′-bipyridine) always show larger ion affinities than the monodentate ligands (4,4′-bipyridine and pyridine), due to the number of active binding sites. Finally, all of the heteroaromatic ligands bind the cations more strongly than does pyrene because $\pi$-bonding interactions are weaker than the coordination bonds formed by donation of the lone pair electrons from the nitrogen atoms to the empty metal orbitals.

**IV. Comparison to Solution Behavior.** Many studies have discussed the measurement of stability constants for interactions of metal ions with heteroaromatic ligands in solution, and the most reliable quantitative values are reported in a comprehensive volume.[50] Several general points are notable when examining the trends reported for the complexation of different metal ions with pyridine, 2,2′-bipyridine, 1,10-phenanthroline, and 2,2′,2″-terpyridine. For instance, complexation of divalent metal ions, including $Zn^{2+}$, $Cu^{2+}$, $Ni^{2+}$, $Co^{2+}$, and $Fe^{2+}$, results in coordination of up to three ligands for the bidentate compounds (2,2′-bipyridine and 1,10-phenanthroline), only one or two ligands for the tridentate terpyridine, and up to four ligands for pyridine. Complexation of monovalent metal ions, such as $Cu^+$ and $Ag^+$,

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**Table 3.** Orders of Metal Ion Affinities

| | |
|---|---|
| $Ag^+$ | 2,2′,2″-terpyridine > 1,10-phenanthroline > 2,2′-bipyridine > pyridine > pyrene |
| $Fe^+$ | 1,10-phenanthroline > 2,2′-bipyridine > pyridine > pyrene |
| $Mg^+$ | 1,10-phenanthroline > 2,2′-bipyridine > pyridine > pyrene |
| $Cu^+$ | 2,2′,2″-terpyridine > 1,10-phenanthroline > 2,2′-bipyridine > pyridine, pyrene |
| $Co^+$ | 2,2′,2″-terpyridine > 1,10-phenanthroline > 2,2′-bipyridine > pyridine |
| $Ni^+$ | 2,2′,2″-terpyridine > 1,10-phenanthroline > 2,2′-bipyridine > pyridine > |
| $H^+$ | 2,2′,2″-terpyridine > 1,10-phenanthroline > 2,2′-bipyridine > pyridine > pyrene |

**Table 4.** log *K* Values for Reactions of Cations with Heterocyclic Ligands in Solution (at 25 °C)[50]

| cation | 1,10-phenanthroline | 2,2′-bipyridine | pyridine | 2,2′,2″-terpyridine |
|---|---|---|---|---|
| $Ag^+$ | 5.0−5.02 | 3.0 | 1.93−2.06 | |
| $Fe^{2+}$ | 5.84−5.86 | 4.20−4.65 | 0.6 | 7.1 |
| $Mg^{2+}$ | 1.2−1.5 | | | |
| $Cu^+$ | 15.82 | 12.95−13.18 | 4.84 | 9.3 |
| $Cu^{2+}$ | 7.4 | 6.33 | 2.50−2.56 | 13.0−13.4 |
| $Cu^{2+}$ ($ML_2$) | 15.8 | 13.5 | 4.5 | 19.1 |
| $Co^{2+}$ | 6.98−7.18 | 5.7−5.9 | 1.15−1.23 | 9.5 |
| $H^+$ | 4.86−5.02 | 4.35−4.67 | 5.24−5.31 | 4.64 |
| $Zn^{2+}$ | 6.4 | 5.12 | 1.04 | 6.0 |
| $Cd^{2+}$ | 5.8 | 4.22 | 1.31 | 5.1 |
| $Ni^{2+}$ | 8.6 | 7.04 | 1.85 | 10.7 |

typically result in coordination of no more than two ligands, regardless of the nature of the ligand. Stability constants for products containing a greater number of ligands than allowed by these guidelines were not reported. Thus, the similar behaviors of the metal ions based only on their valence state, not on their specific electronic configurations, suggests that the complexation process in solution is largely dependent on the relative charge density of the metal ion and not necessarily on the precise number of d electrons available. In many ways, this analysis is similar to that observed in the present gas-phase study. For the most part, all of the monopositive metal ions promote coordination of one or two ligands, and it is only for the bidentate compounds that coordination of three ligands is observed. Just as noted in solution studies, the chelate effect seems to be operative for the reactions involving the bidentate ligands in the gas phase. Of related importance is the observation that coordination of four ligands by any metal ion never occurs in the gas phase. This absence is presumably due to the lower charge density of the monopositive cations in the gas phase, relative to the common divalent ions in solution, a factor which reduces the coordination capabilities of the metal ions in the gas-phase environment.

According to the log K values found in the literature,[50] the results in solution for the stability constants of the various complexes are parallel to many of the gas-phase trends, with the exception of the results involving the measurement of the proton affinity and the coordination of the $Cu^+$ ion. The log K values for the reactions of the metal ions with 2,2′,2″-terpyridine, 1,10-phenanthroline, 2,2′-bipyridine, and pyridine are listed in Table 4. For all of the metal ions except $Cu^+$, the order of stability constants in solution is 2,2′,2″-terpyridine > 1,10-phenanthroline > 2,2′-bipyridine > pyridine. For the proton affinity, pyridine shows the highest basicity in solution, whereas for the $Cu^+$ affinity, both 1,10-phenanthroline and 2,2′-bipyridine show greater log *K* values than terpyridine. With respect to the basicity trend, the origin of the change must be due to the solvation effects on the neutral base or its cationic conjugate acid. Variation in the heats of solvation of the cationic conjugate acids of these bases generally play the largest role in changing the gas-phase basicity orders in solution.[51]

In the gas phase, the trends parallel those observed in solution with two exceptions. For most of the metal ions studied, terpyridine has the greatest relative affinity for the metal cations. However, the order of gas-phase proton affinity differs dramatically from the one observed in solution. The trend in gas-phase basicities correlates directly with ligand polarizability,[51] and thus the largest aromatic ligands show the largest proton affinities. This contrast in the binding affinities between the solution and gas-phase results highlights the well-known important influence of solvent effects on the stabilities of ions in solution. Finally, for complexation of monovalent copper ions, terpyridine again demonstrates the highest affinity in the gas phase, whereas both 1,10-phenanthroline and 2,2′-bipyridine exhibit greater stability constants in solution. In fact, in solution, 2,2′,2″-terpyridine shows low log *K* values for $Ag^+$, $Cu^+$, $Zn^+$, and $Ni^+$, all metal ions that have $d^{10}$ configurations, but shows the highest relative stability constants for all of the divalent metal ions. Thus, there is some yet unidentified influence afforded by the monovalent ions upon complexation in solution, an effect which differs from that of the divalent metal ions, but is likely related directly to the net charge density of the metal ion and not the specific electronic configuration.

## Conclusions

Metal chelates are formed from ion-molecule reactions of monopositive metal ions and aromatic ligands in the gas phase. The extent of coordination in terms of the trends toward dimer and trimer complexation depends on the *n*-dentate nature of the ligand, its size, and the electronic configuration of the metal ion, with a pattern that is not directly predicted from solution results. For example, only dimer products are observed from reactions of $Cu^+$ ions, whereas tris complexes are observed from reactions of $Co^+$ and $Fe^+$ ions. Tetrakis products are never observed. For the bidentate and tridentate ligands, the chelation patterns of $Fe^+$ and $Co^+$ in the gas phase parallel those observed for $Co^{2+}$ and $Ni^{2+}$, the isoelectronic counterparts, respectively, in solution. However, $Ni^+$ complexation in the gas phase does not reflect the solution results for isoelectronic $Cu^{2+}$ in solution, because trimers are consistently produced in solution for the bidentate ligands. This latter difference may be due to the overall lower charge density of $Ni^+$ in the gas phase relative to $Cu^{2+}$ in solution, and the resulting reduced coordination capability.

In general, terpyridine shows the greatest relative metal binding affinity in the gas phase, followed by 1,10-phenanthroline and then 2,2′-bipyridine. The binding affinity trends are predictable based on a knowledge of the relative polarizabilities of the ligands and number of binding sites.

Attachment of one loosely-bound water molecule to the monomer ligand/metal ion complex is observed, but this hydration is not observed for any of the bis or tris complexes. The absence of hydration for the dimers and trimers is attributed to the greater binding strengths of the aromatic ligands relative to that of water, a factor which promotes preferential displacement of the solvent molecule by coordination of a more strongly bound aromatic ligand.

The fact that the gas-phase metal ions are less charge dense, nonsolvated monovalent cations clearly has an influence on the chelation trends relative to solution results, but the observation

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that multiple ligand chelates are produced in abundance in the ion trap is promising, especially for future systematic studies of selectively solvated chelates in the gas phase. Moreover, the fact that the different combinations of metal ions and *n*-dentate ligands demonstrate very specific chelation patterns indicates that the metal ions do not merely behave as uniformly reactive spheres, but retain some chemically distinctive properties in these gas-phase reaction studies.

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