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Solvent displacement in transition metal complexes

Sheryl Blair, Brian Goolsby, Jennifer Brodbelt*

Department of Chemistry and Biochemistry, The University of Texas at Austin, Austin, TX 78712, USA

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Abstract

Ligand exchange reactions of transition metal ions solvated by two acetone or two acetonitrile molecules with multidentate polyethers or pyridyl ligands are undertaken in a quadrupole ion trap mass spectrometer. The ability of the polyether or pyridyl ligand to displace one or both solvent molecules is correlated with the number of binding atoms in the multidentate ligand, the flexibility of the ligand along with its ability to fully coordinate or encapsulate the metal ion, and the strength of the solvent/metal bonds. The smaller polyethers displace one solvent molecule, thus generating stable (M^+ + polyether + solvent) complexes. The larger polyethers rapidly displace both solvent molecules, leading to formation of stable (M^+ + polyether) complexes, because of the ability of the large polyethers to encapsulate or fully coordinate the metal ion. The pyridyl ligands tend to favor formation of (M^+ + pyridyl ligand + solvent) mixed-ligand complexes, regardless of the number of nitrogen atoms or flexibility of the pyridyl ligand. The pyridyl ligands are unable to fully encapsulate the metal ion, so one solvent molecule may remain bound to the metal ion. (Int J Mass Spectrom 185/186/187 (1999) 49–59) © 1999 Elsevier Science B.V.

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1. Introduction

Metal complexation is important in many types of chemical processes such as mechanisms of drug activity, actions of metalloenzymes, selectivity of sensors, and solvation processes [1–3]. Numerous methods have been developed to explore the details of the interactions between metal ions and solvent molecules or organic ligands, including methods in the gas phase that can study the interactions between individual metal ions and either single or multiple ligands. The latter situation is particularly interesting for several reasons. In complexes containing more

than one ligand bound to a metal ion, each ligand does not necessarily possess the same binding energy. There may be cooperation if the ligands are multidentate, and repulsive interactions between two ligands bound to the same metal ion can occur. Thus, strategies for probing the reorganization of ligands around metal ions should give insight into the importance of cooperativity and ligand–ligand repulsions in gas-phase metal coordination chemistry.

The advent of laser desorption [4] and electrospray ionization [5] techniques have allowed the formation of selectively solvated metal ions and metal complexes, including both singly and doubly charged species and complexes that contain more than twelve molecules bound to a single metal ion [6–11]. The use of several tandem mass spectrometric methods has given information about metal–ligand interactions and

* Corresponding author.

Dedicated to Professor Michael T. Bowers on the occasion of his 60th birthday.

has allowed the initial exploration of the transition from solution to the gas phase because of the ability to form and study a variety of clusters containing one or more ligands bound to a single metal ion. For example, energy-resolved threshold collisional activated dissociation has been used to measure bond dissociation energies of various types of metal complexes, including sequential bond dissociation energies when more than one ligand is bound to the metal ion [12,13]. Collisional activated dissociation methods have been used to evaluate the fragmentation pathways of various metal complexes that contain several ligands bound to a single metal ion [8,9].

Previous studies of multiligated metal ions have shown that the first bonds formed to the metal ion are typically the strongest, with a steady progression to lower binding energies for each additional ligand [12,13]. For example, the first two water molecules coordinated with a singly charged transition metal ion, such as Ni^+ , are each bound by 35–45 kcal mol, whereas the third and fourth water molecules are each bound by 10–18 kcal mol [13]. The decreasing bond energy is rationalized by the increase in the degree of ligand–ligand repulsions as the metal ion becomes more crowded and the increase in charge delocalization as each ligand is added. The general trends for alkali metal complexation are similar; however, the bond energies are lower overall [12]. There is a uniform progression to lower bond energies as each ligand is added, and constraints for how the ligands are positioned are less severe because the alkali metal ions do not have specific binding geometries. Interestingly, the total binding energy for four monodentate ligands bound to one metal ion is greater than for two analogous bidentate ligands or one tetradentate ligand bound to one metal ion because the multidentate ligands have less freedom to optimally align their dipoles with the metal ion [12].

In contrast to the quantitative information gained from measurements of bond dissociation energies for metal complexes, ligand exchange reactions undertaken in the gas phase allow qualitative evaluation of the sequence of ligand displacement processes for a range of molecules bound to different types of metal ions [14–16]. Ligand exchange reactions have been

used for years to estimate relative metal binding affinities of organic ligands based on the positive displacement of one type of ligand for another bound to a metal ion [14–16]. The concept can be extended to multiligated metal ions by monitoring the displacement reactions for complexes in which metal ions are surrounded by two or more ligands, a situation in which ligand repulsions and access to the metal ion are important factors. Such exchange processes are especially intriguing if the initial metal complexes incorporate monodentate ligands and react with polydentate ligands because concurrent displacement of several ligands may occur, as illustrated in the present article.

We have undertaken a series of studies aimed at exploring aspects of metal complexation in the gas phase, many specifically focused on the understanding of the intrinsic basis of molecular recognition [17–22] in addition to the systematic evaluation of differences between the reactions of singly versus doubly charged metal ions [23,24]. The reactions of multiligated metal ions with molecules that have several identical binding sites, such as polyethers or pyridyl ligands, are particularly interesting because the multidentate ligands have greater total binding energies than monodentate molecules and should be able to displace one or more of the monodentate solvent ligands initially bound to the metal ion. Thus, by varying the nature of the multidentate polyether or pyridyl ligand, information about structural factors that influence ligand displacement can be obtained, such as the influence of the nitrogen versus oxygen donor atoms, the effect of the number of donor atoms (i.e. the number of oxygen or nitrogen binding sites), and the influence of the flexibility of the ligand. In the present study, transition metal ions solvated by two acetone or two acetonitrile molecules are reacted with multidentate polyether or pyridyl ligands. The ability of the polyether or pyridyl ligands to displace one or both solvent molecules is correlated with the coordination properties of the ligands. The ligands of interest in this study include the pyridyl molecules: 2,2',6',2"-terpyridine, 2,2'-bipyridine, 1,10-phenanthroline, 4,4'-bipyridine, and pyridine, all of which are

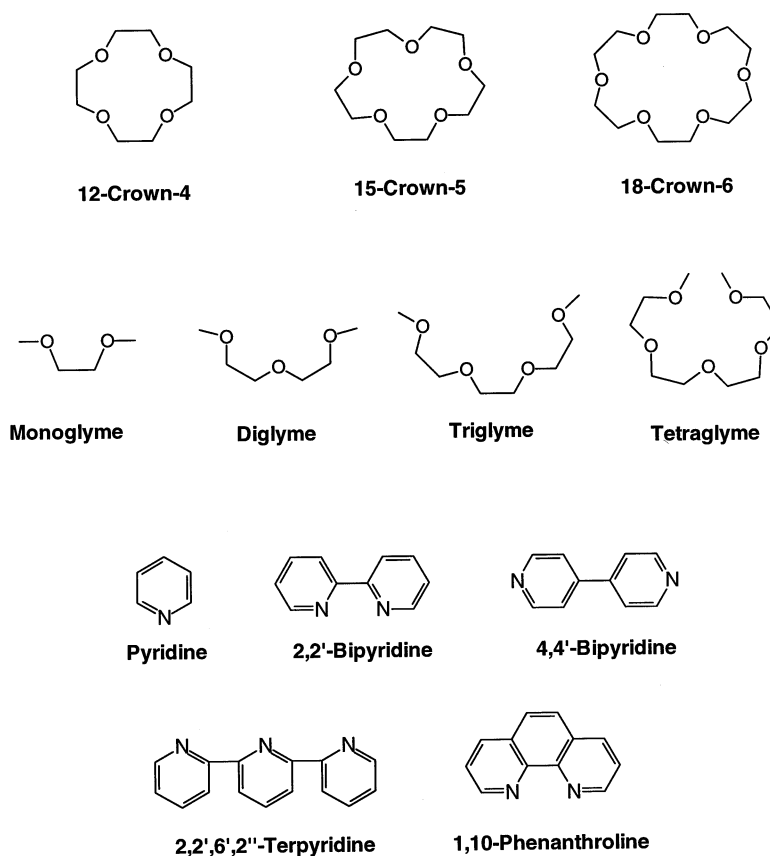


Fig. 1. Polyether and pyridyl structures.

nitrogen donors, and the polyether molecules: 18-crown-6, 15-crown-5, 12-crown-4, tetraethylene glycol dimethyl ether (tetraglyme), triethylene glycol dimethyl ether (triglyme), 2-methoxyethyl ether (diglyme), and ethylene glycol dimethyl ether (monoglyme), all of which are oxygen donors (Fig. 1).

2. Experimental methods

All experiments were performed with a Finnigan MAT quadrupole ion trap mass spectrometer (ITMS) [25] equipped with a probe-mounted fiber optic laser desorption interface [26]. A Nd:YAG laser operated in Q-switch mode supplied the laser pulse that was transmitted through a probe-mounted fiber optic to a metal foil. The power density of the laser pulse was maintained at $\sim 2 \times 10^8$ W/cm².

The metal ions were stored in the trap and subsequently allowed to react with gas-phase acetone or acetonitrile that was admitted through a leak valve. The solvent/metal complex of interest was then isolated and allowed to react for 0–100 ms with a neutral pyridyl or polyether compound that was admitted through a leak valve or solids probe at the same approximate concentration. The resulting metal complexes were then analyzed by operating the ion trap in mass selective instability mode in which an rf voltage applied to the ring electrode is used to eject ions from the trap into an externally mounted electron multiplier. A constant helium buffer gas pressure was maintained at 1 mtorr to promote collisional cooling of the complexes.

Acetone, acetonitrile, and pyridyl and polyether compounds were purchased from Aldrich Chemical

Table 1

Product formation from reactions of ($M^+ + 2 \times \text{acetone}$) ions with polyether ligands^a

Ligand	($Co^+ + 2 \times \text{acetone}$)	($Cu^+ + 2 \times \text{acetone}$)	($Ni^+ + 2 \times \text{acetone}$)
12-Crown-4	($M^+ + 2P$)	($M^+ + 2P$)	($M^+ + 2P$)
	($M^+ + P$)	($M^+ + P$)	($M^+ + P$)
	($M^+ + P + S$)	($M^+ + P + S$)	($M^+ + P + S$)
15-Crown-5	($M^+ + P$)	($M^+ + P$)	($M^+ + P$)
18-Crown-6	($M^+ + P$)	($M^+ + P$)	($M^+ + P$)
Monoglyme	($M^+ + 2P$)	($M^+ + 2P$)	($M^+ + 2P$)
	($M^+ + P + S$)	($M^+ + P + S$)	($M^+ + P + S$)
Diglyme	($M^+ + 2P$)	($M^+ + 2P$)	($M^+ + 2P$)
	($M^+ + P$)	($M^+ + P$)	($M^+ + P$)
	($M^+ + P + S$)		($M^+ + P + S$)
Triglyme	($M^+ + P$)	($M^+ + P$)	($M^+ + P$)
Tetraglyme	($M^+ + P$)	($M^+ + P$)	($M^+ + P$)

^aProducts listed in order of decreasing relative intensity. M = metal ion, P = polyether or pyridyl ligand, S = acetone; the reaction time is 100 ms.

(Milwaukee, WI) and used without further purification.

3. Results and discussion

3.1. Formation of monocationic solvent: transition metal complexes

Metal ions were formed by ablating a metal foil to produce monocationic metal ions. These ions were then allowed to undergo reactions with solvent molecules, either acetone or acetonitrile, that were introduced into the chamber via a leak valve. For reactions with acetone, complexes containing a single metal ion and either one or two solvent ligands were formed, with the most predominant product being the complex with two solvent ligands attached ($M^+ + 2 \times \text{acetone}$). For acetonitrile, complexes containing two solvent ligands, but not one, were formed. This difference in formation of stable 1:1 versus 1:2 metal:solvent complexes can be rationalized by two factors. Acetonitrile is a linear molecule with less steric interference than acetone when trying to achieve an optimal dipole alignment with the metal cation, and it is also known that nitrogen-transition metal bonds are stronger than oxygen-transition metal bonds [1,10,11]. In either case, the complex containing two solvent ligands was isolated and allowed to

react with one of the multidentate compounds for periods of 0–150 ms. Our objective was to compare the abilities of the various multidentate polyether or pyridyl ligands to displace one or both solvent molecules and to form stable complexes containing one solvent molecule and one multidentate ligand. The results of the ligand displacement reaction are summarized in Tables 1–4. Since the product distributions vary with time and are dependent on the concentrations of reactants, the relative product distributions are reported only qualitatively for a single time period (100 ms) to avoid over-interpretation of specific product percentages.

3.2. Ligand displacement of acetone by polyether ligands

The displacement reactions involving the polyether ligands lead to two types of behavior: (1) rapid displacement of both acetone molecules and formation of stable ($M^+ + \text{polyether}$) complexes, and (2) displacement of only one acetone molecule with formation of stable ($M^+ + \text{polyether} + \text{acetone}$) mixed-ligand complexes (Table 1). These two categories of behavior correlate with the coordination capability of each polyether, a factor that is related to the number of oxygen atoms and the flexibility of the ligand. As an example, the products formed from the

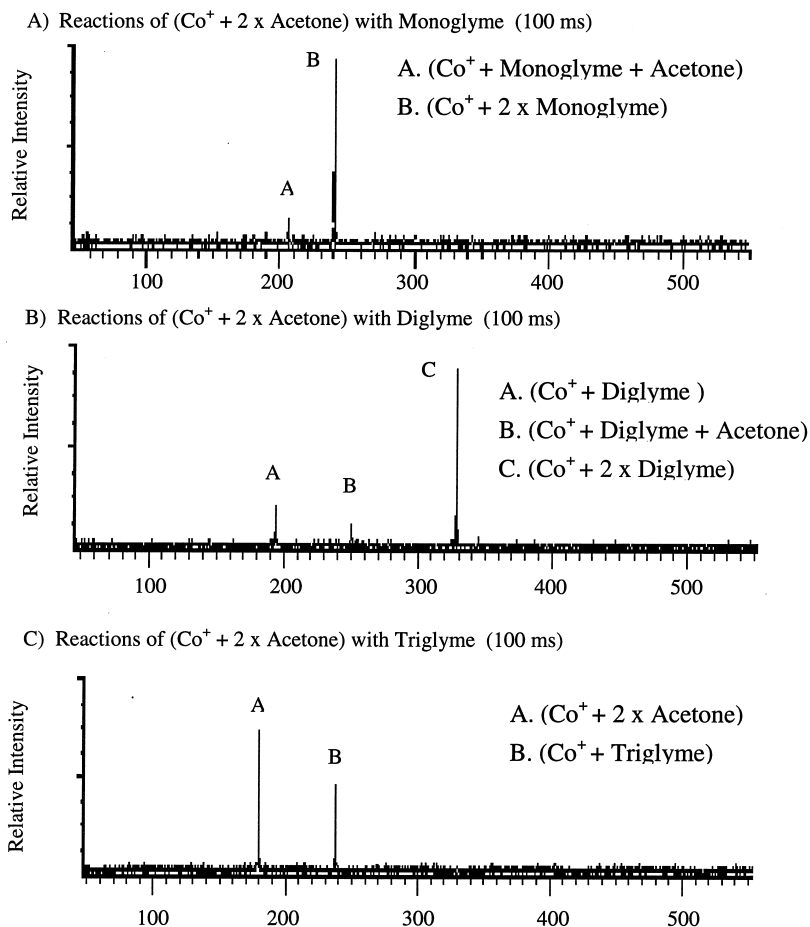


Fig. 2. Effect of polyether size on transition metal binding: (A) reactions of $(\text{Co}^+ + 2 \times \text{acetone})$ with monoglyme (100 ms), (B) reactions of $(\text{Co}^+ + 2 \times \text{acetone})$ with diglyme (100 ms), (C) reactions of $(\text{Co}^+ + 2 \times \text{acetone})$ with triglyme (100 ms).

reaction of monoglyme or diglyme with $(\text{Co}^+ + 2 \times \text{acetone})$ are shown in Fig. 2(A) and (B). The $(\text{Co}^+ + \text{glyme})$ and $(\text{Co}^+ + 2 \times \text{glyme})$ complexes and the mixed-ligand $(\text{Co}^+ + \text{glyme} + \text{acetone})$ complexes are evident in both spectra. In fact, monoglyme, diglyme, and 12-crown-4 are the only three polyether ligands that engage in formation of stable $(\text{M}^+ + \text{polyether} + \text{acetone})$ mixed-ligand complexes upon reaction with the $(\text{M}^+ + 2 \times \text{acetone})$ complexes. 12-Crown-4 has four oxygen atoms and is a fairly rigid ligand. Monoglyme and diglyme have two or three oxygen atoms, respectively, and the relatively small size of these ligands gives them modest flexibility. Because of their degree of flexibility and low

number of oxygen atoms, these three ligands may replace only one of the acetone molecules during the ligand displacement period, thus resulting in the formation of stable $(\text{M}^+ + \text{polyether} + \text{acetone})$ complexes. The flexibility of the polyether is the key feature that influences its ability to orient the oxygen dipoles to optimally coordinate the metal ion. Triglyme, which is larger than monoglyme and diglyme and is the acyclic analog of 12-crown-4, has four oxygen atoms but has greater flexibility because of its acyclic nature. The flexibility of triglyme gives it a much greater ability to re-orient its oxygen dipoles and rapidly displace *both* acetone molecules from the metal ion, and thus the $(\text{M}^+ + \text{triglyme} + \text{acetone})$

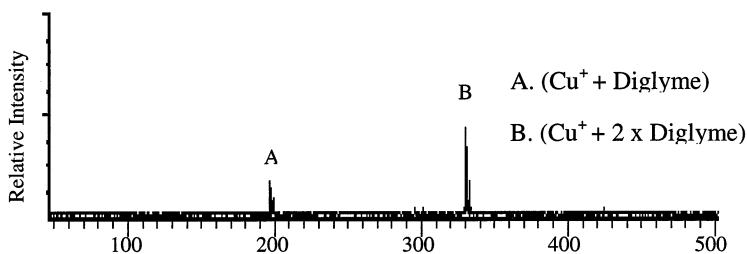


Fig. 3. Reactions of $(\text{Cu}^+ + 2 \times \text{acetone})$ with diglyme (100 ms).

complexes are not observed as stable species [Fig. 2(C)]. Triglyme, tetraglyme, 15-crown-5, and 18-crown-6 all have enough oxygen atoms and sufficient flexibility to allow efficient displacement of both acetone molecules, thus leading to formation of stable $(\text{M}^+ + \text{polyether})$ complexes but not $(\text{M}^+ + \text{polyether} + \text{acetone})$ mixed-ligand complexes.

One exception exists for the ligand displacement reactions of diglyme with $(\text{Cu}^+ + 2 \times \text{acetone})$ versus $(\text{Ni}^+ + 2 \times \text{acetone})$ and $(\text{Co}^+ + 2 \times \text{acetone})$. When reacting with $(\text{Cu}^+ + 2 \times \text{acetone})$, diglyme rapidly displaces both acetone molecules and forms stable $(\text{Cu}^+ + \text{diglyme})$ complexes, but not mixed-ligand complexes (Fig. 3). In contrast, upon reaction with $(\text{Ni}^+ + 2 \times \text{acetone})$ or $(\text{Co}^+ + 2 \times \text{acetone})$, diglyme displaces one acetone molecule to form stable mixed-ligand complexes [Fig. 2(B)]. This difference stems from the different coordination geometry of Cu^+ versus Ni^+ and Co^+ in the gas phase. Cu^+ prefers a linear coordination geometry with two coordination sites in the gas phase, and thus diglyme is sufficiently large and flexible to accommodate this preference and fully coordinate the Cu^+ ion.

3.3. Ligand displacement of acetone by pyridyl ligands

In contrast to the results observed for the displacement reactions involving polyether ligands and $(\text{M}^+ + 2 \times \text{acetone})$ ions in which the formation of mixed-ligand complexes correlated with the flexibility of the polyether, the pyridyl ligands tend to favor formation of $(\text{M}^+ + \text{pyridyl ligand} + \text{acetone})$ complexes for all of the pyridyl ligands, regardless of

the number of nitrogen atoms or the flexibility of the pyridyl ligand (Table 2). An example of this behavior is shown in Fig. 4 for the reactions of $(\text{Co}^+ + 2 \times \text{acetone})$ with pyridine. Fig. 4(A) shows the initial reactions of acetone with Co^+ . The $(\text{Co}^+ + 2 \times \text{acetone})$ complexes are isolated and allowed to react with pyridine. Fig. 4(B) shows the products after 75 ms of reaction time: the mixed-ligand complex $(\text{Co}^+ + \text{pyridine} + \text{acetone})$ is the dominant product, along with formation of $(\text{Co}^+ + 2 \times \text{pyridine})$ complexes. The displacement reactions involving pyridine, 4,4'-bipyridine, 2,2'-bipyridine, 1,10-phenanthroline, and 2,2',6,2''-terpyridine uniformly result in formation of the mixed-ligand complexes with only one exception—the reaction of $(2 \times \text{acetone} + \text{Cu}^+)$ with 2,2',6',2''-terpyridine, as discussed later. The production of stable mixed-ligand complexes for the pyridyl ligands compared to the lack of mixed-ligand complexes for many of the polyethers was somewhat unexpected because nitrogen-metal bonds are stronger than oxygen-metal bonds [1,10]. Therefore, one would imagine that the weakly bound acetone ligands would be rapidly displaced by the more strongly binding pyridyl ligands, similar to the results observed for the ligand displacement reactions involving 15-crown-5, 18-crown-6, triglyme, or tetraglyme. Although the pyridyl ligands form strong bonds to metal ions, they can neither “encapsulate” a metal ion nor fully coordinate it as a larger, more flexible polyether might. Thus, the ligand displacement reactions involving the pyridyl ligands must proceed in a stepwise fashion in which one acetone molecule is displaced by a pyridyl ligand; then a second pyridyl ligand must approach the $(\text{acetone} + \text{M}^+ + \text{pyridyl})$ complex,

Table 2

Product formation from reactions of ($M^+ + 2 \times$ acetone) ions with pyridyl ligands^a

Ligand	($Co^+ + 2 \times$ acetone)	($Cu^+ + 2 \times$ acetone)	($Ni^+ + 2 \times$ acetone)
Pyridine	($M^+ + 2P$)	($M^+ + 2P$)	($M^+ + 2P$)
	($M^+ + P + S$)	($M^+ + P + S$)	($M^+ + 3P$)
4,4'-Bipyridine	($M^+ + P + S$)	($M^+ + P + S$)	($M^+ + P + S$)
	($M^+ + 2P$)	($M^+ + 2P$)	($M^+ + 2P$)
2,2'-Bipyridine	($M^+ + 2P$)	($M^+ + P + S$)	($M^+ + 3P$)
	($M^+ + P + S$)	($M^+ + 2P$)	($M^+ + 2P$)
1,10-Phenanthroline	($M^+ + 3P$)	($M^+ + P + S$)	($M^+ + P$)
	($M^+ + 3P$)	($M^+ + 2P$)	($M^+ + 2P$)
	($M^+ + 2P$)	($M^+ + P + S$)	($M^+ + P + S$)
2,2',6',2''-Terpyridine	($M^+ + P + S$)	($M^+ + 2P$)	($M^+ + 2P$)
	($M^+ + P$)	($M^+ + 2P$)	($M^+ + P + S$)
	($M^+ + 2P$)	($M^+ + P$)	($M^+ + P + S$)

^aProducts listed in order of decreasing relative intensity. M = metal ion, P = polyether or pyridyl ligand, S = acetone; the reaction time is 75–125 ms.

properly orient its nitrogen dipoles and displace the remaining acetone molecule. This sequence results in slower kinetics relative to the case where a larger polyether is already bound to the metal ion in the intermediate (acetone + M^+ + polyether) complex

and must simply dislodge the remaining acetone molecule via a further re-orientation of its free oxygen dipoles.

Differences in the rates of the displacement reactions are noted within the series of pyridyl ligands if

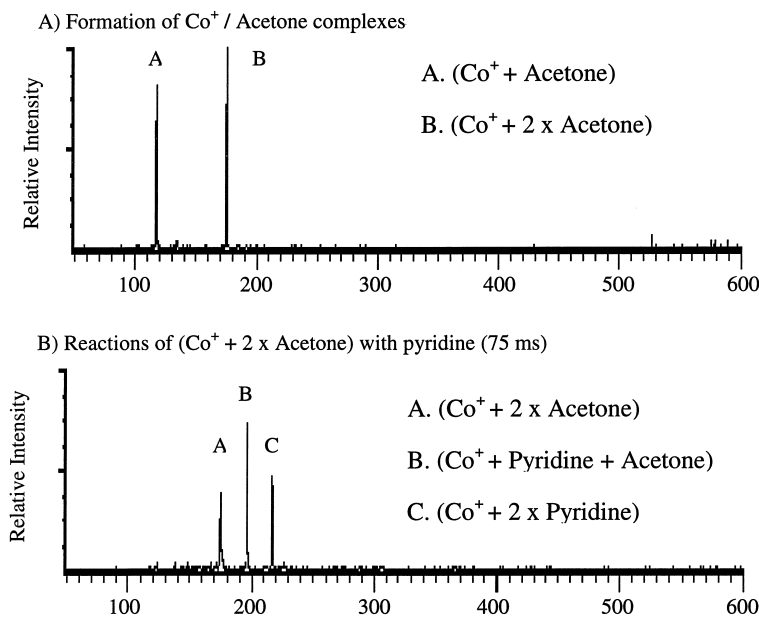


Fig. 4. Stepwise displacement of solvent molecules by a monodentate pyridyl ligands: (A) formation of Co^+ /acetone complexes, (B) reactions of ($Co^+ + 2 \times$ acetone) with pyridine (75 ms).

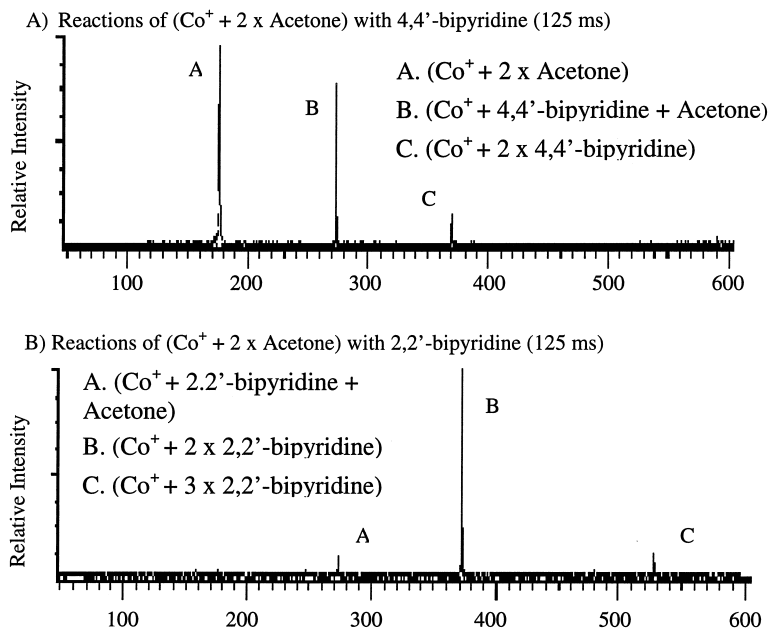


Fig. 5. Reactions of $(\text{Co}^+ + 2 \times \text{acetone})$ with bipyridine ligands: (A) reactions of $(\text{Co}^+ + 2 \times \text{acetone})$ with 4,4'-bipyridine (125 ms), (B) reactions of $(\text{Co}^+ + 2 \times \text{acetone})$ with 2,2'-bipyridine (125 ms).

the product distributions are monitored more closely. For example, the product distributions obtained from the displacement reactions involving $(\text{Co}^+ + 2 \times \text{acetone})$ and 4,4'-bipyridine versus 2,2'-bipyridine are shown in Fig. 5(A) and (B), respectively, using identical reaction conditions. Although only one slice of time is represented by the two spectra, the product distributions can be used to highlight the difference in relative reactivities of the two bidentate pyridyl ligands. For the reactions with 4,4'-bipyridine, the dominant product is the mixed-ligand complex $(\text{Co}^+ + 4,4'\text{-bipyridine} + \text{acetone})$, whereas with 2,2'-bipyridine, the dominant product is the dimer complex $(\text{Co}^+ + 2 \times 2,2'\text{-bipyridine})$. The difference in product distributions reflects the significantly greater metal binding free energy of 2,2'-bipyridine relative to 4,4'-bipyridine, thus increasing the rate of the acetone displacement reactions.

The only exception to the general ligand displacement behavior described above is the reaction of $(\text{Cu}^+ + 2 \times \text{acetone})$ with 2,2',6',2''-terpyridine which results in the formation of $(\text{Cu}^+ + 2,2',6',2''\text{-terpyridine})$ but not mixed-ligand complexes. As mentioned

earlier, Cu^+ prefers a linear coordination geometry, and thus one molecule of 2,2',6',2''-terpyridine may fully coordinate the Cu^+ ion and dislodge both acetone molecules.

3.4. Ligand displacement of acetonitrile by polyether ligands

Acetonitrile is similar to acetone in that it is a common monodentate solvent molecule, but it engages in binding via its nitrogen atom rather than an oxygen atom and thus forms stronger bonds to the monopositive transition metal ions. Comparison of the reactions involving the acetone-solvated metal ions versus acetonitrile-solvated metal ions reflects the ability of the polyether and pyridyl ligands to displace more strongly bound solvent molecules. The reactions were monitored for a subset of three polyether ligands, and the results are summarized in Table 3. In general, the results qualitatively mirror the size-selective trends seen for the reactions of the acetone-solvated metal ions in terms of the formation of mixed-ligand complexes. An example is shown in

Table 3

Product formation from reactions of ($M^+ + 2 \times$ acetonitrile) ions with selected polyether ligands^a

Ligand	($Co^+ + 2 \times$ acetonitrile)	($Cu^+ + 2 \times$ acetonitrile)	($Ni^+ + 2 \times$ acetonitrile)
12-Crown-4	($M^+ + P + S$)	($M^+ + P + S$)	($M^+ + P + S$)
Diglyme	($M^+ + P + S$)	($M^+ + P + S$)	($M^+ + P + S$)
Tetraglyme	($M^+ + P$)	($M^+ + P$)	($M^+ + P$)

^aProducts listed in order of decreasing relative intensity. M = metal ions, P = polyether or pyridyl ligand, S = acetonitrile; the reaction time is 100 ms.

Fig. 6(A) and (B) for the displacement reactions of ($Cu^+ + 2 \times$ acetone) and ($Cu^+ + 2 \times$ acetonitrile) with 12-crown-4. The reactions between ($Cu^+ + 2 \times$ acetone) lead predominantly to ($Cu^+ + 12$ -crown-4) and ($Cu^+ + 2 \times 12$ -crown-4) complexes along with low levels of the key ($Cu^+ + 12$ -crown-4 + acetone) mixed-ligand complexes [Fig. 6(A)]. The reactions between ($Cu^+ + 2 \times$ acetonitrile) lead exclusively to formation of ($Cu^+ + 12$ -crown-4 + acetonitrile) mixed-ligand complexes, thus confirming that 12-crown-4 can displace one but not both of the acetonitrile ligands [Fig. 6(B)]. For both 12-crown-4 and diglyme, stable mixed-ligand complexes are the dom-

inant products, whereas tetraglyme is able to rapidly displace both acetonitrile molecules, thus leading to ($M^+ +$ tetraglyme) complexes.

The critical difference between the displacement reactions involving ($M^+ + 2 \times$ acetone) versus ($M^+ + 2 \times$ acetonitrile) is the ability of 12-crown-4 or diglyme (i.e. the smaller polyethers) to displace the second molecule of solvent. In fact, neither of these polyether ligands is ever able to dislodge a second molecule of acetonitrile from the transition metal ion, whereas these polyethers could easily displace a second molecule of acetone. This difference confirms that acetonitrile is more strongly bound to the metal

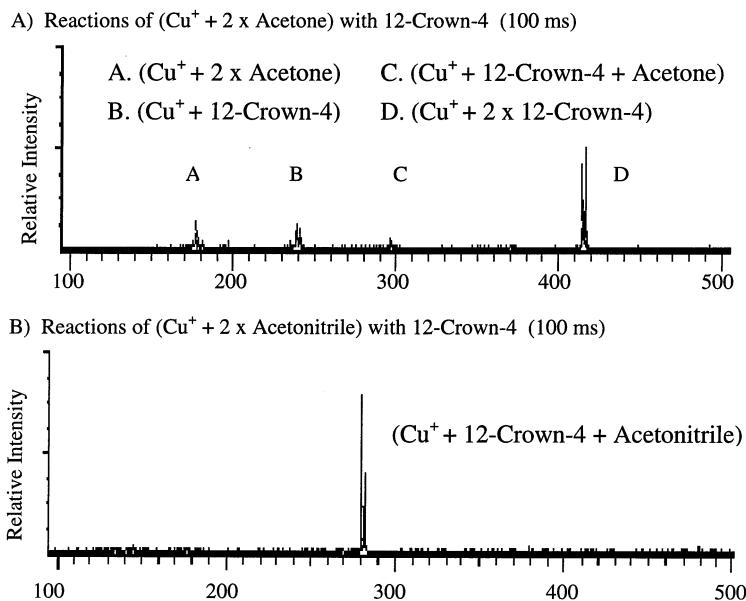


Fig. 6. Reactions of solvated metal ions with 12-Crown-4: (A) reactions of ($Cu^+ + 2 \times$ acetone) with 12-Crown-4 (100 ms), (B) reactions of ($Cu^+ + 2 \times$ acetonitrile) with 12-Crown-4 (100 ms).

Table 4
Product formation from reactions of ($M^+ + 2 \times$ acetonitrile) ions with selected pyridyl ligands^a

Ligand	($Co^+ + 2 \times$ acetonitrile)	($Cu^+ + 2 \times$ acetonitrile)	($Ni^+ + 2 \times$ acetonitrile)
Pyridine	($M^+ + 2P$)	($M^+ + P + S$)	($M^+ + 2P$)
	($M^+ + P + S$)	($M^+ + 2P$)	($M^+ + P + S$)
2,2'-Bipyridine	($M^+ + 2P$)	($M^+ + 2P$)	($M^+ + 2P + S$)
	($M^+ + 3P$)	($M^+ + P + S$)	($M^+ + 2P$)
	($M^+ + P + S$)	($M^+ + P + S$)	($M^+ + P + S$)
1,10-Phenanthroline	($M^+ + 2P$)	($M^+ + 2P$)	($M^+ + P + S$)
	($M^+ + P + S$)	($M^+ + P + S$)	($M^+ + 2P$)

^aProducts listed in order of decreasing relative intensity. M = metal ion, P = polyether or pyridyl ligand, S = acetonitrile; the reaction time is 75–125 ms.

ion than acetone, thus quenching the sequential nature of the displacement reactions for the smaller polyethers.

3.5. Ligand displacement of acetonitrile by pyridyl ligands

The displacement reactions involving the ($M^+ + 2 \times$ acetonitrile) ions were monitored for a subset of three pyridyl ligands, and the results are summarized in Table 4. In general, the results mirror the behavior trends seen for the reactions of the acetone-solvated metal ions. In all cases, stable mixed-ligand complexes are observed, showing that the pyridyl ligands can displace one molecule of acetonitrile rapidly, but the second displacement reaction is slower, allowing the mixed-ligand complexes to survive as stable species on the time scale of the experiment.

One subtle difference in the displacement behavior of the acetone-solvated metal ions versus the acetonitrile-solvated metal ions occurs for the reactions involving pyridine and the solvated Ni^+ ions. For this case alone, formation of ($Ni^+ + 2 \times$ pyridine + acetonitrile) complexes occurs, whereas the analogous trimer complexes [i.e. ($Ni^+ + 2 \times$ pyridine + acetone)] were not observed during the displacement reactions of the acetone-solvated Ni^+ ions. This result confirms that acetonitrile is more strongly bound than acetone to the metal ion, thus allowing the acetonitrile

to remain attached to the Ni^+ ion during the competitive displacement reactions by pyridine.

4. Conclusions

Ligand exchange reactions were used to probe solvent displacement from monopositive transition metal ions. Two general types of behavior were noted throughout the study: (1) the displacement of both solvent molecules by a multidentate ligand, leading to the formation of multidentate ligand/metal complexes, and (2) the displacement of only a single solvent molecule leading to mixed-ligand metal complexes. The primary factors that influence the preference for these two types of behavior include the number of binding atoms in the multidentate ligand, the flexibility of the ligand and its ability to fully coordinate or encapsulate the metal ion, and the strength of the solvent/metal bonds. The larger, more flexible compounds such as tetraglyme and 18-crown-6 are capable of encapsulating the metal ion and rapidly displacing both solvent molecules. Because nitrogen forms stronger bonds to transition metal ions than oxygen, the smaller polyether ligands were not able to dislodge both acetonitrile molecules from the metal ion. The more rigid pyridyl ligands favor the formation of mixed-ligand metal complexes, despite the well-known chelation properties of these ligands and the greater strength of nitrogen-metal versus oxygen-metal bonds. The pyridyl ligands are

unable to fully encapsulate the metal ion, so one solvent molecule may remain bound.

Acknowledgements

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